Reactions of Alkali Benzophenone Ketyls with Alkyl Iodides

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Abstract: Alkali benzophenone ketyls in ethers react with alkyl iodides to give not only alkyldiphenylcarbinols, but also 2- and 4-alkylbenzophenones, benzhydryl alkyl ethers, and alkyldiphenylmethyl alkyl ethers, depending on the metal ion, solvent, and concentrations. Reactions of lithium benzophenone ketyl are especially clean in that no ether products are formed, even in the polar ether THF which promotes formation of these products when other metal ions are used. In THF, lithium benzophenone ketyl reacts with alkyl iodides through initial electron-transfer steps, not through initial nucleophilic displacements. Evidence for this includes a quantitative treatment of the extent of cyclization in the products of reactions of 5-hexenyl iodide. The extent of cyclization implies that the rate constant for the reaction of 5-hexenyl radicals with lithium benzophenone ketyl is 1.5×10^3 times that for the cyclization of 5-hexenyl radicals (room temperature). The latter rate constant is about 10^5 sec^{-1} so the former is about 1.5×10^8 M^{-1} sec^{-1}, an order of magnitude or so less than diffusion controlled. Evidence against an initial nucleophilic displacement in the ketyl-alkyl iodide reactions includes the fact that the second-order rate constants increase through the series methyl iodide, 5-hexenyl iodide, and *tert*-pentyl iodide. Further, none of these reactions gives any products of elimination from the alkyl iodides.

In 1911 Schlenk and Weickel formulated the ketyls, discovered earlier by Beckman and Paul,[1] as free radicals **1**.[2] Part of the evidence was their determination of the products of the reaction of methyl iodide with the ketyl from sodium and dibiphenylyl ketone as those of eq 1.

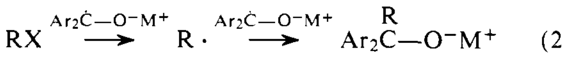
$$\underset{\mathbf{1}}{2Ar_2\dot{C}{-}OM} + MeI \xrightarrow{[H^+\ workup]} MI + Ar_2C{=}O + Ar_2C(Me)OH \qquad (1)$$

Loss of metal atoms from metal adducts of organic compounds seemed reasonable then, as it does today.

Schlenk's formulation of the ketyl structure stands with only minor modifications. Modern workers generally prefer to represent ketyl monomers as ion pairs ($Ar_2\dot{C}{-}O^-M^+$), and it is recognized that there is a pronounced tendency of these ion pairs to aggregate to dimers (ion quadrupoles) and perhaps even higher aggregates. Dimerization to pinacolates, which once seemed important, now appears negligible at moderate concentrations in the more polar ether solvents.[3]

Beginning in 1928, Wooster presented a series of reports on the reaction of sodium benzophenone ketyl with ethyl bromide in liquid ammonia.[4] He considered at least five mechanisms and a variety of experiments designed to test and distinguish among them. He specifically ruled out the dissociation of ketyl to ketone and metal, which would then react with the alkyl halide, and the disproportionation of two ketyl molecules (ion pairs) to benzophenone and benzophenone dianion (disodium benzophenone), which would then react with the alkyl halide.

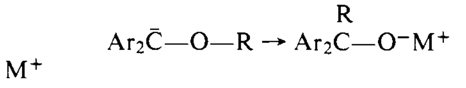
Another mechanism discounted by Wooster, the electron transfer-radical combination process of eq 2, has been popular nonetheless in recent times.



$$RX \xrightarrow{Ar_2\dot{C}{-}O^-M^+} R\cdot \xrightarrow{Ar_2\dot{C}{-}O^-M^+} Ar_2\overset{R}{C}{-}O^-M^+ \qquad (2)$$

The evidence against this was that the yield of recovered benzophenone was found to vary sharply with the speed of addition of ethyl bromide to the ketyl solution. Since benzophenone is generated in the first step of eq 2, and since ethyl bromide is not involved in later steps, the mechanism seems inconsistent with the observations.

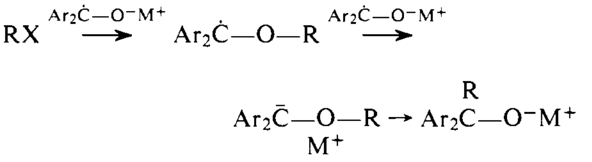
Wooster also considered a mechanism based on what is now known as the Wittig rearrangement (eq 3),[5] which had been described by Schlenk in 1928.[6]



$$\underset{M^+}{Ar_2\bar{C}}{-}O{-}R \rightarrow Ar_2\overset{R}{C}{-}O^-M^+ \qquad (3)$$

(Wittig rearrangement)

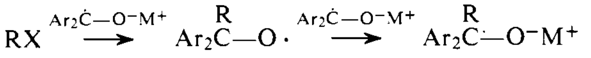
It is possible that the first stage of a ketyl-alkyl halide reaction gives the carbanion which is the starting point for a Wittig rearrangement; the rearrangement itself would complete the reaction, giving the required products (eq 4).



$$RX \xrightarrow{Ar_2\dot{C}{-}O^-M^+} Ar_2\dot{C}{-}O{-}R \xrightarrow{Ar_2\dot{C}{-}O^-M^+} \underset{M^+}{Ar_2\bar{C}}{-}O{-}R \rightarrow Ar_2\overset{R}{C}{-}O^-M^+ \qquad (4)$$

Wooster ruled this out by showing that the rearrangement of the sodium salt of benzhydryl ethyl ether in liquid ammonia is slower than the overall reaction of ethyl bromide with sodium benzophenone ketyl under the same reaction conditions.

In the end, Wooster preferred a direct carbon alkylation of the ketyl by the alkyl halide, giving an intermediate alkoxy radical, which is then reduced by more ketyl (eq 5).



$$RX \xrightarrow{Ar_2\dot{C}{-}O^-M^+} Ar_2\overset{R}{C}{-}O\cdot \xrightarrow{Ar_2\dot{C}{-}O^-M^+} Ar_2\overset{R}{C}{-}O^-M^+ \qquad (5)$$

Warhurst revived the issue in a series of papers dealing with the kinetics of reactions of alkyl halides with a variety of organic radical anions, including ketyls, mostly in dioxane but in some other ethers as well.[7] Morantz and Warhurst posited the mechanism of eq 2,[7a] pointing out its consistency with the reaction products as determined by Schlenk and with the second-order rate law (rate = k[ketyl][alkyl halide]) they found. Since several of the other mechanisms considered by Wooster, notably eq 4 and 5, also fit these criteria, this evidence is not definitive. Further weak evidence supporting eq 2 is the approximately linear relation observed between the free energies of activation and the energies of the molecular orbitals occupied by the odd electrons in a series of ketyls, as calculated from simple molecular orbital theory. This might be anticipated on the basis of eq 2, but it is not necessarily inconsistent with other mechanisms such as those represented by eq 4 and 5.

