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Wittig Rearrangements of Aralkyl Alkyl Ethers

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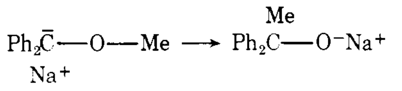
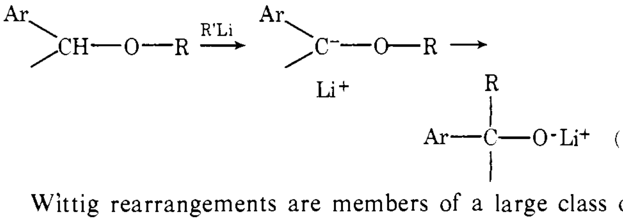
Abstract: Wittig rearrangements of benzhydryl 5-hexenyl ether in THF at room temperature give products containing the cyclopentylmethyl group as well as those containing the 5-hexenyl group. Cyclization occurs in intermediate 5-hexenyl radicals which escape reaction with their geminate partners, but later react with other ketyl molecules. This intermolecular pathway accounts for about 0.16 of the rearrangement, the remaining 0.84 being intramolecular. The intramolecular pathways give only products containing the 5-hexenyl group. The above theory is supported by comparisons of product distributions with appropriate reactions of alkyl iodides with lithium benzophenone ketyl in THF. Further support comes from studies of rearrangements of benzhydryl tetrahydrofurfuryl ether in diethyl ether, a reaction which is not successful in THF. Quantitative considerations suggest that a substantial portion of the intramolecular reaction is something other than secondary recombination of alkyl radical and ketyl. It may be inevitable that concerted processes compete with radical pair processes in electron-sufficient 1,2-shifts. Perhaps primary recombination should not be distinguished from the concerted processes into which it merges. The term "radical-concerted" is proposed to distinguish primary recombination-concerted processes like this from the "allowed" concerted processes of orbital symmetry theory. Data from reactions of benzyl alkyl ethers also support alkyl radical intermediates.

In 1928 Schlenk and Bergmann reported the rearrangement of the sodium salt of benzhydryl methyl ether (generated from benzophenone ketal and sodium) to sodium diphenyl methyl methoxide (eq 1).[1]

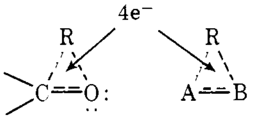


$$\underset{\mathrm{Na^+}}{\mathrm{Ph_2\bar{C}}}\mathrm{{-}O{-}Me} \longrightarrow \mathrm{Ph_2\overset{Me}{C}{-}O^-Na^+} \tag{1}$$

In 1942 a similar process involving alkyllithiums as metallating agents in reactions with benzyl and benzhydryl ethers was reported by Wittig and Lohmann (eq 2),[2] and such reactions have become known as "Wittig rearrangements".



Wittig rearrangements are members of a large class of related reactions such as Stevens, Meisenheimer, and other "ylide" rearrangements. One way to define this class is to focus on the nature of the intermediate or transition state for the 1,2 migration, assuming that it is concerted. For reactions in the class with Wittig rearrangements four electrons are cyclically delocalized over three atomic centers. These may be called "electron-sufficient" rearrangements since the atom to which the migration occurs has a complete octet of electrons in the reactant molecule in each case.

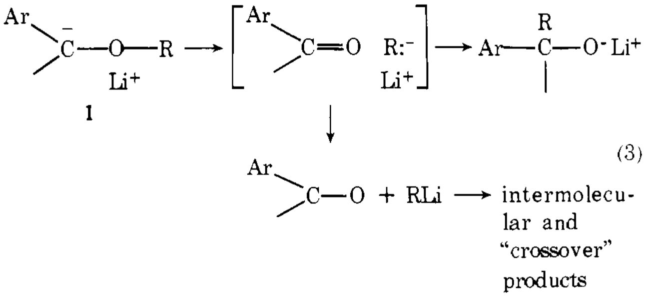


Left: intermediate or transition state for a concerted Wittig rearrangement, metal counterion omitted
Right: intermediate or transition state for a concerted rearrangement of any of the related types, Stevens, Meisenheimer, Wittig, other "ylide" rearrangements, etc (A and B are any atoms).

It has long been recognized that the cyclic delocalization of four electrons over three centers is much less favorable than the similar cyclic delocalization of two electrons and, in recent years, the four-electron systems have been classified as "antiaromatic", contrasting them with the "aromatic" two-electron systems.[3] In electron-deficient species, there are abundant examples of 1,2 migrations through "aromatic" transition states, but it is still a matter of controversy whether significant fractions of the migrations which could occur through "antiaromatic" transition states actually proceed through concerted pathways.

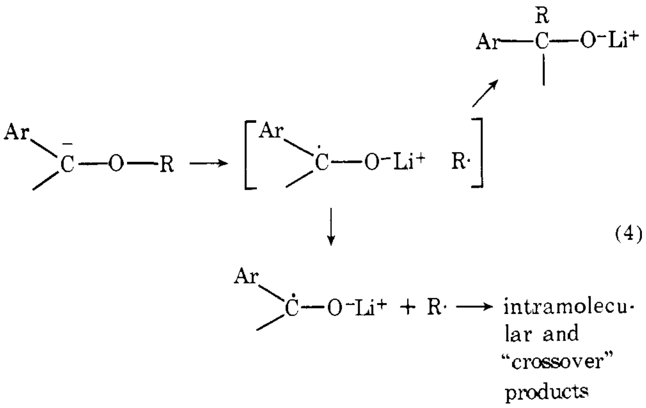
In recent years, evidence of free radical intermediates in many of these reactions has been accumulating.[4-7] Radical pathways account for loss of stereochemical integrity in the migrating group, 1,4 and 1,6 migrations, intermolecularity, and CIDNP. On the other hand, often there is substantially incomplete loss of stereochemistry, often only a small portion of the reaction is intermolecular, and CIDNP is not yet sufficiently quantitative that it can serve as an index to the fraction of the reaction occurring through radicals.[8] Therefore, it can be claimed that the radical pathways may represent only small fractions of the reactions.

For Wittig rearrangements, the evidence for radical pathways is especially indirect. The rearrangement of optically active benzyl *sec*-butyl ether under a variety of conditions occurs with about 70-80% racemization, and the reactions are intermolecular to extents of about 10%.[7a] This evidence was interpreted at first in terms of a heterolytic cleavage-recombination scheme involving carbonyl compounds and carbanions (eq 3).



(3)

Later it was found that the rates of disappearance of the anions **1** correlate better with the stabilities of radicals R· than with those of alkyllithiums RLi, suggesting cleavages to ketyls and alkyl radicals (eq 4).[5]



(4)

A report of CIDNP in a Wittig rearrangement product proved erroneous;[7a] the CIDNP was from an olefinic byproduct.[7d]

Wittig rearrangements seem quite susceptible to variations. α-Elimination occurs instead for benzhydryl phenyl ether in diethyl ether, but the reaction takes its normal course in THF.[9] Allyl groups may migrate through "allowed" concerted pathways in competition with dissociation-recombination processes.[6] The migration of vinyl groups appears to proceed through the anionic cleavage process of eq 3, not the radical cleavage pathway of eq 4.[10]

In view of these variations, and in view of the tenuous evidence for the radical cleavage in Wittig rearrangements involving alkyl group migration, we undertook a study designed to seek more definitive evidence and to disclose new details. We use the 5-hexenyl and tetrahydrofurfuryl groups as special probes for radical and carbanion intermediates, and we compare Wittig rearrangements with corresponding reactions of ketyls with alkyl iodides, reactions which definitely occur through the combinations of alkyl radicals with ketyls.[11] Our experiments were rearrangements promoted by alkyllithiums in THF (sometimes diethyl ether) at room temperature. Our most definitive experiments involved benzhydryl ethers, but some experiments were also performed using benzyl ethers.

Experimental Section

Benzhydryl ethers were prepared as described in the previous paper.[11]

Benzyl 5-Hexenyl Ether. A suspension of 0.053 mol of sodium benzyl alcoholate in 50 ml of DME was prepared from equivalent quantities of sodium hydride and benzyl alcohol. To this was added 8.64 g (0.053 mol) 5-hexenyl bromide and the mixture was stirred 8 hr. After filtration of the insoluble sodium bromide, the filtrate was concentrated and distilled at reduced pressure to yield 4.48 g (44%) of colorless liquid: bp 89-91° (2 Torr); ν_{max} (neat) 1640 ($CH{=}CH_2$), 1100 (C—O—C), 910 and 995 cm^{-1} ($CH{=}CH_2$); δ 1.55 (m, 4 H, $CH_2CH_2CH_2CH_2$), 1.98 (m, 2 H, $CH_2CH{=}CH_2$), 3.36 (t, 2 H, OCH_2CH_2), 4.4 (s, 3 H, $C_6H_5CH_2O$), 4.92 (m, 2 H, $CH{=}CH_2$), 5.65 (m, 1 H, $CH{=}CH_2$), 7.25 ppm (m, 5 H, C_6H_5); mol wt (calcd, 190) parent mass peak *m/e* 190.

Benzyl Tetrahydrofurfuryl Ether. A suspension of 0.05 mol of sodium tetrahydrofurfuryl alcoholate in 25 ml of DME was prepared from 5.1 g (0.05 mol) of tetrahydrofurfuryl alcohol and equivalent sodium hydride. Benzyl chloride (6.4 g, 0.5 mol) in 75 ml of DME was added, and the mixture was stirred 8 hr. Filtration and distillation gave 6.3 g (72%) of product: bp 89° (0.1 Torr) [lit.[11a] bp 141.5-143° (10 Torr)]; ν_{max} (neat) 1100, 1080 cm^{-1} (C—O—C); δ 1.80 (m, 4 H, $CHCH_2CH_2CH_2O$), 3.45 (d, 2 H, OCH_2CHO), 3.80 (m, 3 H, $CH_2CHOCH_2CH_2$), 4.55 (s, 2 H, $C_6H_5CH_2O$), 7.31 ppm (s, 5 H, C_6H_5); mol wt (calcd, 192) parent mass peak *m/e* 192.

Phenyl(cyclopentylmethyl)carbinol and phenyl(5-hexenyl)carbinol were prepared as previously described.[11]

Procedures for Wittig Rearrangements. Reactions were promoted at room temperature (23 ± 1°) by halide-free butyl- or methyllithium (Foote Chemical Co.). The original solvents (diethyl ether or hydrocarbon) were removed in vacuo and replaced by appropriate purified ethers distilled from storage over disodium benzophenone on a vacuum manifold. Concentrations of alkyllithiums were determined by quenching measured aliquots with water and measuring the amount of evolved gas and/or titrating total aqueous base with standard acid. Excess alkyllithium was used in each reaction.

Small-scale reactions were run in 10-ml graduated test tubes fitted with an arm to a vacuum manifold and an arm closed by a serum cap. The vessels were evacuated and flamed on the vacuum manifold. Reagents were added through the septum with syringes flushed with argon.

