The Isomerization of Allyl Phenyl Ether to Propiophenone by Way of a Dianion Intermediate

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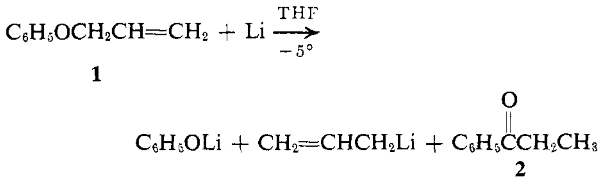
Abstract: Allyl phenyl ether (**1**) isomerizes to propiophenone (**2**) with 2 equiv of *n*-butyllithium in dimethoxyethane–hexane solvent. With only 1 equiv of *n*-butyllithium, allyl phenyl ether gives rise to α-vinylbenzyl alcohol (**3**), a Wittig rearrangement product. Further rearrangement of the alcohol to propiophenone can be brought about with *n*-butyllithium. By quenching with methyl iodide at various time intervals, it is possible to show that the following sequence of reactions is occurring during the isomerization reaction: allyl phenyl ether reacts with *n*-butyllithium to give allyl phenyl ether anion **4**, which rapidly rearranges to α-vinylbenzyl alcohol alkoxide salt **5**; the latter reacts with additional *n*-butyllithium to afford a dianion (**9**), which then abstracts a proton from the solvent to give propiophenone enolate ion (**8**). The effects of sodium amide, potassium amide, and allyllithium on allyl phenyl ether are also reported.

One of the methods of preparing allyllithium is to treat allyl phenyl ether (**1**) with lithium metal in tetrahydrofuran (THF) (eq 1).[1] While preparing allyllithium in this way we noticed that a small amount (*ca.* 5%) of propiophenone (**2**) was also formed. The finding of this unusual by-product prompted us to investigate the mechanism of this allyl phenyl ether rearrangement.



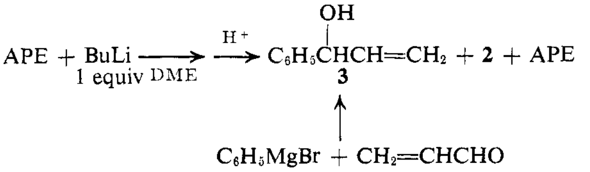
$$\underset{\mathbf{1}}{C_6H_5OCH_2CH{=}CH_2} + Li \xrightarrow[-5^\circ]{THF} C_6H_5OLi + CH_2{=}CHCH_2Li + \underset{\mathbf{2}}{C_6H_5\overset{O}{\overset{\|}{C}}CH_2CH_3} \quad (1)$$

The mechanisms initially considered were (a) a direct lithium metal reaction, possibly involving radical anion intermediates, (b) a base-catalyzed reaction as a result of the presence of allyllithium, or (c) a combination of these two.[2] The effects of allyllithium and other strong bases on allyl phenyl ether (APE) are considered here. However, because of the ease in handling and high yields of propiophenone, *n*-butyllithium was the principal base used in this study.

Results and Discussion

If 2 equiv of *n*-butyllithium in hexane were allowed to react with APE in dimethoxyethane (DME) for 4 hr at room temperature, propiophenone could be isolated in 53% yield (95% pure). Some phenol, a displacement product, was also observed (see Experimental Section). Substituting THF for DME did not significantly affect the yield or purity of the product. However, with pentane–diethyl ether solvent no ketone was observed, only α-vinylbenzyl alcohol (**3**). When pure hexane was employed as the solvent no rearrangements of any kind were detected; the APE was lost, presumably to phenol and 1-heptene.[3] The amount of ketone produced seems to vary directly with the basicity of the solvent, which in turn reflects the nucleophilic character of the carbanion.[4] DME was the principal solvent used in subsequent reactions, mainly because of the cleanliness of the reaction and for comparative purposes to other aspects of the isomerization.[2]

n-Butyllithium (1 equiv) in DME–hexane converted APE into a mixture of propiophenone, α-vinylbenzyl alcohol (**3**), and unreacted APE (eq 2). The structure of **3** was established by comparing its physical properties to that of the alcohol prepared by reacting phenylmagnesium bromide with acrolein.[5] If **3** was treated with 2 equiv of *n*-butyllithium, propiophenone was quantitatively produced. These reactions indicate that α-vinylbenzyl alcohol alkoxide salt (**5**) is a likely intermediate in the isomerization of APE to propiophenone. Ion **5** can arise by way of a Wittig rearrangement[6] of ion **4**, as shown in Scheme I. Based on the observations of Zimmerman and Grovenstein of a "phenanion" intermediate in the rearrangement of 2,2,2-triphenylethyllithium to 1,1,2-triphenylethyllithium,[7] we assume that an intramolecular phenyl migration also occurs in the rearrangement of **4** to **5**. However, it should be pointed out that our results do not rule out possible cleavage–recombination mechanisms.[6c,d]



$$\text{APE} + \text{BuLi} \xrightarrow[\text{1 equiv DME}]{} \xrightarrow{H^+} \underset{\underset{C_6H_5MgBr\, +\, CH_2{=}CHCHO}{\uparrow}}{\underset{\mathbf{3}}{C_6H_5\overset{OH}{\overset{|}{C}}HCH{=}CH_2}} + \mathbf{2} + \text{APE} \quad (2)$$

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[1] J. J. Eisch and A. M. Jacobs, *J. Org. Chem.*, **28**, 2145 (1963).

[2] The effect of alkali metals on allyl phenyl ether is presently under investigation and will be reported at a later date.

[3] Similar solvent effects have been reported by H. Felkin and A. Tambuti [*Tetrahedron Lett.*, 821 (1969)]. They observed both 1,2- and 1,4-Wittig rearrangement products (1-hepten-3-ol and heptanal) for the reaction of *n*-propyllithium with allyl butyl ether in THF–pentane; in pure pentane solvent 1-hexene was the sole product. We have not found any 1,4-Wittig rearrangement products in our studies.

