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

![Scheme I](image)

a: \(R_1 = \text{Ph}, R_2 = \text{H}\), b: \(R_1 = R_2 = \text{CH}_3\), c: \(R_1 = R_2 = \text{H}\)

species formed in TFSA is the O,O-diprotonated β-nitrostyrene (the N,N-dihydroxyiminium-benzyl dication 1a, \(R_1 = \text{Ph}, R_2 = \text{H}\)) (Scheme I).

Initially, we thought that the formation of the dication (1a) depended on the substituent effect of the phenyl group, stabilizing the cation center (C2) by conjugation. However, a similar dication (1b, \(R_1 = \text{Ph} \quad \text{and} \quad \text{R}_2 = \text{CH}_3\)) 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. Furthermore, the parent dication, the N,N-dihydroxyiminium-methylethyl dication
(1c, R1 and R2 = 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).

\[
\begin{align*}
\text{Chart} \\
\end{align*}
\]

β-Methyl-β-nitrostyrene 2d also yields a stable O,O-diprotonated dication 1d (R1 = Ph, R3 = CH3) 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 (R1 = H, R3 = CH3), 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 (CH3), the cation is stable and does not react with another benzene at the
O,O-Diprotonated nitroolefins with benzenes

\[
\begin{align*}
2d-h & \xrightarrow{2H^+} 1d-h \\
& \xrightarrow{\text{TFSA}} \text{C}_6\text{H}_6 \xrightarrow{-40 ^\circ \text{C}} \text{MeOH} \xrightarrow{\text{H}_2\text{O}} 4d-h
\end{align*}
\]

\[
d: R_1 = \text{Ph}, R_3 = \text{CH}_3, e: R_1 = \text{H}, R_3 = \text{CH}_3, f: R_1 = \text{H}, R_3 = \text{Ph},
g: R_1, R_3 = -(\text{CH}_2)_4-, h: R_1, R_3 = -(\text{CH}_2)_5-
\]

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) \textsuperscript{3, 6} with another benzene to give a diphenylated oxime

\[
\begin{align*}
+ & \xrightarrow{\text{C}_6\text{H}_6} \text{CH}_3 \xrightarrow{\text{MeOH}} \text{CH}_3 \rightarrow \text{OCH}_3 \xrightarrow{\text{H}_2\text{O}} \text{CH}_3
\end{align*}
\]

(as shown in Scheme I). \textsuperscript{7} Treatment of the intermediate solution with methanol, followed by aqueous work-up, quantitatively converts the stable protonated \textit{aci} -nitro compound to the corresponding carbonyl compound by a mechanism similar to that of the Nef reaction \textsuperscript{8} (5 $\rightarrow$ 6 $\rightarrow$ 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 \(\alpha\)-phenylacetone: straightforward aqueous quenching of the reaction mixture (5e obtained after 1 min at -40 \(^\circ\) C) gave the ketone 4e in a lower yield (55 \%), together with 1-phenyl-2,2-dinitropropane (13 \%) and \(\alpha\)-phenylacetone oxime (17 \%). \textsuperscript{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

\[
\begin{align*}
1e & \xrightarrow{-40 ^\circ \text{C}} \text{MeOH} \xrightarrow{\text{H}_2\text{O}} 8A, B, C \\
& \xrightarrow{\text{X}} 9A, B, C
\end{align*}
\]

A: \(X = \text{OCH}_3\), B: \(X = \text{CH}_3\), C: \(X = \text{Cl}\)

Scheme IV
similar reaction conditions (Scheme IV). 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-diphenylacetonitrile 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). 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

<table>
<thead>
<tr>
<th></th>
<th>R₁</th>
<th>R₃</th>
<th>Temp.</th>
<th>time</th>
<th>4</th>
<th>10</th>
<th>11 and 12</th>
</tr>
</thead>
<tbody>
<tr>
<td>2e</td>
<td>H</td>
<td>CH₃</td>
<td>-40 °C</td>
<td>1 min</td>
<td>85 %</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2e</td>
<td>H</td>
<td>CH₃</td>
<td>18 °C</td>
<td>10 hr</td>
<td>-</td>
<td>77 %</td>
<td>15 %</td>
</tr>
<tr>
<td>2e</td>
<td>H</td>
<td>CH₃</td>
<td>40 °C</td>
<td>1 hr</td>
<td>-</td>
<td>80 %</td>
<td>16 %</td>
</tr>
<tr>
<td>2f</td>
<td>H</td>
<td>Ph</td>
<td>25 °C</td>
<td>14 hr</td>
<td>-</td>
<td>56 %</td>
<td>23 %</td>
</tr>
<tr>
<td>2g</td>
<td>-(CH₂)₄-</td>
<td>-40 °C</td>
<td>2 hr</td>
<td>72 %</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2g</td>
<td>-(CH₂)₄-</td>
<td>18 °C</td>
<td>20 hr</td>
<td>-</td>
<td>87 %</td>
<td>7 %</td>
<td></td>
</tr>
<tr>
<td>2g</td>
<td>-(CH₂)₄-</td>
<td>40 °C</td>
<td>4 hr</td>
<td>-</td>
<td>87 %</td>
<td>6 %</td>
<td></td>
</tr>
<tr>
<td>2h</td>
<td>-(CH₂)₅-</td>
<td>8 °C</td>
<td>15 hr</td>
<td>-</td>
<td>66 %</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The 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 (R₁, R₃ = -(CH₂)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 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 ¹H-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 TiCl₃.¹¹ 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