Large-scale reactions were run in round-bottomed flasks which had been flamed while being flushed with argon or nitrogen which had been scrubbed in a solution of disodium benzophenone. The flasks were fitted with condensers attached to mercury-filled U tubes. Solvents were distilled directly into the reaction vessels from a solution of disodium benzophenone under argon or nitrogen. Reagents were added through septa with syringes.

Product mixtures were quenched with acetic acid, water, or aqueous ammonium chloride solutions and oxidized by bubbling pure oxygen through them until they were colorless.

Large-Scale Rearrangement of Benzhydryl 5-Hexenyl Ether in THF. To 3.12 g (0.0117 mol) of benzhydryl 5-hexenyl ether in 35 ml of THF was added 35 ml of 0.8 *M* methyllithium (0.028 mol) in THF. After 48 hr, the mixture was quenched, the solvent removed on a rotary evaporator, and the residue taken up in hexane and chromatographed on 100 g of neutral alumina.

Fraction 1 (0.2648 g) was eluted with 100 ml of 1:1 petroleum ether–diethyl ether: ν_{max} ($CHCl_3$) 1660 cm^{-1} (C=O); δ 2.4 ppm (t, Ar$CH_2$$CH_2$); R_f (silica gel) 0.82; VPC retention time, 5 ft × ⅛ in. 10% QF-1 at 230° (standard conditions for retention times reported for other fractions in this experiment), 3.8 min. VPC on a 10 ft × ⅛ in. 20% QF-1 column at 230° gave two peaks, a major component assigned as **6h** (triplet at δ 2.4 ppm) and a minor component **6c** (5.6% of major component).[12] See Results section for coding of compounds.

Fraction 2 (0.1365 g) was eluted with 100 ml of 1:3 petroleum ether–diethyl ether: ν_{max} ($CHCl_3$) 1660 cm^{-1}; δ 2.6 ppm (m); R_f (silica gel) 0.82 and 0.70; VPC retention times 3.2, 8.5, and 11.8 min.

Fraction 3 (0.3119 g) was eluted with 100 ml of pure diethyl ether; R_f (silica gel) 0.82 and 0.70; VPC retention times 3.2, 8.5, and 11.8 min. Oxidation with neutral aqueous potassium permanganate eliminated the VPC peaks at 3.2 and 8.5 min, but did not affect that at 11.0 min. The oxidized mixture was extracted with diethyl ether, which was evaporated and replaced by CCl_4. The residue showed δ 1.6 (m, 9 H, C_6H_5 and C_6H_4 benzene rings), 2.7 (d, 2 H) (ArCH_2CH), and 7.6 ppm (m, 9 H, C_5H_9, cyclopentyl), consistent with **7c**. The peak at 8.5 min was assigned as **7h**.[12]

Fraction 4 (0.0097 g) was eluted with 50 ml of 1:50 methanol–diethyl ether: VPC retention times 8.5 and 11.8 min.

Fraction 5 (2.0163 g) was eluted with 100 ml of 1:3 methanol–diethyl ether: ν_{max} ($CHCl_3$) 3570, 3450 cm^{-1} (OH); VPC retention times 1.8 and 2.6 min; R_f (silica gel) 0.58. This material was stirred 4 hr with solid $AgNO_3$ and 4 drops of water in 15 ml of hexane. The liquid was decanted and the solid treated with cold, concentrated ammonium hydroxide and extracted with ether. Evaporation of the ether gave 1.76 g of material: δ 1.3 (m, 7 H, $Ph_2C(OH)CH_2CH_2CH_2CH_2CH{=}CH_2$), 2.0 (m, 2 H, $CH_2CH_2CH{=}CH_2$), 4.8 (m, 2 H, $CH{=}CH_2$), 5.7 (m, 1 H, $CH_2CH{=}CH_2$), 7.1 ppm (m, 10 H, 2 C_6H_5), consistent with **5h**. These properties also matched those of independently synthesized **5h**.[11] The minor component **5c** was assigned by VPC retention time comparisons by admixture with authentic material.[11]

When chromatography fractions giving single spots on silica gel TLC plates were developed on silica gel plates which had been treated with aqueous silver nitrate, two spots resulted, one of which had the original R_f.

In addition to the VPC columns mentioned above, analyses were performed with a 10 ft × ⅛ in. 10% Carbowax 20M TPA column at 270°, with consistent results. Quantitative NMR analyses for **5h** and **5c** were consistent with VPC analyses.

Rearrangement of Benzhydryl Cyclopentylmethyl Ether in THF. To 4 ml of 0.5 *M* butyllithium in THF was added 0.189 g (0.00071 mol) of benzhydryl cyclopentylmethyl ether. After 3 min, the reaction was quenched with excess water and oxidized. VPC analysis on a 10 ft × ⅛ in. Carbowax 20M TPA column at 270° gave peaks matching those assigned to **5c**, **6c**, and **7c** from the rearrangement of benzhydryl 5-hexenyl ether.

Attempted Rearrangement of Benzhydryl Tetrahydrofurfuryl Ether in THF. In a small-scale reaction, 1 ml of 1.6 *M* butyllithium (1.6×10^{-3} mol) in hexane was placed in the vessel, after evacuating and flaming, and the hexane distilled to a cold trap on the vacuum manifold. Ten milliliters of THF was distilled into the vessel and benzhydryl tetrahydrofurfuryl ether (67.3 mg, 2.51×10^{-4} mol) added. After 1 hr, the solution was quenched with 200 ml of aqueous ammonium chloride. VPC on a 5 ft × ⅛ in. Flexol 8N8 column at 100° gave the yield of 4-penten-1-ol as 94% (internal standard, mesitylene). VPC peaks attributable to **5t**, **6t**, and **7t** (the properties of which are known from independent synthesis (**5t**),[11] products of reactions of tetrahydrofurfuryl iodide with lithium benzophenone ketyl,[11] and rearrangements of benzhydryl tetrahydrofurfuryl ether in diethyl ether (see below)) were absent.

Large-Scale Rearrangements of Benzhydryl Tetrahydrofurfuryl Ether in Diethyl Ether. The reaction of benzhydryl tetrahydrofurfuryl ether (2.105 g, 0.0079 mol) with 50 ml of 0.34 *M* methyllithium (0.017 mol) was quenched after 20 hr with 1.2 ml of acetic acid in 2 ml of water. The white solid which crystallized as the solvent was removed on a rotary evaporator was recrystallized from methanol–water, giving crystals melting at 131–133°: ν_{max} ($CHCl_3$) 3480 cm^{-1} (OH); mixture melting point with authentic diphenyl(tetrahydrofurfuryl)carbinol 133–135°; 0.88 g (43%). VPC on a 12 ft × 0.25 in. 20% Flexol 8N8 column at 100° gave the yield of 4-penten-1-ol as 20%. To ascertain that diphenyl(tetrahydrofurfuryl)carbinol does not react with alkyllithiums to give benzophenone and 4-penten-1-ol, 0.4361 g was treated with 14 ml of 0.23 *M* methyllithium in diethyl ether for 24 hr. On acidification with aqueous ammonium chloride, VPC analyses showed no traces of 4-penten-1-ol.

In another run, 5.34 g of benzhydryl tetrahydrofurfuryl ether (0.0199 mol) reacted with 100 ml of 0.37 *M* methyllithium (0.037 mol) for 48 hr. After quenching, the aqueous layer was extracted four times with 100-ml portions of diethyl ether, which was combined with the original ether layer, dried, and concentrated to about 50 ml. Diphenyl(tetrahydrofurfuryl)carbinol (2.5 g, 0.0093 mol) crystallized, mp 129–131°; 46.9%. VPC analysis as above (internal standard, mesitylene) indicated a 17.4% yield of 4-penten-1-ol.

Large-Scale Rearrangement of Benzhydryl Methyl Ether in Diethyl Ether. Forty milliliters of 1.6 *M* methyllithium (0.064 mol) in diethyl ether was added to 3.08 g (0.0155 mol) of benzhydryl methyl ether in 60 ml of diethyl ether. The progress of the reaction was followed by VPC on a 5 ft × ⅛ in. 10% QF-1 column at 185°. After 48 hr, the mixture was quenched with excess saturated aqueous ammonium chloride. The dried ether solution was concentrated to ca. 5 ml and chromatographed on 100 g of neutral alumina (activity I). Fractions 1–8 (petroleum ether eluent) contained 60 mg of material matching the VPC retention times of 1,1-diphenylethylene (perhaps from the dehydration of some 1,1-diphenylethanol on work-up) and benzhydryl methyl ether. Fractions 9–14 (petroleum ether–benzene eluent) contained three components (total weight 946 mg). Two of these had retention times matching those of 2- and 4-methylbenzophenones. The third component (267 mg) was crystallized from an ethanol solution of fractions 9–14: mp 162–164°; ν_{max} ($CHCl_3$) 1660 cm^{-1} (C=O); λ_{max} ($CHCl_3$) 340 m (ϵ 136); δ 5.45 (s, 1 H), 7.2 ppm (m, 19 H); highest mass peak *m/e* 348. These data are consistent with $(C_6H_5)_2CHC_6H_4COC_6H_5$. The melting point of 4-benzhydrylbenzophenone is reported as 163–164°.[12a] Fractions 15–23 (benzene–diethyl ether and ether eluents) contained 1.511 g (48.2%) of 1,1-diphenylethanol, mp 80–81°, mmp 79–81°.

Large-Scale Rearrangement of Benzyl 5-Hexenyl Ether in THF. After 24 hr, the reaction of a mixture of 25 ml of 0.22 *M* methyllithium (0.0055 mol) in THF with 0.51 g (0.0027 mol) of benzyl 5-hexenyl ether was quenched with water and oxidized by bubbling oxygen through the solution for 15 min. After evaporation of the solvent, the residue was dissolved in petroleum ether and chromatographed on 50 g of neutral alumina. Fraction 2 (3:1 petroleum ether–diethyl ether eluent) contained 57.9 mg (11.4%) of recovered benzyl 5-hexenyl ether. Fractions 5 and 6 contained 103.5 mg (22.9%, corrected for recovered starting material) of a mixture of phenyl(5-hexenyl)carbinol and phenyl(cyclopentylmethyl)carbinol. VPC on a 5 ft × ⅛ in. 10% DEGS column showed 92% of the former and 8% the latter. Fraction 7 contained 127.1 mg (49.5%) of benzyl alcohol containing a small amount of the mixed carbinols.

