[CONTRIBUTION FROM THE RESEARCH LABORATORIES DIVISION, NATIONAL DAIRY PRODUCTS CORPORATION]

Reaction of Peroxyacetic Acid with α-Aralkylidenecyclanones

HENRY M. WALTON

Received February 22, 1957

The reaction of peroxyacetic acid with α-aralkylidenecyclopentanones and α-aralkylidenecyclohexanones in acetic acid media of different acidity resulted in the intrusion of an oxygen atom between the carbonyl and methylidene carbon atoms, with the formation of new 5-enoic-5-hydroxy acid δ-lactones and 6-enoic-6-hydroxy acid ε-lactones. In the presence of massive amounts of potassium acetate further oxidation of the enol lactones under conditions of their formation was effectively suppressed. α-Furfurylidenecyclohexanone reacted similarly.

As part of a program investigating the antimicrobial activity of α,β-unsaturated ketones, a series of α-aralkylidene and α-furfurylidenecyclanones (I) was prepared by the condensation of the requisite aldehydes with cyclopentanone, cyclohexanone, and 3-methylcyclohexanone.

In the course of chemical studies aiming at further utilization of cyclanones (I), their reaction with peroxyacetic acid was investigated. The reagent used in most cases was commercial peroxyacetic acid.[1]

α-Aralkylidene- and α-furfurylidenecyclanones (I) are commonly prepared by condensation of cyclopentanones and cyclohexanones with aldehydes in the presence of basic catalysts.[2a-e] This method of preparation is complicated by the tendency of cyclanones (I) to condense with a second molecule of aldehyde at the remaining activated methylene group to form 2,5- and 2,6-disubstituted products.[3] This tendency is especially pronounced in the preparation of cyclanones (I) from cyclopentanone.[4] In order to minimize the second condensation reaction, it is customary to use the ketone in one- to fourfold molar excess.[2a,5] However, a method by Poggi[2c,d] permits the preparation of I in satisfactory yields on a small scale from equimolecular quantities (0.05–0.1 mole) of benzaldehydes and cyclohexanones. With modifications this method proved capable of extension to larger scale preparations. It also proved possible to prepare α-furfurylidenecyclopentanone and a series of aralkylidenecyclopentanones (I) from the requisite aldehydes and cyclopentanone in equimolecular amounts or slight excess, by stirring the reactants in a mixture of ether and dilute alkali at room temperature. Yields ranging from 24% (*o*-chlorobenzaldehyde) to 72% (*p*-anisaldehyde) were obtained. A series of new cyclanones (I), in addition to known ones, was prepared by these methods; several of these have since been described by other workers.[3,6] Table I lists α-aralkylidenecyclopentanones which apparently have not been described to date.

TABLE I
α-ARALKYLIDENECYCLOPENTANONES (I)

Substituent in R	M.P., °C. or B.P., °C./mm.	Analyses C Calcd.	C Found	H Calcd.	H Found
o-Cl	128/0.15	59.20[a]	59.02[a]	5.35[a]	5.25[a]
p-Cl	82[b,c]	69.73	69.66	5.37	5.33
p-OCH_3	68–69[b]	77.20	77.22	6.98	6.79

[a] Analysis of semicarbazone, m.p. 230° dec., from aq. dioxane. [b] From isopropyl alcohol. [c] Semicarbazone, m.p. 213–218° dec., placed on block at 200° and heated 4°/min., from aq. dioxane. *Anal.* Calcd.: C, 59.20; H, 5.35. Found: C, 59.04; H, 5.20.

The primary oxidation of cyclanones (I) by peroxyacetic acid, with the uptake of one oxygen atom, may *a priori* take three different directions:[7] It may proceed with the addition of an oxygen atom to the ethylenic double bond and formation of oxido compounds II, or with rupture of the bond between the carbonyl group carbon and an adjacent carbon atom, with formation of the lactone structures III and IV. The reaction of peroxidic reagents with ethylenic double bonds has been widely studied. It is recognized that ethylenic bonds in conjugation with carbonyl groups may resist the attack of peroxyacids. Scission of the carbon-to-

(1) Commercial peroxyacetic acid results from the equilibration of 1.5 moles acetic acid with 1.0 mole 90% hydrogen peroxide in the presence of 1% sulfuric acid; it contains about 45% peroxyacetic acid, 6% hydrogen peroxide, and 13% water. *Cf.* F. Greenspan, *Ind. Eng. Chem.*, 39, 847 (1947); U. S. Patent 2,490,800, *Chem. Abstr.*, 44, 2013c (1950).

