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# Reactions of O,O-Diprotonated Nitro Olefins with Benzenes. Formations of Phenylacetones, 4H-1,2-Benzoxazines and Biarylacetone Oximes

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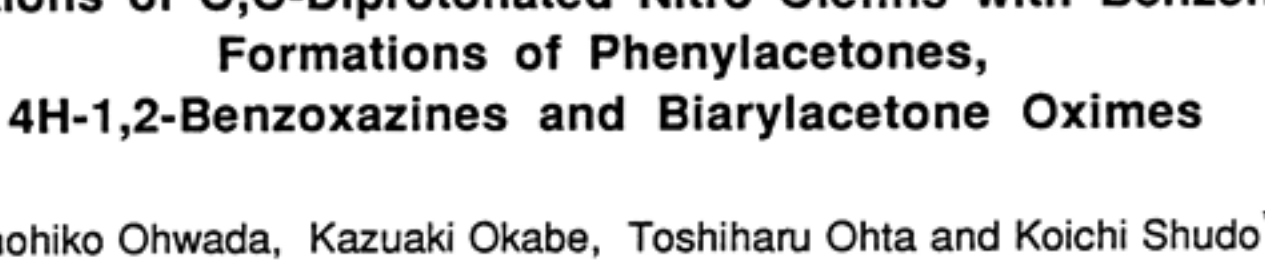
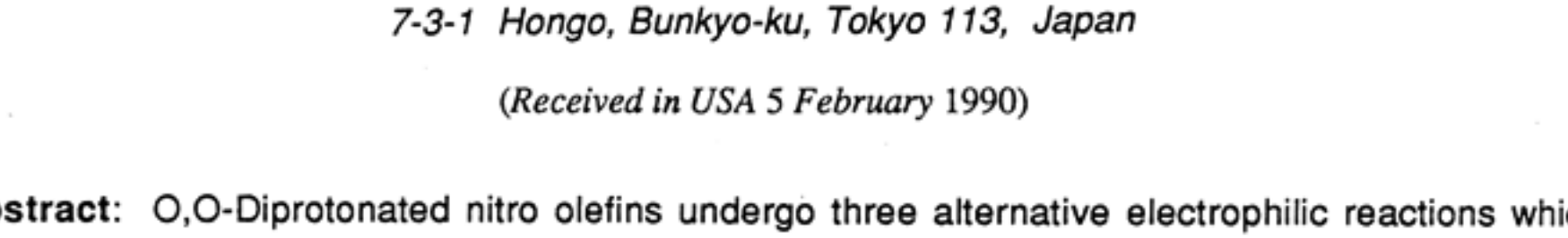
**Abstract**: O,O-Diprotonated nitro olefins undergo three alternative electrophilic reactions which yield α-phenylacetones, 4H-1,2-benzoxazines and biphenylacetone oximes depending on the reaction conditions (temperature and time) and aromatic substrates. Although these reactions are seemingly divergent, a common intermediate of a phenylated protonated *aci*-nitro species, derived from the dication, is postulated to be involved in the reactions. Furthermore, the formation of benzoxazines and biphenylacetone oximes can be interpreted in terms of participation of novel chemical species with phenylethylene dication character derived from the common intermediate.

## Introduction

Nitrostyrene (**2a**) yields a strongly colored stable species formed by protonation in trifluoromethanesulfonic acid (TFSA). On the basis of i-factors in cryoscopic measurements and analysis of the protonation sites by $^{1}H$ and $^{13}C$ NMR spectroscopy, it was concluded that the



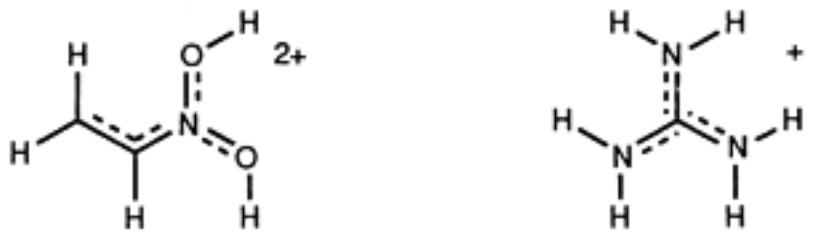

**a**: $R_1$ = Ph, $R_2$ =H, **b**: $R_1$ = $R_2$ = $CH_3$, **c**: $R_1$ = $R_2$ = H




**Scheme I**

species formed in TFSA is the O,O-diprotonated β-nitrostyrene (the N,N-dihydroxyiminium-benzyl dication **1a**, $R_1$ = Ph, $R_2$ = H) (Scheme I). [1] Initially, we thought that the formation of the dication (**1a**) depended on the substituent effect of the phenyl group, stabilizing the cation center ($C_2$) by conjugation. However, a similar dication (**1b**, $R_1$ and $R_2$ = $CH_3$) is formed from 1-nitro-2-methyl-1-propene (**2b**) in TFSA at -5 °C, and is stable enough to be observed by NMR spectroscopy. [2] Furthermore, the parent dication, the N,N-dihydroxyiminium-methylium dication

(**1c**, $R_1$ and $R_2$ = H) itself was concluded to be formed as a discrete entity in the reaction of nitroethylene (**2c**) in TFSA, judging from the reaction product (Scheme I): nitroethylene **2c** reacts with benzene in the presence of TFSA to give deoxybenzoinoxime **3c** in 96 % yield, which corresponds well to the reaction of the dication **1a** with benzene leading to the diphenylated oxime **3a**. [2, 3] The formation of this simple acyclic dication can be ascribed to an intrinsic stabilization, probably by Y delocalization owing to the six π electrons (two π-electrons of the olefinic bond and four electrons of lone pairs of two hydroxy groups). [4] The dications (**1**) are isoelectronic with the guanidinium ion, which has an exceptional stability owing to the Y-shaped configuration of six π-electrons (Chart).



**Chart**

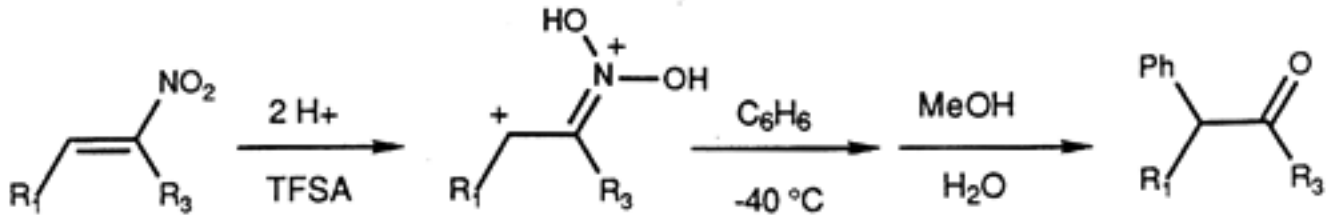
β-Methyl-β-nitrostyrene **2d** also yields a stable O,O-diprotonated dication **1d** ($R_1$ = Ph, $R_3$ = $CH_3$) in TFSA, as was also demonstrated by cryoscopic and NMR spectroscopic measurements.[1]

Electrophilic reactivity of the dications is dependent on the C-1 substituent of the nitro olefin (**2**). [2, 3] A recent study revealed that the dication **1e** ($R_1$ = H, $R_3$ = $CH_3$), formed from 2-nitropropene, reacts with benzene at low temperature (-40 °C) to give a phenylated acetone in high yield after quenching with methanol and water (Scheme II). [5] In this paper we will describe a reaction of the dication **1e** which yields a 4H-1,2-benzoxazine. In this reaction 2- and 4-biphenylacetone oximes are also formed, suggesting intervention of a novel intermolecular nucleophilic attack of benzene on the benzene nucleus of the benzyl cations. In the case of the reaction with substituted benzenes, the dication **1e** predominantly yields the biarylacetone oximes, instead of the 4H-1,2-benzoxazines. Although the two reactions, the formation of the 4H-1,2-benzoxazine and the formation of biphenylacetone oximes are seemingly divergent, we propose the involvement of a common dication intermediate derived from the dication **1e**. We describe here the occurrence of three electrophilic reactions which, depending on the reaction conditions and aromatic substrates, yield α-phenylacetones, 4H-1,2-benzoxazines and biphenylacetone oximes.

## Results and Discussion

### Acid-Catalyzed Reactions of 2-Nitropropene at a Low Temperature. Formation of 1-Phenylacetones.

The dication **1e** of 2-nitropropene reacts with benzene at -40 °C in the presence of TFSA (10 equiv. with respect to the nitro olefin) to give α-phenylacetone **4e** in 85 % yield after methanol-water work-up, i. e., pouring of the reaction mixture after 1 min into a large excess amount of dry methanol (100 ml) cooled at -78 °C with vigorous stirring, subsequent addition of water, and extraction with methylene chloride (Scheme II and Table I). [5] The ketone was formed through a participation of the protonated *aci*-nitro compound. [5] That is, the dication **1e** reacted with benzene to give the α-phenylated protonated *aci* -nitro species **5e**; the dication can thus be regarded as an enoxenium ion equivalent. Since the iminium center of the intermediate **5e** is stabilized by an electron-donating group ($CH_3$), the cation is stable and does not react with another benzene at the

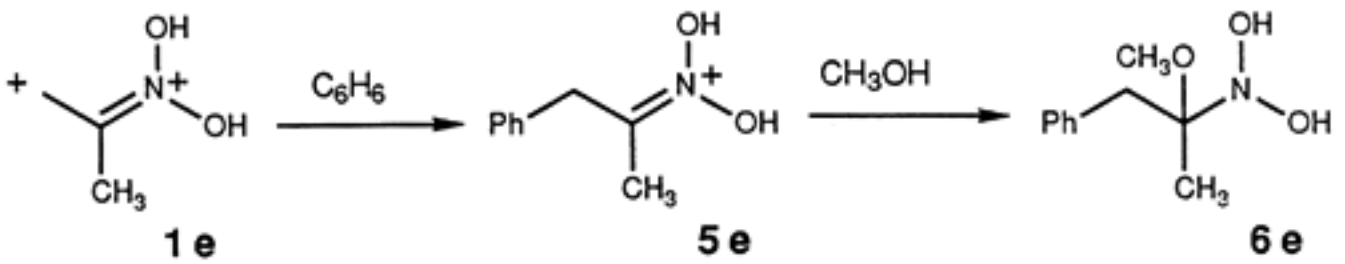



**2d-h** **1d-h** **4d-h**

**d**: $R_1$ = Ph, $R_3$ =$CH_3$, **e**: $R_1$ = H, $R_3$ = $CH_3$, **f** : $R_1$ = H, $R_3$ = Ph,
**g**: $R_1$, $R_3$ = -$(CH_2)_4$-, **h**: $R_1$, $R_3$ = -$(CH_2)_5$-