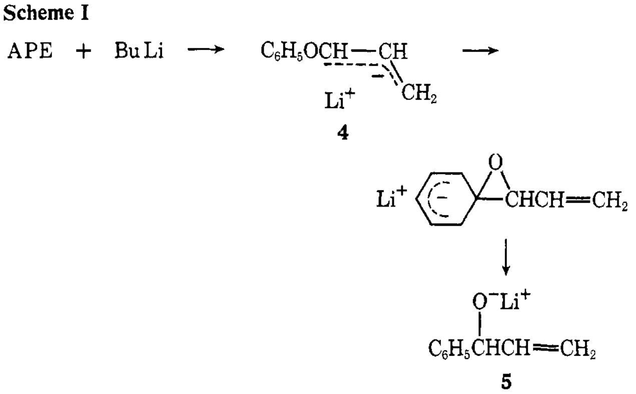
[4] (a) G. E. Coates and K. Wade, "Organometallic Compounds," 3rd ed, Vol. 1, Methuen & Co., London, 1967, p 10; (b) J. M. Mallan and R. L. Bebb, *Chem. Rev.*, **69**, 693 (1969).

[5] R. Delaby and L. Lecomte, *Bull. Soc. Chim. Fr.*, **4**, 738 (1937).

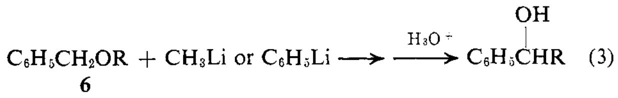
[6] (a) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, pp 230–233; (b) H. Zimmerman in "Molecular Rearrangements," Part I, P. DeMayo, Ed., Interscience, New York, N. Y., 1963, pp 372–377; (c) P. T. Lansbury, V. A. Pattison, J. D. Siller, and J. B. Bieber, *J. Amer. Chem. Soc.*, **88**, 78 (1966); (d) H. Schäfer, U. Schöllkopf, and D. Walter, *Tetrahedron Lett.*, 2809 (1968).

[7] (a) H. E. Zimmerman and A. Zweig, *J. Amer. Chem. Soc.*, **83**, 1196 (1961); (b) E. Grovenstein, Jr., and L. P. Williams, Jr., *ibid.*, **83**, 412, 2537 (1961).

Scheme I

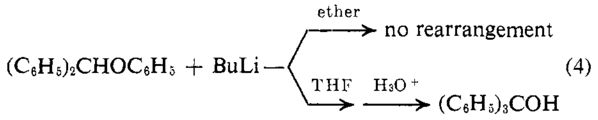


Wittig rearrangements involving phenyl as a migrating group are somewhat rare;[6a,b] for example, benzyl alkyl ethers (**6**, R = alkyl) readily rearrange to alcohols in the presence of methyl- and phenyllithium, while benzyl phenyl ether (**6**, R = C_6H_5) does not rearrange under identical conditions (eq 3).[6a,b]

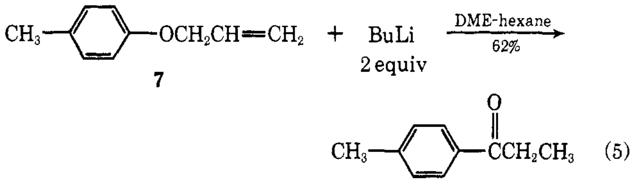


$$\underset{\mathbf{6}}{C_6H_5CH_2OR} + CH_3Li \text{ or } C_6H_5Li \longrightarrow \xrightarrow{H_3O^+} C_6H_5\overset{OH}{\overset{|}{C}}HR \quad (3)$$

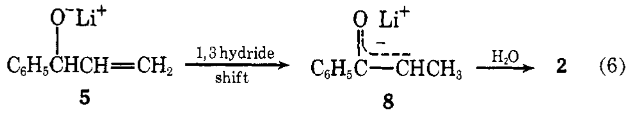
Benzhydryl phenyl ether does not rearrange with *n*-butyllithium in ether, but does rearrange with THF as the solvent (eq 4).[6b]



In contrast to these examples, we observe a good yield of Wittig rearrangement products from APE and *n*-butyllithium. Even some Wittig rearrangement occurs with ether as the solvent. Because of these unexpected differences, the rearrangement of allyl *p*-tolyl ether (**7**) was examined to determine if bond cleavage and formation occur at the same carbon of the aromatic ring as proposed in Scheme I. This, indeed, is the case since **7**, with 2 equiv of *n*-butyllithium, afforded *p*-methylpropiophenone (eq 5). The structure of this latter ketone was easily established from its nmr spectrum and conversion to the known 2,4-dinitrophenylhydrazone derivative.

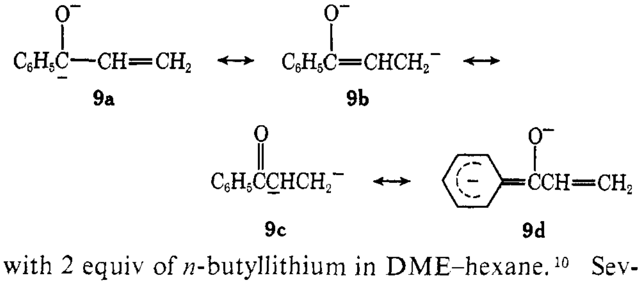


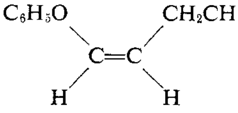
The second step in the isomerization, conversion of ion **5** to propiophenone, required 1 full equiv of *n*-butyllithium for complete reaction. This fact was established by treating APE with 1.2, 1.5, and 1.7 equiv of *n*-butyllithium and observing a proportional increase in the amount of propiophenone produced. Consequently, a simple 1,3-hydride shift from ion **5**, which does not require *n*-butyllithium, can be ruled out (eq 6).