(2a) D. Vorländer and K. Hobohm, *Ber.*, 29, 1836 (1896); (2b) D. Vorländer and K. Kunze, *Ber.*, 59, 2081 (1926); (2c) R. Poggi and V. Guastalla, *Gazz. chim. ital.*, 61, 405 (1931); *Chem. Abstr.*, 26, 105 (1932); (2d) R. Poggi and M. Gottlieb, *Gazz. chim. ital.*, 64, 852 (1934); *Chem. Abstr.*, 29, 2152 (1935); (2e) R. Poggi and P. Saltini, *Gazz. chim. ital.*, 62, 678–86 (1932); *Chem. Abstr.*, 27, 65 (1933).

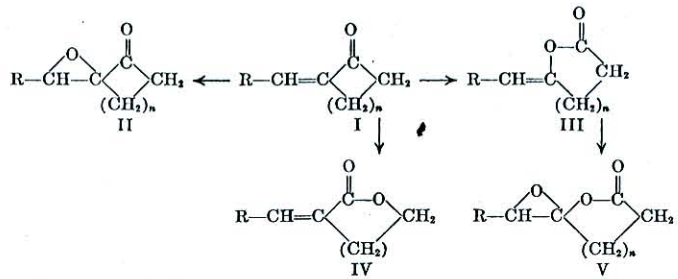
(3) *Cf.* A. C. Huitric and W. D. Kumler, *J. Am. Chem. Soc.*, 78, 614 (1956).

(4) A. Maccioni and E. Marongui, *Gazz. chim. ital.*, 85, 1570 (1955); *Chem. Abstr.*, 50, 10702f (1956).

(5) E. Braude and W. F. Forbes, *J. Chem. Soc.*, 1755 (1951).

(6) G. Vavon and J. M. Conia, *Compt. rend.*, 234, 526 (1952); R. Baltztly, E. Lorz, P. B. Russell, and F. M. Smith, *J. Am. Chem. Soc.*, 77, 624 (1955).

(7) J. Böesecken and C. O. Vermij, *Rec. trav. chim.*, 50, 1023 (1934), found that peroxyacetic acid reacts with furfural with cleavage of the carbonyl group from the furan nucleus. Hence in the case of furfuralcyclanones (I) the possibility must also be considered that they may undergo a similar side-chain cleavage at the furan α-carbon atom.



R = phenyl, substituted phenyl, 2-furyl; n = 3,4.

FIGURE 1.

carbon bond between the carbonyl and an adjacent methylene group in cyclohexanone by means of persulfuric acid has been described by Baeyer and Villiger[8] who obtained ϵ-caprolactone. In formal analogy the reaction of hydrazoic acid with cyclohexanone leads to the formation of ϵ-caprolactam.[9] The formation of lactones from cyclohexanones may also be caused by alkaline hydrogen peroxide.[10] Finally, Böeseken[11] has shown that peroxyacetic acid reacts with benzalacetone and related ketones with the intrusion of an oxygen atom between the carbonyl and styryl groups, resulting in the formation of enol esters of phenylacetaldehyde and benzyl ketones, respectively. Testa[12] has comprehensively surveyed oxidations by hydrogen peroxide and peroxyacids involving cleavage of carbon-carbon bonds. Wenkert and Rubin[13] have advanced a unifying mechanistic interpretation for the main paths that the reaction of peroxyacids and benzalacetone and related ketones might take; their interpretation appears applicable to the present case.

The reaction of peroxyacetic acid with cyclanones (I) was studied at about 30° using the cyclanones in slight molecular excess. Orienting experiments indicated that the nature of the reaction products was strongly affected by the acidity of the reaction medium. Consequently the effect of acidity on the reaction of peroxyacetic acid with cyclanones (I) was studied in three media of different acidity using acetic acid as the solvent. The most acidic media contained 0.1–0.2% sulfuric acid which was introduced *via* the peroxyacetic acid reagent. Less acidic media were obtained by the addition of small amounts of sodium or potassium acetate to the solvent in order to neutralize the sulfuric acid introduced *via* the reagent. Media of repressed acidity involved the use of saturated solutions of potassium acetate in acetic acid as the solvent. This solvent, containing about 20% of potassium acetate, gave color phenomena with various indicators, which corresponded to those obtained at *p*H 4.3–4.5 in water.