A cogent kinetic test of mechanism would be to vary the structure of the alkyl halide in reactions with a given ketyl. The results might be inconsistent with an initial SN2 step, the most likely first step in eq 4 and 5. Unfortunately, of the many ketyl-halide pairs examined by Warhurst and coworkers, only one is pertinent. Isopropyl bromide was found to be slightly more reactive (a factor of about 2) toward sodium benzophenone ketyl in dioxane than *n*-propyl bromide. This could be inconsistent with SN2 processes, but since the products were not examined, the possibility cannot be excluded that a faster elimination component for isopropyl bromide compensates for a slower SN2 component.

Schenk and Matthias reported that reactions of sodium benzophenone ketyl with methyl iodide in various solvents give not only the product of methylation at the carbonyl carbon (diphenylmethylcarbinol), but also products of methylation at carbon atoms of the benzene rings (*o*- and *p*-methylbenzophenones) and even products of methylation at oxygen.[8,9] The nature of the *O*-methyl products was unspecified, the evidence being the NMR spectra of the product mixtures. When the reaction was carried out in 1,2-dimethoxyethane (DME), the product NMR spectrum was reported to show *only* OCH_3 and ArH absorptions but, in dioxane, diethyl ether, isopropyl alcohol, benzene, and hexane, no O-methylation was observed.

Since the Wittig rearrangement pathway would involve O-methylated intermediates, and since the Wittig rearrangement is known to give migration to ring carbon atoms as well as to carbonyl carbon,[10] these findings suggest eq 4 as the reaction mechanism. It could be that this mechanism is subverted in DME by a solvent effect slowing the rearrangement stage, speeding the alkylation stage, or both.

Thus, we have total confusion, with Wooster's data supporting eq 5, Warhurst's favoring eq 2, and Schenk's suggesting eq 4 as the mechanism of ketyl-alkyl halide reactions.

For this reason and because of their likely close relationship to Wittig rearrangements, we have studied reactions of benzophenone ketyls with alkyl iodides in ethers. As it turned out, the cleanest systems are the reactions of lithium ketyls with alkyl iodides,[11] and we believe that our results, described below, definitively rule out the mechanisms of eq 4 and 5. They are consistent with that of eq 2.

Experimental Section

Small Scale Ketyl-Alkyl Iodide Reactions. Reactions were carried out in 10-ml graduated Pyrex test tubes with several attached arms. At the top of each tube was a glass tube leading to a constriction just before a 10/30 tapered ground-glass joint. Between the test tube and the constriction were attached an arm leading to a quartz optical cell, an arm with a fritted disk followed by several constrictions and an open end, and a short arm, bent upward, which could be closed with a rubber septum.

Approximately 100 mg of benzophenone was placed in the test tube through the short side arm, which was then capped with a rubber septum. After an alkali metal was placed in the arm with several constrictions and the end sealed, the vessel was attached through the 10/30 joint to a vacuum manifold and gently flamed during evacuation. Sodium or potassium was distilled through the constriction and deposited as a mirror on the upper part of the arm; the bottom part was then removed. Lithium mirrors were created by liquefying ammonia in the side arm, dissolving lithium, and evaporating the ammonia with splashing up the arm caused by bumping. Cesium was distilled to the upper surface of the arm from a mixture of cesium chloride and calcium metal.

After the solvent was distilled through the vacuum manifold into the reaction vessel from storage over disodium benzophenone, the vessel was cut away from the vacuum manifold at the constriction near the 10/30 joint. The solution of benzophenone was tipped onto the alkali metal mirror through the fritted disk and allowed to react. It was filtered back through this disk into the main vessel. The ketyl concentration was monitored spectrophotometrically. Since Beer's law was not followed at very high concentrations, a concentration-extinction coefficient working curve was established for each metal ion-solvent system. In the construction of these curves, ketyl was determined by quenching with water and titrating the total base with standard hydrochloric acid.

When the desired concentration of ketyl was reached, the solution was frozen in the main body of the reaction vessel with liquid nitrogen while the mirror tube was removed with a torch. The solution was then allowed to come to room temperature, a weighed amount of alkyl halide was injected by syringe through the septum, the reactants were mixed thoroughly by shaking, and the reaction was allowed to proceed. The product solution was quenched with aqueous acid and oxidized by bubbling pure oxygen through it until the yellow color disappeared.

Large Scale Ketyl-Alkyl Iodide Reactions. Two round-bottomed flasks were connected by a tube with a fritted disk and by a smaller tube to equalize their pressures. They were flamed and flushed with ketyl-scrubbed argon. During the flushing, weighed amounts of benzophenone and alkali metal were placed in one flask. An equal amount of benzophenone was added to the other flask, which was attached to a mercury-filled U tube to keep air out. A magnetic stirring bar was placed in each flask.

Solvent was distilled directly into the flask containing the metal from another flask containing a solution of benzophenone ketyl. After transfer of the desired amount, the distillation assembly and U tube were replaced with rubber septa.

The mixture was stirred for at least 4 hr, after which it was assumed (for purposes of yield calculations) that all benzophenone had been converted to its dianion. The solution was transferred through the fritted disk to the other flask and converted to ketyl by reaction with the benzophenone present. A weighed amount of alkyl halide was added by syringe and the solution stirred until reaction was complete.

The product solution was quenched with saturated aqueous ammonium chloride, water, or acetic acid and oxidized by bubbling oxygen through it until the yellow color disappeared.

Materials. Alkyl iodides were obtained commercially or prepared by standard methods. Prior to use they were analyzed by VPC and, if less than 98% purity was indicated, they were further purified by distillation on an annular Teflon spinning-band column or by preparative VPC. Commercial benzophenone was recrystallized to a sharp melting point. Commercial inorganic chemicals (reagent grade or better) were used directly.

For analytical purposes, NMR and VPC characteristics of authentic materials were required. **5m**, **6m**, **7m**, **8m**, **9m**, **5h**, **8h**, **5c**, **8c**, **5t**, and **8t**, all of which were products or possible products of ketyl-alkyl iodide reactions, were independently prepared (see Results and Discussion section for identifying codes). **6h**, **7h**, **6c**, **7c**, **6t**, and **7t** were characterized spectroscopically after isolation or partial isolation from appropriate Wittig rearrangements[12] or ketyl-alkyl iodide reactions and the required VPC characteristics determined. **5p**, **6p**, and **7p** were assumed as products of the reaction of lithium benzophenone ketyl with *tert*-pentyl iodide by analogy with the other ketyl-alkyl iodide reactions, and corresponding VPC peaks were assigned by analogy with the properties of the other compounds **5**, **6**, and **7**.

5m (1,1-Diphenylethanol). Methylmagnesium iodide and benzophenone gave **5m** in 73% yield, mp 80.5-81° from ligroin (lit.[13a] mp 81°).