$$\underset{\mathbf{5}}{C_6H_5\overset{O^-Li^+}{\overset{|}{C}}HCH{=}CH_2} \xrightarrow[\text{shift}]{\text{1,3 hydride}} \underset{\mathbf{8}}{C_6H_5\overset{O\ Li^+}{\overset{\|}{C}}{-}\bar{C}HCH_3} \xrightarrow{H_2O} 2 \quad (6)$$

A likely intermediate for the conversion of ion **5** to propiophenone is a dianion such as that represented by structure **9**.[8] Recent work of Hauser[9] has shown that nonaromatic dianions can be generated from many types of compounds with the aid of strong bases such as potassium amide in liquid ammonia or *n*-butyllithium in THF. In an attempt to trap the dianion **9**, methyl iodide was added 90 sec after mixing APE with 2 equiv of *n*-butyllithium in DME–hexane.[10] Several products were detected by vpc. The major ones (composing about 95% of the product mixture) were isolated by preparative vpc and characterized by spectral evidence and synthesis (see Experimental Section). Three monomethylated products were found: *cis*-butenyl phenyl ether (**10**), derived from methylation of ion **4**, 3-methoxy-3-phenyl-1-propene (**11**), derived from methylation of ion **5**, and isobutyrophenone (**12**), derived from methylation of ion **8**. Two dimethylated compounds were also isolated: pivalophenone (2,2-dimethylpropiophenone) (**13**), which is assumed[11] to arise by further methylation of isobutyrophenone, and 2-methylbutyrophenone (**14**), which would be the expected methylation product of the dianion **9**.





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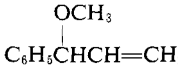
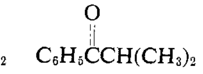


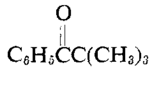
$$C_6H_5\overset{OCH_3}{\overset{|}{C}}HCH{=}CH_2$$

11



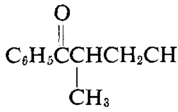
$$C_6H_5\overset{O}{\overset{\|}{C}}CH(CH_3)_2$$

12



$$C_6H_5\overset{O}{\overset{\|}{C}}C(CH_3)_3$$

13



$$C_6H_5\overset{O}{\overset{\|}{C}}\underset{CH_3}{\underset{|}{C}}HCH_2CH_3$$

14

It is of interest to note that the dianion alkylated as if it were a 1,2-dianion of the type **9c**. The dianion was formed by removing the C-1 hydrogen of ion **5**, thus initially generating the 1,2-dianion **9a**. The literature does not report any examples of 1,2-dianions or dianions which are generated one way and react a different way. Actually, a problem of nomenclature arises here since the 1,4-dianion structure **9b** would appear to be the most stable resonance form. Consequently, it is not clear what designation should be given to the dianion, 1,2 or 1,4. The previous nomenclature for dianions was logical in that the protons

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[8] Structure **9** refers to the composite of resonance structures **9a–d**.

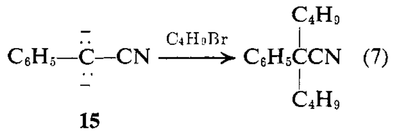
[9] F. E. Henoch, K. G. Hampton, and C. R. Hauser, *J. Amer. Chem. Soc.*, **91**, 676 (1969), and references therein.

[10] The reagents were cooled to 0° before mixing to avoid the excessive heat which was given off with rapid mixing. By monitoring the progress of the isomerization of APE (at room temperature) with vpc, it was possible to show that rearrangement of APE to alcohol **3** was complete in a few minutes and rearrangement to propiophenone was complete after 30 min.

[11] The amount of **13** produced varied with the length of reaction time with methyl iodide and with the amount of **12** formed. A subsequent kinetic run showed that **13** was not formed prior to **12**.

were being removed and replaced at the same site. For example, Kaiser and Hauser[12] refer to dianion **15** as 1,1 because of the way it was generated and the way it reacted (eq 7). However, it is obvious that

$$C_6H_5CH_2CN + 2BuLi \xrightarrow[\text{hexane}]{\text{THF}}$$



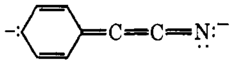
$$C_6H_5{-}\overset{..}{\underset{..}{C}}{-}CN \xrightarrow{C_4H_9Br} C_6H_5C(C_4H_9)_2CN \quad (7)$$

15

other resonance forms such as **15a** and **15b** (which are 1,3 and 1,7 dianion contributors) aid in the stability of the ion but are not alkylated as such.

$C_6H_5\overset{-}{\ddot{C}}{=}C{=}\ddot{N}:^-$

15a



15b

The amount of 2-methylbutyrophenone (**14**) produced after methylation at 90 sec reaction time was quite small—about 0.5%. The major methylated products at this time were **10** (18%) and **11** (58%). Assuming that the added methyl iodide effectively quenched all intermediates at approximately the same rate, the low yield of **14** at this early reaction time means a low concentration of dianion. If methyl iodide was added after 30 min reaction time the relative amount of **14** was much higher; actual composition was 73.5% **12**, 10.5% **14**, 8% **13**, 5.5% **11**, and 2.5% **10**. Methylation after 3 hr afforded only **12** and **13**. Since no 2-methylbutyrophenone (**14**) was observed at this longer reaction time, the dianion must have picked up a proton to yield ion **8**—the predominate species at the conclusion of the isomerization. To substantiate the limited lifetime of the dianion, the progress of the isomerization was monitored by quenching with methyl iodide at various time intervals and analyzing by vpc; the results are shown in Figure 1.[13] The data show that the concentration of dianion built in the beginning remained constant (*ca.* 10%) for a while and diminished at long reaction time.