**Scheme II**

low temperature (Scheme III). In the case of the corresponding iminium intermediate, formed from a nitro olefin bearing a hydrogen atom at the $C_1$ carbon atom (such as 1-nitroethylene), it reacts (after further protonation; data not shown) [3, 6] with another benzene to give a diphenylated oxime



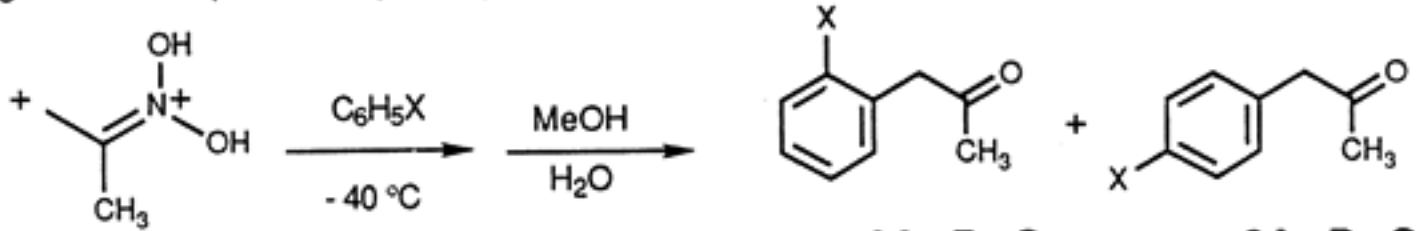

**1e** **5e** **6e**

**7e** **4e**

**Scheme III**

(as shown in Scheme I). [7] Treatment of the intermediate solution with methanol, followed by aqueous work-up, quantitatively converts the stable protonated *aci* -nitro compound to the corresponding carbonyl compound by a mechanism similar to that of the Nef reaction [8] (**5**→ **6**→ **7**), involving attack of more nucleophilic methanol on the cation **5e** through a ketal intermediate which could be isolated by careful work-up (Scheme III). This work-up procedure is important to get a high yield of the α-phenylacetone: straightforward aqueous quenching of the reaction mixture (**5e** obtained after 1 min at -40 °C) gave the ketone **4e** in a lower yield (55 %), together with 1-phenyl-2,2-dinitropropane (13 %) and α-phenylacetone oxime (17 %). [9] The stepwise work-up eliminates the complex accompanying reactions.

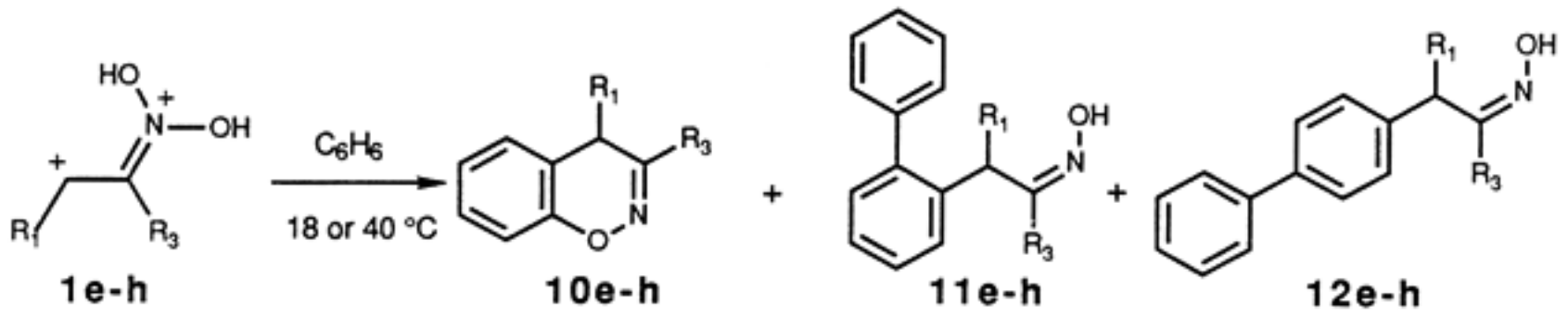
The reactions of the dication **1e** with substituted benzenes (anisole, toluene or chlorobenzene) give *ortho*- (**8A**, **B**, **C**) and *para*-substituted arylacetones (**9A**, **B**, **C**) in high yields under




**1e** **8A, B, C** **9A, B, C**

**A**: X = $OCH_3$, **B**: X=$CH_3$, **C**: X = Cl

**Scheme IV**




**Scheme V**

similar reaction conditions (Scheme IV). [5] The *ortho*/*para* ratios of the ketones were determined from the $^1$H NMR spectra. In the case of anisole, the *ortho* isomer **8A** is favored over the *para* isomer while in the cases of toluene and chlorobenzene, the *para* isomers (**9B**,**C**) are favored over the *ortho* isomers.

The dication **1d** formed from β-methyl-β-nitrostyrene (**2d**) also reacted with benzene at -40 °C, and the methanol-water work-up gave 1,1-diphenylacetone **4d** in 65 % yield, suggestive of the involvement of the protonated *aci*-nitro **5d**.

### Acid-Catalyzed Reactions of 2-Nitropropene at a Higher Temperature. Formation of 4H-1,2-Benzoxazines

In the presence of TFSA (10 equiv with respect to the nitro olefin), the reaction of 2-nitropropene **2e** with benzene at 18 °C for 10 hrs, followed by aqueous work-up, gave 3-methyl-4H-1,2-benzoxazine **10e** (78 %), together with biphenylacetone oximes (2-isomer **11e**, 5 % and 4-isomer **12e**, 10 %) (Scheme V). The 4H-1,2-benzoxazine is a novel heterocyclic compound, obtained for the first time by this reaction. The structure of the 4H-1,2-benzoxazine was elucidated on the basis of the $^1$H and $^{13}$C NMR spectra and combustion analysis, and was confirmed by X-ray crystallographic analysis of the 4H-1,2-benzoxazine **10g** similarly obtained from 1-nitrocyclohexene (*vide infra*). The benzoxazine ring is planar with bond lengths of N-O (1.44 Å), C-N (1.27 Å) and C-O (1.51 Å). [10] The 4H-1,2-benzoxazine is deduced to be formed by cyclization between the oxygen atom and the benzene ring. The reaction requires a longer reaction time and a higher reaction temperature as compared with the acid-catalyzed reaction of a nitro olefin leading to the α-phenylacetone **4e** (-40 °C, 1 min). The reaction can be accelerated by heating at 40 °C (Table I). Quenching the reaction after an insufficient reaction time (1 hr at 18 °C) yielded a significant amount of the phenylacetone together with the 4H-1,2-benzoxazine. This result indicates common intervention of the protonated *aci*-nitro compound (**5e**) in the formation of the benzoxazine, and, we suggest, in the formation of the biphenylacetone oximes (see Proposed Reaction Mechanisms).

In order to examine the generality of formation of the novel heterocycles, 4H-1,2-benzoxazines, the acid-catalyzed reactions of some nitro olefins bearing a 1-alkyl substituent were investigated. The results are summarized in Table I. The reaction of α-nitrostyrene **2f** ($R_1$ = H, $R_3$ = Ph) resulted in the formation of the benzoxazine **10f** (56 %), together with biphenyloximes (**11f** and **12f**) (23 %). A similar reaction occurred with 1-nitro-1-cyclohexene **2g** ($R_1$, $R_3$ = -$(CH_2)_4$-): the reaction with benzene in the presence of TFSA at 15 °C for 20 hrs (or 4 hrs at 40 °C) gave the

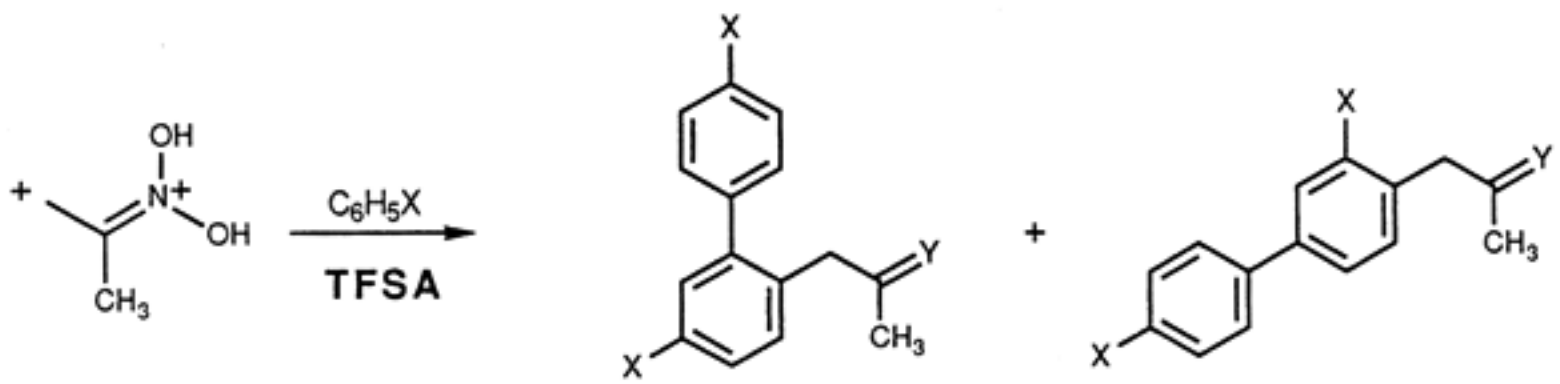
**Table I Acid-catalyzed Reactions of Nitro Olefins with Benzene**

| | $R_1$ | $R_3$ | Temp. | time | **4** | **10** | **11** and **12** |
|---|---|---|---|---|---|---|---|
| **2e** | H | $CH_3$ | - 40 °C | 1 min | 85 % | - | - |
| **2e** | H | $CH_3$ | 18 °C | 10 hr | - | 77 % | 15 % |
| **2e** | H | $CH_3$ | 40 °C | 1 hr | - | 80 % | 16 % |
| **2f** | H | Ph | 25 °C | 14 hr | - | 56 % | 23 % |
| **2g** | | $-(CH_2)_4-$ | -40 °C | 2 hr | 72 % | - | - |
| **2g** | | $-(CH_2)_4-$ | 18 °C | 20 hr | - | 87 % | 7 % |
| **2g** | | $-(CH_2)_4-$ | 40 °C | 4 hr | - | 87 % | 6 % |
| **2h** | | $-(CH_2)_5-$ | 8 °C | 15 hr | - | 66 % | - |

corresponding 4H-1,2-benzoxazine **10g** (87 %) and biphenyloximes ( 2-isomer **11g**, 2 % and 4-isomer **12g**, 5 %). In the reaction of 1-nitro-1-cycloheptene **2h** ($R_1$, $R_3$ = $-(CH_2)_5-$), the corresponding 4H-1,2-benzoxazine **10h** was also formed in 66 % yield under similar conditions.