6m (2-Methylbenzophenone). 2-Methylbenzophenone was prepared by the method of Ador and Rilliet.[13b] To 2.72 g (0.02 mol) of *o*-toluic acid in 25 ml of dry benzene was added 3 ml of thionyl chloride; the solution was refluxed 1 hr. After evaporation of excess thionyl chloride and benzene, the residue was again taken up in benzene (25 ml). The acid chloride solution was added to 4 g of aluminum chloride in 25 ml of benzene and the mixture refluxed until HCl evolution ceased; it was poured into ice-water and extracted with several portions of benzene. After drying over calcium sulfate and removing the benzene, the crude product was chromatographed on 80 g of neutral alumina (Merck) to give 2.2 g (56%) of colorless liquid, ν_{max} (neat) 1665 cm^{-1} (C=O).

7m (4-Methylbenzophenone). Following the identical procedure as for **6m**, using *p*-toluic acid, **7m** was obtained in 69% yield, white crystals from ligroin mp 55-56° (lit.[14] mp 58-59°).

8m (Benzhydryl Methyl Ether). To 1.23 g (0.053 mol) of freshly cut sodium in 100 ml of DME was added 5 ml of methanol and the mixture stirred for 1 hr. Following addition of 5.9 g (0.029 mol) of benzhydryl chloride, the solution was refluxed 6 hr, whereupon it was filtered, concentrated to ca. 10 ml, poured into ice and 10% HCl, and extracted with ether. The ether solution was washed with aqueous sodium bicarbonate and with saturated aqueous sodium chloride, then dried over magnesium sulfate, and filtered. Distillation gave 3.5 g (60%) of colorless liquid, bp 99-100° (0.5-0.8 Torr) [lit.[15] bp 104-105° (3-5 Torr)].

9m (Diphenyl(methyl)carbinyl Methyl Ether). The reaction of the sodium salt of **5m** with methyl iodide in DME gave **9m** in 74% yield, bp 109-112° (0.9-1.0 Torr) [lit.[16a] bp 140° (12 Torr)].

5h (Diphenyl(5-hexenyl)carbinol). 5h was prepared from phenyl(5-hexenyl)carbinol by oxidizing it to the ketone and adding phenylmagnesium bromide.

Phenyl(5-hexenyl)carbinol. To 1.27 g of Mg in 75 ml of ether was added 8.64 g (0.053 mol) of 5-hexenyl bromide in portions small enough to generate moderate reflux. The Grignard reagent was allowed to react with 5.62 g (0.053 mol) of benzaldehyde, and the reaction mixture was poured into ice and saturated aqueous ammonium chloride. This mixture was extracted with ether, and the ethereal solution was washed with 5% sodium bicarbonate and saturated sodium chloride aqueous solutions and then dried over anhydrous magnesium sulfate. It was filtered, concentrated, and distilled at reduced pressure to yield 6.53 g (67%) of colorless liquid: bp 111-113° (1.5-2.0 Torr); $\nu_{\max}$ (neat) 3350 (OH), 1640 ($CH{=}CH_2$), 910 and 995 cm^{-1} ($CH{=}CH_2$); δ 1.35 (m, 6 H, $CH_2CH_2CH_2$), 1.85 (m, 2 H, $C\mathit{H}_2CH{=}CH_2$), 3.31 (s, 1 H, OH), 4.25 (t, 1 H, $HOC\mathit{H}$), 4.70 (m, 2 H, $CH{=}C\mathit{H}_2$), 5.45 (m, 1 H, $C\mathit{H}{=}CH_2$), 6.90 ppm (s, 5 H, C_6H_5); mol wt (calcd, 190) parent mass peak *m/e* 190.

Diphenyl(5-hexenyl)carbinol. To 2.00 g (0.0105 mol) of phenyl(5-hexenyl)carbinol in 25 ml of acetone was added Jones reagent until an orange color persisted. The color was discharged with isopropyl alcohol. Following neutralization with sodium bicarbonate, the acetone layer was separated. The aqueous layer was extracted with ether, and the ether and acetone layers were combined and dried over anhydrous magnesium sulfate. After filtration, the solvents were removed in vacuo, and the residue was taken up in dry ether and added to excess phenylmagnesium bromide in ether. Standard Grignard work-up gave a pale yellow oil weighing 2.5 g (83%). Chromatography on alumina (1:1 ether:petroleum ether as eluent) gave pure colorless material: $\nu_{\max}$ ($CHCl_3$) 3430 (OH), 1645 ($CH{=}CH_2$), 910 and 995 cm^{-1} ($CH{=}CH_2$); δ 1.3 (m, 6 H, $CH_2CH_2CH_2$), 2.0 (m, 3 H, $C\mathit{H}_2CH{=}CH_2$, $O\mathit{H}$), 4.75 (m, 2 H, $CH{=}C\mathit{H}_2$), 5.5 (m, 1 H, $C\mathit{H}{=}CH_2$), 7.1 ppm (m, 10 H, C_6H_5); mol wt (calcd, 266) highest mass peak *m/e* 249 (M − 17).

5c (Diphenyl(cyclopentylmethyl)carbinol). 5c was prepared from phenyl(cyclopentylmethyl)carbinol by oxidizing it to the ketone and adding phenylmagnesium bromide.

Phenyl(cyclopentylmethyl)carbinol. Excess benzaldehyde was added to the Grignard reagent prepared from 19.6 g (0.12 mol) of cyclopentylmethyl bromide and magnesium in ether. Standard work-up followed by distillation gave 18.3 g (80%) of a colorless oil bp 114° (1.8 Torr). On standing, the oil crystallized to a white solid: mp 37-38°; δ 1.55 (m, 11 H, C_6H_{11}), 3.85 (s, 1 H, OH), 4.40 (t, 1 H, $C\mathit{H}OH$), 7.08 ppm (s, 5 H, C_6H_5); mol wt (calcd, 190) parent mass peak *m/e* 190.

Diphenyl(cyclopentylmethyl)carbinol. Following the procedure above for diphenyl(5-hexenyl)carbinol, 1.0 g of phenyl(cyclopentylmethyl)carbinol gave rise to 0.85 g of diphenyl(cyclopentylmethyl)carbinol (61%): mp 42-43°; $\nu_{\max}$ ($CHCl_3$) 3440 cm^{-1} (OH); δ 1.5 (m, 9 H, C_5H_9), 2.25 (d, 2 H, $C\mathit{H}_2C_5H_9$), 7.0 ppm (m, 10 H, C_6H_5); mol wt (calcd, 266) mass peak *m/e* 249 (M − 17).

