Experimental

Ultraviolet spectra were obtained on a Beckman Model DB spectrophotometer in 95% ethanol (mean deviation ±1.0 mμ). Infrared spectra were taken on a Perkin-Elmer Model 21 spectrophotometer equipped with sodium chloride optics. The n.m.r. spectra were obtained on a Varian Model A-60 spectrometer using tetramethylsilane as an internal reference and are reported in τ (p.p.m.) units. Melting points were taken in capillaries on a Mel-Temp melting point apparatus.

Dehydroacetic Acid (II).—The enol acetate of ethyl acetoacetate [b.p. 83° (5 mm.), $n^{25}\mathrm{D}$ 1.4423, 61.2 g.], freshly distilled cyclopentadiene (19.8 g.), and hydroquinone (0.2 g.) were mixed in a glass liner and placed in a high pressure bomb at 190° for 20.5 hr. under 2000 p.s.i. of an inert gas (hydrogen). On removal from the bomb, 4 g. of polymer was filtered off and the liquid was distilled, yielding three fractions. The low-boiling fraction consisted of mainly cyclopentadiene and was stripped off and discarded. The higher boiling material was fractionated to give 35 g. of unreacted enol acetate and 6.3 g. of a white crystalline material, b.p. 126° (7 mm.), m.p. 99–100°, which melted at 110° following recrystallization from carbon tetrachloride. The solid was identified as dehydroacetic acid, giving no melting point depression on admixture with an authentic sample, m.p. 110°, prepared by the method of Arndt.[11] The acid gave the following spectral properties: ultraviolet, $\lambda_{\max}$ 225.5 mμ (log ϵ 3.99) and 311.0 mμ (log ϵ 4.05); infrared, $\lambda_{\max}^{\mathrm{CCl}_4}$ 5.70 (s), 5.75 (m), 6.06 (s), 6.16 (m), and 6.40 (s) μ; $\lambda_{\max}^{\mathrm{Nujol}}$ 5.82 (s), 6.06 (s), 6.16 (s), and 6.42 (s) μ; $\lambda_{\max}^{\mathrm{KBr}}$ 5.78 (s), 6.05 (s), 6.17 (m), and 6.40 (s) μ; n.m.r. ($CDCl_3$), τ 7.84 (3H, doublet, J = 0.8 c.p.s.), 7.43 (3H, singlet), and 4.22 (1H, quartet).

A sample of dehydroacetic acid was dissolved in D_2O containing sodium deuterioxide and examination of the n.m.r. spectrum showed rapid deuteration of the 3-acetyl group as indicated by the disappearance of the singlet at τ 7.43. No exchange with the 6-methyl was observed.

Sodium Dehydroacetate.[12]—Sodium dehydroacetate was obtained as a white salt from ethanol–water: $\lambda_{\max}$ 230 mμ (log ϵ 4.22) and 295.5 mμ (log ϵ 3.92); $\lambda_{\max}^{\mathrm{KBr}}$ 5.93 (s), 6.02 (s), 6.25 (sh), 6.34 (s), and 6.51 (ms) μ; $\lambda_{\max}^{\mathrm{Nujol}}$ 5.93 (s), 6.02 (s), 6.31 (m), 6.34 (s), and 6.51 (ms) μ.

Silver Dehydroacetate.[12]—Silver dehydroacetate was obtained as white crystals from hot water which turned gray on drying: $\lambda_{\max}$ 229 mμ (log ϵ 4.21) and 297 mμ (log ϵ 3.92); $\lambda_{\max}^{\mathrm{KBr}}$ 5.93 (s), 6.03 (s), 6.35 (s), and 6.52 (m) μ; $\lambda_{\max}^{\mathrm{Nujol}}$ 5.93 (s), 6.08 (s), and 6.41 (s) μ.

Methyl Dehydroacetate.[12]—Methyl dehydroacetate was obtained as faintly yellow needles on recrystallization from carbon tetrachloride: m.p. 91–92° (lit.[12] m.p. 93–95°); $\lambda_{\max}$ 224.5 mμ (log ϵ 3.98) and 314.5 mμ (log ϵ 3.94); $\lambda_{\max}^{\mathrm{CCl}_4}$ 5.78 (s), 5.83 (s, sh), 5.89 (s, sh), 6.08 (m), and 6.56 (m) μ; $\lambda_{\max}^{\mathrm{Nujol}}$ 5.78 (ms, sh), 5.86 (s), 5.98 (s), 6.09 (m), and 6.66 (s) μ; $\lambda_{\max}^{\mathrm{KBr}}$ 5.76 (ms, sh), 5.83 (s), 5.95 (s), 6.06 (m), and 6.64 (s) μ; n.m.r. ($CDCl_3$), τ 7.68 (3H, doublet, J = 0.8 c.p.s.), 7.55 (3H, singlet,) 6.04 (3H, singlet), and 3.77 (1H, quartet).