Large-Scale Rearrangement of Benzyl Tetrahydrofurfuryl Ether in Diethyl Ether. After 65 hr, the reaction of 4.12 g (0.0214 mol) of benzyl tetrahydrofurfuryl ether with 100 ml of 0.6 *M* methyllithium (0.06 mol) in diethyl ether was quenched with 5 ml of glacial acetic acid and oxidized with oxygen. After filtration and evaporation of the solvent, the residue was dissolved in carbon tetrachloride and analyzed by VPC. VPC on a 5 ft × ⅛ in. 5% 8N8 Flexol column at 100° revealed no 4-penten-1-ol; less than 1% could have been detected. Analysis on a 5 ft × ⅛ in. 10% QF-1 column at 180° showed two main components; these were collected from another VPC run on a 5 ft × ⅛ in. 5% SE-30 column at 195°. The material giving the smaller peak had a retention time and NMR spectrum identical with that of benzyl alcohol. The material giving the larger peak had spectral characteristics consistent with phenyl(tetrahydrofurfuryl)carbinol: δ (CCl_4) 1.8 (m, 6 H, $CHCH_2CHCH_2CH_2CH_2O$), 2.7 (m, 4 H, $CHOCH_2$ and OH), 4.8 (t, 1 H, $C_6H_5CH(OH)CH_2$), 7.2 ppm (m, 5 H, C_6H_5); mol wt (calcd, 192) parent mass peak *m/e* 192. Analysis of the reaction mixture by NMR showed 33% benzyl alcohol and 67% phenyl(tetrahydrofurfuryl)carbinol.

In other similar runs, phenyl(tetrahydrofurfuryl)carbinol was isolated in 58 and 38% yields, respectively, by column chromatography on neutral alumina and by fractional distillation and an annular Teflon still. From phenyl(tetrahydrofurfuryl)carbinol so obtained, diphenyl(tetrahydrofurfuryl)carbinol was prepared by oxidation to the ketone and reaction with phenylmagnesium bromide.[11]

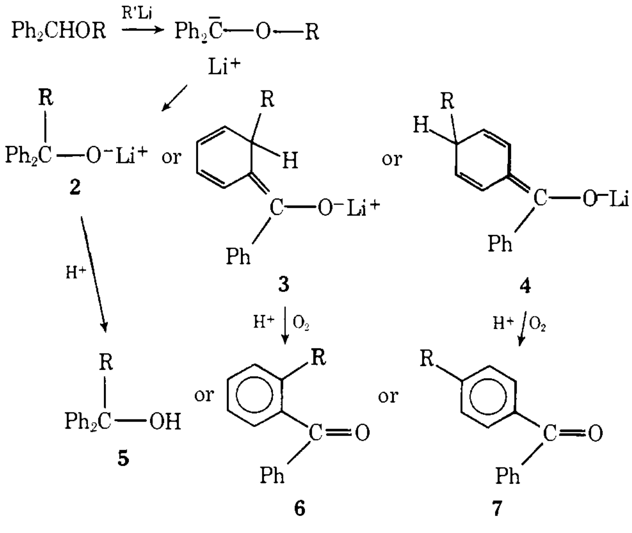
Quantitative Analyses. Most of the quantitative analyses reported in the tables were done by VPC on product mixtures from small-scale reactions, using columns and conditions indicated in footnotes to the tables. Occasional duplicate analyses by NMR agreed with those by VPC. The bases for assignments of VPC peaks for all compounds **5** were comparisons with independently synthesized materials. The bases for assignments of **6h**, **6c**, **7h**, and **7c** are given above.[12] **6t** and **7t** were assigned by VPC characteristics correlated between Wittig rearrangements and reactions of tetrahydrofurfuryl iodide with lithium benzophenone ketyl.[11] **6b** and **7b** were assigned from VPC characteristics correlated among Wittig rearrangements of benzhydryl butyl ether, Wittig rearrangements of benzhydryl tetrahydrofurfuryl ether promoted by butyllithium in THF and in diethyl ether (in which **5b**, **6b**, and **7b** are formed by crossover), and reactions of butyllithium with benzophenone.

Kinetics. Kinetic runs with benzhydryl methyl ether were carried out in 10-ml reaction vessels to which a quartz optical cell was attached. Runs were at toom temperature (23 ± 1°). Metallation of benzhydryl methyl ether to give the colored lithio benzhydryl methyl ether was competitive, in each case, with the decomposition of the lithio ether, so that the optical density in the visible rose initially, then reached a maximum and decreased. Optical densities were taken at the $\lambda_{\max}$ in the visible region. When log (OD) was plotted against time, the points for the later stages of the reaction formed an excellent straight line. Clearly, metallation was complete through this range, which spanned 2-3 half-lives. From this slope, the first-order rate constant for decomposition of the lithio ether was computed.

Results

Mass balances were obtained for many experiments and they were generally excellent, with 90% or more of the reactants accounted for. Products of Wittig rearrangements of benzhydryl ethers include not only the carbinols **5**, but also the 2- and 4-alkylbenzophenones **6** and **7**. These arise on work-up from precursor anions **2**, **3**, and **4** (Scheme I). **2**, **3**, **4**, **5**, **6**, and **7** are coded as in the preceding paper on ketyl-alkyl iodide reactions[11] to facilitate comparisons of the two sets of results.

Scheme I



m, R = methyl
c, R = cyclopentylmethyl
t, R = tetrahydrofurfuryl
b, R = butyl
h, R = 5-hexenyl

Table I. Products of Reactions of Benzhydryl 5-Hexenyl Ether with Alkyllithiums in THF at Room Temperature[a]

Alkyllithium	5h	6h	7h	5c	6c	7c
BuLi	77	14	10	47	5	48
MeLi	77	13	9	60	4	36

[a] Relative yields normalized so that (5h + 6h + 7h) = (5c + 6c + 7c) = 100. Yields were determined by VPC using the following columns: (1) 10 ft × $^1/_8$ in. 10% Carbowax (20M-TPA) on 80–100 mesh acid-washed DMCS-treated Chromosorb W at 240–250°. Phenyl biphenylyl ketone was the internal standard. Total yields (absolute) of the above products were ca. 90% in each case by VPC and, in the case of the methyllithium reaction, 92% was isolated by chromatography on alumina. In the butyllithium reaction, 5c, 6c, and 7c accounted for 15% of the products listed above and, in the methyllithium reaction, 16%. Initial concentrations of benzhydryl 5-hexenyl ether were 0.1–0.2 *M*, and alkyllithiums were present in twofold excess or greater.

Table II. Products of Reactions of Benzhydryl Tetrahydrofurfuryl Ether with Butyllithium in THF and Diethyl Ether at Room Temperature[a]

Solvent	4-Penten-1-ol	5t	6t	7t	5b	6b	7b
THF[b]	*94*	0	0	0	96	1.4	3.0
DEE[c]	*19*[d]	74 (*47*)[e]	14	12	42	7	51

[a] Italicized figures are absolute percent yields. The other figures are relative yields normalized so that (5t + 6t + 7t) = (5b + 6b + 7b) = 100. Analyses were by VPC as described in footnote *a* of Table I. [b] Initial concentration of BuLi = 0.16 *M*. Initial concentration of benzhydryl tetrahydrofurfuryl ether = 0.025 *M*. Experiments with methyllithium gave comparable yields of 4-penten-1-ol. [c] Initial concentration of butyllithium = 0.16 *M*. Initial concentration of benzhydryl tetrahydrofurfuryl ether = 0.10 *M*. [d] Not determined for the butyllithium reaction described in footnote *c*, but the average (of 17 and 20) determined from similar experiments using methyllithium. [e] Italicized figure is isolated yield (see Experimental Section).

Table III. Products of Reactions of Benzhydryl Cyclopentylmethyl Ethers with Butyllithium in THF at Room Temperature[a]

Benzhydryl ether	5c or 5b	6c or 6b	7c or 7b
Cyclopentylmethyl	68	19	13
Butyl	77	9	14

[a] Relative yields; (5c + 6c + 7c) = (5b + 6b + 7b) = 100. Analyses by VPC as in footnote *a* of Table I.

Rearrangements of benzhydryl 5-hexenyl ether (Table I) give not only products **5h**, **6h**, and **7h**, which contain the 5-hexenyl group, but also products **5c**, **6c**, and **7c**, which contain the cyclopentylmethyl group. The ratios **5h:6h:7h** are very different from the ratios **5c:6c:7c.**

Table II contains data for reactions of benzhydryl tetrahydrofurfuryl ether in both THF and diethyl ether. There is a striking solvent effect: the reaction proceeds normally in diethyl ether but it is completely subverted in THF. In THF a 94% yield of 4-penten-1-ol is found instead of the normal rearrangement products. Only about 19% 4-penten-1-ol is found in the comparable reaction in diethyl ether. Of especial import are the ratios among the "crossover" products (**5b**, **6b**, **7b**) obtained in these reactions, that is, the products in which the alkyl group (butyl) of the promoting alkyllithium (butyllithium) appears in the products instead of the alkyl group (tetrahydrofurfuryl) of the reactant ether. The ratios **5b:6b:7b** are widely different from reactions in THF and diethyl ether.

Table III contains product distributions from rearrangements of benzhydryl alkyl ethers which lead to no special products, that is, no products in which the migrating alkyl group has rearranged and no significant yields of crossover products. The migrating groups are butyl and cyclopentylmethyl, and the partitioning among products **5**, **6**, and **7** is very similar for these groups.

Table IV. Products of Reactions of Alkyllithiums with Benzophenone[a]

RLi	$[RLi]_0$[b]	[Benzophenone]$_0$[b]	Solvent	Mixing order	5	6	7
MeLi	0.64	0.16	DEE[c]	Ketone to RLi	100	0	0
BuLi	0.27	0.08	$\frac{5\ \text{THF}}{1\ \text{hexane}}$	RLi to ketone	91	3	5
BuLi	0.27	0.44	$\frac{5\ \text{THF}}{1\ \text{hexane}}$	RLi to ketone	93	3	4
BuLi	0.15	0.10	$\frac{10\ \text{THF}}{1\ \text{hexane}}$	RLi to ketone	91	3	7
BuLi	0.15	0.10	$\frac{10\ \text{THF}}{1\ \text{hexane}}$.	Ketone to RLi	93	3	4

[a] Relative yields by VPC; 10 ft × $^1/_8$ in. 10% Carbowax 20M TFA at 220°. [b] Initial molar concentrations in reaction mixture. [c] Diethyl ether. [d] Volume/volume ratios before mixing.

Table V. Products of Reactions of Benzhydryl Methyl Ethers with Methyllithium in THF and Diethyl Ether at Room Temperature[a]

$[MeLi]_0$	$[Ph_2CHOMe]_0$	$[MeLi]_0/[Ph_2CHOMe]_0$	5m	6m	7m
		In THF			
0.050	0.075	0.67	90	3.8	6.3
0.57	0.40	1.43	82	6.6	11.6
0.925	0.50	1.85	90	2.5	7.6
1.14	0.40	2.85	84	6.4	9.7
0.075	0.025	3.00	87	4.5	8.9
0.47	0.100	4.70	90	3.8	6.7
		Av:	87	5	8
		In DEE[b]			
		0.37	91	3.4	5.8
		1.85	85	4.6	10.5
		3.70	84	4.7	11.7
		4.63	81	5.1	14
		4.63	79	5.8	15
		4.63	86	5.4	8.8
		4.63	82	6.2	11.5
		Av:	84	5	11

[a] Relative percent yields determined by NMR. In several cases in THF absolute yields determined by VPC at 165° on a 5 ft × $^1/_8$ in. 10% QF-1 on DMCS-treated Chromosorb W column were greater than 95%. [b] Diethyl ether.