5t (Diphenyl(tetrahydrofurfuryl)carbinol). To 2.3 g (0.012 mol) of phenyl(tetrahydrofurfuryl)carbinol[17] in 25 ml of acetone was added Jones reagent until a permanent orange color developed. The color was discharged by dropwise addition of isopropyl alcohol and the mixture neutralized with sodium bicarbonate. The acetone layer was separated and dried over anhydrous magnesium sulfate. After filtration, the acetone was stripped off and the residue dissolved in ether. The ether solution was added to excess phenylmagnesium bromide and the resulting mixture worked up following standard procedures. After solvents were removed the material crystallized. Recrystallization from ether-petroleum ether gave 0.99 g (31%) of white crystals: mp 134-135°; $\nu_{\max}$ (CCl_4) 3480 cm^{-1} (OH); δ 1.9 (m, 6 H, $CH_2C\mathit{H}_2C\mathit{H}_2CHC\mathit{H}_2COH$), 3.5 (m, 3 H, $CH_2C\mathit{H}OC\mathit{H}_2CH_2$), 7.0 ppm (m, 10 H, C_6H_5); mol wt (calcd, 268) mass peak *m/e* 251 (M − 17).

8h (Benzhydryl 5-Hexenyl Ether). To 1.3 g (0.054 mol) of sodium hydride suspended in DME was added 9.94 g (0.054 mol) of benzhydrol in DME (total volume ca. 150 ml). The resulting mixture was stirred 24 hr with a slight excess (9.8 g, 0.06 mol) of 5-hexenyl bromide. After filtration and concentration, the material was placed on a column of 150 g of neutral alumina (activity 1). Elution with 30-60° petroleum ether gave 8.7 g (61%) of light yellow oil. Distillation on an Nester-Faust annular Teflon still at 127-128° (0.5 Torr) gave 3.3 g of material showing no impurities by VPC: $\nu_{\max}$ (neat) 1635 ($CH{=}CH_2$), 1110 (C—O—C), 915 and 1000 cm^{-1} ($CH{=}CH_2$); δ 1.55 (m, 4 H, $CH_2C\mathit{H}_2C\mathit{H}_2$), 1.98 (m, 2 H, $C\mathit{H}_2CH{=}CH_2$), 3.25 (t, 2 H, OCH_2), 4.78 (m, 2 H, $CH{=}C\mathit{H}_2$), 5.08 (s, 1 H, $OCHPh_2$), 5.60 (m, 1 H, $C\mathit{H}{=}CH_2$), 7.10 ppm (s, 10 H, C_6H_5); mol wt (calcd, 266) parent mass peak *m/e* 266.

8t (Benzhydryl Tetrahydrofurfuryl Ether). To 20.3 g (0.1 mol) of benzhydryl chloride in 100 ml of DMF was added 51 g (0.5 mol) of tetrahydrofurfuryl alcohol containing 20 ml of pyridine. After stirring 2 hr at 70°, most of the excess alcohol was removed by distillation at atmospheric pressure. The residue was cooled and poured into water, and the aqueous layer was separated. The organic layer was dissolved in 200 ml of ether and dried over anhydrous magnesium sulfate, after which it was filtered and the ether stripped off in vacuo. Distillation gave 25.1 g (94%) of liquid with: bp 168-171° (0.7-1.2 Torr); $\nu_{\max}$ (neat) 1100, 1080 cm^{-1} (C—O—C); δ 1.85 (m, 4 H, $CH_2C\mathit{H}_2C\mathit{H}_2CH$), 3.28 (d, 2 H, $OC\mathit{H}_2CHO$), 3.65 (m, 3 H, $CH_2C\mathit{H}OC\mathit{H}_2CH_2$), 5.19 (s, 1 H, $OCHPh_2$), 7.10 ppm (s, 10 H, $C_6\mathit{H}_5$); mol wt (calcd, 268) parent mass peak *m/e* 268.

8c (Benzhydryl Cyclophenylmethyl Ether). Using cyclopentylmethanol instead of tetrahydrofurfuryl alcohol, the procedure for **8t** was followed, giving **8c** in 85% yield: bp 142-144° (0.4 Torr); $\nu_{\max}$ (neat) 1090 cm^{-1} (C—O—C); δ 1.45 (m, 9 H, C_5H_9), 2.5 (d, 2 H, $OC\mathit{H}_2CH$), 4.9 (s, 1 H, $OCHPh_2$), 6.9 ppm (s, 10 H, C_6H_5); mol wt (calcd, 266) parent mass peak *m/e* 266.

Analyses. Solutions of reaction products were analyzed directly by VPC, or they were concentrated and then analyzed by VPC or chromatographed on alumina. For solutions to be analyzed by NMR, the solvent was stripped off and replaced by chloroform. After analyses by NMR, some mixtures were also analyzed by VPC, a procedure which always gave consistent results.

Columns, conditions, and internal standards are given in the footnotes to the tables of results.

Kinetics. Reaction mixtures were prepared as above under "Small Scale Reactions". Reaction progress was monitored spectrophotometrically at 6200 Å. Conventional integrated second-order plots gave excellent linearity with very little scatter. All reactions were at 23 ± 1°.

Results and Discussion

Approach to the Problem. We first surveyed the gross effects on product distributions of variations in solvent, concentration, and metal ion in the reactions of alkali benzophenone ketyls with methyl iodide. In many situations, products of O-methylation were found. However, O-methylation was never found for lithium benzophenone ketyl. This is very fortunate because alkyllithiums are the conventional promoters of Wittig rearrangements, and we hoped to be able to apply the results of these studies to the mechanisms of Wittig rearrangements. Since Wittig rearrangements are often carried out in THF, we chose reactions of lithium benzophenone ketyl with alkyl iodides in THF for detailed study. For these systems, kinetic and product probes were used. 5-Hexenyl iodide and tetrahydrofurfuryl iodide provided special product probes, the former testing for alkyl radical intermediates, which are indicated, and the latter for alkyl anion intermediates, which are not indicated.

Yields. In most cases our analyses indicate 50-70% total

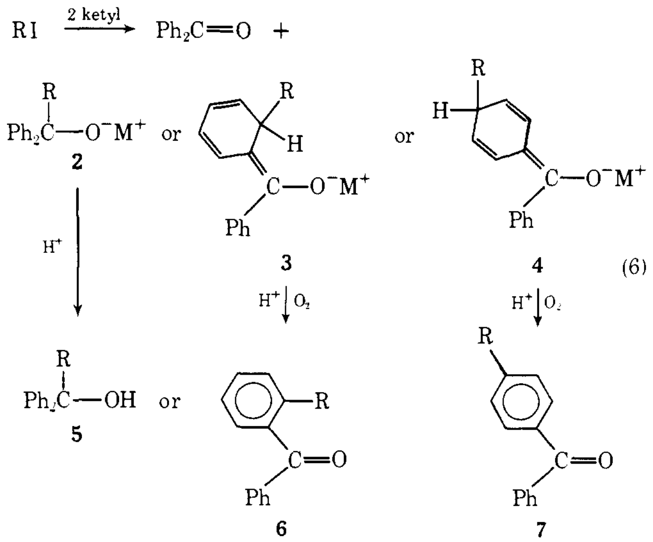
Table I. Products of Reactions of Sodium Benzophenone Ketyl with Methyl Iodide in Diethyl Ether at Room Temperature