Ethyl Dehydroacetate.[12]—Ethyl dehydroacetate was obtained as white needles on recrystallization from carbon tetrachloride: m.p. 90–91° (lit.[12] m.p. 93–94°); $\lambda_{\max}$ 225.5 mμ (log ϵ 3.96) and 313.5 mμ (log ϵ 3.91); $\lambda_{\max}^{\mathrm{CCl}_4}$ 5.79 (s), 5.87 (s, sh), 6.07 (m), and 6.53 (ms) μ; $\lambda_{\max}^{\mathrm{Nujol}}$ 5.83 (s, sh), 5.89 (s), 6.09 (m), and 6.54 (s) μ; $\lambda_{\max}^{\mathrm{KBr}}$ 5.69 (m), 5.83 (s), 5.89 (s, sh), 6.07 (m), and 6.54 (s) μ; n.m.r. ($CDCl_3$), τ 8.57 (3H, center of triplet), 7.40 (3H, doublet, J = 0.8 c.p.s.), 7.55 (3H, singlet), 5.78 (2H, center of quartet), and 3.93 (1H, quartet).

A small sample of ethyl dehydroacetate was shaken in D_2O in the presence of sodium deuterioxide for 20 min. and extracted with chloroform-*d*. The diminished singlet at τ 7.55 in the n.m.r. indicated partial deuteration of the 3-acetyl methyl group while no exchange of the 6-methyl was observed.

Ethyl dehydroacetate (2.5 g.) was hydrogenated on a Parr hydrogenation apparatus (60 p.s.i.) using 5% Pd–C (0.5 g.) as catalyst in 35 ml. of absolute ethanol. The catalyst was removed by filtration and the ethanol solution exhibited an ultraviolet $\lambda_{\max}$ at 264.5 mμ. The solvent was removed under vacuum to give 1.5 g. of a dark oil which gave a strong, positive ferric chloride test in both water and alcohol. This material was assigned the structure of 3-acetyl-6-methyl-2-pyrone on the basis of the spectral evidence: $\lambda_{\max}^{\mathrm{CCl}_4}$, 5.81 (w–m), 6.04 (s), 6.19 (s), and 8.00 (s) μ; $\lambda_{\max}^{\mathrm{neat}}$ 5.75 (s), 6.04 (s), 6.19 (s), and 8.00 (s) μ; n.m.r. (CCl_4), τ 8.63 (3H, center of doublet, J = 7 c.p.s.), 8.07 (3H, singlet), 5.87 (1H, multiplet), and 7.84–8.50 (5H, unresolved multiplets). This oil rapidly exchanged deuterium with the 3-acetyl hydrogens as was observed by the disappearance of the singlet at τ 8.07. The deuterium exchange reactions were carried out in D_2O at *ca.* 10–15° with only a trace of sodium deuterioxide present so as to minimize any chance of β-keto ester cleavage. A quantitative hydrogenation of a 1.0-g. sample using 5% Pd–C in absolute ethanol gave absorption of 3.2 mole equiv. of hydrogen. The ethanol solution was examined by ultraviolet and showed an absence of absorptions at 225 and 313 but gave an absorption at 264.5 mμ indicating hydrogenation was complete. Hydrogenation using PtO_2 in ethanol led to a yellow oil, $n^{24}\mathrm{D}$ 1.4924, which had $\lambda_{\max}$ 294 mμ and $\lambda_{\max}^{\mathrm{CCl}_4}$ 5.74 (m, sh,) 5.85 (s), 6.05 (ms), 6.39 (s), 6.90 (ms), 7.21 (ms), 7.41 (m), 7.52 (wm), and 7.81 (s) μ. This material, which was obviously different from the product using Pd–C as catalyst, was not identified.