Table VI. Products of Reactions of Benzyl 5-Hexenyl Ether with Methyllithium in THF and Diethyl Ether at Room Temperature[a]

Solvent	$C_6H_5CH_2OH$	C_6H_5(5-Hex)CHOH[b]	C_6H_5(CPM)CHOH[c]
THF[d]	50	21	1.8
DEE[e]	57[f]	36[f]	Trace[f]

[a] Values tabulated are absolute percentage yields corrected for recovered starting material. Carbonyl compounds (2- and 4-alkylbenzaldehydes are likely products) were not determined. [b] Phenyl(5-hexenyl)carbinol. [c] Phenyl(cyclopentylmethyl)carbinol. [d] Initial concentration of methyllithium = 0.22 *M*. Initial concentration of benzyl 5-hexenyl ether = 0.11 *M*. See Experimental Section for analytical details. [e] Diethyl ether. Initial concentration of methyllithium = 1.0 *M*. Initial concentration of benzyl 5-hexenyl ether = 0.2 *M*. [f] Determined by VPC on a 5 ft × $^1/_8$ in. DEGS column at 190°.

Table VII. Products of Reactions of Benzyl Tetrahydrofurfuryl Ether with Methyllithium in THF and Diethyl Ether at Room Temperature[a]

Solvent	$C_6H_5CH_2OH$	C_6H_5(THFF)-CHOH[b]	$CH_2{=}CHCH_2$-CH_2CH_2OH
THF[c]	31[c]	69[c]	*5.25*[d]
DEE[e]	33 *(28)*[e]	67 *(57)*[e]	*0*

[a] Values not in italics are relative yields of benzyl alcohol and phenyl(tetrahydrofurfuryl)carbinol given as percentages. Italicized values are absolute percentage yields. Carbonyl compounds (2- and 4-tetrahydrofurfurylbenzaldehydes are likely products) were not determined. [b] Phenyl(tetrahydrofurfuryl)carbinol. [c] Initial concentration of methyllithium = 0.6 *M*. Initial concentration of benzyl tetrahydrofurfuryl ether = 0.2 *M*. Relative yields from NMR analyses. [d] Average of two experiments giving 4 and 6.5% yields of 4-penten-1-ol. Determined by VPC on a 5 ft × $^1/_8$ in. 5% 8N8 Flexol column at 100°. [e] Diethyl ether. Relative yields are averages from four experiments in which the yield of benzyl alcohol was 29–37% and that of phenyl(tetrahydrofurfuryl)carbinol was 63–71%. In two of these experiments, the absolute yields of benzyl(tetrahydrofurfuryl)carbinol were determined, 59.7% by VPC on a 5 ft × $^1/_8$ in. Carbowax 20M column at 225° using benzhydrol as the internal standard and assuming a relative (flame ionization detector) response factor of unity (on a weight basis), and 57.7% isolated by chromatography on neutral alumina (activity 1, eluent 4:1 diethyl ether–methanol). To obtain the absolute yield values tabulated, the ratios of these absolute yields to the relative yields in the same experiments were averaged and the average factor was applied to the average relative yields from four experiments. See Experimental Section for detailed description of one large-scale experiment.

Table IV contains data from reactions of alkyllithiums with benzophenone. The resulting ratios of products **5, 6,** and **7** are pertinent to discussions of the anion cleavage mechanism since the anion cleavage mechanism invokes product formation through these reactions. Additions of alkyllithiums to benzophenone give only small quantities of **6**, and **7**, if any, in contrast to both Wittig rearrangements and the related reactions of lithium benzophenone ketyl with alkyl iodides.

Table V contains the results of Wittig rearrangements of benzhydryl methyl ether in diethyl ether and THF. In diethyl ether there was obtained, in addition to **5m, 6m,** and **7m,** a small amount of a compound with spectral characteristics of a benzhydrylated benzophenone, $(C_6H_5)_2CHC_6H_4COC_6H_5$ (see Experimental Section). In THF this product is apparently absent or insignificant since **5m, 6m,** and accounted for greater than 95% of the benzhydryl methyl ether consumed. It is seen that the ratios **5m:6m:7m** are essentially unaffected by the nature of the solvent.

Table VI gives the products of Wittig rearrangements of benzyl 5-hexenyl ether promoted by methyllithium in diethyl ether and in THF. Here 50–57% of the reaction is elimination to benzyl alcohol (and 1,5-hexadiene, presumably) rather than rearrangement; this finding is in excellent agreement with those of Lansbury and Pattison, who found a ratio of elimination to rearrangement of 1.2 in reactions of metalated benzyl primary alkyl ethers. In both THF and diethyl ether, phenyl(cyclopentylmethyl)carbinol was detected among the products, in addition to phenyl(5-hexenyl)carbinol, and in THF the cyclic product was 8% of the phenyl(alkyl)carbinols. Carbonyl compounds among the products, e.g., alkylbenzaldehydes, were not examined. Among the products which were determined, there is very little solvent effect on the yields.

Table VII gives the yields of products of Wittig rearrangements of benzyl tetrahydrofurfuryl ether promoted by methyllithium in diethyl ether and THF. Again, elimination is significant, benzyl alcohol accounting for 29–37% of the combined alcohols. In contrast to the similar reaction of benzhydryl tetrahydrofurfuryl ether, which fails in THF, the reaction takes a normal course in both diethyl ether and THF. 4-Penten-1-ol was not determined in diethyl ether, but in THF its yield is 4–7%. Assuming no solvent effect on the yield of phenyl(tetrahydrofurfuryl)carbinol, this is 8% of the combined phenyl(tetrahydrofurfuryl)carbinol and 4-penten-1-ol yields.

Table VIII. Rate Constants for the Decomposition of Lithio Benzhydryl Methyl Ether at Room Temperature[a]

Solvent	$[\mathrm{RLi}]_0, M$	$[(\mathrm{C_6H_5})_2\mathrm{CHOCH_3}]_0, M$	$k, M^{-1}\ \mathrm{sec}^{-1}$
DME	0.7[b]	0.00562	0.00045
	0.7[b]	0.00263	0.00043
		Av:	0.00044
THF	0.4[b]	0.00454	0.0015
	0.4[b]	0.00454	0.0013
		Av:	0.0014
DEE[d]	0.17[c]	0.00504	0.00068

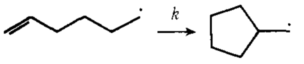
[a] See Experimental section for method of dissecting rate constant for decomposition of the metallated ether from the overall process of metallation and decomposition. [b] RLi = methyllithium. [c] RLi = butyllithium. [d] Diethyl ether.

Table VIII contains rate constants for the decomposition of lithio benzhydryl methyl ether in DME, THF, and diethyl ether at room temperature. Solvent effects are very small.

Discussion

We focus first on the intermolecular products of Wittig rearrangements, including crossover products. Later we discuss intramolecular Wittig rearrangement products.

Intermolecular Products (5c, 6c, 7c) from Wittig Rearrangements of Benzhydryl 5-Hexenyl Ether. Products **5c**, **6c**, and **7c** from the Wittig rearrangement of benzhydryl 5-hexenyl ether (Table I) can be formed by cyclization of some 5-hexenyl intermediate. Cyclization is well-known for the 5-hexenyl radical (eq 5).[13] A control experiment showed



$k = 1 \times 10^5\ \mathrm{sec}^{-1}$ (5)

that 5-hexenyllithium does not cyclize in THF at room temperature.[14] Thus, we hypothesize intermediate 5-hexenyl radicals.

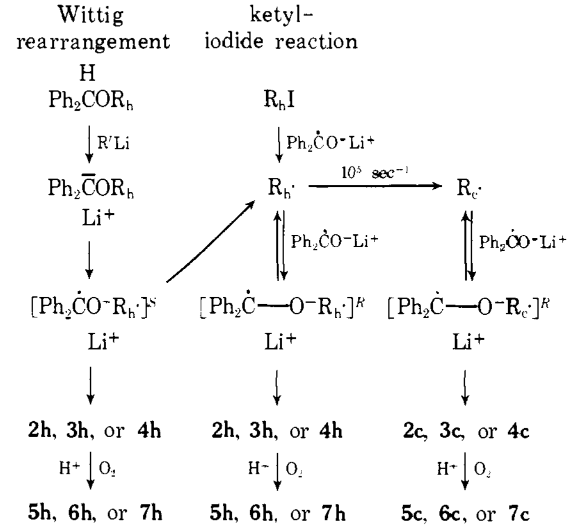
According to the radical cleavage mechanism (eq 4), the intramolecular products are formed in geminate recombinations (cage reactions) of radicals formed in the homolysis of the ether anion. Since geminate recombination must be essentially complete within about 10^{-9} sec,[15] the cyclization of 5-hexenyl radicals to cyclopentylmethyl radicals, for which the rate constant is about $10^5\ \mathrm{sec}^{-1}$,[13] cannot compete with geminate recombination, and products **5c**, **6c**, and **7c** must result from the cyclization of 5-hexenyl radicals which *escape* geminate recombination. Thus, according to the radical cleavage mechanism, **5c**, **6c**, and **7c** must be *intermolecular* products.

Scheme II is an expanded and specialized version of the radical cleavage mechanism which treats both the Wittig rearrangement of benzhydryl 5-hexenyl ether and the reaction of lithium benzophenone ketyl with 5-hexenyl iodide. The mechanism shown for the latter reaction is supported by convincing evidence.[11] According to Scheme II, the product-determining seps of the *intermolecular* portion of the Wittig rearrangement are identical with the product-determining steps of the ketyl-alkyl iodide reaction. Thus Scheme II leads to the prediction that the ratios **5c**:**6c**:**7c** should be the same for both reactions.

This prediction is realized. From the Wittig rearrangement of benzhydryl 5-hexenyl ether promoted by butyllithium in THF, **5c**:**6c**:**7c** = 47:5:48 (Table I), and from the reaction of lithium benzophenone ketyl with 5-hexenyl iodide the same ratios are 41:11:48, identical within experimental error.

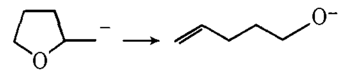
In contrast, if the anion cleavage mechanism (eq 3) were to apply, the intermolecular Wittig rearrangement products would be formed in reactions of alkyllithiums with benzophenone. Again, it would be very unlikely that cyclization of 5-hexenyllithium (if it could occur at all) could compete with intramolecular product formation, so that again **5c**, **6c**, and **7c** would be assigned as intermolecular products. The results in Table IV show that reactions of alkyllithiums with benzophenone give greater than 90% **5** and smaller amounts of **6** and **7**. Thus, not only do the intermolecular product distributions agree quantitatively with the radical cleavage mechanism, but also they are in sharp disagreement with predictions based on the anion cleavage mechanism.