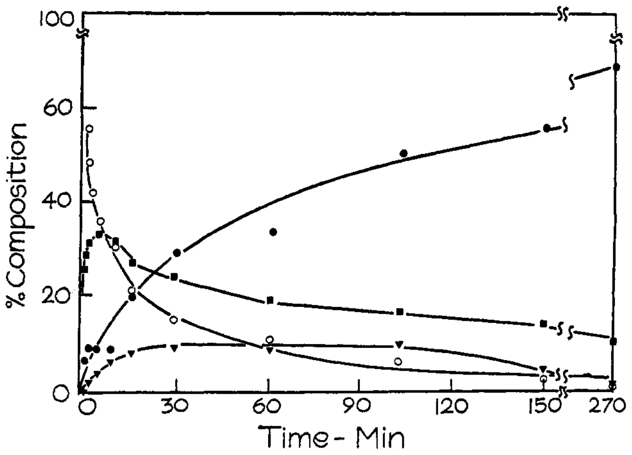
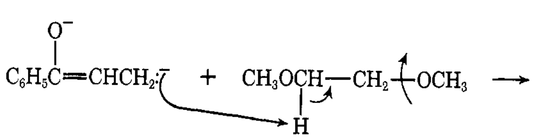


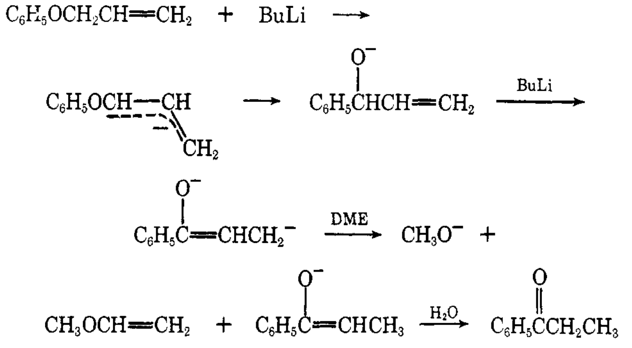
Figure 1. Product composition resulting from the methylation of APE at various time intervals: ○, amount of **10** (from ion **4**); ■, amount of **11** (from ion **5**); ▲, amount of **14** (from dianion **9**); ●, amount of **12**, **13**, and 1-methoxy-1-phenyl-1-propene (from ion **8**).

The most obvious source of protons for converting the dianion into propiophenone enolate is the solvent DME.[14] If this were the case, methyl vinyl ether (**16**) and methoxide ion should be formed (eq 8). Indeed, it was possible to detect methyl vinyl ether escaping from the isomerization reaction mixture by passing the exiting gases through 2,4-dinitrophenylhydrazine reagent, which contained sulfuric acid, and observing acetaldehyde 2,4-dinitrophenylhydrazone. Actually, it is not too surprising that dianion **9** is so reactive since, unlike most other reported dianions, it does not possess good anion stabilizing groups, like a carbonyl or cyano. A controlled experiment showed that *n*-butyllithium reacted slowly with DME, producing methyl vinyl ether. The rapid consumption of *n*-butyllithium by the reactants, however, would seem to preclude any significant reaction with the solvent. Kaiser, Henoch, and Hauser[15] have also reported an example of a reactive dianion abstracting a proton from its solvent; however, in their case the solvent was THF. It is now possible to summarize the sequence of steps involved in the isomerization of APE with *n*-butyllithium. This is shown in Scheme II.



$$\mathbf{8} + \underset{\mathbf{16}}{CH_3OCH{=}CH_2} + CH_3O^- \quad (8)$$

Scheme II



Another approach taken to study the mechanism of this rearrangement was to examine the isomerization of α,α-dideuterioallyl phenyl ether (**17**). Under a variety of conditions, however, no propiophenone was ever obtained from **17** with *n*-butyllithium. The disappearance of APE-d_2 was quite slow; in fact, the starting material was recovered—with no loss of label—in about 50% yield when 2 equiv of *n*-butyllithium were used.

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[12] E. M. Kaiser and C. R. Hauser, *J. Amer. Chem. Soc.*, **88**, 2348 (1966).

[13] In order to slow the reaction and give somewhat more accurate data, the reaction temperature employed for this run was −5° instead of the usual room temperature conditions. However, the data are still only of qualitative nature because of partial overlapping of peaks in the vpc and because corrections for differences in thermal conductivity were not made.

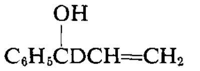
[14] The butane produced from the *n*-butyllithium reactions and the solvent hexane are unlikely proton candidates due to their volatility and inertness. The possibility that dianion **9** reacts with ion **5** to exchange a proton to yield **9** (from **5**) and **8** (from **9**) can be discounted because only a catalytic amount over 1 equiv of *n*-butyllithium would be needed to isomerize APE to propiophenone when actually 2 equiv are needed.

[15] E. M. Kaiser, F. E. Henoch, and C. R. Hauser, *J. Amer. Chem. Soc.*, **90**, 7287 (1968).

The only products that could be characterized in these reactions were phenol and 1-deuterio-1-phenyl-2-propen-1-ol (**18**). Further rearrangement of **18** with excess *n*-butyllithium could not be achieved.

$C_6H_5OCD_2CH{=}CH_2$

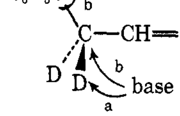
17



$C_6H_5\overset{\overset{\textstyle OH}{|}}{C}DCH{=}CH_2$

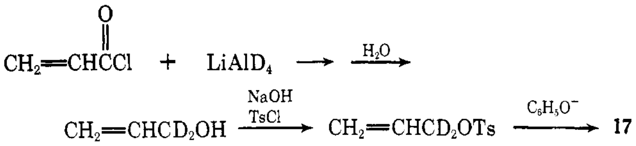
18

Obviously, we did not expect this unusually large isotope effect. The Wittig rearrangement begins with abstraction of an α-proton (path a below), a process which should be slowed by the replacement of α-hydrogens by deuteriums. Displacement of phenoxide ion (path b), which occurs to some extent with nondeuterated APE, should be relatively unaffected by substitution of α-deuteriums. Possibly the α-deuteriums significantly disrupt the balance between these competing reactions. As mentioned, the rate of disappearance of APE-d_2 was much slower than regular APE. With these longer reaction times, loss of *n*-butyllithium by reaction with the solvent[4b] could be a factor. It is not clear to us why **18** is also so unreactive.