Experiment	$[\mathrm{Ketyl}]_0$[a]	$[\mathrm{MeI}]_0/[\mathrm{ketyl}]_0$[a]	**5m**[b]	**6m**[b]	**7m**[b]
3-7-67-a	0.037	0.48	20	ND	30
3-19-67-2	0.037	0.50	18	ND	38
4-2-67-1	0.017	2.9	21	ND	36
3-23-69	~0.05	0.50	(33)[c]	(7)[c]	(60)[c]

[a] $[\,]_0$ = initial molar concentration. [b] Absolute percent yields, based on limiting reagent, determined by VPC on a 5 ft × $^1/_8$ in. 10% QF-1 column operated at 165° using 4,4'dimethylbenzophenone as an internal standard. [c] Relative percent yields from the NMR spectrum of the product mixture.

yields. There were no unaccounted-for peaks in the VPC traces, and occasionally the total yield was quite high (≥90%). For the large-scale reactions at least, these variations may reflect uncertainty in the initial ketyl concentration.

Survey of Reactions of Methyl Iodide. Table I gives the product distribution for reactions of sodium benzophenone ketyl with methyl iodide in diethyl ether. Diphenylmethylcarbinol (**5m**) is accompanied by *2*- and *4*-methylbenzophenones (**6m** and **7m**). It is presumed that these products result from precursors **2m, 3m,** and **4m** on hydrolytic and oxidative work-up, as shown in eq 6. The yellow color of the



(6)

m, R = methyl
h, R = 5-hexenyl
c, R = cyclopentylmethyl
t, R = tetrahydrofurfuryl
p, R = *tert*-pentyl

product solutions is consistent with the presence of the quinoid anions **3** and **4**; it is discharged when air is admitted. No O-methylation results. The yield of 4-methylbenzophenone is greater than the yield of diphenylmethylcarbinol. Only a few percent of the product is 2-methylbenzophenone. The ratio **7m**:**5m** is 1.5–1.8, and it does not change when methyl iodide is placed in excess (expt 4-2-67-1).

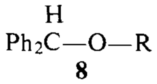
The data of Table I are in good agreement with those of Schenk and Matthias,[8] who determined the ratios **5m**:**6m**:**7m** as 27:6:67. Whatever the reaction mechanism, it must account definitely for the formation of **6** and **7** as well as **5**.

Table II gives the effects of solvent variation on the products of reactions of sodium benzophenone ketyl with methyl iodide. Diethyl ether is unique among the three ethers used in not promoting O-alkylation. Both **8m** and **9m** are formed in DME, but only **8m** in THF under the conditions of the experiment. Our results in DME are not consistent with the report of Schenk and Matthias that only O-alkylation occurs.[8] We confirmed our products by examination of NMR spectra (the method employed by Schenk and Matthias) as well as VPC analyses. We have no explanation for the discrepancy.

Table II. Solvent Effect on Products of Reactions of Sodium Benzophenone Ketyl with Methyl Iodide at Room Temperature[a]

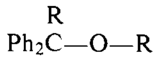
Experiment	Solvent	**5m**	**6m**	**7m**	**8m**	**9m**	**7m**-(abs)[b]
3-23-69	DEE[c]	33	7	60	0	0	(36)[d]
3-30-69	THF	44	7	34	15	0	17.4
3-23-67-2[e]	DME	35	ND	29	36[f]	ND	28

[a] Relative percent yields of **5m, 6m, 7m, 8m,** and **9m** from NMR spectra of product mixtures. Initial concentration of ketyl, ca. 0.05 *M*. Initial molar ratio [MeI]/[ketyl], 0.5. [b] Absolute yield of 7*m* determined by VPC on a 5 ft. × $^1/_8$ in. 10 % QF-1 on DMCS-treated Chromosorb W column at 165°; internal standard *p,p'*-dimethylbenzophenone. [c] Diethyl ether. [d] Average from four other similar experiments; see Table I. [e] Initial ketyl concentration. 0.032 *M*. Initial ratio [MeI]/[ketyl]; 0.54. Analyses as in footnote *b*. [f] **9m**, the product of both O- and carbonyl C-methylation, was definitely formed, as shown by later experiments but, at the time of this experiment, the column had deteriorated and was not separating **8m** from **9m**. The yield of **8m** includes a contribution from 9*m*.



$$\mathrm{Ph_2\overset{H}{C}{-}O{-}R}$$

8

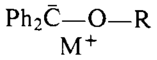


$$\mathrm{Ph_2\overset{R}{C}{-}O{-}R}$$

9

[letter codes **m, h, c, t,** and **p** are the same as for **2, 3, 4, 5, 6,** and **7**]

Since multiple alkylation must occur in stages, we thought that perhaps there was no formation of the carbanionic precursor (**10**) of **8**, but that all O-alkylation could occur in reactions of **2m** with methyl iodide. If so, then it might be possible to suppress O-alkylation completely by using an excess of ketyl over methyl iodide. Table III gives the results of a series of experiments in which the proportions of sodium benzophenone ketyl and methyl iodide were varied. A twofold excess of methyl iodide (expt 3-23-67-1) gives about the same products as the stoichiometric ratio of reactants (0.50), but a twofold excess of ketyl (expt 3-30-67-1 and 4-1-67-1) gives sharply decreased yields of O-alkylation products and correspondingly increased yields of **5m,** with the yield of **7m** unaffected. This is clear support for the hypothesis that a substantial fraction of the O-alkylation comes about through the reaction of the alkoxide ion **2m** with methyl iodide. However, later experiments in THF (Table II) showed clearly that benzhydryl methyl ether (**8m**) is definitely a product so that not all O-methylation occurs by methylation of **2m.** The residual yields of O-methylated products even in the presence of excess ketyl in DME are also consistent with the formation of **8m.**



$$\mathrm{Ph_2\underset{M^+}{\bar{C}}{-}O{-}R}$$

10

[letter codes are the same as for other structures, e.g., **2–9**]

We sought the possible elimination of O-methylation through metal ion effects. These are summarized in Table IV. The influence of metal ion is quite pronounced. Lithium benzophenone ketyl gives no O-methylation, while sodium, potassium, and cesium ketyls give increasing amounts. Surprisingly, cesium benzophenone ketyl gives no diphenylmethylcarbinol (**5m**), the only type of product reported in the earlier literature of ketyl-alkyl halide reactions. With the potassium and cesium ketyls, especially, there is a large amount of benzhydryl methyl ether (**8m**), the product of

Table III. Effects of Variations in Proportions of Reactants on the Product Distribution from Reactions of Sodium Benzophenone Ketyl with Methyl Iodide in DME at Room Temperature[a]