Scheme II[a]

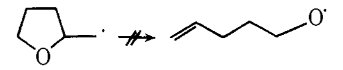


[a] R_h = 5-hexenyl; R_c = cyclopentylmethyl. No particular states of ion aggregation are implied by the representations above. *S* designates initially electronic singlet radical pairs. *S* pairs in the scheme above would be formed with particular initial geometries. *R* pairs are formed when independently generated radicals diffuse together with random spins and geometries.

Crossover Products from Wittig Rearrangements, or Attempted Wittig Rearrangements, of Benzhydryl Tetrahydrofurfuryl Ether. Since tetrahydrofurfuryl anions (as in tetrahydrofurfurylsodium, tetrahydrofurfurylmagnesium halides, etc.) undergo a facile ring opening (eq 6),[16] but the similar ring opening for tetrahydrofurfuryl radicals (eq 7) is

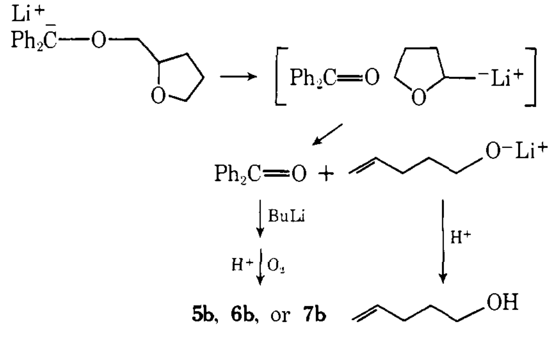


(6)



(7)

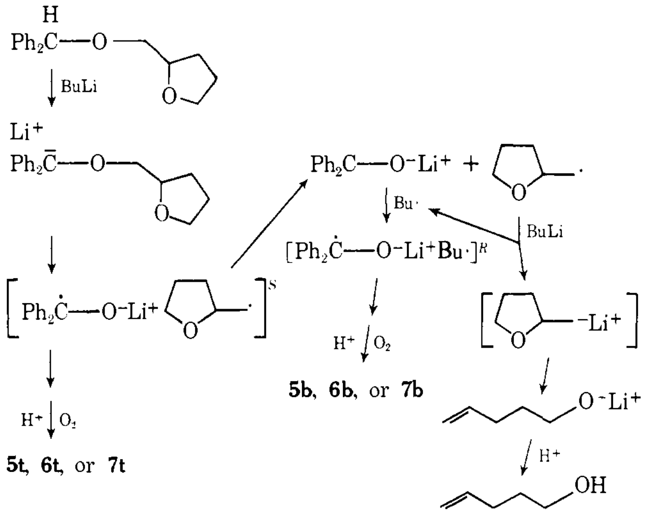
quite unfavored thermodynamically and does not occur,[17] the presence or absence of 4-penten-1-ol from rearrangements of benzhydryl tetrahydrofurfuryl ether is significant. In THF, 4-penten-1-ol is formed in 94% yield and the normal rearrangement products **5t**, **6t**, and **7t** are not formed at all. If butyllithium is used in the reaction, in their places are found **5b**, **6b**, and **7b**, which may result either from reactions of butyl radicals with lithium benzophenone ketyl



(8)

(from an initial radical cleavage, eq 4) or from reactions of butyllithium with benzophenone (from an initial anion cleavage, eq 3). Equation 8 illustrates the pathway through which crossover products might be expected to form following an initial anion cleavage, while Scheme III illustrates crossover product formation following an initial radical cleavage. If the high yield of 4-penten-1-ol from the reaction in THF reflects an anionic cleavage (eq 8), then the distribution of crossover products should be typical of additions of alkyllithiums to benzophenone. In fact, the ratios **5b:6b:7b** are 96:1.3:4 (Table II), which compare well with the similar ratios 92:3:5 from the addition of butyllithium to benzophenone (Table V). Thus, it is clear that the reaction of benzhydryl tetrahydrofurfuryl ether with butyllithium in THF follows an anionic cleavage pathway.

Scheme III[a]



[a] See footnote to Scheme II for significance of radical pair designations *S* and *R*.

We regard the anionic cleavage of benzyhydryl tetrahydrofurfuryl ether in THF as a special case to which we will return after considering the analogous reaction in diethyl ether.

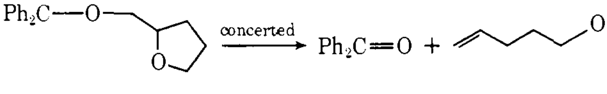
In diethyl ether, the reaction takes a different course. There is a much lower yield of 4-penten-1-ol than in THF and, although some crossover products **5b, 6b,** and **7b** are formed, the bulk of the reaction is a normal rearrangement leading to **5t, 6t,** and **7t** (Table II). These facts accord better with a radical cleavage than an anion cleavage since a large fraction of the tetrahydrofurfuryl groups succeed in migrating in the normal fashion. The yields of **5t, 6t,** and **7t** total 64% when the relative yield data are combined with the isolated yield of **5t**; since isolation invariably involves losses, the absolute yield is undoubtedly higher.

It seems unlikely that processes involving reactions of tetrahydrofurfuryl radicals with butyllithium could compete with geminate recombination, but once tetrahydrofurfuryl radicals escape geminate recombination, it is reasonable that they might suffer an electron transfer (lithium transfer) reaction with butyllithium, which is present in excess (see Scheme III). This would lead to butyl radicals and 4-penten-1-ol, and the crossover products would be formed through reactions of independently generated butyl and lithium benzophenone ketyl radicals, just as in reactions of alkyl iodides with lithium benzophenone ketyl. In fact, the ratios **5b:6b;7b** are 42:7:51, which are typical of the ratios found in reactions of lithium benzophenone ketyl with primary alkyl iodides. For example, 5-hexenyl iodide reacts with lithium benzophenone ketyl in THF to give ratios **5h:6h:7h** of 44:9:47. Thus, the data are quite consistent with the radical cleavage process of Scheme III.

Suppose that the 4-penten-1-ol in diethyl ether had arisen from an anion cleavage in competition with the radical cleavage. Then the crossover products would have been formed at least partly according to eq 8, and **5b** should have been favored. The fact that **5b** was formed in nearly exact quantitative agreement with typical radical coupling processes suggests that the anion cleavage process can be neglected in diethyl ether.

We return now to the reaction of benzhydryl tetrahydrofurfuryl ether with butyllithium in THF. From other experiments (Table V), there is no significant solvent effect, between THF and diethyl ether, on the product distributions from rearrangements of benzhydryl methyl ether. Thus, the nature of the solvent is ordinarily not a factor affecting mechanism. However, the tetrahydrofurfuryl group is not an ordinary alkyl group; it contains an electronegative atom and a very favorable potential anionic fragmentation mode. We propose that the normal process for benzhydryl alkyl ethers is the radical cleavage in both diethyl ether and THF, and that reactions of tetrahydrofurfuryl ether are special in that they are subject to control through solvation factors.

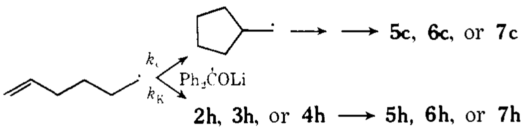
Further insight into the reaction in THF comes from comparisons of kinetic results. The reaction of the anion **1** is not much faster than the metallation of benzhydryl methyl ether by butyl- or methyllithium in THF or diethyl ether at room temperature. This is evidenced by the fact that the spectrum of **1** builds up in the initial stages of these reactions. However, we could detect no such buildup in the reaction of benzhydryl tetrahydrofurfuryl ether in THF, suggesting that the rate constant for the reaction of **1** is much faster than normal in that case. This result is consistent with either an anion cleavage (facilitated by the inductive effect of the oxygen of tetrahydrofurfuryl) or a concerted fragmentation (eq 9).



(9)

It is not clear just how the solvent, which interacts primarily with the associated lithium ions, presumably, influences reaction 3 or 9, but it is worth noting that lithium ion pairs of anions **1** are most likely solvent-separated ion pairs in THF but contact ion pairs in diethyl ether.[19]

Intramolecular Rearrangement Products of Reactions of Benzhydryl Alkyl Ethers. We argued above that **5c, 6c,** and **7c** were exclusively *intermolecular* rearrangement products of benzhydryl 5-hexenyl ether; now we consider whether **5h, 6h,** and **7h** are exclusively *intramolecular* products. Is it reasonable to assume that essentially *all* the 5-hexenyl radicals escaping geminate recombination cyclize to cyclopentylmethyl radicals before reacting? Yes. Under conditions where essentially all the alkyl radicals are scavenged in reactions with ketyl, the following is the competition to be considered (eq 10).



(10)

The ratio k_K/k_C has been estimated as $\sim 1.5 \times 10^3\ M^{-1}$,[18] and k_C is $\sim 1 \times 10^5$ sec^{-1}, so that k_K is $\sim 1.5 \times 10^8\ M^{-1}$ sec^{-1}. We must estimate the concentration of ketyl that builds up during the course of the Wittig rearrangement. Consider the following mechanistic scheme (eq 11)

$$\begin{aligned} \mathrm{A} &\xrightarrow{k_1} a\mathrm{K} + a\mathrm{R} + (1-a)\mathrm{B} \\ \mathrm{K} + \mathrm{R} &\xrightarrow{k_\mathrm{K}} \mathrm{B} \\ 2\mathrm{R} &\xrightarrow{k_1} \mathrm{C} \end{aligned} \tag{11}$$

where A = benzhydryl alkyl ether; R = alkyl radical; K = ketyl; B = **5**, **6**, or **7**; C = alkyl coupling or disproportionation product. Since alkyl radicals are quite reactive toward one another but ketyls are totally unreactive toward one another, and since k_t (ca. $2 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$) is greater than k_K, in the very early stages of the reaction the concentration of ketyl will build up rapidly. Assuming a steady state [R], eq 12 governs this buildup.

$$-\frac{\mathrm{d}[\mathrm{K}]}{\mathrm{d}[\mathrm{A}]} = \frac{2k_\mathrm{t}[\mathrm{R}]^2}{k_1[\mathrm{A}]} = a - \frac{k_\mathrm{K}[\mathrm{K}][\mathrm{R}]}{k_1[\mathrm{A}]} \tag{12}$$

$$\frac{\mathrm{d}[\mathrm{R}]}{\mathrm{d}t} = 0 = ak_1[\mathrm{A}] - k_\mathrm{K}[\mathrm{K}][\mathrm{R}] - 2k_\mathrm{t}[\mathrm{R}]^2 \tag{13}$$

$$\frac{-\mathrm{d}[\mathrm{K}]}{\mathrm{d}[\mathrm{A}]} = \frac{2k_1k_\mathrm{t}[\mathrm{A}]}{(k_\mathrm{K}[\mathrm{K}])^2}\left(a + \frac{\mathrm{d}[\mathrm{K}]}{\mathrm{d}[\mathrm{A}]}\right)^2 \tag{14}$$

Using the steady-state equation for [R] (eq 13), this can be transformed to eq 14, the integration of which would give [K] at any stage of the reaction. An upper limit on [K] reached during the course of a Wittig rearrangement under the conditions of our experiments can be estimated without solving this equation exactly (see Appendix). Using $k_1 = 10^{-3}\ \mathrm{sec}^{-1}$,[19] $k_2 = 10^8\ M^{-1}\ \mathrm{sec}^{-1}$, $k_3 = 2 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$, and $[\mathrm{A}]_0 = 0.1\ M$, we calculate that a is 0.16 and the [K] reached is no more than $5.3 \times 10^{-5}\ M$. This leads to the estimate that *at least* 95% of the 5-hexenyl radicals which escape geminate recombination will cyclize. Thus, the contribution of nongeminate processes involving the 5-hexenyl radical to the yield of **5h** in the rearrangement of benzhydryl 5-hexenyl ether is negligible.