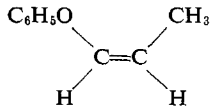


The sequence of reactions used to synthesize APE-d_2 is shown in Scheme III. Both mass spectroscopy and nmr confirmed that the APE-d_2 was greater than 98% d_2 and the label was located exclusively on the α position. Our results parallel those of Barner and Schmid,[16] who found no scrambling of ^{14}C label when treating 3-^{14}C-allyl bromide with sodium phenolate, thereby indicating that a simple S$_N$2 displacement took place at the methylene carbon of allyl bromide.

Scheme III



The action of other bases on allyl phenyl ether was also examined. Sodium amide in DME brought about an isomerization of the double bond to give a mixture of phenyl propenyl ethers, 97% cis (**19**) and 3% trans (**20**). Potassium amide in liquid ammonia, a commonly used system for generating dianions,[6] also gave a mixture of phenyl propenyl ethers; here the ratio was 65 cis:35 trans, which corresponds exactly to the reported equilibrium mixture of **19** and **20**.[17] Apparently, one does not get past the ion **4** stage with these base systems.



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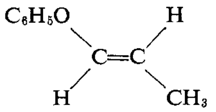

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Finally, allyllithium, prepared from tetraallyltin,[18] was mixed with a THF solution of APE and refluxed for 90 min to yield a mixture of 78% APE, 13% propiophenone (**2**), and 9% α-vinylbenzyl alcohol (**3**). Consequently, it is possible that the allyllithium produced in the cleavage of APE (eq 1) could account for the small amount of propiophenone observed in the reaction. Work is presently under way to define the scope and usefullness of these reactions for synthetic purposes.

Experimental Section

Melting points and boiling points are uncorrected. Proton magnetic resonance spectra were obtained with a Varian A-60D spectrometer using tetramethylsilane as the reference. Infrared spectra were recorded on a Perkin-Elmer Model 137B Infracord. Mass spectra were taken on a Consolidated Electrodynamics Corp. 103C mass spectrometer. Preparative and analytical analyses of liquid products were performed on a 6 ft × 0.25 in. aluminum column packed with 20% SE30 on 80–100 mesh Chromosorb W and a 13 ft × 0.25 in. aluminum column packed with 20% diethylene glycol succinate (DEGS) on 80–100 mesh Chromosorb W using an F & M Model 700 gas chromatograph equipped with a thermal conductivity detector.

All reaction solvents, except diethyl ether which was Mallinckrodt anhydrous reagent grade, were distilled directly before use. Dimethoxyethane was distilled from Na–K alloy and tetrahydrofuran from lithium aluminum hydride. The *n*-butyllithium was purchased from Alfa Inorganics, Inc., as a 22% solution in hexane; the strength of this solution changes with use and, consequently, it was necessary to titrate the solution with standardized sulfuric acid from time to time to determine its actual strength.

Allyl Phenyl Ether (1) Isomerization to Propiophenone (2). In a thoroughly dry apparatus, under nitrogen atmosphere, 5.6 ml (22.2 mmol) of *n*-butyllithium in hexane was added rapidly to a cooled solution of 1.5 g (11.1 mmol) of allyl phenyl ether[19] dissolved in 30 ml of anhydrous DME. A dark red color developed instantaneously and persisted throughout the stirring period. The reaction mixture was stirred for 4 hr at room temperature and then emptied into 30 ml of distilled water. Ether was added and the organic layer was separated. The aqueous layer was extracted with fresh ether. The combined ether extracts were washed with water, dried over sodium sulfate, and evaporated by means of a flash evaporator. Vacuum distillation of the residue afforded 0.80 g (53% yield) of propiophenone: bp 75–84° (5 mm), 2,4-DNP mp 188° (from ethanol) [lit.[20] bp 75° (3 mm), 2,4-DNP mp 187–189°]. The nmr and mass spectra of the product were identical with an authentic sample[21] of propiophenone. The mass spectrum displayed a molecular ion at *m/e* 134 and abundant peaks at *m/e* 105 (100%), 77 (37%), and 51 (20%). Analysis by vpc (DEGS) showed a purity of at least 95%.

The aqueous layer of the work-up, which was quite basic, was acidified with 10% hydrochloric acid and extracted twice with ether. The ether extracts were washed with 5% aqueous $NaHCO_3$ and water, dried (Na_2SO_4), and evaporated to yield 0.22 g (22%) of phenol.

If a trap containing 2,4-dinitrophenylhydrazine, dissolved in aqueous sulfuric acid, was attached to the apparatus and the gases being evolved from the isomerization reaction passed through the trap, a precipitate settled out. The precipitate was collected by filtration and recrystallized from ethanol to give acetaldehyde 2,4-dinitrophenylhydrazine, mp 148–149.5° (lit.[22] mp 146°).

Allyl Phenyl Ether and 1 Equiv of *n*-Butyllithium. To a solution of 2.7 g (20 mmol) of allyl phenyl ether in 30 ml of anhydrous DME was added 12.5 ml (20 mmol) of *n*-butyllithium in hexane. After stirring at room temperature for 30 min, the reaction was worked up[23] to give 1.0 g of colorless liquid, bp 130–148° (85 mm). An-

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(21) Purchased from Aldrich Chemical Co., Milwaukee, Wis.