The addition of the peroxyacetic acid reagent to acetic acid resulted in the expected formation of additional peroxyacetic acid at the expense of the hydrogen peroxide in the reagent.[1] Addition of the reagent to acetic acid saturated with potassium acetate caused the decomposition of the hydrogen peroxide. The decomposition was substantially complete in several hours at room temperature and was accompanied by a slower decomposition of peroxyacetic acid.

Cyclohexanone in acetic acid and peroxyacetic acid reacted with formation of ϵ-caprolactone,[14] indicating the possibility of reaction (I) → (VI).[15] Benzalcyclanones (I, R = phenyl, n = 2,3) in acetic acid reacted vigorously with peroxyacetic acid; at the same time the hydrogen peroxide in the reagent was consumed rapidly. Complex reaction mixtures resulted and it was difficult to isolate primary oxidation products, even though the reaction was quenched when only molecular or slightly smaller proportions of active oxygen had been consumed.

When the reaction was carried out under less acidic conditions (addition of small amounts of alkali acetate to the solvent), benzalcyclopentanone yielded products which apparently resulted from further oxidation of primary oxidation products. Benzalcyclohexanone, used in 25% excess under the same conditions, afforded a moderate yield of the primary oxidation product of structure III.

When the reaction of peroxyacetic acid with (I) was conducted in acetic acid saturated with potassium acetate, peroxyacetic acid was consumed more rapidly than in the more acidic media, and hydrogen peroxide consumption was slowed. Primary oxidation products of structure III were easily isolated in yields of 60–80%. Lactones of structure III obtained by this method are listed in Table II. This table also lists lactones of structure V which were isolated from mixtures obtained by using acetic acid containing small amounts of alkali acetate as the solvent.

(8) A. v. Baeyer and V. Villiger, *Ber.*, **32**, 3625 (1899); **33**, 858 (1900).

(9) J. v. Braun and A. Heymons, *Ber.*, **63**, 502 (1930).

(10) J. Reese, *Ber.*, **75**, 384 (1942).

(11) J. Böeseken, *et al.*, *Rec. trav. chim.*, **50**, 827 (1931); **52**, 874 (1933); **55**, 786 (1936).

(12) E. Testa, *Oxydationen durch Wasserstoffperoxyd und Persäuren die zur Spaltung von C-C-Bindungen führen*, Juris Verlag, Zurich (1950).

(13) E. Wenkert and M. Rubin, *Nature*, **170**, 708 (1952).

(14) Recently reported by P. S. Starcher and B. Phillips, *Abstracts, 130th Meeting, American Chemical Society*, Atlantic City, N. J., p. 16P, September 1956.

(15) During this reaction the hydrogen peroxide contained in the reagent tended to persist although one might have expected it to be consumed, at least through continued equilibration with the acetic acid as the peroxyacetic acid was consumed. The observed protective effect of cyclohexanone on hydrogen peroxide might be ascribed to their tendency to form addition compounds, of which several are known; *cf.* R. A. Raphael, in *Chemistry of Carbon Compounds*, E. H. Road, ed., IIa, Elsevier Publishing Company, N. Y., 1953, pp. 196–7.

When the lactones (III) were obtained as solids generally having higher melting points than the antecedent ketones. They were stored in the dark under nitrogen. Without these precautions the lactones, especially the lower melting ones, tended to decompose on storage.

The structure of the new lactones follows from elemental analysis, positive tests for unsaturation, positive Legal test[16] and their ready saponification with the formation of ketoacids which were characterized as semicarbazones. These semicarbazones are listed in Table III.

Saponification of 6-phenyl-5-hydroxy-5-hexenoic acid δ-lactone (lactone 1, Table II) yielded 85% of 6-phenyl-5-oxohexanoic acid. Structure III was further supported by potassium permanganate oxidation of 7-phenyl-6-heptenoic acid ϵ-lactone (lactone 8, Table II) which afforded benzoic and adipic acid.