On this basis, **5h, 6h,** and **7h** are products of intramolecular processes. The ratios of the intramolecular products, **5h:6h:7h** = 77:14:10, contrast with those for intermolecular products.

Another estimate of the product distribution from intramolecular processes comes from the reaction of benzhydryl tetrahydrofurfuryl ether with butyllithium in diethyl ether. Our hypothesis is that essentially all the tetrahydrofurfuryl radicals escaping geminate recombination react with the excess butyllithium according to Scheme III, leaving **5t, 6t,** and **7t** as intramolecular products only. We have no compelling justification for this assumption, but the electron (lithium atom) exchange between tetrahydrofurfuryl radicals and butyllithium apparently *does* occur (see earlier discussion of evidence), and it is probably thermodynamically favored. Many thermodynamically favored electron transfer reactions are nearly diffusion controlled. The yield of 4-penten-1-ol (19%), reflecting the intermolecular component of the reaction, is in good agreement with the estimate of the intermolecular component of the rearrangement of benzhydryl 5-hexenyl ether. It is gratifying to find also that the ratios **5t:6t:7t** (74:14:12) are also in excellent agreement with the ratios **5h:6h:7h** (77:14:10) from the intramolecular portion of the rearrangement of benzhydryl 5-hexenyl ether.

Thus 81–85% of the Wittig rearrangements of each of these benzhydryl primary alkyl ethers is intramolecular, while 15–19% proceeds intermolecularly through ketyl and alkyl radicals which escape geminate recombination.

Intermolecular and Intramolecular Product Ratios. By assuming that 0.19 is also the fraction of intermolecular rearrangement in reactions of benzhydryl, cyclopentylmethyl and benzhydryl butyl ethers and accepting the intermolecular ratios **5:6:7** derived from independent sources, the ratios **5:6:7** for the intramolecular portions of these Wittig rearrangements can also be estimated (eq 15).

$$P_i = 0.81P_{gi} + 0.19P_{ni} \text{ or } P_{gi} = \frac{P_i - 0.10P_{ni}}{0.81} \tag{15}$$

Here P_i is the net proportion of the ith product (**5, 6,** or **7**), P_{gi} is the percentage of the intramolecular (geminate) process leading to that product, and P_{ni} is the percentage of the intermolecular (nongeminate) process leading to that product. All the data are collected, together with the results of these calculations, in Table IX.

Table IX. Ratios 5:6:**7** of Products Formed Intermolecularly and Intramolecularly in Wittig Rearrangements of Benzhydryl Alkyl Ethers in THF

Alkyl group	Intermolecular	Intramolecular
5-Hexenyl	44:9:47[a]	77:14:10[b]
Tetrahydrofurfuryl	35:9:56[c]	74:14:12 (DEE)[d]
Cyclopentylmethyl	44:8:48[e]	(74:22:5)[f]
Butyl	42:7:51 (DEE)[g]	(85:10:5)[f]

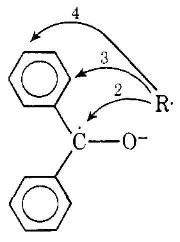
[a] From the reaction of 5-hexenyl iodide with lithium benzophenone ketyl. [b] From the Wittig rearrangement of benzhydryl 5-hexenyl ether. [c] From the reaction of tetrahydrofurfuryl iodide with lithium benzophenone ketyl. [d] From the Wittig rearrangement of benzhydryl tetrahydrofurfuryl ether in diethyl ether. [e] Average of values from the reaction of 5-hexenyl iodide with lithium benzophenone ketyl and the Wittig rearrangement of benzhydryl 5-hexenyl ether. [f] Calculated (eq 15) from the intermolecular ratios and the data of Table III. [g] From the Wittig rearrangement of benzhydryl tetrahydrofurfuryl ether in diethyl ether in the presence of excess butyllithium.

There is a remarkable consistency among the ratios **5:6:7** for both the intermolecular and intramolecular processes. The grand average for intermolecular processes is **5:6:7** = 41:8:51, while that for intramolecular processes is 77:15:8.

The fact that the ratios for the inter- and intramolecular processes differ could be interpreted in terms of fundamentally different inter- and intramolecular processes. Alternatively, the processes could be fundamentally the same, but differing somehow in the dynamics which determine the product ratios.

For economy, we pursue the latter idea. We see two possible kinds of distinctions between radical pairs formed by homolysis of the O–R bond of a lithium benzhydryl alkyl ether (*S* pairs) and the random spin radical pairs (*R* pairs) formed when independently generated ketyl and alkyl radicals diffuse together. First, the *S* pairs are formed with a definite, restricted set of initial geometries, while the *R* pairs are formed from randomly oriented individual radicals. Second, the *S* pairs and *R* pairs may be formed in different states of aggregation and cationic solvation.

An *S* pair results from simple stretching of the O-R bond. Some simultaneous bond bending may also occur but, in any event, in an *S* pair, R· is located initially near the carbonyl region of the ketyl. The amount of relative movement required for R· to bond at either the carbonyl carbon or the ortho ring carbon is very small. A much larger movement is required for bonding at the para ring carbon atom. If the radicals recombine rapidly, before they separate and



suffer complete rotational relaxation relative to one another, coupling at the carbonyl and ortho ring carbon atoms should be favored by these geometric factors. The observed ratios **5**:**6**:**7** are, in fact, 77:15:8. This consideration would be meaningless, of course, if it turned out that the inherent reactivities at the positions leading to **5**, **6**, and **7** stood in similar ratios. But these relative reactivities are measured by the product distributions from *R* pairs, and they are very different, the para position of the ketyl being slightly more reactive than the carbonyl carbon; **5**:**6**:**7** = 41:8:51. Thus, the difference in initial radical pair geometries leads to a correct prediction of the qualitative difference between inter- and intramolecular product distributions.

Ketyls are probably contact ion pairs, and the ion pairs tend to form paramagnetic dimers (ion quadrupoles). Nothing is known of the state of aggregation and solvation of lithio benzhydryl alkyl ethers in THF but, by analogy with other hydrocarbon anion systems, they might be expected to exist as solvent-separated ion pairs or as a closely balanced mixture of solvent-separated and contact ion pairs.[18] The state of solvation and aggregation of the lithium benzophenone ketyl in an *S* pair may reflect that of its lithio benzhydryl alkyl ether precursor. Thus, the differences in product distributions from *S* pairs and *R* pairs could reflect the differences in the state of ion aggregation and solvation of the lithium benzophenone ketyls in these radical pairs.

Both *R*-pair and *S*-pair product distributions seem nearly independent of solvent between THF and diethyl ether. Since these solvents have very different metal ion solvating capacities, so that rather different states of ion aggregation and solvation are expected in them, the data suggest that perhaps the ion aggregation and solvation factors affect the product distributions in only minor ways. Supporting this are product distributions from *R* pairs in ketyl-alkyl iodide reactions, where the ketyls are at rather high concentrations, and Wittig rearrangements, where the ketyls are at much lower concentrations and in the presence of other organolithium compounds (alkyllithiums and lithio benzhydryl alkyl ethers). The ketyl aggregates may be very different; yet the product distributions are similar.

Thus, the most satisfying radical pair theory of these Wittig rearrangements attributes the differences in product distributions from *S* pairs and *R* pairs to differences in initial geometries.

Contribution of Secondary Recombination to the Intramolecular Rearrangement. *Secondary geminate recombination* results when a pair of radicals which have separated from adjacent positions in solution (i.e., from an encounter) diffuse together again and react.[15] Secondary recombination accounts for the entire "cage" reaction when the radical pair source generates the radicals in a separated condition, as in decompositions of azo compounds, etc., where nitrogen or other small molecules intervene initially between the radicals.

Molecular rotations seem to be fast compared with secondary recombination. Experiments of Kopecky[20] and of Greene[21] gave 80-90% racemized cage coupling products when chiral radical pairs were generated by thermolyses of azo compounds.

To estimate the contribution of secondary recombination to the intramolecular portions of the Wittig rearrangements considered here, we use eq 16

$$P_{g7} = 0.80F_{sec}P_{n7} \qquad (16)$$

where F_{sec} is the fraction of the intramolecular process proceeding by secondary recombination. The bases of this equation are the following assumptions: (1) that if rotational relaxation of ketyl relative to R· were complete, P_{n7} would be the fraction of secondary recombination leading to **7**; (2) that such rotational relaxation is 80% complete in secondary recombination (see above); and (3) that intramolecular processes other than secondary recombination produce no **7**. Using the data of Table IX, F_{sec} is estimated as in Table X.

Table X. Estimated Maximum Contributions of Secondary Recombination to Intramolecular Wittig Rearrangements of Benzhydryl Alkyl Ethers[a]

Alkyl group	F, sec
5-Hexenyl	0.27
Tetrahydrofurfuryl	0.27
Cyclopentylmethyl	(0.13)[b]
Butyl	(0.13)[b]

[a] From data of Table IX and eq 15. For assumptions, see text. [b] Additional assumptions were required for these estimates; see Table IX and text.

With respect to variation in the amount of **7** formed in intramolecular processes other than secondary recombination, assumption 3 *maximizes* the estimated contribution of secondary recombination. Thus, while these estimates are of value only as qualitative indicators, the strong indication is that substantial portions of the intramolecular processes occur through pathways other than secondary recombination.