<table>
<thead>
<tr>
<th>Nitro Olefin</th>
<th>Aromatic</th>
<th>Temp</th>
<th>time</th>
<th>Biarylacetone oximes (Biarylacetone)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2e</td>
<td>benzene</td>
<td>18°C</td>
<td>10 hr</td>
<td>15 % a,b</td>
</tr>
<tr>
<td>2e</td>
<td>anisole</td>
<td>15°C</td>
<td>16 hr</td>
<td>61 % c (54 %)</td>
</tr>
<tr>
<td>2e</td>
<td>toluene</td>
<td>15°C</td>
<td>16 hr</td>
<td>83 % d (75 %)</td>
</tr>
<tr>
<td>2e</td>
<td>chlorobenzene</td>
<td>15°C</td>
<td>19 hr</td>
<td>86 % e (76 %)</td>
</tr>
</tbody>
</table>

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). 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, which is in accord with experimental observation. 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 = OCH₃), which can be formed from α-carbomethoxy-diphenyl-
methanol in the presence of TFSA, cyclizes to the fluorene (Scheme VII). 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 pentadienyl cation 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 C2 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. 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 (18d, 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 (19c), in a similar manner to the dication 17. The increased delocalization of positive charge of the dication 19 facilitates intramolecular 6\pi
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 (18d, 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). 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

\[
\begin{align*}
\text{2d, i, j} & \quad 2\text{H}^+ \quad \text{TFSA} \\
\text{1d, i, j} & \quad \text{C}_6\text{H}_6 \\
\text{23d, i, j} & \quad \text{24d, i, j} \\
\text{10d, i, j} & \\
\end{align*}
\]

\[d: R_1 = \text{Ph} \quad R_3 = \text{CH}_3, \quad i: R_1 = \text{CH}_3 \quad R_3 = \text{CH}_3, \quad j: R_1 = \text{C}_9\text{H}_7 \quad R_3 = \text{C}_9\text{H}_7\]

\[
\begin{align*}
\text{2k} & \quad \text{C}_6\text{H}_6 \quad \text{TFSA} \\
\text{10k} & \quad \text{26} \\
\end{align*}
\]

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 presence of TFSA to give the corresponding 4H-1,2-benzoxazine, together with the products formed by C-C bond cleavage: 2i (R₁ and R₃ = CH₃) yields 10i (37 %), 23i (24 %), and 24i (21 %); 2j (R₁ and R₃ = C₃H₇) yields 10j (46 %), 23j (44 %) and 24j (44 %); 2k (R₁, R₃ = -(CH₂)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 C₁ 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 olefins. This reaction can be interpreted in terms of electrocyclic ring closure of the cisoid phyleneethylene 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 phyleneethylene 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 CDCl₃ as the solvent. ¹³C NMR spectra were recorded on either a JEOL FX-100 (at 25.5 MHz) or a JEOL GX-400 (at 100 MHz) in CDCl₃ 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 with phthalic anhydride (1.35 equiv.) by heating to 140 °C under reduced pressure (78 mmHg). The distilled yellow oil was dried over CaCl₂, and the filtrate was redistilled to give pure 2e as yellow low-melting-point crystals (59 °C/80 mmHg, lachratory). ¹H 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 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 (CH₂Cl₂; n-hexane 1:5) to give α-nitrostyrene (2f) in 59 % yield.