**Formation of Biarylacetone Oximes**

In the case of the reaction of the dication **1e** with substituted benzenes, the formation of biphenylacetone oximes prevails over that of 4H-1,2-benzoxazines (Scheme VI): in the presence




**1e** Y = N-OH **13A, B, C** **14A, B, C**

**A**: X = $OCH_3$, **B**: X = $CH_3$, **C**: X = Cl Y = O **15A, B, C** **16A, B, C**

**Scheme VI**

of TFSA, 2-nitropropene **2e** reacted with anisole, toluene or chlorobenzene (30 equiv.) to give the corresponding biarylacetone oximes (**13A**, **B**, **C** and **14A**, **B**, **C**, respectively) in high yields (Table II). The reaction conditions used were similar to those in the case of benzene (16 hrs at 15 °C or 2 hrs at 40 °C). In no case did we find evidence for formation of the corresponding 4H-1,2-benzoxazine. The structures of biarylacetone oximes were determined on the basis of the $^1$H-NMR spectra (presence of seven aromatic protons and two methylene protons). The structures were also confirmed as the biarylketones (**15A**, **B**, **C** and **16A**, **B**, **C**) after hydrolysis by the action of aqueous $TiCl_3$.[11] In the case of anisole, the major product was (3,4'-dimethoxy-4-biphenyl)-

**Table II Acid-catalyzed Reactions of 2-Nitropropene (2e) with Aromatics**

| Nitro Olefin | Aromatic | Temp | time | Biarylacetone oximes (Biarylacetone) |
|---|---|---|---|---|
| **2e** | benzene | 18°C | 10 hr | 15 % [a, b] |
| **2e** | anisole | 15 °C | 16 hr | 61 % [c] (54 %) |
| **2e** | toluene | 15 °C | 16 hr | 83 % [d] (75 %) |
| **2e** | chlorobenzene | 15 °C | 19 hr | 86 % [e] (76 %) |

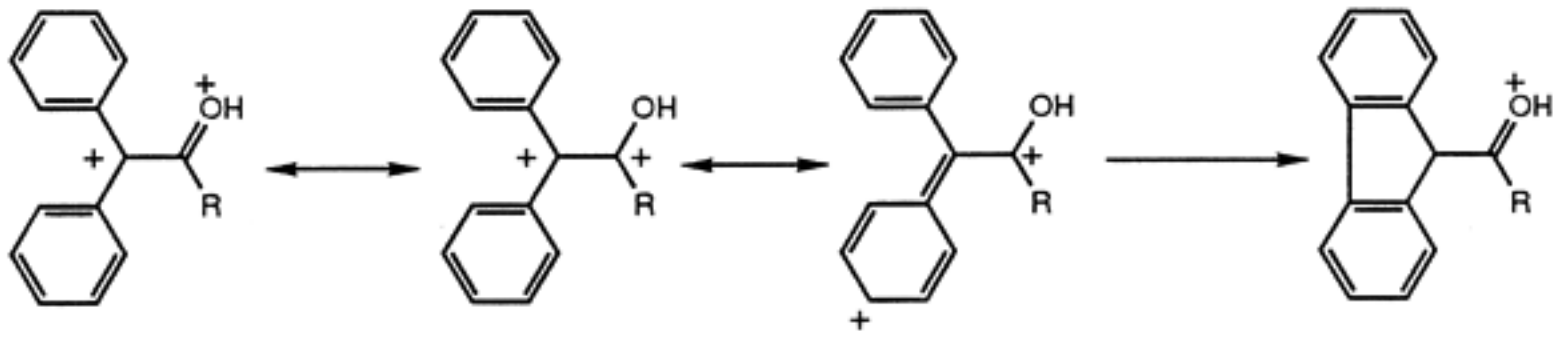
a) **11e**:**12e** = 1: 2. b) **10e** is also formed in 77 % yield. See Table I. c) Predominantly **14A**. d) **13B**:**14B** = 1: 2. e) **13C**:**14C** = 1: 2.5. The yields are given in terms of the total amount of isomeric biarylacetone oximes. The yields shown in parentheses are based on the isolated biarylacetones .

acetone (**16A**) in the yield of 48 %. In the case of toluene, (4',5-dimethyl-2-biphenyl)acetone (**15B**) and (3,4'-dimethyl-4-biphenyl)acetone (**16B**) were obtained in yields of 25 % and 50 %, respectively. In the case of chlorobenzene, (4',5-dichloro-2-biphenyl)acetone (**15C**) was obtained in 50 % yield. A mixture of the ketones obtained in the reaction with chlorobenzene was hydrodehalogenated over Pd-on-C in ethanol to give (2-biphenyl)acetone (53 %, based on the ketone) and 1-(4-biphenyl)-2-propanol (22 %).

The formation of the predominant biarylacetone oximes can be interpreted as follows: the dication **1e** reacts with the first molecule of the aromatic at the *ortho* position (the major pathway in the case of anisole) or at the *para* position (in the case of toluene and chlorobenzene). [12] The second aromatic molecule, at its *para* position, attacks the first phenyl ring. The formation of the biaryl products can only be interpreted in terms of an involvement of nucleophilic attack of the aromatic on the benzene ring of the intermediate cationic derivatives. Theoretical studies showed that the electrophilicity of the simple benzyl cation is localized on the α-carbon atom, [13] which is in accord with experimental observation. [14] Thus, the formation of the biphenyl products suggests the involvement of an electrophile more reactive than the benzyl cation, the phenylethylene dication.

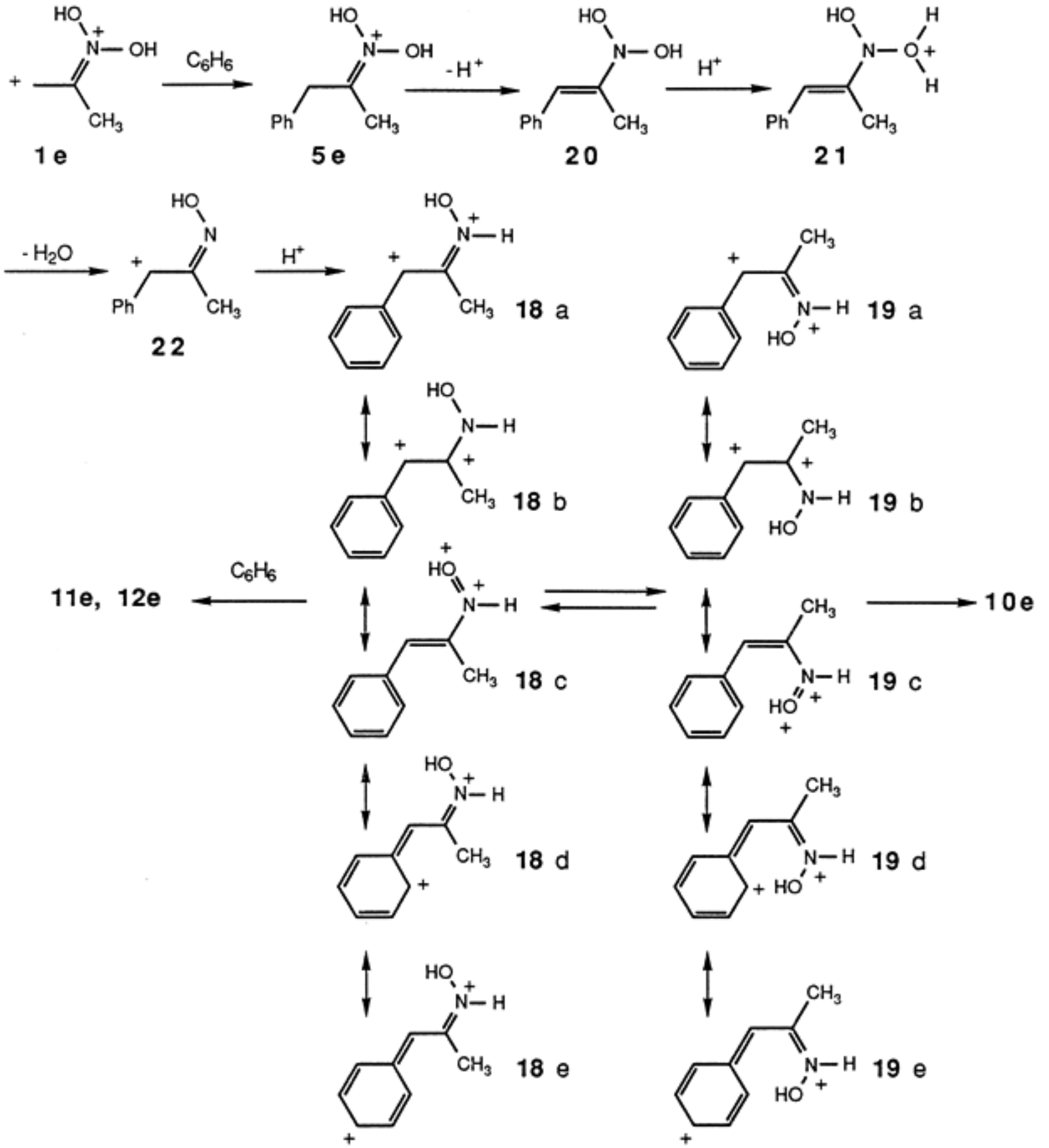
## Proposed Reaction Mechanisms

We have studied the formation and electrocyclic reaction of the phenylethylene dications **17**. The dication **17** (for example, R = $OCH_3$), which can be formed from α-carbomethoxy-diphenyl-