Intramolecular Pathways Other than Secondary Recombination. It may not be possible to distinguish experimentally the conceivable intramolecular pathways other than secondary recombination. One of these is *primary geminate recombination* of radicals, which occurs when a radical pair is generated with the radicals adjacent in solution and they react without ever having separated from adjacent positions.[15] Others include a broad spectrum of "concerted" migration pathways, which are quite conceivable in spite of the "antiaromatic" character of the transition states for such process. Both primary recombination and concerted reactions can occur with retention of configuration at the migrating group, and neither will give rise to CIDNP. Thus, it appears that all the probes conventionally used really probe only the intermolecular process and the secondary recombination portion of the intramolecular process, leaving the specification of the intramolecular pathways other than secondary recombination as matters of conjecture.

Approximate quantum mechanical calculations are sophisticated conjectures and, for model Stevens rearrangements, these predict concerted rearrangement pathways.[22,23] On a slightly lower level of sophistication, the following argument makes it plausible that "concerted" pathways compete with radical pathways in electron-sufficient 1,2-shifts and that "concerted" and radical pathways merge. Consider the rearrangement of R-A-B: to :A-B-R. In Figure 1 a coordinate position (x,y) is a system-representative point which also directly reflects the position of the migrating group R. The line of centers A-B defines the x axis, and the midpoint A and B is taken as the coordinate origin. As the system-representative point moves in the x,y plane, the A-B distance is allowed to adjust to minimum energy and R is maintained in its most favorable attitude for bonding. The dashed line represents schematically the ridge of highest energy separating R-A-B: from :A-B-R.[24] At sufficiently large y, this ridge passes smoothly into the broad plane representing dissociated radicals.

Suppose that there were no path from R-A-B: to :A-B-R with a lower energy barrier than that for homolytic dissociation. Then *every point on the ridge* (dashed line) *would have to be higher in energy than separated radicals*; that is, every point on the ridge would have to be antibonding with respect to separated radicals. The two sites for bonding of R· to :A–B· are so close to one another (on adjacent atoms) that it is impossible to conceive of a point along the dashed line where R· is not interacting with both sites. Since R· and :A–B· are mutually reactive radicals, the normal anticipation is that at least some points along the dashed line should be bonding. Thus, the normal expectation is that there should exist a pathway from R–A–B: to :A–B–R which involves less than complete separation to radicals. This would be a "concerted" pathway.

One can imagine a spectrum of such "concerted" pathways which merge into primary recombination. Whether a pathway is classified as "concerted" or as part of primary recombination is somewhat ambiguous; one must decide arbitrarily on the degree of interaction between R· and :A–B· below which they would be classified as a radical pair and above which as an intermediate state for a "concerted" process. Perhaps such a distinction should not be attempted.

The antiaromaticity of the systems along the dashed line of Figure 1 does not imply that these system are antibonding with respect to separated radicals, it merely implies that they are much less bonding than corresponding aromatic (or nonaromatic) systems would be. Consequently, the "concerted" pathways may be closely competitive with paths through separated free radicals (secondary recombination and intermolecular reactions).

Such "concerted" reactions should be distinguished from the "allowed" concerted reactions of orbital-symmetry theory. A feature of the latter is that bond making compensates for bond breaking at intermediate stages of the reactions. "Antiaromatic" transition states provide for little or no such compensation. We suggest the adjective "radical-concerted" to describe concerted pathways which are closely competitive with and closely akin to dissociation to free radicals. Further, we propose that radical-concerted pathways be regarded as a normal component of primary geminate recombination of radicals; i.e., "primary recombination" should be understood to include possible radical-concerted pathways. Thus, we may speak of electron-sufficient 1,2-shifts as homolytic dissociation–recombination reactions and have it understood that this may include radical-concerted components.

Consistency of Rate Constant and Cage Effect. Consider the consistency of the rate constant (10^8 M^{-1} sec^{-1}) for the reaction of 5-hexenyl radicals with lithium benzophenone ketyl in THF with the magnitude (0.8) of the cage effect, assuming a homolytic dissociation recombination mechanism for the entire process. Since a diffusion-controlled rate constant for the reaction of independently formed radicals would be about 2×10^9 M^{-1} sec,[25] only about $\frac{1}{20}$ of the electronic singlet engagements[24] of independently formed radicals results in reaction. On the other hand, when the radical pairs are formed by homolytic cleavage of ether anions, 0.8 of the engagements (100% electronic singlet) results in reaction. Thus, singlet components of R pairs are only $\frac{1}{16}$th as reactive as S pairs.

Is this reasonable? Two obvious explanations are (1) that singlet R pairs and S pairs have identical reactivities, but that a large portion of the intramolecular reaction proceeds through concerted processes, not through radical pairs, and (2) that R pairs and S pairs have different reactivities because of the different states of ionic aggregation and solvation of their ketyl moieties. Laying these aside, there is yet another reasonable explanation. The geometry of an S pair during the beginning of its initial encounter is favorable for immediate reaction. The alkyl radical is already situated in the vicinity of a reaction site, the carbon atom of the "carbonyl" group of the ketyl. This is not the case with R pairs, which are formed initially with random geometries. Thus, R pairs may be expected to undergo many collisions before finding a favorable geometry for reaction, which is not required for S pairs. This could easily account for a small factor like 16 in the relative reactivities of similarly constituted R and S pairs. Again, the description of rapid primary recombinations may merge with that of concerted processes in which dissociation to independent radicals is not quite achieved.

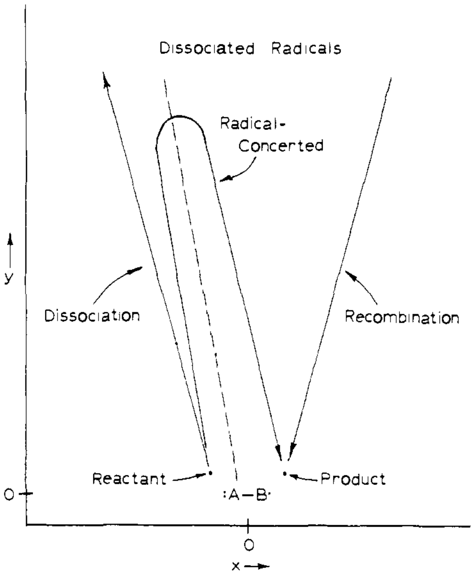


Figure 1. Schematic representation of pathways for electron-sufficient rearrangements of R–A–B: to :A–B–R. Points in the x-y plane represent the location of R with respect to A–B; the points representing R–A–B: and :A–B–R are labeled "reactant" and "product", respectively. All points at sufficiently large r ($r = (x^2 + y^2)^{1/2}$) represent dissociated radicals R· and :A–B·. The dashed line is the ridge of highest energy separating the regions of reactant and product. If all points on the dashed line are at a higher energy than that of dissociated radicals, the dissociation–recombination pathway will be the most favored pathway. However, if any points along the dashed line are of lower energy than dissociated radicals, there will exist a pathway (or a set of pathways) for a concerted rearrangement which is energetically more favored than dissociation–recombination. The rearrangement would then follow a distribution of paths govern by both energy and entropy factors. One of the paths shown crosses the dashed line just short of dissociation to independent radicals; this is a "radical-concerted" pathway. The dashed line leans to the reactant side purposely; this reflects the fact that all practical examples of electron-sufficient rearrangements are strongly favored thermodynamically, due to favorable redistributions of charge. These favorable charge redistributions also accompany radical dissociation. In the case of the Wittig rearrangement, negative charge moves from carbon to oxygen, a process which is strongly favored.

It should also be noted that, if S-pair encounters *after* the initial one are essentially like R-pair encounters, geometric randomization having occurred between the initial and subsequent encounters, then the measured rate constant for 5-hexenyl radical–lithium benzophenone ketyl reactions implies that the contribution of secondary recombination to the cage effect is very small; if the cage effect is 0.80, then 0.79 is assigned by this reasoning to primary recombination and 0.01 to secondary recombination.[26] This is consistent with the previous estimate of the maximum amount of secondary recombination based on product distributions.

Rearrangements of Benzhydryl Methyl Ether. The available facts are consistent with Scheme II. The absence of **6m** and **7m** from additions of methyllithium to benzophenone (Table IV) and their presence among the products of both Wittig rearrangements of benzhydryl methyl ether (Table V) and the reactions (through methyl radicals)[12] of lithium benzophenone ketyl with methyl iodide strongly suggest the involvement of methyl radicals in the Wittig rearrangement.

Rearrangements of Benzyl 5-Hexenyl Ether. The appearance of cyclopentylmethyl-containing products is consistent with Scheme II. The fact that they form a smaller proportion of the products than in corresponding rearrangements of benzhydryl ethers suggests that there is less intermolecularity in rearrangements of benzyl ethers than those of benzhydryl ethers. This would be consistent with a higher radical-radical reactivity for benzaldehyde radical-anion than for benzophenone radical-anion (ketyl), which is rational since the former is less delocalized and less sterically hindered than the latter.

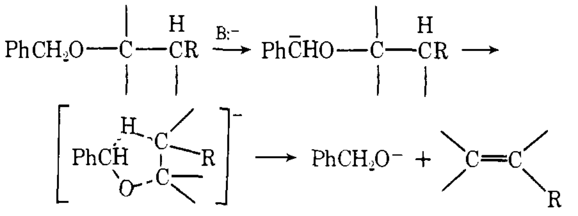
The data suggest that the intermolecular component of the reaction is insignificant in diethyl ether, but detectable, though small, in THF. A similar effect was noted in rearrangements of benzyl tetrahydrofurfuryl ether (see below).

Rearrangements of Benzyl Tetrahydrofurfuryl Ether. The fact that the rearrangement of benzyl tetrahydrofurfuryl ether in THF takes a normal course while that of benzhydryl tetrahydrofurfuryl ether fails requires comment, but no clear, unique rationalization suggests itself. Perhaps lithio benzyl tetrahydrofurfuryl ether exists primarily as contact ion pairs, while lithio benzhydryl tetrahydrofurfuryl ether exists as solvent-separated ion pairs. This is consistent with the less delocalized charge, leading to tighter ion pairs, presumably, of the anion from the benzyl ether. One might then assume, as suggested earlier, that solvent-separated ion pairs suffer an anionic cleavage while contact ion pairs suffer the radical cleavage in aralkyl tetrahydrofurfuryl ethers. Actually, it may not be necessary for there to be shifts in the actual types of reactant ion pairs present. The phenomenon could be stated more generally by positing that "tighter" ion pairs tend toward the radical cleavage and "looser" ion pairs toward the the anion cleavage, where "tightness" and "looseness" refer to the ease of ionic dissociation without specifically invoking different ion pair subspecies like "contact" and "solvent-separated" ion pairs.

As in the case of benzyl 5-hexenyl ether, there is evidence here that the intermolecular pathway is negligible in diethyl ether, but detectable in THF. Thus, 4-penten-1-ol is formed (probably as in Scheme III) in THF but not in diethyl ether.