2f: ¹H NMR: 7.40 (5H, m), 6.49 (1H, 2H), 5.86 (1H, brs). 1-Nitro-1-phenyl-2-ethanol: mp 74.5-75.5 °C (colorless needles; recrystallized from CH₂Cl₂/n-hexane). Anal. Calcd. for C₇H₅NO₃, C, 57.48; H, 5.43; N, 8.38. Found: C, 57.20; H, 5.32; N, 8.46. ¹H NMR: 7.42 (m, 5H), 5.62 (d, 1H, 4H, 10H), 4.58 (1H, d, d, 13H, 10H, 3H), 3.94 (1H, d, d, 13H, 4H), 2.28 (s, OH). ¹³C 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-1-nitrocycloheptane. ²⁰ ²¹ 2h: yellow oil: bp 59-61 °C/1 mmHg>. ¹H NMR: 7.40 (1H, t, 7H), 2.80 (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. ¹H NMR: 7.20 (1H, q, 6H), 2.18 (3H, s), 1.90 (3H, d, 6H). ¹³C 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). 2-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. ¹H NMR: 5.88 (1H, t), 2.40 (4H, sextet), 1.48 (4H, m), 0.96 (6H, t). ¹³C 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 N₂O₄ on cyclooctene as described previously. ²² The crude product was separated by flash column chromatography (CH₂Cl₂; n-hexane 2:1), and was purified by distillation under reduced pressure (70-71 °C/1 mmHg>). ¹H NMR: 7.28 (1H, t, 9H), 2.76 (2H, t, 6H), 2.32 (2H, t, 2, 9H), 1.92-1.40 (8H, m). ¹³C 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) in a dry ice-acetone bath. After being warmed to ambient temperature (10-15 min), the resultant yellow solution was diluted with water (150 ml), neutralized with powdered NaHCO₃ and saturated with NaCl. The solution was extracted with CH₂Cl₂ (400 ml), dried over Na₂SO₄, and concentrated, and the residue was flash-chromatographed (CH₂Cl₂; 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 C₁₅H₁₄N₄O₄ (2,4-dinitrophenylhydrazone): C,
O,O-Diprotonated nitroolefins with benzenes

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\(_2\)Cl\(_2\) (400 ml), dried over Na\(_2\)SO\(_4\), and evaporated, and the residue was flash-chromatographed (CH\(_2\)Cl\(_2\): n-hexane 1:2, subsequently, AcOEt: CH\(_2\)Cl\(_2\) 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\(_9\)H\(_{10}\)N\(_2\)O\(_4\): 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, 41.2, 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 (8H, 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\(_{16}\)NO\(_4\): 0.5 (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, t, 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\(_{16}\)NO\(_4\): 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 C9H10ClNO: C, 58.87; H, 5.49; N, 7.63. Found: C, 58.91; H, 5.54; N, 7.64. 1H 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 C15H13ClN4O4: C, 51.66; H, 3.76; N, 16.07. Found: C, 51.66; H, 3.78; N, 16.00. 1H 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-Nitroprene at a Higher Temperature. Formation of 3-Methyl-4H-1,2-benzoxazine (10e)