(22) "Dictionary of Organic Compounds," 4th ed, Vol. 1, Oxford University Press, New York, N. Y., 1965, p 7.

(23) The work-up of the reaction was similar to that described for the isomerization of **1** to **2**.

alysis of the product by gas chromatography (DEGS) indicated a composition of approximately 40% **2**, 23% **1**, and 30% α-vinylbenzyl alcohol (**3**). The latter compound was separated by preparative vpc and identified by comparison of its retention time, ir, nmr, and mass spectrum to that of **3** synthesized from phenylmagnesium bromide and acrolein.[5] The spectral properties are: ir[6] (film) 3.0 (O–H), 6.09, 10.10, 10.78 ($-CH{=}CH_2$), 13.1, 13.5, 14.3 μ (Ph); nmr (CCl_4) δ 4.87–5.35 (m, 3, $-CHC{=}CH_2$), 5.62–6.20 (m, 1, $-CH{=}$), 7.00–7.35 (m, 5, Ph); mass spectrum (70 eV) *m/e* (rel intensity) 134 (61), 133 (70), 115 (44), 105 (88), 79 (82), 78 (60), 77 (100), 51 (72).

Propiophenone (2) from Rearrangement of α-Vinylbenzyl Alcohol (3). To a solution of 0.9 g (6.7 mmol) of **3** in 20 ml of anhydrous DME was added 12.5 ml (13.4 mmol) of *n*-butyllithium in hexane. A red color developed instantaneously. After stirring for 5 hr, the reaction was worked up[23] to afford 0.8 g of propiophenone, bp 64–69° (3.2 mm). Analysis by vpc and nmr indicated a purity of about 97%.

Isomerization of Allyl *p*-Tolyl Ether (7). To a solution of 2.4 g (16.3 mmol) of **7**[19] in 30 ml of anhydrous DME was added 10.7 ml (32.6 mmol) of *n*-butyllithium in hexane. A dark red color immediately developed. After stirring for 4 hr, the reaction was worked up[23] to yield 1.34 g of liquid, bp 60–160° (0.5 mm). Both vpc and nmr indicated that the product was a mixture of three components. The major compound (62%) was *p*-methylpropiophenone, 2,4-DNP mp 202–203° (lit.[20] 2,4-DNP mp 201°); nmr (CCl_4) δ 1.05 (t, 3, J = 7.0 Hz, CH_3), 2.17 (s, 3, CH_3), 2.62 (q, 2, J = 7.0 Hz, $-CH_2-$), 6.84 (d, 2, J = 8.0 Hz, aryl H ortho to CH_3), and 7.49 (d, 2, J = 8.0 Hz, aryl H ortho to keto group). The long retention time component (13%) was *p*-cresol, based on nmr and retention time comparison to an authentic sample of *p*-cresol. The short retention time component (19%) was not identified.

Methylation of the Intermediates in the Allyl Phenyl Ether Isomerization. To a solution of 3.0 g (22.4 mmol) of **1** in 37 ml of anhydrous DME, cooled to 0°, was added 11.0 ml (44.8 mmol) of *n*-butyllithium in hexane all at one time. Exactly 90 sec later, a cooled solution of 6 ml (80 mmol) of methyl iodide in 10 ml of DME was added rapidly. The mixture was stirred at room temperature for 3 hr and worked up[23] to afford 2.2 g of liquid, bp 47–105° (0.4 mm). Analysis by vpc (SE30) showed several components, the majority of which were collected by preparative vpc. The properties of the five compounds collected are reported in the following way: compound; per cent of the mixture; retention time (SE30, 85°, flow = 80 ml of He/min); major ir bands; nmr; major mass spectral peaks; other pertinent data.

3-Methoxy-3-phenyl-1-propene (11): 58%; 16 min; ir (film) 9.09 (C–O–C), 10.04, 10.76 ($-CH{=}CH_2$), 13.26, 14.36 μ (Ph); nmr (CCl_4) δ 3.23 (s, 3, $-OCH_3$), 4.52 (d, 1, J = 5.5 Hz, $>CHO-$), 5.0–5.4 (m, 2, $=CH_2$), 5.6–6.2 (m, 1, $=CH-$), 7.22 (s, 5, Ph); mass spectrum (70 eV) *m/e* (rel intensity) 148 (100), 115 (96), 94 (92), 77 (92), 51 (88); identical with a sample of **11** prepared by treating **3** with 1 equiv of *n*-butyllithium in DME–hexane and then 1 equiv of methyl iodide.

***cis*-Butenyl phenyl ether (10)**: 18%; 22 min; ir (film) 8.10 (C_6H_5-O-C), 6.02 (C=C), 13.30, 14.52 μ (Ph); nmr (CCl_4) δ 1.00 (t, 3, J = 7.5 Hz, CH_3), 2.20 (d of p, 2, J = 7.5 Hz, J = 1.5 Hz, $-CH_2-$), 4.76 (q, 1, J = 6–7 Hz, $=CHCH_2-$), 6.28 (t of d, 1, J = 1.5 Hz, J = 6.0 Hz, $-OCH{=}$), 6.7–7.4 (m, 5, Ph); mass spectrum (70 eV) *m/e* (rel intensity) 148 (64), 94 (100), 77 (67), 55 (63), 51 (65).

Isobutyrophenone (12): 21%; 31 min; ir (film) 5.95 μ (C=O); nmr (CCl_4) δ 1.18 (d, 6, J = 7.0 Hz, CH_3), 3.50 (septet, 1, J = 7 Hz, $>CH-$), 7.3–8.0 (m, 5, Ph); mass spectrum (70 eV) *m/e* (rel intensity) 148 (8), 105 (100), 77 (78), 51 (40); identical with an authentic sample[21] of **12**.