**17** R =$OCH_3$, OH, Ph

**Scheme VII**



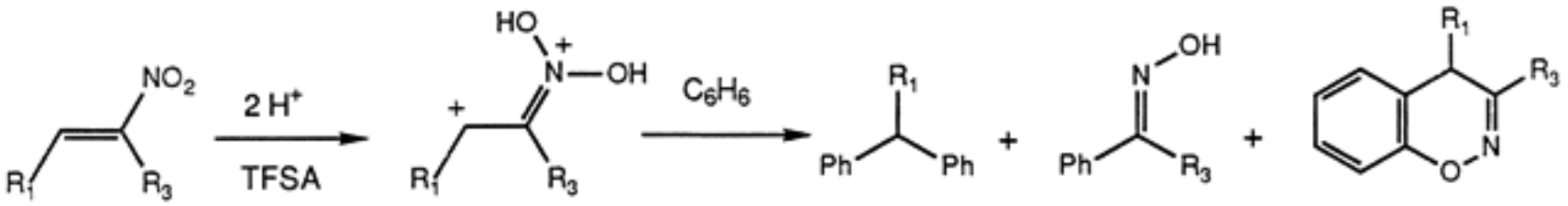

**Scheme VIII**

methanol in the presence of TFSA, cyclizes to the fluorene (Scheme VII).[14] The positive charge of this ion, because of charge-charge repulsion, is more delocalized onto the aromatic ring as compared with that of the benzyl cation. The species with the positive charge substantially delocalized over the aromatic rings has a pentadienylium character, resulting in the facile 4π electrocyclization reaction. For the present reactions, we propose a similar mechanism involving phenylethylene dications **18** and equilibrating cisoid **19** substituted with hydroxylamine, which

can be formed from the common intermediate **5e** through elimination of a proton at the $C_2$ position (**20**) and subsequent elimination of water from **20** (via **21**) (Scheme VIII). In the course of the elimination of water, *trans* elimination about the C-N bond may be preferred. [15] The oxime-cation **22** must be protonated in the strong acid to give **18**. The dication (**18**) would have a substantial contribution of quinoid resonance structures (**18**d, e). The dication can also be in equilibrium with the dication **19**(a-e), exhibiting a U-shaped hexatrienylium character, represented by an N,O-diprotonated ene-nitroso character (**19**c), in a similar manner to the dication **17**. [14] The increased delocalization of positive charge of the dication **19** facilitates intramolecular 6π electrocyclization in a disrotatory mode to form the 4H-1,2-benzoxazine **10e**. The dication **18** would react intermolecularly with another benzene on the aromatic nucleus to give biphenylacetone oximes **11e** and **12e**. The positive charge delocalization over the aromatic ring may be enhanced in favor of the resonance structures (**18**d, e) by the presence of an electron-donating group on the aromatic ring of **18**. Predominant formation of biaryl products (**13** and **14**) in the case of substituted benzenes may be due to this extensive charge delocalization onto the ring and slow equilibration with the corresponding cisoid dication, like **19** . The formation of biphenylacetone oximes is the first example of an intermolecular reaction on the benzene ring of phenylethylene dications.

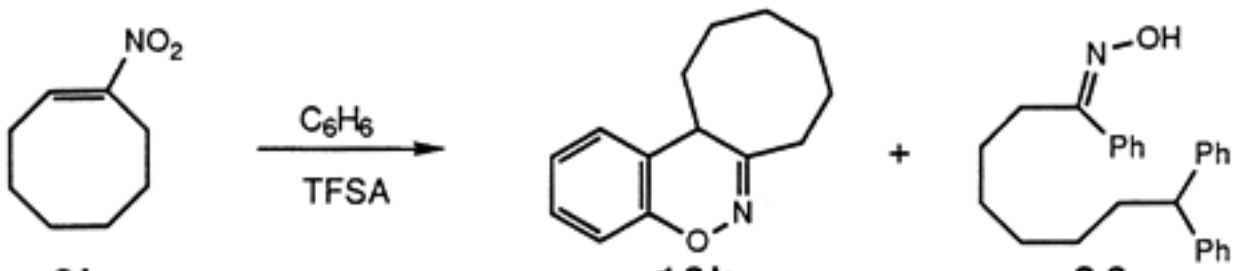
### Substituent Effects of the Reaction

In our previous study we showed that the dication **1d** formed from β-methyl-β-nitrostyrene **2d** reacts with benzene at 8 °C for 6 hr to yield triphenylmethane **23d** (77 %) and acetophenone oxime **24d** (90 %) , together with acetophenone (10%) and 3-methyl-4-phenyl-4H-1,2-benzoxazine **10d** (10 %) (Scheme IX). [3] The former products are formed from a diphenylated intermediate derived from the dication **1d**: the protonated *aci*-nitro species **5d** reacts with the second benzene under the strongly acidic conditions (i.e., after further protonation) to afford the intermediate, the N,N-dihydroxylamine or its protonated form (**25d**) (Scheme X). The intermediate **25d** eliminates water, accompanied with C-C bond cleavage, forming the stable diphenylmethyl cation and acetophenone oxime (**24d**). The former cation reacts with another benzene to give **23d** (Scheme X). This C-C bond cleavage reaction also takes place in 1,2-dialkyl-substituted acyclic




**2d, i, j** **1d, i, j** **23d, i, j** **24d, i, j** **10d, i, j**

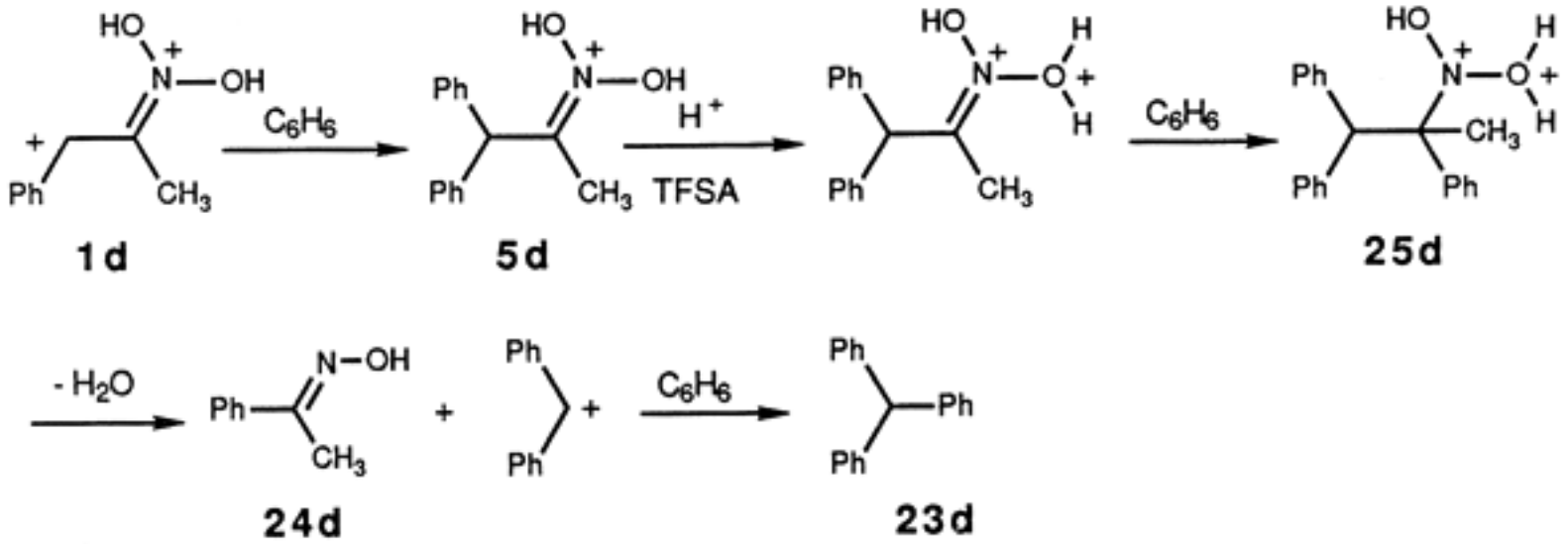
**d**: $R_1$ = Ph $R_3$ = $CH_3$, **i** $R_1$ = $CH_3$ $R_3$ = $CH_3$, **j**: $R_1$ = $C_3H_7$ $R_3$ = $C_3H_7$




**2k** **10k** **26**

**Scheme IX**

nitro olefins (such as 2-nitro-2-butene **2i** or Z-4-nitro-4-octene **2j**) and medium-sized cyclic nitro olefins (such as 1-nitro-1-cyclooctene **2k**). These nitro olefins react with benzene in the




**Scheme X**

presence of TFSA to give the corresponding 4H-1,2-benzoxazine, together with the products formed by C-C bond cleavage: **2i** ($R_1$ and $R_3 = CH_3$) yields **10i** (37 %), **23i** (24 %), and **24i** (21 %); **2j** ($R_1$ and $R_3 = C_3H_7$) yields **10j** (46 %), **23j** (44 %) and **24j** (44 %); **2k** ($R_1$, $R_3 = -(CH_2)_6-$) yields **10k** (28 %) and **26** (25 %). The divergent reaction modes can be attributed to steric and electronic effects. The reaction pathway to the benzoxazine may be retarded by the steric crowding in the protonated *aci*-nitro compounds formed from 1,2-dialkyl-substituted acyclic nitro olefins. Also the electrofugal leaving ability of the $C_1$ moiety is enhanced by the phenyl and alkyl substituents.

## Conclusion

O,O-Diprotonated nitro olefins undergo three alternative electrophilic reactions which yield α-phenylacetones, 4H-1,2-benzoxazines and biphenylacetone oximes depending on the reaction conditions (temperature and time) and aromatic substrates. The first involves quenching of an intermediate *aci*-nitro species with methanol and then water at low temperature to give 1-phenylacetones. The second mode involves the formation of 4H-1,2-benzoxazines in good yield from benzene and variously substituted O,O-diprotonated nitro olefines. This reaction can be interpreted in terms of electrocyclic ring closure of the *cisoid* phenylethylene dication intermediate **19**. The third mode involves the attempted extension of these 4H-1,2-benzoxazine forming conditions to monosubstituted benzenes whereby biarylacetone oximes were produced in moderate to good yields. The biarylacetone oximes are also postulated to be formed by an intramolecular reaction on the benzene ring of the *transoid* phenylethylene dication intermediate. These reactions provided versatile synthetic methods for novel aromatics.

## Experimental Section

**General Methods** All the melting points were measured with a Yanagimoto hot-stage melting point apparatus and are uncorrected. Proton NMR spectra were measured on either a JEOL FX 100-MHz NMR spectrometer or a JEOL GX 400-MHz NMR spectrometer with TMS as an internal reference in $CDCl_3$ as the solvent. $^{13}C$ NMR spectra were recorded on either a JEOL FX-100 (at 25.5 MHz) or a JEOL GX-400 (at 100 MHz) in $CDCl_3$ and chemical shifts are

reported in ppm, referenced by assignment of the middle resonance of deuteriochloroform as 77.0 ppm from TMS. Ultraviolet spectra were measured on a Shimadzu UV 200S at ambient temperature in 95 % EtOH. Column chromatography was performed by using silica gel (Wakogel C-200, Wako Chemical Co.) and flash column chromatography was performed on silica gel (Kieselgel 60, 230-400 mesh, Merck) with the specified solvent. Combustion analyses were carried out in the microanalytical laboratory of this Faculty.