For purposes of comparison, commercial peroxyacetic acid was treated with acetic anhydride, resulting in a 26% peroxyacetic acid reagent which contained less than 0.4% hydrogen peroxide. Benzalcyclopentanone reacted with this reagent under conditions of different acidity with results which were similar to those obtained with commercial peroxyacetic acid. In acetic acid saturated with

TABLE II

LACTONES III AND V[a]

Lactone No.[b]	Substituent in R	n	M.P. or B.P., °C./mm.	Recrystallized from[c]	Analyses C Calcd.	C Found	H Calcd.	H Found	Sapon. Equiv. Calcd.	Sapon. Equiv. Found
1[2a]	None	2	79–80	E	76.57	76.39	6.43	6.29	188	189
2	None[d]	2	80	E	70.57	70.72	5.93	5.99	204	207
3[d]	*o*-Cl	2	113.5–114.5	A	64.72	64.91	4.98	5.10	222.7	223
4[d]	*p*-Cl	2	111–112	A	15.92[e]	15.82[e]				
5[d]	*p*-CH_3O	2	72–73	A	71.54	71.30	6.54	6.49		
6	*p*-CH_3O[d]	2	64	A	66.65	66.81	6.02	6.12		
7[f]	3,4-OCH_2O	2	96–97	E + A	67.23	66.99	5.22	5.30		
8[g]	None	3	70–71	E	77.20	76.99	6.98	6.94	202	202
9[h]	*p*-Cl	3	103–104	A	65.96	65.49	5.53	5.6		
10[2c]	*p*-CH_3O	3	67	E	72.39	72.35	6.94	6.92		
11[2e]	None	[i]	63.5	E	77.75	77.40	7.46	7.33		
12[j]	*o*-Cl	3	88–89	A	Analyzed as semicarbazone of saponification product; cf. Table III					
13[15]	R = 2-furyl	3	137/1.5		68.73	69.10	6.30	6.33	192	192

[a] Lactones V are listed following the corresponding lactones III and designated [a]. [b] Properties of the parent α-aralkylidene- and α-furfurylidenecyclanones (I) are described in the references given in this column. [c] E = isopropyl ether; A = isopropyl alcohol. [d] See Table I. [e] Cl. [f] G. Vavon and J. M. Conia, *Compt. rend.*, 234, 526 (1952). [g] O. Wallach, *Ber.*, 40, 71 (1907). [h] A. C. Huitric and W. D. Kumler, *J. Am. Chem. Soc.*, 78, 1150 (1956). [i] From 3-methyl-6-benzalcyclohexanone. [j] R. Baltzly, E. Lorz, P. B. Russell, and F. M. Smith, *J. Am. Chem. Soc.*, 77, 624 (1955).

TABLE III

SEMICARBAZONES OF KETOACIDS $RCH_2CO(CH_2)_nCO_2H$

From Lactone No.	M.P., °C.	Recrystallized from[a]	Analyses C Calcd.	C Found	H Calcd.	H Found	Neut. Equiv. Calcd.	Neut. Equiv. Found
1	162–163.5	A	59.30	59.65	6.56	6.70	263	264
5	157	A	57.31	57.31	5.62	5.62		
8	158–159	A	60.63	60.83	6.90	6.70	277	271
9	163–163.5	D	13.48[b]	13.76[b]				
12	188–189 dec.	D	11.37[b]	11.35[b]				
13	150	M	53.92	53.52	6.41	6.11	267	269

[a] A = aqueous alcohol; D = aqueous dioxane; M = aqueous methanol. [b] Cl.

(16) *Cf.* H. Meyer, *Analyse und Konstitutionsbestimmung Organischer Verbindungen*, 5th ed., Julius Springer Verlag, Vienna, 1938, p. 550.

potassium acetate, the corresponding lactone (III) was formed in somewhat higher yield than by the reaction of commercial peroxyacetic acid.

The reaction of benzalacetone, in acetic acid saturated with potassium acetate, with the 26% peroxyacetic acid reagent afforded a 65% yield of once-distilled phenylacetaldehyde enol acetate, b.p. 88–89°/1.4 mm., n_D^{20} 1.5615.[17]

Lactones of structure III, containing a double bond not conjugated with a carbonyl group, could be expected to react readily with peroxyacetic acid, a reaction which was previously inferred from the isolation of more highly oxygenated lactones presumed to have structure V (Table I). This oxidation was also effected by treating 6-phenyl-5-hydroxy-5-hexenoic acid δ-lactone (Lactone I, Table II) with peroxyacetic acid in solutions of different acidity. In this case, too, the presence of massive amounts of potassium acetate in the reaction mixture proved beneficial in channeling the reaction toward a clearly defined product containing an additional atom of oxygen; presumably it had the oxido structure V.

