Analysis by vpc using cyclopentane as the internal standard indicated 0.07 mole of isobutylene/mole of chlorotriphenylmethane. The reaction mixture was then diluted to 10 ml with benzene and the triphenylmethane yield was determined by comparison with a standard solution using equivolume injections of standard and reaction mixture. The triphenylmethane yield was 0.24 mole/mole of chlorotriphenylmethane. A control experiment was identical with that just described except that the *t*-butyl sulfide was omitted. The control gave no isobutylene, but a triphenylmethane yield of 0.19 moles/mole of chlorotriphenylmethane.

Reduction of Triphenylcarbinol and Sulfides 3a and 4a.[54] Triphenylcarbinol (0.540 g, 2.0 mmoles) was dissolved in 10 ml of acetic acid with warming on a steam bath. To this solution was added 1.5 ml of 47% HBr. After heating the solution on a steam bath for 5 min, 1.5 ml of 47% HI was added and the solution was heated for 1 hr. After cooling the solution to room temperature, 1 g of sodium bisulfite in 10 ml of water was added, and the acids were neutralized by the addition of sodium carbonate. The solution was extracted twice with benzene. Drying of the benzene extracts with sodium sulfate followed by evaporation of the solvent yielded 0.500 g (98.5%) of triphenylmethane, mp 92–93.5°.

Similar treatment of a mixture of triphenylmethyl *t*-butyl sulfide (0.051 g, 0.153 mmole) and 4-biphenylyldiphenylmethyl *t*-butyl sulfide (0.050 g, 0.123 mmole) gave 77 mg of reduction product which was dissolved in 4 ml of benzene. Comparison of the vpc of this solution with that of a standard solution using known injection volumes showed the yield of triphenylmethane was 89% and that of 4-biphenylyldiphenylmethane was 100%.

(54) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass, 1955, p. 81.

Acknowledgment. This work was supported, in part, by Public Health Service Research Grant CA-06535 from the National Cancer Institute.

Reactions of α-Hydroxybenzyl Free Radicals. III.[1] Processes for α-Hydroxycyclopropylcarbinyl Radical Formation

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Abstract: The reactions of arylcyclopropylcarbinols with di-*t*-butyl peroxide and aryl cyclopropyl ketones with 2-butanol and di-*t*-butyl peroxide have been investigated. Factors influencing the stability of the free-radical intermediates have been evaluated. Mechanisms for the formation of α-hydroxybenzyl free radicals from the corresponding ketone have been studied. Direct hydrogen-atom transfer from an α-hydroxyalkyl radical to the aromatic ketone is proposed. Evidence concerning the nature of α-hydroxycyclopropylcarbinyl free radicals suggests that substituents on the cyclopropane ring affect the rate of formation of the radical but that the product composition is highly dependent on radical lifetime.

The cyclopropylcarbinyl free radical has generated neither the interest nor the controversy of its carbonium-ion counterpart. Although the cyclopropylcarbinyl free radical shows a tendency to undergo ring-opening rearrangement reactions, there is no evidence to favor a bicyclobutonium-type reaction intermediate. Whereas the cyclopropylcarbinyl carbonium ion tends to equilibrate with cyclobutyl and allylcarbinyl species, allylcarbinyl products only are most often observed when the radical is generated.[3] Only one tentative report of cyclobutyl radical products from cyclopropylcarbinyl radical intermediates has appeared.[4] Furthermore, although the cyclobutyl carbonium ion shows a tendency to equilibrate with the corresponding allylcarbinyl and cyclopropylcarbinyl structures, reactions of the cyclobutyl free radical generally lead only to unrearranged products.[5,6]

In spite of the apparent lack of equilibration of the cyclopropylcarbinyl and allylcarbinyl free radicals with the corresponding four-membered ring species, the ring strain associated with the cyclopropyl group adjacent to the radical site is sufficient to provide the cyclopropylcarbinyl radical with some unusual properties. For example, in almost every case ring opening of the cyclopropylcarbinyl radical to the allylcarbinyl radical occurs concomitant with an unusually large rate of formation of the species. Thus, in every known case the cyclopropylcarbinyl radical is more easily formed than sterically analogous species.[7–12]

In an earlier communication[9] we reported that α-hydroxycyclopropylcarbinyl free radicals underwent ring-opening rearrangement to give enolate radicals which, after chain transfer and tautomerization, gave straight-chain ketones. We now report these studies in detail and discuss their bearing on the problem of cyclopropylcarbinyl free-radical intermediates. Further, we report studies pertinent to the mechanism of the reaction of α-hydroxyalkyl radicals with aromatic ketones.

(1) Part II: D. C. Neckers, J. Hardy, and A. P. Schaap, *J. Org. Chem.*, **31**, 622 (1966).
(2) National Science Foundation Undergraduate Research Participant, 1965.
(3) (a) N. Demjanov, *Ber.*, **40**, 4393 (1907); (b) *ibid.*, 4961 (1907); (c) R. Skrabel, *Monatsch.*, **70**, 420 (1927); (d) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951).
(4) C. Walling and P. S. Fredricks, *ibid.*, **84**, 3326 (1962).
(5) H. C. Brown and M. Borkowski, *ibid.*, **74**, 1894 (1952).
(6) D. Schuster, Ph.D. Thesis, California Instituite of Technology, 1960.
(7) C. G. Overberger and A. Lebovits, *J. Am. Chem. Soc.*, **76**, 2722 (1954).
(8) E. S. Huyser and J. D. Taliaferro, *J. Org. Chem.*, **28**, 3442 (1963).
(9) D. C. Neckers, *Tetrahedron Letters*, 1889 (1965).
(10) H. Hart, and R. A. Cipriani, *J. Am. Chem. Soc.*, **84**, 3697 (1962).
(11) H. Hart and D. P. Wyman, *ibid.*, **81**, 4891 (1959).
(12) E. S. Huyser and D. H. Wang, *J. Org. Chem.*, **29**, 2720 (1964).