**Materials** 2-Nitropropene (**2e**) was prepared by elimination of water from 2-nitro-1-propanol [16] with phthalic anhydride (1.35 equiv.) by heating to 140 °C under reduced pressure (78 mmHg).[17] The distilled yellow oil was dried over $CaCl_2$, and the filtrate was redistilled to give pure **2e** as yellow low-melting-point crystals (59 °C/ 80 mmHg, *lachrymatory*). $^1$H NMR: 6.42 (1H, brs), 5.60 (1H, brs), 2.26 (3H, s). 2-Nitro-1-propanol was prepared by the condensation reaction of formalin (37 % in water) and nitroethane in the presence of NaOH at ambient temperature for 3 hr (bp. 57 °C/ 1.5 mmHg). α-Nitrostyrene (**2f**) was prepared *in situ* from 1-nitro-1-phenyl-2-ethanol, which was itself prepared by the condensation reaction of formalin (37 % aq) and α-phenylnitromethane [18] in the presence of triethylamine (1 equiv.) in dioxane at -10 °C (2 hr). A solution of 1-nitro-1-phenyl-2-ethanol in ethyl acetate was treated with mesityl chloride in the presence of triethylamine. The reaction mixture was poured into 2 N aq HCl, and extracted with ethyl acetate. The organic solvent was evaporated, and the resultant residue was flash chromatographed ($CH_2Cl_2$; n-hexane 1:5) to give α-nitrostyrene (**2f**) in 59 % yield. [19] **2f**: $^1$H NMR: 7.40 (5H, m), 6.49 (d, 1H, 2 Hz), 5.86 (1H, brs). 1-Nitro-1-phenyl-2-ethanol : mp 74.5-75.5 °C (colorless needles: recrystallized from $CH_2Cl_2$/n-hexane). Anal. Calcd. for $C_8H_9NO_3$, C, 57.48; H, 5.43; N, 8.38. Found: C, 57.20; H, 5.32; N, 8.46. $^1$H NMR: 7.42 (m, 5H), 5.62 (d, d, 1H, 4 Hz, 10 Hz), 4.58 (1H, d, d, d, 13 Hz, 10 Hz, 3 Hz), 3.94 (1H, d, d, 13 Hz, 4 Hz), 2.28 (s, OH). $^{13}$C NMR: 131.3 (s), 130.1 (d), 129.1 (d), 127.6 (d), 92.4 (d), 63.7 (t). 1-Nitro-1-cycloheptene (**2h**) was prepared by oxidative deselenylation of 1-phenylselenyl-2-nitrocycloheptane. [20, 21] **2h** : yellow oil: bp 59-61 °C/ 1 mmHg>. $^1$H NMR: 7.40 (1H, t, 7 Hz), 2.88 (2H, m), 2.36 (2H, m), 1.96-1.40 (6H, m). 2-Nitro-2-butene (**2i**) was prepared as in the case of **2e**. **2i**: bp. 60 °C/17 mmHg. $^1$H NMR: 7.20 (1H, q, 6 Hz), 2.18 (3H, s), 1.90 (3H, d, 6 Hz). $^{13}$C NMR: 151.0 (s), 131.3 (d), 34.6 (t), 30.1 (t), 22.2 (t), 20.5 (t), 13.6 (q), 13.1 (q). Z-4-Nitro-4-octene (**2j**) was prepared by a similar procedure to that used in the case of **2h**. **2j**: bp. 67-69 °C/ 6 mmHg. $^1$H NMR: 5.68 (1H, t), 2.40 (4H, sextet), 1.48 (4H, m), 0.96 (6H, t). $^{13}$C NMR: 151.0 (s), 131.3 (d), 34.6 (t), 30.1 (t), 22.2 (t), 20.5 (t), 13.6 (q), 13.1 (q). 1-Nitro-1-cyclooctene (**2k**) was prepared by the action of $N_2O_4$ on cyclooctene as described previously. [22] The crude product was separated by flash column chromatography ($CH_2Cl_2$: n-hexane 2:1), and was purified by distillation under reduced pressure (70-71 °C/ 1 mmHg>). $^1$H NMR: 7.28 (1H, t, 9 Hz), 2.76 (2H, t, 6 Hz), 2.32 (2H, t x 2, 9 Hz), 1.92-1.40 (8H, m). $^{13}$C NMR: 152.0 (s), 135.9 (d), 29.0 (t), 28.2 (t), 26.6 (t), 26.4 (t), 25.7 (t), 24.8 (t).

**Acid-Catalyzed Reaction of 2-Nitropropene with Benzene at Low Temperature. Formation of Phenylacetone 4e**

**(A) Methanol and Water Work-up:** A solution of 2-nitropropene (**2e**) (299 mg) in benzene (total amount of benzene used was 30 equiv.) was added to a well-stirred mixture of TFSA (10 equiv. with respect to **2e**) and benzene with methylene chloride as a co-solvent (30 equiv. with respect to **2e**) cooled to -40 °C in a dry ice-acetone bath. The reaction mixture was poured after 1 min into a large excess of dry methanol (100 ml), cooled to -78 °C, with vigorous stirring. After being warmed to ambient temperature (10-15 min), the resultant yellow solution was diluted with water (150 ml), neutralized with powdered $NaHCO_3$ and saturated with NaCl. The solution was extracted with $CH_2Cl_2$ (400 ml), dried over $Na_2SO_4$, and concentrated, and the residue was flash-chromatographed ($CH_2Cl_2$: n-hexane 12:7) to give pure 3-phenylpropan-2-one (**4e**), 392 mg (85 %), as a colorless oil. **4e**: mp 152.5-153.5 °C (as the 2,4-dinitrophenylhydrazone, recrystallized from methanol). Anal. Calcd. for $C_{15}H_{14}N_4O_4$ (2,4-dinitrophenylhydrazone): C,

57.32; H, 4.49; N, 17.83. Found: C, 57.10; H, 4.56; N, 17.95. $^1$H NMR: 7.34 (2H, t, 7.0 Hz, 7.0 Hz), 7.27 (1H, t, 7.0 Hz, 7.0 Hz), 7.20 (2H, d, 7.0 Hz), 3.69 (2H, s), 2.15 (3H, s).

**(B) Aqueous Work-up**: The reaction mixture, obtained at -40 °C from 2-nitropropene **2e** (300.2 mg) as in **(A)** was poured after 1 min into a large excess of ice-water (200 ml). The mixture was extracted with $CH_2Cl_2$ (400 ml), dried over $Na_2SO_4$, and evaporated, and the residue was flash-chromatographed ($CH_2Cl_2$: n-hexane 12:7, subsequently, AcOEt: $CH_2Cl_2$ 1:10) to give **4e** (254.6 mg; 55 %), together with 2,2-dinitro-1-phenylpropane (94.9 mg; 13 %) and phenylacetone oxime (89.4 mg; 17 %). 2,2-Dinitro-1-phenylpropane: mp 69.0-70.0 °C, colorless needles (recrystallized from n-hexane). Anal. Calcd. for $C_9H_{10}N_2O_4$: C, 51.43; H, 4.79; N, 13.33. Found: C, 51.39; H, 4.75; N, 13.27. $^1$H NMR: 7.40-7.07 (5H, m), 3.82 (2H, s), 2.02 (3H, s). $^{13}$C NMR: 130.4, 130.0, 129.1, 128.8, 119.6, 42.4, 21.8. Phenylacetone oxime: the latter product was identical to an authentic sample in terms of the IR and $^1$H NMR spectra.

**Acid-catalyzed Reaction of 1-Nitrocyclohexene with Benzene at Low Temperature. Formation of Phenylated Ketone 4g**

The crude products, obtained from 1-nitrocyclohexene **1g** (303.5 mg) in the similar way as described above for **2e** (-40 °C, 2 hr), was flash-chromatographed (AcOEt: n-hexane 1:10) to give 2-phenylcyclohexanone **4g** (297.2 mg; 72 %). The reaction also yielded a small amount (1 %) of the 4H-1,2-benzoxazine **10g** (*vide infra*). **4g**: mp 58.0-59.0 °C , colorless needles (recrystallized from n-hexane). Anal. Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.54; H, 8.15. $^1$H NMR: 7.24-7.07 (5H, m), 3.61 (1H, d, d, 12 Hz, 6 Hz), 2.66-1.50 (8 H, m). $^{13}$C NMR: 209.4 (s), 138.6 (s), 128.3 (d), 128.0 (d), 126.4 (d), 57.1 (d), 42.0 (t), 35.0 (t), 27.6 (t), 25.1 (t).

**Acid-catalyzed Reactions of 2-Nitropropene with Substituted Benzenes at Low Temperature. Formation of Arylacetones 8A-C and 9A-C**

**(A) Anisole**: In the same way as described for the reaction with benzene, 2-nitropropene **2e** (306.0 mg) was allowed to react with anisole (30 equiv.) in the presence of TFSA (10 equiv.) at -40 °C. The reaction mixture was quenched after 1 min by pouring into methanol precooled to -78 °C and then water. The resultant crude products were separated by flash column chromatography (AcOEt: n-hexane 1:9) to give 377.6 mg (66 % yield) of o-methoxyphenylacetone (**8A**) and 153.4 mg (27 %) of p-methoxyphenylacetone (**9A**). o-Methoxyphenylacetone **8A**: mp 169.0-170.5 °C (as the 2,4-dinitrophenylhydrazone). Anal. Calcd. for $C_{16}H_{16}N_4O_5$ (as the 2,4-dinitrophenylhydrazone): C, 55.81; H, 4.68; N, 16.27. Found: C, 55.85; H, 4.68; N, 16.18. $^1$H NMR: 7.26 (1H, t, d, 2 Hz, 8 Hz), 7.13 (1H, d, d, 7.0 Hz, 1.5 Hz), 6.92 (1H, d, t, 7 Hz, 1 Hz), 6.88 (1H, d, 8.0 Hz), 3.81 (3H, s), 3.67 (2H, s), 2.13 (3H, s). p-Methoxyphenylacetone **9A**: mp 82.5-83.0 °C (as the 2,4-dinitrophenylhydrazone). Anal. Calcd. for $C_{16}H_{16}N_4O_5$: C, 55.81; H, 4.68; N, 16.27. Found: C, 56.15; H, 4.78; N, 15.97. $^1$H NMR: 7.12 (2H, d, 9.0 Hz), 6.87 (2H, d, 9 Hz), 3.80 (3H, s), 3.63 (2H, s), 2.14 (3H, s).