EXPERIMENTAL

All melting points were taken on a Fisher-Johns melting point block; the thermometer was calibrated with Keufler "Testsubstanzen." Boiling points are uncorrected.

Preparation of cyclanones (I). *p-Anisalcyclopentanone.* A mixture of *p*-anisaldehyde (28.5 g., 0.208 mole), cyclopentanone (18.0 g., 0.214 mole), ether (200 ml.), and 1*N* sodium hydroxide solution (200 ml.) was stirred for 64 hr. at room temperature. The aqueous layer was separated and extracted with ether. The combined ethereal solutions were washed to neutrality, dried briefly over magnesium sulfate, and concentrated by distillation. Vacuum distillation of the residue yielded the product, b.p. 175°/25 mm., as a light yellow oil which crystallized (30.0 g., m.p. 63–65°). Recrystallization from isopropyl alcohol afforded light yellow crystals, m.p. 68–69°.

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.22; H, 6.79.

A somewhat higher yield was obtained when the same reactants in ether (100 ml.) and 1*N* sodium hydroxide solution (450 ml.) were shaken for 15 hr. at room temperature. More reactive aldehydes required less stirring time.

Furfurylidenecyclopentanone. A mixture of redistilled furfural (32.0 g., 0.33 mole), cyclopentanone (28.0 g., 0.33 mole), ether (150 ml.), and 0.1*N* sodium hydroxide solution (300 ml.) was stirred with external cooling to moderate the exothermic reaction. After about 30 min., yellow crystalline material (presumably difurfurylidenecyclopentanone) began to separate in rapidly increasing amounts. After having been stirred for a total of 45 min., the mixture was filtered with suction. The filtered solid material as well as the separated aqueous layer of the filtrate were extracted with ether. The combined ethereal solutions were washed twice with water and concentrated on the steam bath. The residue was distilled *in vacuo*. After distillation of unreacted starting material, the product was obtained as a yellow oil having b.p. 154°/15 mm., which readily crystallized (55 g., 60% yield). After recrystallization from isopropyl ether it had m.p. 59–60°; reported m.p. 60.5°.[4]

Benzalcyclohexanone. A mixture of benzaldehyde (212 g., 2.0 moles), cyclohexanone (218 g., 2.2 moles), and 1*N* sodium hydroxide solution (1000 ml.) was stirred and heated under reflux for about 3 hr., allowed to cool and stand at room temperature overnight. Methylene chloride was added to the mixture; the aqueous layer was separated and extracted with the same solvent. The combined methylene chloride solutions were washed with water and then with water containing a few drops of acetic acid. After drying over magnesium sulfate the combined solutions were concentrated and distilled *in vacuo*. The product was obtained as a yellow oil, b.p. 173–183°/10 mm. (273 g., 73% yield). It was taken up in low boiling petroleum ether (90 ml.) and seeded. Crystallization was allowed to proceed for several hours. The liquid was decanted from the coarse crystalline material and the material was then washed with a small amount of low boiling petroleum ether. After air-drying, it had the reported melting point, 54°.[2b]

When substituted benzaldehydes were condensed with cyclohexanones, heating under reflux was applied for 5–6 hr. With less reactive aldehydes (*o*- and *p*-chlorobenzaldehyde), twofold molar quantities of cyclohexanone gave improved yields.

Furfurylidenecyclohexanone. Furfural (196 g., 2.0 moles), in two equal portions, was added to a stirred mixture of cyclohexanone (200 g., 2.05 moles) and 1*N* sodium hydroxide solution (2000 ml.). After addition of the first half-portion, the reaction mixture warmed up gradually to 34°. After 2 hr., when the temperature of the mixture had dropped to 30°, the remainder of the furfural was added and stirring continued for a total of 21 hr. A yellow precipitate was obtained which was separated by filtration and washed by slurrying with water and filtering. When this washing procedure was repeated twice, a neutral filtrate was obtained. The filter cake was washed with low boiling petroleum ether and subjected to distillation *in vacuo*. The oil obtained at 103°/0.2 mm. represented a yield of 60.5% (217 g.). The oil solidified rapidly; yellow crystals were obtained which had m.p. 46–47°, reported m.p. 47°.[18]