Pivalophenone (13): 4%; 38 min; ir (film) 5.95 μ (C=O) [lit.[24] 5.95 μ for (C=O)]; nmr (CCl_4) δ 1.34 (s, 9, CH_3), 7.2–7.8 (m, 5, Ph); mass spectrum (70 eV) *m/e* (rel intensity) 162 (7), 105 (100), 77 (41), 51 (26).

2-Methylbutyrophenone (14): 0.5%; 55 min; ir (film) 5.90 μ (C=O); nmr (CCl_4) δ 0.89 (t, 3, J = 7.5 Hz, CH_3), 1.14 (d, 3, J = 7.0, CH_3), 1.57 (m, 2, $-CH_2-$), 3.36 (m, 1, $>CH-$), 7.2–8.0 (m, 5, Ph); mass spectrum (70 eV) *m/e* (rel intensity) 162 (7), 105 (100), 77 (47), 51 (27); 2,4-DNP mp 129–130° (from ethanol) (lit.[25] 2,4-DNP 128–129°); identical with a sample of **14** prepared by ethylation of propiophenone, using sodium amide as the base, ethyl iodide as the alkylating agent, and ether as the solvent.[26]

Monitoring the Progress of the APE Isomerization by Methylation. To a solution of 2.07 g (15.6 mmol) of APE in 30 ml of anhydrous DME, cooled to −5°, was added 11.0 ml (31.2 mmol) of *n*-butyllithium in hexane. While keeping the reaction mixture at 0°, 3-ml aliquots were removed at time intervals of 0.5, 1, 2, 4, 8, 15, 30, 60, 100, 150, and 270 min and added to a solution of 1.5 ml of methyl iodide in 1.5 ml of DME. After standing a few minutes, each sample was diluted with water and extracted with 4 ml of ether. The ether solution was dried (Na_2SO_4), concentrated, and gas chromatographed (SE30). The peak area of all the components were calculated using the triangle method (peak height × width at half-height). The results are shown in Figure 1.

A peak of early retention time, similar to the other ethers, building proportionately to the amount of **12**, was observed and, consequently, assumed to be 1-methoxy-1-phenyl-1-propene (the O-methylated product of propiophenone enolate ion **8**). This product was not observed before, probably because there the methyl iodide was added to the ions and here it is just the reverse order. The peak disappears from the chromatogram if the samples are treated with 6 M H_2SO_4. Varying amounts of anisole, from methylation of phenol, were also observed in the chromatograms.

α,α-Dideuterioallyl Phenyl Ether (17). A freshly prepared[27] ethereal solution of 4.5 g (75 mmol) of α,α-dideuterioallyl alcohol was mixed with 15.5 g (82 mmol) of recrystallized *p*-toluenesulfonyl chloride. To this solution, cooled to 0°, 8.7 g (210 mmol) of pulverized sodium hydroxide was slowly added, while maintaining a temperature of 0–5°.[28] After stirring for 45 min, the reaction mixture was poured into ice–water. The aqueous phase was extracted twice with ether. The combined ether extracts were washed with water and concentrated on a flash evaporator. The residue was not distilled since violent decomposition of allyl tosylate can occur[29] upon distillation.

The crude allyl tosylate was then mixed with 6.7 g (72 mmol) of phenol and 13 ml of 6 N sodium hydroxide.[30] After stirring at room temperature for 2 days, the solution was extracted twice with ether. The combined ether extracts were washed with water, dried over $MgSO_4$, and concentrated on a flash evaporator. About 40 ml of hexane was added to the residue and this was stored in a freezer overnight. The precipitated, excess, *p*-toluenesulfonyl chloride was removed by filtration. The filtrate was concentrated and vacuum distilled to give 5.5 ml of liquid, bp 61–103° (5.2 mm). Redistillation afforded 3.5 g of **17**: bp 42–60° (1 mm); nmr (CCl_4) δ 5.10 (d of d, 1, J = 10 Hz, J = 2 Hz, $-CH{=}CH_2$, cis), 5.22 (d of d, 1, J = 18 Hz, J = 2 Hz, $-CH{=}CH_2$ trans), 5.93 (d of d, 1, J = 18 Hz, J = 10 Hz, $-CH{=}CH_2$), 6.7–7.4 (m, 5, Ph); ir (film) 4.57, 4.79 μ (C–D); mass spectrum (70 eV) *m/e* (rel intensity) 136 (74), 135 (32), 65 (40), 43 (100), 40 (34), 39 (54). Analysis by vpc (SE30) showed a purity of >98%. Because of the interference of the M − 1 peak in the mass spectrum of APE, nmr was used to set the limits of deuterium content at >98% d_2 at the α position (total absence of a methylene peak at δ 4.2).

Attempted Isomerization of α,α-Dideuterioallyl Phenyl Ether (17). To a solution of 0.26 g (1.9 mmol) of **17** in 30 ml of anhydrous DME was added 1.5 ml (4.2 mmol) of *n*-butyllithium in hexane. A light yellow-red color developed. The solution was stirred for 4 hr and worked up as usual.[23] Analysis of the ether solution of the product by vpc (SE30) showed three major components. These were separated by preparation vpc and found (ir, nmr, mass spectra, and vpc) to be phenol, APE-α,α-d_2 (**17**), and 1-deuterio-1-phenyl-2-propen-1-ol (**18**): ir (film) 2.95 (–OH), 4.60, 4.75 (C–D), 5.98, 10.12, 10.82 ($-CH{=}CH_2$), 13.3, 14.3 μ (Ph); nmr (CCl_4) δ 4.8–5.3 (m, 2, $=CH_2$), 5.5–6.2 (m, 1, $-CH{=}CH_2$), 7.01 (s, 5, Ph); mass spectrum (70 eV) *m/e* (rel intensity) 135 (89), 134 (80), 116 (38), 105 (86), 80 (100), 79 (54), 78 (98), 77 (84), 51 (81).