**(B) Toluene**: 2-Nitropropene **2e** (306.7 mg) was allowed to react with toluene (30 equiv.) in the presence of TFSA (10 equiv.) at -40 °C, and the resultant reaction mixture was quenched as described above (after 1 min). The resultant residue was flash-chromatographed to give 477.2 mg (92 %) of a mixture of o-methylphenylacetone (**8B**) and p-methylphenylacetone (**9B**) (1: 1.35, estimated from the $^1$H NMR spectrum). All spectral data were identical with those of the corresponding authentic samples, prepared from p- and o-tolylacetic acid by treatment with methyl lithium, in terms of the $^1$H NMR spectra. o-Methylphenylacetone **8B**: $^1$H NMR: 7.20-7.12 (4H, m), 3.71 (2H, s), 2.25 (3H, s), 2.14 (3H, s). $^{13}$C-NMR: 206.0 (s), 136.6 (s), 133.1 (s), 130.3 (d), 130.2 (d), 127.2 (d), 126.1 (d), 48.9 (t), 29.0 (q), 19.4 (q). p-Methylphenylacetone **9B**: $^1$H NMR: 7.14 (2H, d, 8.0 Hz), 7.09 (2H, d, 8.0 Hz), 3.65 (2H, s), 2.33 (3H, s), 2.14 (3H, s). $^{13}$C-NMR: 206.7 (s), 136.6 (s), 131.2 (s), 129.4 (d), 129.2 (d), 50.6 (t), 29.1 (q), 21.0 (q).

**(C) Chlorobenzene**: 2-Nitropropene **2e** (304.7 mg) was allowed to react with chlorobenzene (30 equiv.) in the presence of TFSA (10 equiv.) at -40 °C. After 30 min the reaction mixture was quenched as described above. The

resultant residue was flash-chromatographed (AcOEt: n-hexane 1: 10) to give 153.0 mg (26 %) of o-chlorophenylacetone (**8C**) and 388.6 mg (66 %) of p-chlorophenylacetone (**9C**). o-Chlorophenylacetone **8C**: mp 123.0-124.0 °C (as the oxime, recrystallized from n-hexane). Anal. Calcd. for $C_9H_{10}ClNO$: C, 58.87; H, 5.49; N, 7.63. Found: C, 58.91; H, 5.54; N, 7.64. $^1$H NMR: 7.40 (1H, m), 7.26-7.20 (3H, m), 3.85 (2H, s), 2.21 (3H, s). p-Chlorophenylacetone **9C**: mp 120.5-121.0 °C (as the 2,4-dinitrophenylhydrazone, recrystallized from methanol). Anal. Calcd. for $C_{15}H_{13}ClN_4O_4$: C, 51.66; H, 3.76; N, 16.07. Found: C, 51.66; H, 3.78; N, 16.00. $^1$H NMR: 7.31 (2H, d, 8 Hz), 7.13 (2H, d, 8 Hz), 3.68 (2H, s), 2.17 (3H, s).

**Acid-catalyzed Reaction of 2-Nitropropene at a Higher Temperature. Formation of 3-Methyl-4H-1,2-benzoxazine (10e)**

A solution of 2-nitropropene **2e** (296.8 mg) in benzene was added in portions to an ice-cooled mixture of 3.0 ml (10 equiv.) of TFSA and benzene (total amount of benzene used was 30 equiv., 9 ml) with vigorous stirring. Stirring was continued at 18 °C (water temperature) for 10 hr. The reaction mixture was then poured into 250 ml of ice and water, and extracted with 3 x 100 ml portions of $CH_2Cl_2$. The extract was dried over $Na_2SO_4$ and concentrated under reduced pressure. The residue was flash-chromatographed ($CH_2Cl_2$: n-hexane 12:7, then AcOEt: $CH_2Cl_2$ 1: 12) to afford 386.3 mg (77 % yield) of 3-methyl-4H-1,2-benzoxazine **10e** and 112.3 mg (15 % yield) of α-biphenylacetone oximes (*o/p* ratio 1:2, estimated from the $^1$H NMR spectrum). The α-biphenylacetone oximes were separated by a combination of fractional recrystallization (from n-hexane) and flash column chromatography to yield 2-biphenylacetone oxime **11e** (two separable isomers of the oxime) and 4-biphenylacetone oxime **12e** (a mixture of the *anti* and *syn* isomers of the oxime). **10e**: mp 47-48 °C, colorless plates (recrystallized from n-hexane). Anal. Calcd. for $C_9H_9NO$: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.16; H, 6.18; N, 9.49. $^1$H NMR: 7.30-6.88 (4H, m), 3.32 (2H, s), 2.12 (3H, s). $^{13}$C NMR: 155.9 (s), 152.1 (s), 127.4 (d), 126.9 (d), 122.9 (d), 115.7 (s), 113.4 (d), 26.6 (t), 20.5 (q). **11e** (*anti*): mp 132.0-132.5 °C (recrystallized from n-hexane). Anal. Calcd. for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 79.95; H, 6.83; N, 6.27. $^1$H NMR: 8.52 (brs, OH), 7.36-7.28 (9H, m), 3.47 (2H, s), 1.67 (s, 3H); mass spectrum: m/e 225 ($M^+$). $^{13}$C NMR: 157.6 (s), 142.4 (s), 141.4 (s), 134.2 (s), 130.1 (d), 129.6 (d), 129.2 (d), 128.1 (d), 127.5 (d), 127.0 (d), 126.6 (d), 39.4 (t), 13.6 (q). **11e** (*syn*): mp 124-126 °C (recrystallized from n-hexane). $^1$H NMR: 7.07 (bs, 1H, OH), 7.37- 7.25 (m, 9H), 3.74 (s, 2H), 1.63 (s, 3H). Mass spectrum: m/e 225 ($M^+$). **12e** : a mixture of *anti* and *syn* isomers of the oxime: mp 137-139 °C (recrystallized from n-hexane). Anal. Calcd. for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 79.82; H, 6.76; N, 6.29. $^1$H NMR: 7.59-7.26 (9H, m), 3.79 ($CH_2$, s, *syn*), 3.55 ($CH_2$, s, *anti*), 1.88 ($CH_3$, s, *syn*), 1.87 ($CH_3$, s, *anti*). $^{13}$C NMR: 140.8 (s), 139.7 (s), 139.5 (s), 135.8 (s), 129.4 (d), 128.7 (d), 127.3 (d), 127.1 (d), 41.9 (t, *anti*), 34.7 (t, *syn*), 20.0 (q, *syn*), 13.5 (q, *anti*). UV: $\lambda_{max}$ 255 nm (log ε $\lambda_{max}$ : 4.2); mass spectrum: m/e 225 ($M^+$). The structures of the biphenylacetone oximes **11e** and **12e** were confirmed by the independent synthesis starting from 2- and 4-biphenylacetic acid by methyl lithium treatment, followed by usual oximation.

A similar reaction also took place at 40 °C: heating brought about a considerable reduction in the reaction time (1 hr). A solution of 2-nitropropene **2e** (299.4 mg) in benzene was added in portions to an ice-cooled mixture of 3.0 ml (10 equiv.) of TFSA and benzene (total 9 ml, 30 equiv.) with vigorous stirring. Immediately after the addition, the mixture was heated in an oil bath at 40 °C for 1 hr with stirring. Aqueous work-up, extraction, and evaporation of the organic solvent, as described above, yielded a crude residue, which was separated by flash column chromatography ($CH_2Cl_2$: n-hexane 12: 7, then $CH_2Cl_2$: AcOEt 12: 1) to afford 404.8 mg (80 %) of **10e** and 123.3 mg of **11e** and **12e** (ratio1: 2 , estimated from the $^1$H NMR spectrum).

**Acid-catalyzed Reaction of α-Nitrostyrene 2f at a Higher Temperature. Formation of 3-Phenyl-4H-1,2-benzoxazine (10f).**

α-Nitrostyrene (**2f**) (325.4 mg) reacted in a mixture of 1.93 ml (10 equiv.) of TFSA and 5.8 ml (30 equiv.) of benzene at 25 °C for 14 hr. The crude residue was separated by flash column chromatography with $CH_2Cl_2$: n-hexane (1: 2, then 2:1) to afford 3-phenyl-4H-1,2-benzoxazine **10f** (255.1 mg, 56 %) and biphenyloximes (142.5 mg, 23 %, o/p 1:2 (**11f** and **12f**), estimated from the $^1$H NMR spectrum). **10f**: mp 101.5-102.5 °C (recrystallized from n-hexane). Anal. Calcd. for $C_{14}H_{11}NO$: C, 80.36; H, 5.30; N, 6.69. Found: C, 80.18; H, 5.32; N, 6.88. $^1$H NMR: 7.78 (2H, m), 7.44 (3H, m), 7.24-6.96 (4H, m), 3.78 (2H, s). $^{13}$C NMR: 155.2 (s), 152.2 (s), 133.7 (s), 130.2 (d), 128.4 (d), 127.9 (d), 127.7 (d), 125.9 (d), 123.7 (d), 115.9 (s), 113.8 (d), 24.2 (t). **11f**: mp 140.5-141.5 °C (recrystallized from n-hexane). Anal. Calcd. for $C_{20}H_{17}NO$: C, 83.60; H, 5.96; N, 4.87. Found: C, 83.39; H, 6.00; N, 5.02. Mass spectrum: m/e 287 ($M^+$). $^1$H NMR: 8.17 (brd, OH, 1H), 7.30 (14H, m), 4.12 (2H, s). **12f**: mp 157.0-158.0 °C (recrystallized from n-hexane). Anal. Calcd. for $C_{20}H_{17}NO$: C, 83.60; H, 5.96; N, 4.87. Found: C, 83.73; H, 6.00; N, 4.96. $^1$H NMR: 8.50 (1H, brs, OH), 7.68-7.22 (14H, m), 4.25 (2H, s); mass spectrum: m/e 287 ($M^+$).