Solvent Effects. In several cases we have carried out reactions in both THF and diethyl ether. A major solvent effect, the failure of the Wittig rearrangement of benzhydryl tetrahydrofurfuryl ether in THF and its success in diethyl ether, was discussed above. The apparent increase in intramolecularity of rearrangements of benzyl alkyl ethers in going from THF to diethyl ether is a minor effect which we will not attempt to rationalize. It is noteworthy that solvent effects on the rates of decomposition of lithio benzhydryl methyl ethers (Table VIII), the distributions of products from the same reaction (Table V), and the competition between α',β-elimination and the Wittig rearrangement in benzyl alkyl ethers (Tables VI and VII, see below) are negligibly small, while the solvent effect on the competition of α-elimination and the Wittig rearrangement is quite significant (see below).

α',β-Elimination. Earlier studies have demonstrated the competition of α',β-elimination with Wittig rearrangements of benzyl ethers.[4,27] In this process the base removes a benzylic (α') hydrogen initially, but a β-hydrogen of the alkyl group is later lost. Letsinger and Pollard proposed an intramolecular syn elimination (eq 17),[27] and Lansbury et al. used the same process in competition with the homolytic cleavage of the metallated ether to rationalize their findings that elimination is very important for primary alkyl ethers but negligible for tertiary alkyl ethers, with secondary alkyl ethers intermediate.[4] The argument is that the intramolecular syn elimination of eq 17 is competitive with a homolytic cleavage (Scheme II), the rate of which increases with the stability of the radicals being formed. Both this argument and the lower basicity of benzyhydrylic anions than benzyl anions[27] rationalize the fact that this elimination is less significant for benzhydryl alkyl ethers than for benzyl alkyl ethers. For benzhydryl alkyl ethers reacting with alkyllithiums in THF, it is insignificant. In light of the evidence,[4,27] eq 17 seems satisfactory, but we are puzzled by the absence of a solvent effect on the competition between the internal syn elimination and the homolytic cleavage of Scheme II. Further, we are puzzled by the finding of Lansbury et al. that, in a rigid system (dibenzobicyclo[2.2.2]octadien-2-ol), only 83% of the elimination is syn. What process accounts for the 17% anti elimination?

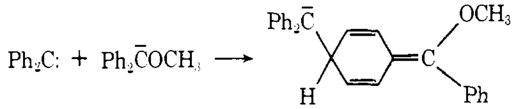


(17)

α-Elimination. Wittig and Clausnizer found phenol in 80% yield from metallated benzhydryl phenyl ether in diethyl ether but normal rearrangements in THF and DME.[9] α-Elimination would generate phenoxide ion and diphenylcarbene (eq 18).

$$\mathrm{Ph_2\bar{C}{-}O{-}R \rightarrow Ph_2C\colon + RO^-} \qquad (18)$$

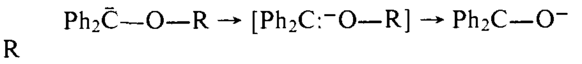
Wittig and Happe reported an unknown compound, mp 165.5–168°, from the reaction of benzhydryl methyl ether with phenyllithium in diethyl ether.[28] From the reaction of benzhydryl methyl ether with methyllithium in diethyl ether, we obtained 4-benzhydrylbenzophenone, mp 162–164° (see Experimental Section). This is a reasonable product if diphenylcarbene is formed in the reaction. One likely initial step in the formation of this product is represented by eq 19.



(19)

A shift in reaction medium to THF eliminates the 4-benzhydrylbenzophenone.

One might suppose that α-elimination followed by a carbene insertion into the C-O bond of RO⁻ (eq 20) might be the general mechanism of the Wittig rearrangement.


(20)

$$\mathrm{Ph_2\bar{C}{-}O{-}R \rightarrow [Ph_2C\colon^{-}O{-}R] \rightarrow \underset{R}{Ph_2C}{-}O^-} \qquad (20)$$

In addition to questions of the feasibility of process 20 itself, this hypothesis makes no provision for the formation of 2- and 4-alkylbenzophenones. Further, it seems inconsistent with the fact that 4-benzhydrylbenzophenone, a product of α-elimination, is absence in many reactions of benzhydryl alkyl ethers (in THF) in which the rearrangement proceeds smoothly.

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Appendix. Upper Limit of [K]

The initial behavior of the system (eq 11, parameters as given in text) was investigated using an iterative finite difference method and a computer. [R] reaches its maximum, steady-state value in about a millisecond, at which time [K] is less than 10^{-5} M and [A] is virtually unchanged from its original value. Subsequently, [R] slowly decreases as [K] builds up.

Equation 14 can be approximated as eq 21.

$$-\mathrm{d}[\mathrm{K}]/\mathrm{d}[\mathrm{A}] = (2a^2k_1k_t[\mathrm{A}])/(k_\mathrm{K}[\mathrm{K}])^2 \qquad (21)$$

Since d[K]/d[A] is a negative quantity, eq 21 (compare eq 14) *overestimates* −d[K]/d[A]. Integration of 21 between limits $t = t_\mathrm{s}$ and $t = \infty$ gives eq 22, which *overestimates* $[\mathrm{K}]_\infty$.

$$[\mathrm{K}]_\infty = \left[\frac{3a^2k_1k_y[\mathrm{A}]_\mathrm{s}^2}{k_\mathrm{K}^2} + [\mathrm{K}]_\mathrm{s}^3\right]^{1/3} \qquad (22)$$

The initial values $[\mathrm{A}]_\mathrm{s}$ and $[\mathrm{K}]_\mathrm{s}$ are not those for $t = 0$ because eq 14 is derived from a steady-state expression for [R]. Thus, $[\mathrm{A}]_\mathrm{s}$ and $[\mathrm{K}]_\mathrm{s}$ may be chosen for any time after the steady state on [R] is reached. From the computer calculations, we can set $[\mathrm{A}]_\mathrm{s} = [\mathrm{A}]_0 = 0.1$ and $[\mathrm{K}]_\mathrm{s}$ = values in the range 10^{-7} M upward. For values of $[\mathrm{K}]_\mathrm{s}$ less than about 10^{-4} M, it turns out that $[\mathrm{K}]_\mathrm{s}$ in eq 22 is negligible. Since there are valid values of $[\mathrm{K}]_\mathrm{s}$ less than 10^{-4} M, this term can always be neglected.

If $a = 1$, eq 22 gives the maximum value of [K] as 1.82×10^{-4} M. If this were the constant value of [K] throughout the reaction, the fraction of free 5-hexenyl radicals which would cyclize would be $k_\mathrm{c}/k_\mathrm{c} + k_\mathrm{K}[\mathrm{K}]) = 0.846$. In fact, 0.15 of the migrating groups cyclize. Thus, the maximum possible value of a is $0.15/0.846 = 0.177$. When this value of a is assumed, $[\mathrm{K}]_\infty = 5.73 \times 10^{-5}$ M is calculated. Repetition of the entire process until self-consistency is obtained gives $a_\mathrm{max} = 0.16$, $[\mathrm{K}]_\mathrm{max} = 5.3 \times 10^{-5}$ M, and the minimum fraction of "free" (cage-escaped) 5-hexenyl radicals which cyclize = 0.95. Since the maximum fraction of 5-hexenyl radicals cyclizing is 1.00, a lies between the limits 0.15 and 0.16.

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(12) 2-Alkylbenzophenones are taken to be eluted from neutral alumina with less polar solvents, to have smaller VPC retention times on QF-1 (a fluorosilicon), and to be formed in smaller amounts in reactions of alkyl iodides with lithium benzophenone ketyl than isomeric 4-alkylbenzophenones. In each of our cases, these are all the properties of a particular member of the pair. The chromatographic properties are those expected on general grounds of molecular polarity; a 2-alkylbenzophenone should be less polar than its 4 isomers. 2- and 4-methylbenzophenones, for which these criteria are not the basis of structural assignment, conform to each of them. (a) G. Wittig, L. Gonsior, and H. Vogel, *Justus Liebigs Ann. Chem.*, **688**, 1 (1965).

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(14) Lithium naphthalene in THF was allowed to react with 5-hexenyl chloride at room temperature. The product solution was divided into two portions, one of which was quenched with D_2O for 2 min and the other for 2 hr after the reaction. The ratio methylcyclopentane/1-hexene was the same (12) for both portions, while mass spectra showed 35% monodeuteriohydrocarbons from the 2-min quench and none from the 2-hr quench. Thus, 5-hexenyllithium was initially present, but not after 2 hr, and it failed to cyclize, rather than react with solvent, to a detectable extent during this period.

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(18) By analogy with fluorenyllithium and other lithium-delocalized carbanion ion pairs. See J. Smid in "Ions and Ion Pairs in Organic Reactions", M. Szwarc, Ed., Wiley-Interscience, New York, N.Y., 1972, pp 85–151.

(19) This value seems a fair estimate in view of the rate constants for decomposition of lithio benzhydryl methyl ethers (Table VIII). While rate constants for decompositions of lithio benzhydryl 5-hexenyl ethers might be expected to be a little larger,[5] the facts that metallation must precede decomposition of the metallated ether and that metallation is competitive with decomposition of the metallated ether mean that the actual rate of production of ketyl and 5-hexenyl radicals will be lower than that estimated as if the metallated ether were formed instantly.

(20) K. R. Kopecky and T. Gillian, *Can. J. Chem.*, **47**, 2371 (1969).

(21) F. D. Greene, M. A. Berwick, and J. C. Stowell, *J. Am. Chem. Soc.*, **92**, 867 (1970); J. P. Engstrom and F. D. Green, *J. Org. Chem.*, **37**, 968 (1972).

(22) M. J. S. Dewar, calculations presented at the 23rd National Organic Symposium of the American Chemical Society, Tallahassee, Fla., June 1973.

(23) G. L. Closs, private communication, 1975.

(24) The entire sequence of initial encounter, temporary separations, and geminate reencounters constitute an engagement: J. F. Garst, F. E. Barton, II, and J. I. Morris, *J. Am. Chem. Soc.*, **93**, 4310 (1971).

(25) A typical rate constant for engagements is about 10^{10} M^{-1} sec^{-1}. The initial electronic singlet character of these is one-fourth. If the triplet component cannot react, the maximum rate constant is $2\text{–}3 \times 10^9$ M^{-1} sec^{-1}, which agrees well with typical rate constants found for reactions between very reactive radicals.

(26) If α_0 is the probability of primary recombination, β' is the probability of reaction (ever) of singlet R pairs, and the initial reencounter is identical with the initial R-pair encounter, then

$$b = \alpha_0 + (1 - \alpha_0)\beta'$$

where b is the cage effect. Setting b to 0.80 and β' to 0.05 gives $\alpha_0 = 0.79$ and $(1 - \alpha_0)\beta'$ (secondary recombination) = 0.01.

(27) R. F. Letsinger and D. F. Pollard, *J. Am. Chem. Soc.*, **78**, 6079 (1956).

(28) G. Wittig and Happe, *Justus Liebigs Ann. Chem.*, **557**, 205 (1947).