Experiment	$[\text{Ketyl}]_0$	$[\text{MeI}]_0/[\text{kctyl}]_0$[b]	Relative yield (absolute) 5m	7m	8m–9m[c]
3-23-67-1	0.028	1.08	24 (22)	27 (23)	49 (41)
3-23-67-2	0.032	0.59	32 ND	32 ND	35 ND
3-24-67-1	0.024	0.58	39 (30)	34 (26)	27 (21)
3-24-67-1	0.032	0.54	35 (34)	29 (28)	36 (35)
3-19-67-1	0.061	0.54	14? ND	30? ND	57? ND
3-19-67-3	0.032	0.52	40 ND	24 ND	36 ND
3-24-67-3	0.046	0.45	34 (20)	23 (13)	43 (25)
3-30-67-1	0.030	0.28	56 (43)	39 (31)	5 (4)
4-1-67-1	0.025	0.23	62 (56)	28 (25)	10 (9)

[a] Percent yields, based on limiting reagents. Products were analyzed by VPC on a 5 ft × $^1/_8$ in. 10% QF-1 on Chromosorb W column at 165° using 4,4'-dimethylbenzophenone as an internal standard. Relative yields are not in parentheses, absolute yields are. [b] For the formation of monomethyl products, the stoichiometric ratio of reactants is 0.50. [c] The column used did not separate **8m** and **9m**. Yields are calculated as if the VPC peak were due entirely to **8m**.

methylation in oxygen. The significance of the metal ion effect with respect to mechanism and reactivity was not pursued. We have concluded (see later) that the lithium ketyl-alkyl iodide reactions follow the mechanism of eq 2 (ET). The metal ion effect suggests the possibility of a change in mechanism with metal ion. The incursion of S$_N$2 initial steps is one possibility for the reactions of methyl iodide with benzophenone ketyls formed from the alkali metals of higher atomic number than lithium.

Comparison of Products of the Reaction of Lithium Benzophenone Ketyl with Those of the Wittig Rearrangement of Benzhydryl Methyl Ether under Comparable Conditions. Before turning to other types of reactions, we cite evidence that reactions of lithium benzophenone ketyl with methyl iodide do not proceed through Wittig rearrangements as in eq 4. If they did, then the distribution of products arising from the Wittig rearrangement of benzhydryl methyl ether (**8m**) and the reaction of lithium benzophenone ketyl with methyl iodide would be the same since both reactions would proceed through the same intermediate **10m.** In fact, from the ketyl-iodide reaction, the ratios of products **5m**:**6m**:**7m** are 58:5:38 (Table IV), while from the Wittig rearrangement the same ratios are 87:5:8.[12] Thus, the ketyl-iodide reactions do not proceed exclusively through a Wittig rearrangement intermediate stage. Evidence presented later will suggest that no significant fraction of reactions of primary alkyl iodides with lithium benzophenone ketyl in THF proceeds through eq 4.

Kinetics of Reactions of Lithium Benzophenone Ketyl with Alkyl Iodides in THF. The kinetic data gave good fits to the integrated second-order equation. The derived rate constants are given in Table V. It is seen that there is a slight trend to larger rate constants with increased branching at the carbon bearing the halogen; *tert*-pentyl iodide reacts 4–5 times as rapidly as methyl iodide. Further, the presence of olefins among the reaction products was excluded by the absence of corresponding VPC peaks. Since no alkanes result either, the products must be entirely those of substitution. Consequently, it cannot be argued that there may be an elimination component that is responsible for the increasing rate constant with branching in the alkyl iodide.

The observed trend is certainly inconsistent with initial classical S$_N$2 steps, for which rate constants are typically 1000 times slower for secondary alkyl halides than for the corresponding methyl halide, with tertiary halides being slower yet.[18] Thus, reactions through eq 4 and 5 with S$_N$2 initial steps are excluded, suggesting that reaction occurs through eq 2.

Table IV. Metal Ion Effects on the Distribution of Products from Reactions of Benzophenone Ketyls with Methyl Iodide in THF at Room Temperature[a]

Experiment	Metal	5m	6m	7m	8m	9m	7m-(abs)[b]
3-30-69	Li	58	5	38	0	0	18
3-30-69	Na	44	7	34	15	0	17
3-30-69	K	24	3	23	34	16	14
3-30-69	Cs	0	6	10	43	41	ND

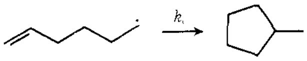
[a] Relative percent yields obtained by NMR. Initial concentrations of ketyl, ca. 0.05 *M*. Ratio $[\text{MeI}]_0/[\text{ketyl}]_0$, 0.50. [b] Absolute yield determined by VPC on a 5 ft × $^1/_8$ in. QF-1 on DMCS-treated Chromosorb W column at 165° using 4,4'-dimethylbenzophenone as an internal standard.

Table V. Rate Constants for Reactions of Lithium Benzophenone Ketyl with Alkyl Iodides in THF at Room Temperature (22–23°)

Experiment	Alkyl iodide	$[\text{Ketyl}]_0$[a]	$[\text{RI}]_0$[a]	k[b]
9-22-70-1	Methyl iodide	0.0225	0.0168	0.039
9-16-70-1	Methyl iodide	0.0240	0.0173	0.027
	Methyl iodide		Av:	0.033
9-16-70-2	5-Hexenyl iodide	0.0275	0.0162	0.084
9-16-70-2a	5-Hexenyl iodide	0.0235	0.0160	0.088
	5-Hexenyl iodide		Av:	0.086
9-16-70-3	*tert*-Pentyl iodide	0.0225	0.0168	0.15

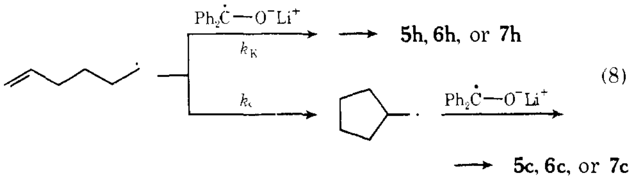
[a] Initial molar concentration. [b] Second-order rate constant defined by $-d[\text{ketyl}]/dt = 2k[\text{ketyl}][\text{RI}]$. The factor of 2 on the right side of the rate law accounts for the consumption of a second ketyl molecule (ion pair) in a rapid step following the initial (slow) bimolecular step.

Products of Reactions of 5-Hexenyl Iodide with Lithium Benzophenone Ketyl in THF. 5-Hexenyl radicals cyclize irreversibly to cyclopentylmethyl radicals with a rate constant ca. 1 × 10^5 sec^{-1} (eq 7).[19]



$k_c = 1 \times 10^5$ sec^{-1} (7)

If eq 2 applies, reactions of 5-hexenyl iodide with lithium naphthalene should give not only products **5h, 6h,** and **7h** (containing the 5-hexenyl group) but also products **5c, 6c,** and **7c** (containing the cyclopentylmethyl group). Since the extent of cyclization is determined by the competition of eq 8, it should be dependent on the concentration of ketyl, lower concentrations favoring formation of **5c, 6c,** and **7c.**



(8)

The results of experiments of this type are in Table VI. The products listed account for all the major VPC peaks. No C$_6$ hydrocarbons were found; both 1-hexene and 1,5-hexadiene are absent, as well as the related cyclic alkanes. All six of the alkylation products anticipated on the basis of eq 2 and 8 were found. Also, the prediction of the effect of the concentration of ketyl was realized. The ratio (**5h** + **6h** + **7h**):(**5c** + **6c** + **7c**) decreases from about 16 for 0.05 *M* ketyl to about 0.5 for 0.001 *M* ketyl.