A solution of 2-nitroprene 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 CH2Cl2. The extract was dried over Na2SO4 and concentrated under reduced pressure. The residue was flash-chromatographed (CH2Cl2: n-hexane 12:7, then AcOEt: CH2Cl2 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 (α/β ratio 1:2, estimated from the 1H 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 C9H9NO: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.16; H, 6.18; N, 9.49. 1H NMR: 7.30-6.88 (4H, m), 3.32 (2H, s), 2.12 (3H, s). 13C 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 C15H15NO: C, 79.97; H, 6.71; N, 6.22. Found: C, 79.95; H, 6.83; N, 6.27. 1H 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+). 13C 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). 1H 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 C15H15NO: C, 79.97; H, 6.71; N, 6.22. Found: C, 79.82; H, 6.76; N, 6.29. 1H NMR: 7.59-7.26 (9H, m), 3.79 (CH2, s, syn), 3.55 (CH2, s, anti), 1.88 (CH3, s, syn), 1.87 (CH3, s, anti). 13C 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: λmax 255 nm (log ε λmax : 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-nitroprene 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 (CH2Cl2: n-hexane 12:7, then CH2Cl2: AcOEt 12:1) to afford 404.8 mg (80 %) of 10e and 123.3 mg of 11e and 12e (ratio1:2, estimated from the 1H 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 CH₂Cl₂: n-hexane (1: 2, then 2:1) to afford 3-phenyl-4H-1,2-benzoazine 10f (255.1 mg, 56 %) and biphenyloximes (142.5 mg, 23 %, o/p 1:2 (11f and 12f), estimated from the 1H NMR spectrum). 10f: mp 101.5-102.5 °C (recrystallized from n-hexane). Anal. Calcd. for C₁₄H₁₁NO: C, 80.36; H, 5.30; N, 6.69. Found: C, 80.18; H, 5.32; N, 6.88. 1H NMR: 7.78 (2H, m), 7.44 (3H, m), 7.24-6.96 (4H, m), 3.78 (2H, s). 13C 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 C₂₀H₁₇NO: 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+). 1H NMR: 8.17 (b rd, OH, 1H), 7.30 (14H, m), 4.12 (2H, s). 12f: mp 157.0-158.0 °C (recrystallized from n-hexane). Anal. Calcd. for C₂₀H₁₇NO: C, 83.60; H, 5.96; N, 4.87. Found: C, 83.73; H, 6.00; N, 4.96. 1H 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-benzoazine 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 Et₂O/n-hexane). Anal. Calcd. for C₁₂H₁₃NO: 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+). 1H 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). 13C 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 CH₂Cl₂: n-hexane). Anal. Calcd. for C₁₈H₁₉NO: C, 81.48; H, 7.22; N, 5.28. Found: C, 81.20; H, 7.19; N, 5.39. 1H 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). 1H 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 C₁₉H₁₉NO: C, 81.48; H, 7.22; N, 5.28. Found: C, 81.19; H, 7.32; N, 5.01. 1H NMR: 7.28 (9H, 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 C₁₉H₁₉NO: C, 81.48; H, 7.22; N, 5.28. Found: C, 81.23; H, 7.32; N, 5.12. 1H NMR: 7.62-7.20 (9H, m), 3.50 (1H, t, 7 Hz), 2.95 (1H, m), 2.36-1.30 (7H, m).

Deoxygenation of Biphenylcyclohexanone Oximes 11g and 12g

A mixture of the biphenyl oximes (11g and 12g) obtained in the above reaction was deoxygenated by McMurry's procedure (by the action of 17 % aq TiCl₃). 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+). 1H NMR: 7.44-7.12 (9H, m), 3.66 (1H, d, d, 12 Hz, 6 Hz), 2.60-1.60 (8H, m). 13C 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 C₁₉H₁₉O: C, 86.36; H, 7.25. Found: C, 86.22; H, 7.19. 1H 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). 13C 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: λ_max 255 nm (log ε 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. 1H NMR: 7.20-6.60 (4H, m), 2.36 (1H, m), 2.20 (1H, s), 2.0-1.2 (m, 9H). 13C 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-Nitropropane with Substituted Benzenes. Formation of Biarylacetone Oximes.