Peroxyacetic acid oxidation of cyclanones (I). *General procedure.* The peroxyacetic acid reagent was added rapidly with stirring to a slight molecular excess of cyclanone (I), dissolved or suspended in a five- to sixfold amount of the appropriate solvent system. The ensuing reaction was strongly exothermic. By means of external cooling the reaction mixture was maintained at 30 ± 2°. The disappearance of peroxyacetic acid and of hydrogen peroxide was followed by titration of 1-ml. samples of the mixture.[19] After 20–30 min., the reaction usually slowed down, as was shown by spontaneous cooling of the reaction mixture [chlorinated cyclanones (I) reacted more slowly]. When the temperature of the reaction mixture had returned to within 2 degrees of room temperature, 93–95% of the peroxyacetic acid had usually been consumed. At this point or, alternately, when 1.0 atom of active oxygen had been consumed, the reaction was quenched by the addition of ether and water and the product was isolated from the ethereal solution.

When the ethereal solutions that were obtained from reaction mixtures containing massive amounts of potassium acetate were evaporated on the steam bath, the evaporation residue usually crystallized on cooling, furnishing crude lactones (III); in a few cases partial purification of the crude product by vacuum distillation was necessary to bring about crystallization.

Characterization of the lactones (III) by saponification and semicarbazone formation involved saponification of the lactones in a slight excess of aqueous-alcoholic alkali and treatment of the saponification mixture with semicarbazide reagent.

6-Phenyl-5-hydroxy-5-hexenoic acid δ-lactone (Lactone 1, Table II) from (I) (*R = phenyl, n = 2*). Commercial peroxyacetic acid[20] (12 ml. containing 0.076 mole peracid) was added with stirring during 10 min. to benzalcyclopentanone (14.05 g., 0.082 mole) in glacial acetic acid saturated with potassium acetate (70 ml.). After 40 min., about 93% of the peroxyacetic acid and 53% of the hydrogen peroxide content of the reagent had been consumed; after 70 min. about 95% and 68%, respectively, had been consumed. Ether and water (100 ml. each) were added to the reaction mixture. The aqueous layer was separated and extracted twice with ether (50 ml.). The ethereal solutions were combined, washed consecutively with water (3 × 50 ml.), sodium carbonate solution (2 × 25 ml.), and again with water (2 × 50 ml.). After filtration through magnesium sulfate and concentration on the steam bath, a residue was obtained which solidified on cooling. By recrystallization from isopropyl ether it yielded colorless flakes, m.p. 79–80° (8.4 g.).

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.58; H, 6.43. Found: C, 76.39; H, 6.29.

Somewhat less pure additional material (1.0 g.) was isolated from the recrystallization mother liquors. Total yield obtained: 67% on the basis of peroxyacetic acid, 62% on the basis of the ketone used.

Potassium permanganate oxidation of 7-phenyl-6-hydroxy-6-heptenoic acid ε-lactone (VII). The lactone (2.02 g., 0.01 mole) was oxidized by stirring it with 2% potassium permanganage solution (450 ml.) for 16 hr. at room temperature. Potassium carbonate (5.0 g.) was added and stirring continued for 2 hr. Several small portions of oxalic acid were added to the mixture with warming on the steam bath, until the purple color of the solution was discharged. The resulting mixture was filtered and the filtrate evaporated on the steam bath. The solution of the residue in water (50 ml.) was acidified to *p*H 5. Solid benzoic acid separated and was removed by filtration. The filtrate was extracted twice with ether (15.10 ml.). On concentration, the ethereal extracts yielded adipic acid. Both acids were identified by their neutralization equivalents and melting points, taken separately and admixed with authentic specimen.

Peroxyacetic acid oxidation of lactones (III). A solution of 6-phenyl-5-hydroxy-5-hexenoic acid δ-lactone (Lactone I, Table II) in acetic acid saturated with potassium acetate (12 ml. solution containing 1.30 g., 5.9 millimoles, of lactone) was treated with peroxyacetic acid (2 ml. containing 6.8 millimoles of peracid and less than 0.24 millimole of hydrogen peroxide). After 1 hr., the peroxyacetic acid had been consumed. The reaction mixture was poured into water (30 ml.) and the precipitated oil was allowed to crystallize. The crystallized material was separated by filtration, washed with water and low boiling petroleum ether; after recrystallization from isopropyl ether it had m.p. 80° (0.73 g., 52% yield). Additional material was obtained by working up the recrystallization mother liquors.

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.57; H, 5.93; Sapon. equiv. 204. Found: C, 70.72; H, 5.99; Sapon. equiv. 207.