The concentration effect can be treated quantitatively to obtain the rate constant ratio $k_K/k_c = r$. Assuming the mechanism of eq 2, and assuming that the ketyl is monomeric (ion pairs), the appropriate relationship between r, x_0 (initial ketyl concentration), and s [ratio of (**5h** + **6h** + **7h**) to (**5c** + **6c** + **7c**)] is eq 9

Table VI. Products of Reactions of Lithium Benzophenone Ketyl with 5-Hexenyl Iodide in THF at Room Temperature[a]

x_0[b]	y_0[c]	5h	6h	7h	5c	6c	7c	(5h+ 6h+ 7h)	(5c+ 6c+ 7c)	k_K/k_c[d]
0.051	0.025	40	10	44	3	1	2	94	6	1.4×10^3
0.024	0.017	41	7	44	3	1	4	92	8	2.0×10^3
0.0010	0.0006	15	3	14	28	7	34	32	69	1.0×10^3
Average product ratios:					5h:6h:7h = 44:9:47					
					5c:6c:7c = 41:11:48					
Average rate constant ratio:					$k_K/k_c = 1.5 \times 10^3\ M^{-1}$					
If $k_c = {\sim}1 \times 10^5$ sec^{-1}, then:					$k_K = {\sim}1.5 \times 10^8\ M^{-1}$ sec^{-1}					

[a] Relative yields; absolute yields ca. 50%. Two columns were used for these analyses, $^1/_8$ in. × 10 ft 10% Carbowax 20M-TPA on 80–100 mesh acid-washed DMCS-treated Chromosorb W and $^1/_8$ in. × 20 ft 20% QF-1 or Chromosorb W, at 240–250°; internal standard; phenyl biphenyl ketone. [b] Initial molar concentration of lithium benzophenone ketyl. [c] Initial molar concentration of 5-hexenyl iodide. [d] k_K = rate constant governing the reactions of 5-hexenyl radicals with lithium benzophenone ketyl computed as if ketyl were monomeric. k_c = rate constant for cyclization of 5-hexenyl radicals to cyclopentylmethyl radicals.

$$rx_0 + 1 = e^{(rx_0)/(1+s)} \qquad (9)$$

provided that 5-hexenyl iodide is in excess of or equivalent to ketyl.[20] Table VI contains the values k_K/k_c computed from this relationship for the various initial ketyl concentrations. It is seen that although x_0 and s vary widely, the computed values of k_K/k_c are all in the range 1-2 × $10^3\ M^{-1}$. Thus, the data are consistent with a stringent quantitative test of eq 2.

The rate constant k_K for the reaction of 5-hexenyl radicals with lithium benzophenone ketyl is ~1.5 × $10^8\ M^{-1}$ sec^{-1} if k_c is taken as ~1 × 10^5 sec^{-1}. This is one order of magnitude less than the similar rate constant k_N for the corresponding reaction with sodium naphthalene in DME. It is also at least one order of magnitude, and probably 1.5, less than diffusion controlled.

It should be noted that the distribution among products, **5**, **6**, and **7**, is independent of the ketyl concentration and of the fraction of product with cyclized alkyl groups. This is, of course, as it should be.

Products of Reactions of Tetrahydrofurfuryl and *tert*-Pentyl Iodides with Lithium Benzophenone Ketyl in THF. Table VII contains the results of analyses of reactions of tetrahydrofurfuryl and *tert*-pentyl iodides with lithium benzophenone ketyl in THF. The ratios **5t:6t:7t** and **5p:6p:7p** are quite similar to the ratios **5h:6H;7h** and **5c:6c:7c** and to the ratio **5m:6m:7m.** The only notable trend among these ratios is the slight tendency toward formation of **7** at the expense of **5** with the more sterically hindered alkyl radicals.

Of more significance is the complete absence of 4-penten-1-ol among the products of the reaction of lithium benzophenone ketyl with tetrahydrofurfuryl iodide. This implies directly that no portion of the reactions between tetrahydrofurfuryl radicals and lithium benzophenone ketyl ion pairs (or higher aggregates) is electron transfer (eq 10).

$$\text{R}\cdot + \text{Ph}_2\dot{\text{C}}\text{—O}^-\text{Li}^+ \rightarrow \text{R:}^-\text{Li}^+ + \text{Ph}_2\text{C}{=}\text{O} \qquad (10)$$

Tetrahydrofurfuryl anions (in lithium reagents, Grignard reagents, etc.) undergo facile ring opening to 4-pentene 1-oxide ions, which would have led to 4-penten-1-ol had the anions been formed.[21] Instead, the reactions take the normal course for alkyl iodide-lithium benzophenone ketyl reactions. This point is important because the products could have been formed by way of reaction 10 followed by reaction of the alkyllithium so formed with benzophenone. Such a pathway is excluded not only by the absence of 4-penten-1-ol from the tetrahydrofurfuryl iodide reaction but also by the fact that the ratios **5:6:7** from all the alkyl iodide-lithium benzophenone ketyl reactions are quite different from the corresponding ratios obtained when alkyllithiums add to benzophenone in THF.

Table VII. Products of Reactions of Lithium Benzophenone Ketyl with Tetrahydrofurfuryl and *tert*-Pentyl Iodides in THF at Room Temperature[a]

Alkyl iodide[b]	[Ketyl]$_0$[c]	[RI]$_0$[c]	5t or 5p	6t or **6p**	7t or 7p
t[d]	0.051	0.025	35	9	56
p	0.050	0.025	38	8	55
p	0.023	0.017	41	3	56

[a] Relative yields; absolute yields ca. 50%. See footnote *a* of Table VI for details of VPC analyses. [b] t = tetrahydrofurfuryl iodide; **p** = *tert*-pentyl iodide. [c] Initial molar concentration. [d] No trace of 4-penten-1-ol was found by VPC in the product mixture.

The absence of 4-penten-1-ol also excludes the mechanism of eq 4, which involves an intermediate Wittig rearrangement stage. When the Wittig intermediate **10t** is formed in THF from benzhydryl tetrahydrofurfuryl ether and butyllithium, a 94% yield of 4-penten-1-ol results.[12] Assuming that the same species would behave in the same fashion under the closely similar conditions of the two reactions, this excludes the formation of **10t** in the ketyl-tetrahydrofurfuryl iodide reaction, so that the reaction cannot follow eq 4.