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

(A) Anisole: 2-Nitropropane 2e (304.3 mg) reacted in a mixture of 3.1 ml of TFSAs (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 CH2Cl2: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 deoxygenation of the oximes to the ketone was carried out by the action of aq TiCl4 in dioxane (reflux for 1 hr). The major component (80 %) was (3,4'-dimethoxy-2-biphenyl)acetone (16A) and two other components were also assigned as the isomers of dimethoxy-substituted biphenylacetone, based on the 1H NMR spectrum (seven aromatic protons and two methylene protons) and GC-mass spectrum (m/e: 270 (M+), (3,4'-Dimethoxy-2-biphenyl)acetone 16A: mp 104.5-106.0 °C, colorless needles (recrystallized from n-hexane). 1H 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-2-biphenyl)acetone oxime (anti 14A): mp 125.5-127.0 °C. Anal. Calcd. for C_{17}H_{19}NO: C, 71.56; H, 6.71; N, 4.91. Found: C, 71.28; H, 6.76; N, 4.90. 1H 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-2-biphenyl)acetone oxime (syn 14A): mp 120.0-121.5 °C. Anal. Calcd. for C_{17}H_{19}NO: C, 71.56; H, 6.71; N, 4.91. Found: C, 71.28; H, 6.68; N, 4.97. 1H 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-Nitropropane 2e (304.3 mg) was treated with a mixture of 3.1 ml of TFSAs (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 (CH2Cl2) to give 732.8 mg (83 % yield) of dimethyl-substituted biphenylacetone oximes. Deoxygenation of the oximes to the corresponding ketones was conducted by the action of aqueous TiCl4 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 1H 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_{4}O_{4}: C, 66.02; H, 5.30; N, 13.39. Found: C, 66.27; H, 5.35; N, 13.63. 1H-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: λmax 237 nm and 214 nm. (3,4'-Dimethyl-4-biphenyl)acetone 16B: 1H-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 (3H, s), 2.30 (3H, s), 2.18 (s, 3H). UV: λmax 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 (CH2Cl2) to afford 874.1 mg (86 % yield) of dichlorobiphenylacetone oximes. The mixture of the oximes was deoxygenated by the action of 17 %aq TiCl4 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: mp 152.5-153.5 °C (as the 2,4-dinitrophenylhydrazone) (recrystallized from methanol-CH2Cl2). Anal. Calcd. for C21H16N4O4Cl2: C, 54.92; H, 3.51; N, 12.20. Found: C, 55.06; H, 3.48; N, 12.12. 1H 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 hydrodehalogened 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 C15H16O: C, 84.87; H, 7.60; N, 0.0. 1H 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 CH2Cl2: 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-diphenylethylamine 23 and 89.0 mg (21 %) of acetophenone oxime 241. 10i: volatile colorless oil. Mass spectrum: m/e 161 (M+). 1H NMR: 7.22-6.80 (4H, m), 3.38 (1H, q, 7 Hz), 2.12 (3H, s), 1.36 (3H, d, 7 Hz). 13C 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). 23: the IR spectrum of 23i was identical with that of an authentic sample. 241: 1H NMR: 7.68-7.58 (2H, m), 7.54-7.24 (3H, m), 2.25 (3H, s). 13C 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 (CH2Cl2: 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 phenylbutanoxime 24j. 10j: colorless oil, purified by molecular distillation (25 °C (ext)/ 1 mmHg). Anal. Calcd. for C14H19NO: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.11; H, 8.97; N, 6.53. 1H NMR: 7.32-7.20 (2H, m), 7.10-6.96 (2H, m), 3.36 (1H, t), 2.80-2.32 (3H, m), 1.80-1.12 (7H, m), 1.00-0.84 (4H, m). 13C 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). 1H NMR: 7.21 (10H, m), 3.90 (1H, t), 2.98 (2H, q), 1.28 (2H, m), 0.92 (3H, t). 13C 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-butenone. 24j: mp 44-45 °C, purified by molecular distillation: 33 °C (ext)/ 1 mmHg. Anal. Calcd. for C10H13NO: C, 73.59; H, 8.03; N, 8.58. Found: C, 73.34; H, 8.04; N, 8.40. 1H 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). 13C 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 resultant 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. 1H NMR 7.34-7.0 (4H, m), 3.50 (1H, m), 2.84-2.40 (2H, m), 2.0-1.2 (10H, m). 13C 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. 1H 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). 13C 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).

References

(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 trifluoroacetic 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.
(9) These latter products are proposed to be formed through the following redox reactions (eq. 1-3): the aci-nitro compound (5e) was reduced to α-phenylacetone oxime by the Nef hydrolysis by-product, i.e. nitroxy (HNO) or its equivalent (eq. 1 and 2). Subsequent nitrosation of the aci-nitro compound by the action of the resultant nitrous acid yielded a geminal nitroso nitro compound which was oxidized to 1-phenyl-2,2-dinitropropane probably by the oxidizing aci-nitro compound (eq. 3).

\[ \text{R}_1\text{R}_2\text{C}=\text{N}^+\text{(OH)}\text{O}^- \rightarrow \text{R}_1\text{R}_2\text{C}=\text{O} + \text{H}^+ + \text{HNO} + \text{H}_2\text{O} \quad (\text{eq. 1}) \]
\[ \text{R}_1\text{R}_2\text{C}=\text{N}^+\text{(OH)}\text{O}^- + \text{HNO} \rightarrow \text{R}_1\text{R}_2\text{C}=\text{N-OH} + \text{HNO}_2 \quad (\text{eq. 2}) \]
\[ \text{R}_1\text{R}_2\text{C}=\text{N}^+\text{(O')O}^- + \text{NO}^+ \rightarrow \text{R}_1\text{R}_2\text{C(NO)(NO)}_2 \rightarrow \text{R}_1\text{R}_2\text{C(NO)}(\text{NO})_2 \quad (\text{eq. 3}) \]


(10) Unpublished results. We Thank Dr. Kentaro Yamaguchi, School of Pharmaceutical Sciences, Showa University for the X-ray structure analysis and helpful discussion.


(12) The ortho and para ratio of the biarylacetone oximes at this stage corresponds reasonably well to that of α-arylacetone (Table II), suggesting an involvement of the protonated aci-nitro species as a common intermediate in the formation of both the biarylacetone oximes and arylacetones.


(15) The biphenylacetone oximes 11 and 12 are isomerized to a mixture of anti and syn oximes during isolation, but, the initial products are mainly syn isomers (as shown in Scheme V).