Allyl Phenyl Ether and Sodium Amide in DME. A solution of 2.5 g (18.6 mmol) of APE in 7.5 ml of anhydrous DME was added rapidly to a solution of 1.6 g (41 mmol) of $NaNH_2$ in 30 ml of anhydrous DME. After stirring for 3 hr at room temperature, the reaction mixture was worked up[23] to give 1.36 g of liquid, bp 40–42° (1.2 mm). By nmr and vpc (SE30) the product composition

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was found to be 97% *cis*-propenyl phenyl ether (**19**) and 3% *trans*-propenyl phenyl ether (**20**). Spectral evidence for **19** is the following: ir (film) 8.00 (Ph–O–R), 13.28, 14.50 μ (Ph); nmr (CCl_4) δ 1.70 (d of d, 3, J = 7.0 Hz, J = 1.5 Hz, CH_3), 4.75 (p, 1, J = 7 Hz, $=CHCH_3$), 6.30 (d of d, 1, J = 6.3 Hz, J = 1.5 Hz, $-OCH=$), 6.80–7.30 (m, 5, Ph) [lit.[31] **19**, J = 6.0 Hz for *cis*-$CH=CH-$].

Allyl Phenyl Ether and Potassium Amide in Liquid Ammonia. To a grey solution of approximately 50 mmol of KNH_2 in liquid ammonia—prepared by dissolving 2.24 g (57 mg-atoms) of potassium in 120 ml of liquid ammonia containing a pinch of hydrated ferric nitrate—was rapidly added 2.5 g (18.6 mmol) of APE. A red color developed immediately. The solution was stirred for 3 hr and then, while the ammonia evaporated, 40 ml of ether was added. After the ammonia had all evaporated, the ether solution was worked up[23] to afford 1.0 g of liquid, bp 50–55° (2.0 mm). By nmr and vpc (SE30) the product was found to be a mixture of 68% phenol and 32% of a mixture of 65% *cis*-propenyl phenyl ether (**19**) and 35% *trans*-propenyl phenyl ether (**20**). The nmr evidence for **20** is the following: (CCl_4) δ 1.48 (d of d, 3, J = 7.0 Hz, J = 1.5 Hz, CH_3) and 5.28 (d of q, 1, J = 11.0 Hz, J = 7.0 Hz, $=CH\text{-}CH_3$); the other protons were obscured by phenol peaks [lit.[31] for *trans*-$CH=CH-$ of **20** is J = 11.3 Hz].

Isomerization of Allyl Phenyl Ether with Allyllithium. In a completely dry apparatus and under nitrogen atmosphere, 3.5 ml (9.8 mmol) of *n*-butyllithium in hexane was mixed with 1.34 g (4.7 mmol) of tetraallyltin.[18] The solution was stirred at room temperature for 45 min and then the precipitated allyllithium was filtered under nitrogen, washed twice with pentane, and dissolved in about 20 ml of anhydrous THF. By titration, this solution was found to contain 9 mmol of base (allyllithium). To the solution was added 0.5 g (3.8 mmol) of APE. After stirring at room temperature for 2 hr and at reflux for 1.5 hr, the reaction was worked up[23] to give an ether residue of 78% APE, 13% propiophenone (**2**), and 9% α-vinyl benzyl alcohol (**3**), by vpc (DEGS). Similarly, with DME as the solvent, the ether residue was found to contain 90% APE, 4% **1**, and 6% **3**.

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The Neighboring Peroxide Anion and the 1,2-Dioxetane Intermediate. A Kinetic and Product Study of the Basic Decomposition of Chloro-*tert*-butyl Hydroperoxide

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Abstract: A kinetic and product study of the basic decomposition of chloro-*tert*-butyl hydroperoxide (**1**) in aqueous methanol suggests a neighboring peroxide anion reaction (ND_I-($^-$OO-4)). Based on this mechanism, the pK_a of **1**, obtained from kinetic data, is in good agreement with predicted values. Anchimeric assistance in the ND_I-($^-$OO-4) reaction is estimated to be approximately 10^4 and the α effect is 37 relative to the ND_I($^-$O-4) reaction. The products and light emission from the basic decomposition of **1** are in accord with a 1,2-dioxetane intermediate (**5**). Spectral data and light emission from an isolated sample of **5** provide further support. A kinetic treatment, which draws on iodometric and light emission data, allows the calculation of rate coefficients for the reactions of **5**. Activation parameters for unimolecular decomposition of **5** in 60% aqueous methanol with 1.58 *M* ionic strength are: E_a = 19.1 ± 0.3 kcal/mol and log A = 10.9. The products of this reaction are acetone and formaldehyde. A base-catalyzed decomposition of **5** also occurs to give, in part, 2-methyl-1,2-propanediol (**4**). A combination of kinetic and product data suggests that the initial product of the basic decomposition of **5** is α-hydroxyisobutyraldehyde. The latter compound, with formaldehyde and base, is proposed to give **4**. Activation parameters for the basic decomposition of **5** are: E_a = 16.3 ± 0.3 kcal/mol and log A = 9.42. Direct reaction of bromide ion and formaldehyde (at high concentration) with **5** is observed and rate coefficients are calculated.

The synergetic relationship between a functional group and the reaction site has fascinated chemists for a number of years. Although numerous groups are reported to enter into neighboring group reactions,[1] little is known about peroxy group participation in these reactions. For this reason, we have undertaken a comprehensive study of neighboring peroxide group reactions.[2] Our study was begun with a search for a four-ring peroxide anion ND_I reaction ($^-$OO-4), which employed the basic decomposition of chloro-*tert*-butyl hydroperoxide (**1**).[4] This hydroperoxide fulfilled the requirements of avoiding complicating basic elimination reactions which

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(2) This type of neighboring group reaction is defined by Traylor[3] as "internal nucleophilic displacement" and abbreviated as ND_I.

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