Saponification of lactone (V). The above lactone (0.10 g.) was saponified in 0.2*N* potassium hydroxide in 50% alcohol (3 ml.) at room temperature. The saponification mixture was acidified with hydrochloric acid; the precipitated organic acid was filtered and washed with water, after air-drying, the acid was recrystallized from a mixture of carbon tetrachloride and petroleum ether and then from carbon tetrachloride; it had m.p. 62° and neut. equiv. 221 (calcd., 222).

Acknowledgment. The author is indebted to S. J. Tassinari for the microanalyses reported.

OAKDALE, N. Y.

(17) J. Böeseken and A. Kremer, *Rec. trav. chim.*, **50**, 827 (1931), using distilled peroxyacetic acid, obtained a yield of 38% of twice-distilled material, n_D^{20} 1.555; as obtained by means of peroxybenzoic acid the ester had b.p. 144°/24 mm., n_D^{25} 1.559.

(18) N. Wolff, *Compt. rend.*, **174**, 1469 (1922).

(19) The method of F. P. Greenspan and D. G. Mackellar, *Anal. Chem.*, **20**, 1061 (1948) was used.

(20) "Becco 40% Peracetic Acid" was obtained from the Becco Chemical Division, Food Machinery and Chemical Corp., Buffalo 7, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Preparation and Stability of Some Organolithium Compounds in Tetrahydrofuran

HENRY GILMAN AND BERNARD J. GAJ

Received April 15, 1957

Methyl-, *n*-butyl-, and phenyllithium have been prepared in tetrahydrofuran by the interaction of methyl chloride, *n*-butyl chloride, *n*-butyl bromide, and bromobenzene, respectively, with lithium wire. The stability of these reagents in tetrahydrofuran at several temperatures has been studied. The order of stability was found to be: methyl- > phenyl- > *n*-butyllithium.

A number of studies concerned with the cleavage of ethers by organometallic reagents have been reported;[1] however, only three of these studies[1i, 1s, 1t] involved reactions of tetrahydrofuran

(1) (a) K. Ziegler and A. Colonius, *Ann.*, **479**, 135 (1930); (b) J. W. Cook, C. L. Hewett, and C. A. Lawrence, *J. Chem. Soc.*, 1936, 71; (c) W. Huckel and H. Bretschneider, *J. prakt. Chem.*, **151**, 61 (1938); (d) A. Lüttringhaus and G. Wagner-v. Sääf, *Angew. Chem.*, **51**, 915 (1938); (e) A. H. Haubein, *Iowa State Coll. J. Sci.*, **18**, 48 (1943) [*Chem. Abstr.*, **38**, 716 (1944)]; (f) A. A. Morton, *Chem. Revs.*, **35**, 21 (1944); (g) A. Lüttringhaus, G. Wagner-v. Sääf, E. Sucker, and G. Borth, *Ann.*, **557**, 46 (1947); (h) B. C. McKusick, *J. Am. Chem. Soc.*, **70**, 1976 (1948); (i) G. Wittig and A. Rückert, *Ann.*, **566**, 101 (1950); (j) K. Ziegler and H. G. Gellert, *Ann.*, **567**, 185 (1950); (k) S. J. Cristol, J. R. Douglass, and J. S. Meek, *J. Am. Chem. Soc.*, **73**, 816 (1951); (l) D. H. Gould, K. H. Schaaf, and W. L. Ruigh, *J. Am. Chem. Soc.*, **73**, 1263 (1951); (m) R. L. Letsinger, A. W. Schnizer, and E. Bobko, *J. Am. Chem. Soc.*, **73**, 5708 (1951); (n) R. L. Letsinger, J. H. Traynham, and E. Bobko, *J. Am. Chem. Soc.*, **74**, 399 (1952); (o) P. D. Bartlett, S. Friedman, and M. Stiles, *J. Am. Chem. Soc.*, **75**, 1771 (1953); (p) R. L. Letsinger and E. Bobko, *J. Am. Chem. Soc.*, **75**, 2649 (1953); (q) A. A. Morton and E. Brachman, *J. Am. Chem. Soc.*, **76**, 2973 (1954); (r) H. Gilman, A. H. Haubein, and H. Hartzfeld, *J. Org. Chem.*, **19**, 1034 (1954); (s) H. Normant, *Compt. rend.*, **239**, 1510 (1954); (t) R. L. Letsinger and D. F. Pollart, *J. Am. Chem. Soc.*, **78**, 6079 (1956).