**Acid-catalyzed Reaction of 1-Nitrocyclohexene at a Higher Temperature. Formation of the 4H-1,2-Benzoxazine 10g.**

A solution of 302.9 mg of 1-nitrocyclohexene **2g** in benzene (total benzene was 6.3 ml, 30 equiv.) was added dropwise to a mixture of 2.1 ml of TFSA (10 equiv.) and benzene cooled to 0 °C. Stirring was continued at 18 °C for 20 hr before aqueous work-up. The resultant residue was flash-chromatographed with AcOEt: n-hexane (1: 10) as the eluent to give the 4H-1,2-benzoxazine **10g** (387.3 mg, 87 % yield) and 42.5 mg of the biphenylcyclohexanone oximes **11g** and **12g** (ratio 1: 2). **10g**: mp 63.5-64.5 °C, pale yellow plates (recrystallized from $Et_2O$/n-hexane). Anal. Calcd. for $C_{12}H_{13}NO$: C, 76.97; H, 7.00; N, 7.48. Found: C, 77.00; H, 7.06; N, 7.18. Mass spectrum: m/e 187 ($M^+$). $^1$H NMR: 7.2-6.8 (4H, m), 3.34 (1H, d, d, 13 Hz, 5 Hz), 2.66 (1H, d, 13 Hz), 2.4-1.4 (7H, m). $^{13}$C NMR: 158.4 (s), 150.4 (s), 127.6 (d), 126.1 (d), 122.6 (d), 117.3 (s), 112.9 (d), 35.1 (t), 32.4 (t), 26.6 (t), 25.4 (t). 2-(2-Biphenyl)cyclohexanone oxime **11g** (*anti*): mp 193.0-193.5 °C, colorless needles (recrystallized from $CH_2Cl_2$: n-hexane). Anal. Calcd. for $C_{18}H_{19}NO$: C, 81.48; H, 7.22; N, 5.28. Found: C, 81.20; H, 7.19; N, 5.39. $^1$H NMR: 7.16 (9H, m), 3.42 (2H, s & t, 8 Hz), 2.00-1.60 (7H, m). **11g** (*syn*): mp 153.0-154.0 °C, white powder (recrystallized from n-hexane). $^1$H NMR: 7.30 (9H, m), 4.56 (1H, t, 5 Hz), 2.50 (2H, m), 2.04-1.20 (6H, m). Mass spectrum: m/e 265 ($M^+$). 2-(4-Biphenyl)cyclohexanone oxime **12g** (*syn*): mp 142.5-143.5 °C (recrystallized from n-hexane). Anal. Calcd. for $C_{18}H_{19}NO$: C, 81.48; H, 7.22; N, 5.28. Found: C, 81.19; H, 7.32; N, 5.01. $^1$H NMR: 7.28 (9 H, m), 4.86 (1H, m), 2.60-1.40 (8H, m). **12g** (*anti*): mp 184.0-185.0 °C, colorless needles (recrystallized from n-hexane). Anal. Calcd. for $C_{18}H_{19}NO$: C, 81.48; H, 7.22; N, 5.28. Found: C, 81.23; H, 7.32; N, 5.12. $^1$H NMR: 7.62-7.20 (9H, m), 3.50 (1H, t, 7 Hz), 2.95 (1H, m), 2.36-1.30 (7H, m).

**Deoximation of Biphenylcyclohexanone Oximes 11g and 12g**

A mixture of the biphenyl oximes (**11g** and **12g**) obtained in the above reaction was deoximated by McMurry's procedure (by the action of 17 % aq $TiCl_3$).[11] The crude ketones were separated by flash column chromatography (AcOEt: n-hexane 1:12) to give 2-(2-biphenyl)cyclohexanone and 2-(4-biphenyl)cyclohexanone (40 % and 10 % yields, respectively). 2-(2-Biphenyl)cyclohexanone: mass spectrum: m/e 250 ($M^+$). $^1$H NMR: 7.44-7.12 (9H, m), 3.66 (1H, d, d, 12 Hz, 6 Hz), 2.60-1.60 (8H, m). $^{13}$C NMR: 210.5 (s), 142.1 (s), 141.6 (s), 136.7 (s), 129.9 (d), 129.0 (d), 128.6 (d), 128.1 (d), 127.4 (d), 127.0 (d), 126.5 (d), 54.4 (d), 42.4 (t), 36.0 (t), 27.8 (t), 25.8 (t). 2-(4-Biphenyl)cyclohexanone: mp 105.0-106.0 °C, white powder (recrystallized from n-hexane). Anal. Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.22; H, 7.19. $^1$H NMR: 7.58 (2H, d, d, 9 Hz, 1 Hz), 7.42 (2H, t, 8 Hz), 7.32 (1H, t, 7 Hz), 7.56 (2H, d, 8.5 Hz), 7.21 (2H, d, 8.5 Hz), 3.65 (1H, d, d, 12 Hz, 5 Hz), 2.60-2.42 (2H, m), 2.36-2.24 (1H, m), 2.23-1.95 (3H, m), 1.90-1.77 (2H, m). $^{13}$C NMR: 209.9 (s), 141.0 (s), 139.7 (s), 137.8 (s), 128.9 (d), 128.7 (d), 127.1 (d), 57.2 (d), 42.3 (t), 35.3 (t), 28.0 (t), 25.5 (t). UV: $\lambda_{max}$ 255 nm (log ε $\lambda_{max}$ 4.3).

**Acid-catalyzed Reaction of 1-Nitro-1-cycloheptene 2h. Formation of the 4H-1,2-Benzoxazine (10h).**

A solution of 1-nitro-1-cycloheptene **2h** (205.3 mg) in 1 ml of dry benzene was added to an ice-cooled mixture (5 °C ) of 1.2 ml (10 equiv.) in 2.7 ml of dry benzene (total 30 equiv.) with vigorous stirring. Stirring was continued at 8 °C for 15 hr. Aqueous work-up yielded 66 % (192.7 mg) of the 4H-1,2-benzoxazine **10h**. **10h**: colorless oil: purified by molecular distillation (33 °C (ext)/ 1 mmHg>). Anal. Calcd. for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.74; H, 7.69; N, 6.80. $^1$H NMR: 7.20-6.60 (4H, m), 2.36 (1H, m), 2.20 (1H, s), 2.0-1.2 (m, 9H). $^{13}$C NMR: 164.3 (s), 153.4 (s), 126.8 (d), 125.3 (d), 123.4 (d), 122.6 (s), 113.8 (d), 32.6 (t), 32.4 (t), 28.6 (t), 27.3 (t), 25.7 (t). Mass spectrum: m/e 210 ($M^+$).

**Acid-catalyzed Reactions of 2-Nitropropene with Substituted Benzenes. Formation of Biarylacetone Oximes.**

The acid-catalyzed reaction of 2-nitropropene with a substituted benzene was performed as described in the case of the reaction with benzene.

**(A) Anisole**: 2-Nitropropene **2e** (304.3 mg) reacted in a mixture of 3.1 ml of TFSA

(10 equiv.) and 11.3 g (30 equiv.) of anisole at 15 °C for 16 hrs. The residue, obtained by aqueous work-up, was purified twice by flash column chromatography with $CH_2Cl_2$: n-hexane and with AcOEt: n-hexane to give 609.0 mg (61 % yield) of dimethylbiphenylacetone oximes (**13A** and **14A**). In this reaction methoxyphenylacetone was also formed in 10 % yield(*o/p* ratio 7: 3). The deoximation of the oximes to the ketone was carried out by the action of aq $TiCl_3$ in dioxane (reflux for 1 hr). The major component (80 %) was (3,4'-dimethoxy-4-biphenyl)acetone (**16A**) and two other components were also assigned as the isomers of dimethoxy-substituted biphenylacetone, based on the $^1$H NMR spectrum (seven aromatic protons and two methylene protons) and GC-mass spectrum (m/e: 270 ($M^+$). (3,4'-Dimethoxy-4-biphenyl)acetone **16A**: mp 104.5-106.0 °C, colorless needles (recrystallized from n-hexane). $^1$H NMR: 7.52 (2H, d, 9 Hz), 7.16 (1H, d, 8 Hz), 7.10 (1H, d, d, 8 Hz, 2 Hz), 7.03 (1H, d, 1.5 Hz), 6.97 (2H, d, 9 Hz), 3.87 (3H, s), 3.85 (3H, s), 3.70 (2H, s), 2.17 (3H, s). *anti*-(3,4'-Dimethoxy-4-biphenyl)acetone oxime (*anti* **14A**): mp 125.5-127.0 °C. Anal. Calcd. for $C_{17}H_{19}NO_3$: C, 71.56; H, 6.71; N, 4.91. Found: C, 71.28; H, 6.76; N, 4.90. $^1$H NMR: 7.52 (2H, d, 8.4 Hz), 7.18 (1H, d, 7.7 Hz), 7.09 (1H, d, d, 7.9 Hz, 1.7 Hz), 7.04 (1H, d, 1.5 Hz), 6.97 (2H, d, 8.8 Hz), 3.90 (3H, s), 3.85 (3H, s), 3.54 (2H, s), 1.86 (3H, s). *syn*-(3,4'-dimethoxy-4-biphenyl)acetone oxime (*syn* **14A**): mp 120.0-121.5 °C. Anal. Calcd. for $C_{17}H_{19}NO_3$: C, 71.56; H, 6.71; N, 4.91. Found: C, 71.28; H, 6.68; N, 4.97. $^1$H NMR: 7.52 (2H, d, 8.8 Hz), 7.19 (1H, d, 7.7 Hz), 7.09 (1H, d, d, 7.9 Hz, 1.6 Hz), 7.03 (1H, bs), 6.98 (2H, d, 8.4 Hz), 3.90 (3H, s), 3.86 (3H, s), 3.76 (2H, s), 1.79 (3H, s).

**(B) Toluene**: 2-Nitropropene **2e** (304.3 mg) was treated with a mixture of 3.1 ml of TFSA (10 equiv.) and 9.65 g (30 equiv.) of toluene at 15 °C for 16 hr. Aqueous work-up and extraction yielded the residue, which was separated by flash column chromatography ($CH_2Cl_2$) to give 732.8 mg (83 % yield) of dimethyl-substituted biphenylacetone oximes. Deoximation of the oximes to the corresponding ketones was conducted by the action of aqueous $TiCl_3$ in dioxane, and the resultant residue was flash-chromatographed (AcOEt: n-hexane 1:12) to give **15B** and **16B** (622 mg, **15B**/**16B** 2: 1, estimated from the $^1$H NMR spectrum). (5,4'-Dimethoxy-2-biphenyl)acetone **15B**: mp 171.0-172.5 °C, yellow needles (as the 2,4-dinitrophenylhydrazone, recrystallized from n-hexane). Anal. Calcd. for $C_{23}H_{22}N_4O_4$: C, 66.02; H, 5.30; N, 13.39. Found: C, 66.27; H, 5.35; N, 13.63. $^1$H-NMR : 7.20 (2H, d, 8 Hz), 7.13 (3H, m), 7.12 (2H, d, 8 Hz), 3.65 (2H, s), 2.39 (3H, s), 2.36 (3H, s), 1.99 (3H, s). UV: $\lambda_{max}$ 237 nm and 214 nm. (3,4'-Dimethyl-4-biphenyl)acetone **16B**: $^1$H NMR: 7.48 (2H, d, 8 Hz), 7.40 (brs, 1H), 7.39 (1H, d, 8 Hz), 7.23 (2H, d, 8 Hz), 7.18 (1H, d, 8 Hz), 3.74 (2H, s), 2.39 (s, 3H), 2.30 (s, 3H), 2.18 (s, 3H). UV: $\lambda_{max}$ 257 nm, 210 nm.