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The Peroxide-Induced Decarbonylation of Phenoxyacetaldehyde

JAMES W. WILT AND MARTIN P. STUMPF[1]

Department of Chemistry, Loyola University,
Chicago, Illinois 60626

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Our interest[2] in the neophyl-radical rearrangement prompted an investigation of a possibly analogous oxygen to carbon migration by phenyl. This report concerns our efforts to convert the phenoxymethyl radical (**1**) into the benzyloxy radical (**2**). Several

$$\underset{\textbf{1}}{\mathrm{Ph{-}O{-}CH_2\cdot}} \xrightarrow{?} \underset{\textbf{2}}{\mathrm{\cdot O{-}CH_2{-}Ph}}$$

items in the literature made such an investigation seem worthwhile. (1) The rearrangement appeared possible even though no steric compression exists in **1**, since Slaugh[3] found some rearrangement of phenyl in $C_6H_5CH_2CH_2\cdot$ (using labeled compounds) and showed thereby that compressional strain in the radical is not necessary for rearrangement to occur. (2) Oxygen radicals of the type sought do not usually undergo the reverse of the above rearrangement unless three aryl groups are present. Thus, **3** does not rearrange to **4**,[4] while **5** does rearrange to **6** (the Wieland rearrange-

$$\underset{\textbf{3}}{\mathrm{Ph{-}CH(CH_3){-}O\cdot}} \not\longrightarrow \underset{\textbf{4}}{\mathrm{CH_3\dot{C}H{-}OPh}}$$

$$\underset{\textbf{5}}{\mathrm{Ph_3C{-}O\cdot}} \longrightarrow \underset{\textbf{6}}{\mathrm{Ph_2\dot{C}{-}OPh}}$$

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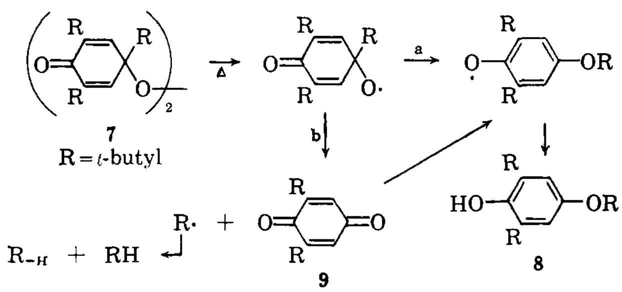
[1] From the M.S. Thesis of M. P. S., Loyola University, June 1962.

[2] J. W. Wilt and C. A. Schneider, *J. Org. Chem.*, **26**, 4196 (1961), and earlier papers.

[3] L. H. Slaugh, *J. Am. Chem. Soc.*, **81**, 2262 (1959).

[4] N. Kornblum and H. E. De La Mare, *ibid.*, **74**, 3079 (1952). This work is incorrectly ascribed to N. Kornblum and C. Teitelbaum in both Gould's text[5] and in C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 473.

ment).[6] It has been noted,[5] however, that the study of **3** was perhaps not done under conditions favorable for rearrangement (thiophenol was present); thus this example is possibly not apt. Another instance where a rearrangement of this type might have occurred was in the thermal decomposition of bis(1,3,5-tri-*t*-butyl-2,5-cyclohexadien-4-one) peroxide (**7**).[7] Some 2,6-di-*t*-butyl-4-*t*-butoxyphenol (**8**) was isolated, possibly formed as the result of the process shown as path a.



Some quinone (**9**), isobutane, and isobutylene were isolated also, however, and the formation of **8** could be accommodated just as well by a β-cleavage–readdition pathway (path b). (3) The general ease of oxygen–oxygen homolysis compared with carbon–carbon homolysis indicates a somewhat greater stability for the oxy radicals, and the enthalpic change associated with the rearrangement of **1** to **2** might therefore be favorable. This last is further borne out by the heats of formation of alkyl *vs.* alkoxy radicals; the former are in the range of 4 to 30 kcal./mole (excluding the exceptionally stable trifluoromethyl radical, whose heat of formation is -117 ± 2 kcal./mole), while the latter are in the range of -0.5 to -30 kcal./mole.[8] While not necessarily so by any means, such literature items indicate that the process **1** → **2** might proceed.

The di-*t*-butyl peroxide (DTBP) induced decarbonylation of phenoxyacetaldehyde was therefore performed. It proceeded only partially to completion, however, and yielded *only* anisole as a monomeric product. No evidence was found for the rearrangement of **1** to **2**.

$$\mathrm{PhOCH_2CHO} \xrightarrow[\Delta]{\text{DTBP}} \mathrm{PhOCH_3} + \text{polymer} + \mathrm{CO}$$

The results of the several runs made are given in Table I.