Tetrahydrofurfuryl radicals do not open to 4-penten-1-oxy radicals[22] so the data are perfectly consistent with the mechanism of eq 2.

The lack of electron transfer from lithium benzophenone ketyl to tetrahydrofurfuryl radicals probably means that it does not occur with other alkyl radicals either. In reactions of alkyl radicals with naphthalene radical anions (alkali naphthalenes), electron transfer competes with radical combination. However, naphthalene is less readily reduced than benzophenone, and naphthalene radical anion should yield its "extra" electron more readily than benzophenone radical anion so that it is quite reasonable that alkyl radicals are reduced by the radical anion of naphthalene but not that of benzophenone.

Summary of Conclusions

Our major conclusions follow. (1) The initial reaction step between lithium benzophenone ketyl and an alkyl iodide is a dissociative electron transfer generating an alkyl radical (first step, eq 2). An initial S$_N$2 step at either carbon or oxygen of the ketyl is specifically ruled out. (2) Intermediate alkyl radicals are scavenged completely by lithium benzophenone ketyl. No products of reactions of alkyl radicals with solvent or of reactions among alkyl radicals are formed. (3) Reactions of alkyl radicals with lithium benzophenone ketyl occur by radical combination exclusively (second steps, eq 2). There is no electron transfer from the ketyl to the alkyl radical, even when the alkyl radical is tetrahydrofurfuryl. (4) Alkyl radical-ketyl combination occurs at three sites of the ketyl, the "carbonyl" carbon and ortho and para positions of the phenyl groups. No combination occurs at the oxygen atom of the ketyl. Such combination would form anions capable of undergoing Wittig rearrangements. Wittig rearrangements are not part of the reaction mechanism. (5) For primary alkyl radicals, about 90% of the combination with lithium benzophenone ketyl occurs at the "carbonyl" carbon and the para positions of the phenyl rings, with only about 10% at the ortho positions. Combination is proportioned about equally between the two major positions. (6) The second-order rate constant for combination of 5-hexenyl radicals with lithium benzophenone ketyl is about 1.5 × $10^8\ M^{-1}$ sec^{-1}.

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References and Notes

(1) E. Beckman and T. Paul, *Justus Liebigs Ann. Chem.*, **266**, 1 (1891).
(2) W. Schlenk and T. Weickel, *Chem. Ber.*, **44**, 1182 (1911).
(3) N. Hirota and S. I. Weissman, *J. Am. Chem. Soc.*, **86**, 2538 (1964).
(4) (a) C. B. Wooster, *J. Am. Chem. Soc.*, **50**, 1388 (1928); (b) *ibid.*, **51**, 1856 (1929); (c) C. B. Wooster and W. E. Holland, *ibid.*, **56**, 2438 (1934); (d) C. B. Wooster and J. G. Dean, *ibid.*, **57**, 112 (1935).
(5) G. Wittig and L. Lohmann, *Justus Liebigs Ann. Chem.*, **550**, 260 (1942).
(6) W. Schlenk et. al., *Justus Liebigs Ann. Chem.*, **464**, 22 (1928).
(7) (a) D. J. Morantz and E. Warhurst, *Trans. Faraday Soc.*, **51**, 1375 (1955); (b) E. Warhurst and R. Whittaker, *ibid.*, **62**, 707 (1966); and intervening papers.
(8) G. Schenk and G. Matthias, *Tetrahedron Lett.*, 699 (1967).
(9) See also J. F. Garst and C. D. Smith, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, paper O-20. However, this abstract contains errors of fact based on data from a deteriorated VPC column. Our present data do *not* agree with the report of Schenk and Matthias to the extent indicated by the abstract cited above.
(10) U. Schollkopf and W. Fabian, *Angew. Chem.*, **72**, 570 (1960).
(11) Part of this work has been reported in preliminary form: J. F. Garst and C. D. Smith, *J. Am. Chem. Soc.*, **95**, 6870 (1973).
(12) J. F. Garst and C. D. Smith, *J. Am. Chem. Soc.*, the following paper in this issue.
(13) (a) *Beilstein*, **6**, 685; (b) E. Ador and A. A. Rilliet, *Chem. Ber.*, **12**, 2296 (1879).
(14) *Beilstein*, **7**, 440.
(15) *Beilstein, 3rd Suppl.*, **6**, 3395.
(16) (a) *Beilstein, 2nd Suppl.*, **6**, 639; (b) J. J. Eisch and G. R. Husk, *J. Am. Chem. Soc.*, **87**, 4194 (1965).
(17) From the Wittig rearrangement of benzyl tetrahydrofurfuryl ether. See Experimental Section of ref 12.
(18) See, for example, J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure", McGraw-Hill, New York, N.Y., 1968, p 281.
(19) D. J. Carlsson and K. U. Ingold, *J. Am. Chem. Soc.*, **90**, 7047 (1968); D. Lal, D. Griller, S. Husband, and K. U. Ingold, *ibid.*, **96**, 6355 (1974).
(20) J. F. Garst and F. E. Barton, II, *J. Am. Chem. Soc.*, **96**, 523 (1974).
(21) This ring opening is the basis of a preparation of 4-penten-1-ol: L. A. Brooks and H. R. Snyder in "Organic Syntheses", Collect. Vol. III, E. C. Horning, Ed., Wiley, New York, N.Y., 1955, p 698.
(22) J. F. Garst, *Prepr., Div. Pet. Chem., Am. Chem. Soc.*, **13**, D65 (1968).

Wittig Rearrangements of Aralkyl Alkyl Ethers

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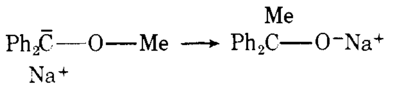
Abstract: Wittig rearrangements of benzhydryl 5-hexenyl ether in THF at room temperature give products containing the cyclopentylmethyl group as well as those containing the 5-hexenyl group. Cyclization occurs in intermediate 5-hexenyl radicals which escape reaction with their geminate partners, but 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.

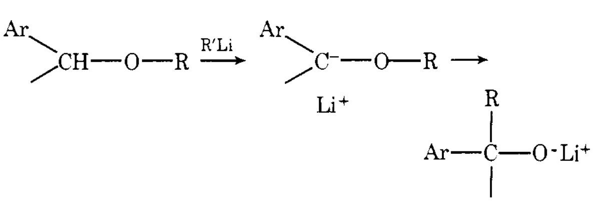
In 1928 Schlenk and Bergmann reported the rearrangement of the sodium salt of benzhydryl methyl ether (generated from benzophenone ketal and sodium) to sodium diphenyl methyl methoxide (eq 1).[1]



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

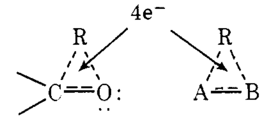
(1)

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".



(2)

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 classi-