**(C) Chlorobenzene**: 2-Nitropropene **2e** (299.7 mg) was treated with a mixture of 3.05 ml (10 equiv.) of TFSA and 11.63 g (30 equiv.) of chlorobenzene at 15 °C for 19 hrs. The residue, after aqueous work-up, was flash-chromatographed ($CH_2Cl_2$) to afford 874.1 mg (86 % yield) of dichlorobiphenylacetone oximes. The mixture of the oximes was deoximated by the action of 17 % aq $TiCl_3$ in dioxane (10 ml) under reflux for 2 hr. After aqueous work-up, the crude product was flash-chromatographed (AcOEt: n-hexane 1:9) to give 732.4 mg of ketones (76 % from **2e**). The major component of the ketones was (4, 5'-dichloro-2-biphenyl)acetone **16C**. (4, 5'-Dichloro-2-biphenyl)acetone **16C**: mp 152.5-153.5 °C (as the 2,4-dinitrophenylhydrazone) (recrystallized from methanol-$CH_2Cl_2$). Anal. Calcd. for $C_{21}H_{16}N_4O_4Cl_2$: C, 54.92; H, 3.51; N, 12.20. Found: C, 55.06; H, 3.48; N, 12.12. $^1$H NMR: 7.38 (2H, d, 8 Hz), 7.32 (1H, d, d, 8 Hz, 2 Hz), 7.24 (1H, d, 2 Hz), 7.14 (1H, d, 8 Hz), 7.15 (2H, d, 8.5 Hz), 3.63 (2H, s), 2.03 (3H, s). The mixture of ketones (732.4 mg) was hydrodehalogenated over Pd-on-C in EtOH at ambient temperature for 24 hrs, and the products were separated by flash column chromatography (AcOEt: n-hexane 1: 4) to give 290.0 mg (53 %) of (2-biphenyl)acetone and 119.5 mg (21.5 %) of 1-(4-biphenyl)-2-propanol. 1-(4-Biphenyl)-2-propanol: mp 59.5-60.5 °C, white powder (recrystallized from n-hexane). Anal. Calcd. for $C_{15}H_{16}O$: C, 84.87; H, 7.60; N, 0.0. Found: C, 84.64; H, 7.60; N, 0.0. $^1$H NMR: 7.58 (2H, d, d, 7 Hz, 1.5 Hz), 7.55 (2H, d, 8 Hz), 7.43 (2H, d, d, 7 Hz, 7 Hz), 7.34 (1H, t, t, 7 Hz, 1.5 Hz), 7.29 (2H, d, 8 Hz), 4.07 (1H, m), 2.84 (1H, d,d, 13 Hz, 5 Hz) 2.73 (1H, d, d, 13 Hz, 8 Hz), 1.56 (1H, brs, OH), 1.28 (3H, d, 6 Hz).

**Acid-catalyzed Reaction of 2-Nitro-2-butene 2i**

A solution of 2-nitro-2-butene **2i** (321.2 mg) in 2 ml of dry benzene was added dropwise to a mixture of 2.65 ml (10 equiv.) of TFSA and 6 ml of benzene (total benzene used was 30 equiv.) at 0 °C with stirring. Stirring was continued at 18 °C (in a water bath) for 15 hrs before usual aqueous work-up. The crude residue was separated by flash column chromatography with $CH_2Cl_2$: n-hexane (2: 3) as the eluent to give 189.4 mg (37 %) of the 4H-1,2-benzoxazine **10i**, 138.2 mg (24 %) of 1,1-diphenylethane **23i** and 89.0 mg (21 %) of acetophenone oxime **24i** . **10i**: volatile colorless oil. Mass spectrum: m/e 161 ($M^+$). $^1$H NMR: 7.22-6.80 (4H, m), 3.38 (1H, q, 7 Hz), 2.12 (3H, s), 1.36 (3H, d, 7 Hz). $^{13}$C NMR: 160.3 (s), 152.3 (s), 127.3 (d), 126.2 (d), 123.4 (d), 122.0 (s), 113.7 (d), 31.9 (d), 19.6 (q), 19.0 (q). **23i**: the IR spectrum of **23i** was identical with that of an authentic sample. **24i**: $^1$H NMR: 7.68-7.58 (2H, m), 7.54-7.24 (3H, m), 2.25 (3H, s). $^{13}$C NMR: 155.8 (s), 136.3 (s), 129.0 (d), 128.3 (d), 125.9 (d), 12.4 (q).

**Acid-catalyzed Reaction of Z-4-Nitro-4-octene 2j**

A solution of Z-4-nitro-4-octene **2j** (314.8 mg) in 1.3 ml of dry benzene was added to an ice-cooled mixture of 1.76 ml (10 equiv) of TFSA and 4 ml of benzene (total benzene used was 30 equiv.). Stirring was continued at 18 °C for 15 hrs before usual aqueous work-up. The resultant crude products were separated by flash column chromatography ($CH_2Cl_2$: n-hexane 2: 3) to give 201.8 mg (46 %) of the 4H-1,2-benzoxazine **10j**, 184.5 mg (44 %) of 1,1-diphenylbutane **23j** and 142.8 mg (44 %) of phenylbutanonoxime **24j**. **10j**: colorless oil, purified by molecular distillation (25 °C (ext)/ 1 mmHg>) Anal. Calcd. for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.11; H, 8.97; N, 6.53. $^1$H NMR: 7.32-7.20 (2 H, m), 7.10-6.96 (2 H, m), 3.36 (1 H, t), 2.80-2.32 (3H, m), 1.80-1.12 (7 H, m), 1.00-0.84 (4H, m). $^{13}$C NMR: 163.0 (s), 153.4 (s), 127.3 (d), 127.2 (d), 123.2 (d), 121.5 (s), 114.1 (d), 37.2 (d), 35.8 (t), 35.4 (t), 19.5 (t x 2), 13.8(q x 2). **23j**: colorless oil, purified by molecular distillation (32 °C (ext)/ 1 mmHg). $^1$H NMR: 7.21 (10H, m), 3.90 (1H, t), 2.98 (2H, q), 1.28 (2H, m), 0.92 (3H, t). $^{13}$C NMR: 145.2 (s), 128.2 (d), 127.7 (d), 125.8 (d), 51.1 (d), 38.0 (t), 21.2 (t), 14.1 (q). The IR spectrum of **23j** was identical with that of an authentic sample, prepared by hydrogenation of 1,1-diphenyl-1-butene. **24j**: mp 44-44.5 °C, purified by molecular distillation: 33 °C (ext)/ 1 mmHg>. Anal. Calcd. for $C_{10}H_{13}NO$: C, 73.59; H, 8.03; N, 8.58. Found: C, 73.34; H, 8.04; N, 8.40. $^1$H NMR: 7.64-7.40 (2H, m), 7.40-7.00 (3H, m), 2.88-2.60 (2H, t), 1.80-1.32 (2H, sextet), 1.08-0.80 (3H, t). $^{13}$C NMR: 159.4 (s), 135.8 (s), 128.9 (d), 128.4 (d), 126.2 (d), 28.2 (t), 19.9 (t), 14.3 (q).

**Acid-catalyzed Reaction of 1-Nitro-1-Cyclooctene 2k**

1-Nitrocyclooctene **2k** (938.6 mg) reacted with benzene (100 equiv.) in the presence of TFSA (10 equiv.) at 18 °C for 15 hrs. The resulatant residue was chromatographed with AcOEt: n-hexane (1: 4) to give 369.3 mg (28 % yield) of the 4H-1,2-benzoxazine **10k** and 583.3 mg (25 % yield) of the C-C bond cleavage product **26**. **10k**: mp 77-77.5 °C (recrystallized from n-hexane). Anal. Calcd. for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51. Found: C, 78.10; H, 8.09; N, 6.24. $^1$H NMR 7.34-7.0 (4H, m), 3.50 (1H, m), 2.84-2.40 (2H, m), 2.0-1.2 (10H, m). $^{13}$C NMR: 166.6 (s), 154.1 (s), 126.9 (d), 125.9 (d), 124.6 (s), 123.6 (d), 114.3 (d), 37.3 (d), 36.5 (t), 32.8 (t), 27.9 (t), 24.6 (t), 23.8 (t), 21.7 (t); mass spectrum: m/e 215 ($M^+$). **26**: mp 68 °C (recrystallized from n-hexane). Anal. Calcd. for $C_{26}H_{29}NO$: C, 84.05; H, 7.87; N, 3.77. Found: C, 83.94; H, 8.01; N, 3.77. $^1$H NMR: 7.88 (1H, brs, OH), 7.62-7.42 (2H, m), 7.40-7.0 (13H, m), 3.86 (1H, t), 2.76 (2H, m), 2.00 (2H, m), 1.74-1.00 (8H, m). $^{13}$C NMR: 159.3 (s), 145.0 (s), 135.5 (s), 128.9 (d), 128.3 (d), 128.1 (d), 127.6 (d), 126.0 (d), 125.8 (d), 51.2 (d), 35.7 (t), 29.2 (t), 27.8 (t), 26.2 (t).

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(6) Nitronic acids react with benzene at the *ipso* position of the nitro group to give the phenylated oximes in the presence of TFSA. The reaction with benzene is not catalyzed by trifluoro-acetic acid, which is sufficiently acidic to monoprotonate a nitronic acid to the protonated aci-nitro form. The reaction requires a stronger acid, trifluoromethane sulfonic-acid, suggesting intervention of the dication formed by N,O-diprotonation of *aci*-nitro aikanes rather than the monoprotonated *aci*-nitro alkane.

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$$R_1R_2C{=}N^+(OH)O^- \rightarrow R_1R_2C{=}O + H^+ + HNO + H_2O \quad \text{(eq. 1)}$$

$$R_1R_2C{=}N^+(OH)O^- + HNO \rightarrow R_1R_2C{=}N\text{-}OH + HNO_2 \quad \text{(eq. 2)}$$

$$R_1R_2C{=}N^+(O^-)O^- + NO^+ \rightarrow R_1R_2C(NO)(NO_2) \rightarrow R_1R_2C(NO_2)(NO_2) \quad \text{(eq. 3)}$$

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