TABLE I

PHENOXYACETALDEHYDE DECARBONYLATIONS

Run	Time, hr.	% CO[a]	% anisole[a]
1	4.75	21	6
2[b]	6.25	63	21
3[c]	6.25	53	21
4[d]	9.0	52	21
5[e]	8.5	81	81

[a] Based on the aldehyde consumed. Usually 30–50% of the aldehyde was recoverable. [b] Excess peroxide was used. Normally 30 mole % of DTBP was employed (*e.g.*, run 1) at a temperature of 172°. Here, however, 225 mole % of DTBP was employed at this temperature. [c] 290 mole % of DTBP at 175°. [d] The aldehyde was 1 *M* in chlorobenzene at reflux temperature. [e] The aldehyde was 1 *M* in chlorobenzene at reflux with 5 mole % of benzyl mercaptan present.

It is seen that the yield of anisole was usually low and that generally only about one-third of the phenoxymethyl radicals (**1**) terminated as anisole. The exception was run 5 where the benzyl mercaptan present completely trapped out **1**. In all runs made, careful searching failed to find any products likely from **2** such as benzyl alcohol or benzaldehyde. Of course, neither of these two products would probably be inert under the reaction conditions. Benzaldehyde is converted to *meso*-dihydrobenzoin dibenzoate by DTBP,[9] and benzyl alcohol would be expected to give other products *via* the α-hydroxybenzyl radical.[10] The absence of either substance to the limit of detection (about 3 mole %), particularly under more dilute conditions, is considered significant.

The reported attack of phenoxymethyl radicals upon anisole[11] to yield (*inter alia*) isomeric phenoxymethylanisoles, as shown, gave a clue to the nature of the

$$\mathrm{PhOCH_3} \xrightarrow[\Delta]{\text{DTBP}} o,m,p\text{-}\mathrm{C_6H_5OCH_2{-}C_6H_4OCH_3}$$

(disappointingly intractable) residues that made up the bulk of the product in several of the runs made. These residues showed intense ether absorption (8.1 μ) in the infrared. On the other hand, only weak carbonyl absorption was noted. This argues against much *meso*-dihydrobenzoin dibenzoate[9] in the residue. Small amounts nevertheless could have been there. These facts, together with the observed molecular weight of over 400 for these residues, suggest that **1** attacked phenoxyacetaldehyde in much the same manner as **1** attacks anisole. The ensuing radicals appear to be poor chain carriers, however, because the 30 mole % of peroxide needed in this decarbonylation, rather than the 10 mole % normally effective,[2] indicates a shorter chain length than normal. Further complicating work on these residues, however, was the observation that phenoxyacetaldehyde resinified upon heating to 150° and undoubtedly thereby made up a portion of the residue itself.

It is conceivable that **2** was formed to some extent from **1** but that such rearrangement was then obscured through consumption of **2** by paths as yet unknown. The available evidence, however, suggests that the rearrangement did not occur. Dilution did not afford any change in the monomeric product, contrary to the results obtained in other systems.[12] Also, the ability of benzyl mercaptan to trap all of **1**, with no sign of rearranged products, indicated that if **1** rearranged, it did so at a slower rate than it underwent chain transfer. While this in itself is not uncommon, neither is it uncommon to observe still some rearrangement in the presence of the hydrogen donor.[12] Nonetheless, we feel that the present conditions, though worth trying, did not afford the best opportunity to observe the

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desired rearrangement. Our efforts to find this and other "hetero" analogs of the neophyl rearrangement are therefore continuing.

Experimental

Phenoxyacetaldehyde was prepared by the oxidation of glycerol α-phenyl ether (a gift from the Miner Laboratories, Chicago, Ill.) with lead tetraacetate according to Speer and Mahler[13] (48%, b.p. 82° at 4 mm., semicarbazone m.p. 144.5–145.5°, 2,4-dinitrophenylhydrazone m.p. 137.5–138°, in agreement with literature values[13]). The decarbonylations were performed as described in other work.[2] The reaction material was processed *via* gas chromatography (g.c.) on a Perkin-Elmer Model 154C instrument equipped with a column of Union Carbide X-525 silicone oil (15% on firebrick, 6 ft. × 0.25 in., 128°, helium carried gas pressure 20 p.s.i.g.) Assignment of structure to the products isolated by g.c. was *via* infrared and g.c. comparison with knowns. Mixing experiments indicated that about 3 mole % of benzyl alcohol and benzaldehyde each could readily be detected in the residues from decarbonylation. Carbon monoxide was collected over water and determined by absorption in cuprous sulfate–β-naphthol in a Fisher–Orsat apparatus. The molecular weights of the nonvolatile reaction residues from several runs were determined cryoscopically by the freezing point depression of benzene. Further details of the experiments performed may be found in Table I.

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The Thermal Decomposition of *sec*-Butyllithium

William H. Glaze, Jacob Lin, and E. G. Felton[1]

Department of Chemistry, North Texas State University, Denton, Texas

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Although the thermal decomposition of ethyllithium and *n*-butyllithium have been reported by Ziegler[2] and Bryce-Smith,[3] no systematic investigation of the reaction has been made. In the course of such a study we have examined the products of the decomposition of *sec*-butyllithium in the pure, liquid state and in hydrocarbon solutions. The solid product has been identified as virtually pure lithium hydride. With the exception of a small amount (<1%) of *n*-butane, the organic product consists of the isomers of butene shown in Table I.

Table I

Product Distributions from the Decomposition of *sec*-Butyllithium

		Olefin products (%)		
Temp., °C	Solvent	1-Butene	*cis*-2-Butene	*trans*-2-Butene
78	Pure liquid	34	51	15
80	Octane (1.84 *M*)	40	34	26

The unusual nature of this reaction is apparent when one examines other β-elimination reactions from *sec*-C_4H_9X systems. DePuy and King[4] have tabulated the distribution of butene isomers for β-elimination reactions which have been identified as typical E1, E2, or *cis*-elimination processes. It is significant that in no case does the *cis*:*trans* ratio exceed unity, and in most cases does not deviate appreciably from the "equilibrium value" which favors the *trans* isomer by a factor of 3:1 at 25°.[4]

We are unable at this time to describe the exact mechanism of the elimination of lithium hydride from alkyllithium compounds. It is clear, however, that the preference for the *cis* isomer is indicative of unusual steric requirements in the activated complex. This may be due to the well-known association of alkyllithium compounds in both the pure state and in organic solvents. Thus the crystal structure of ethyllithium consists of tetramers,[5] while hexamers and tetramers are indicated in the vapor phase[6] and in benzene.[7] *t*-Butyllithium is tetrameric in benzene.[8]

It is conceivable, for example, that the orientation of a *sec*-butyllithium tetramer into the proper conformation for *cis* β-elimination results in the preference of *cis*-2-butene over the *trans* isomer. The increase in the percentage of the latter in octane may be accounted for by a rapid equilibrium between tetramers (or hexamers) and dimers in which the steric requirements are less rigid.

Experimental

Preparation and Purification of *sec*-Butyllium.—The preparation was carried out under an argon atmosphere in a three-necked 1-l. reaction flask equipped with a Hirschberg stirrer, Friedrichs reflux condenser, and a dropping funnel. Lithium sand was prepared by rapidly shaking molten lithium metal (1.1 g.-atoms with 2% sodium,[9] Lithium Corporation of America) in mineral oil, with sodium oleate added to disperse the metal as it solidified. The metal was filtered after cooling and transferred to the flask along with 250 ml. of dry pentane (Phillip's Pure grade). *sec*-Butyl chloride (0.5 mole, Eastman Kodak, purified), mixed with 150 ml. of pentane, was placed in the dropping funnel. Approximately 10% of the chloride and a slight amount of heat were added to initiate the reaction, as evidenced by the formation of a purple-colored coating on the metal. The remainder of the halide was added dropwise over a period of 4–5 hr. After refluxing for 2 hr. longer, the reaction vessel was taken into a drybox and the mixture was filtered. The pentane solution of *sec*-butyllithium was concentrated by vacuum distillation.

Approximately 15 ml. of concentrated *sec*-butyllithium solution was transferred to a flask while still in the drybox. The flask was connected through a U-tube trap to a vacuum stopcock. The apparatus was removed from the drybox and attached to a high-vacuum line. After pumping on the system to remove the last traces of solvent, the flask was heated in a mineral oil bath at approximately 90°. The *sec*-butyllithium distilled and collected in the U-tube which was cooled with liquid air. *sec*-Butyllithium distils easily under these conditions yielding a clear, viscous liquid at room temperature. The residual pressure in the system was approximately 50 μ. The distillation flask was then sealed off, leaving the U-tube containing the *sec*-butyllithium on the vacuum line.

Thermal Decomposition of *sec*-Butyllithium.—For the decomposition of the pure liquid a thermoregulated oil bath at the desired temperature (±0.05°) was raised around the U-tube, and decomposition was followed manometrically. When the decomposition was carried out in octane solution the alkyllithium compound was transferred after distillation to the drybox where the solution was prepared. After analysis by the Gilman double titration method,[10] an appropriate amount of the solution was placed in a boiling flask with condenser attached.[11] The flask was transferred to the vacuum line and the decomposition was carried

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