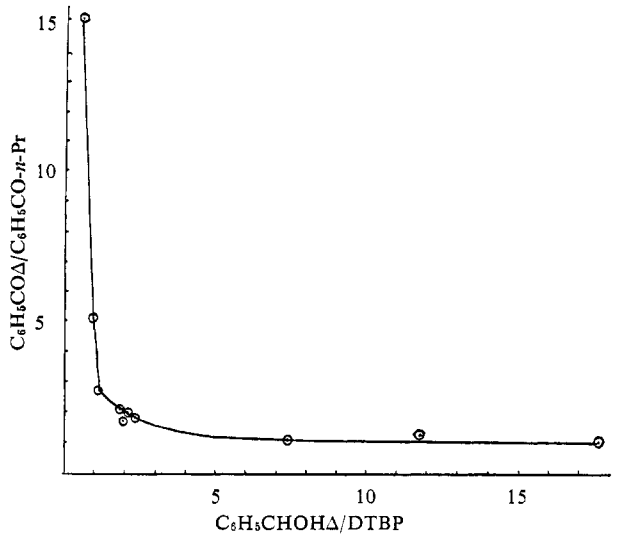


Figure 1.

Results

Ring-opening rearrangement reactions occur when α-hydroxycyclopropylcarbinyl radicals are generated by hydrogen-atom abstraction from cyclopropylphenylcarbinol.[9] The results of a typical experiment are shown in Table I. With cyclopropylmethylcarbinol and di-*t*-butyl peroxide (DTBP), a similar ring opening rearrangement reaction is observed, and the ring-opened product is the only isolated product at 130°. No cyclopropyl methyl ketone is observed. The results of a typical experiment are given in Table II. Bimolecular coupling products are also formed and were qualitatively identified by mass spectrometric analysis. Thus a minor product from reaction of cyclopropylmethylcarbinol with DTBP is 2,9-decanedione. With cyclopropylmethylcarbinol-O-*d*, the exclusive deuterium-containing 2-pentanone obtained from reaction with di-*t*-butyl peroxide at 130° is 2-pentanone-3-*d*.

Table I. Reaction of Cyclopropylphenylcarbinol with DTBP at 130°

Reactant	mmole	Product	mmole
Cyclopropylphenylcarbinol	6.94	*t*-Butyl alcohol	0.64
DTBP	0.73	Acetone	0.11
		Butyrophenone	0.41
		Cyclopropyl phenyl ketone	0.43
		Cyclopropylphenylcarbinol (residual)	4.54

Table II. Reaction of Cyclopropylmethylcarbinol with DTBP at 130°

Reactant	mmoles	Product	mmoles
Cyclopropylmethylcarbinol	14.14	Acetone	0.68
DTBP	1.78	*t*-Butyl alcohol	2.22
		2-Pentanone	5.28
		Cyclopropylmethylcarbinol (residual)	4.67

The products of the reaction of cyclopropylphenylcarbinol with di-*t*-butyl peroxide were observed to be dependent upon the concentration of peroxide. At higher peroxide concentrations, the ratio of unrearranged to rearranged product was relatively high. As the concentration of peroxide was lowered, the ratio of cyclopropyl phenyl ketone to butyrophenone decreased. Using molar concentration ratios of DTBP to phenylcyclopropylcarbinol lower than 0.1, a constant ratio of cyclopropyl phenyl ketone to butyrophenone was obtained. The results of a number of experiments are shown in Figure 1.

Substituents on the aryl ring of cyclopropylarylcarbinols affected the constant ratio of cyclopropyl aryl ketone to substituted butyrophenone. In Table III the ratios of unrearranged to rearranged products as a function of the aryl substituent are given. As expected, as the relative ability of the substituent to stabilize the developing free radical by resonance interactions increases, or as the substituent becomes a more efficient electron donor, the ratio of unrearranged to rearranged product increases.

Table III. Reaction of Substituted Cyclopropylphenylcarbinols with DTBP at 130°

Substituent	$\frac{X\text{-Ph-}COC_3H_5}{X\text{-Ph-}CO(CH_2)_2CH_3}$
H	2.34 ± 0.16
p-OMe	3.76 ± 0.14
p-Me	2.84 ± 0.25
p-F	3.57 ± 0.06
m-CF_3	1.86 ± 0.03

With substituents on the cyclopropane ring, the ratio of unrearranged to rearranged product is virtually unaffected. The results of a typical experiment with 2-methylcyclopropylphenylcarbinol and DTBP are given in Table IV. The ratio of valerophenone to isovalerophenone obtained upon rearrangement of the α-hydroxy(2-methyl)cyclopropylphenylcarbinyl radical is constant and favors the valerophenone 9.33 ± 0.07 to 1.

Table IV. The Reaction of 2-Methylcyclopropylphenylcarbinol with DTBP at 130°

Reactant	mmole	Product	mmole
2-Methylcyclopropylphenylcarbinol	0.621	Isovalerophenone	0.006
		Valerophenone	0.054
DTBP	0.161	2-Methylcyclopropyl phenyl ketone	0.112
		2-Methylcyclopropylphenylcarbinol (residue)	0.394
		Acetone	0.035
		t-Butyl alcohol	0.270

We have also reported that rearrangement products characteristic of α-hydroxycyclopropylcarbinyl free-radical intermediates are observed when DTBP is decomposed in a solution of cyclopropyl phenyl ketone and 2-butanol. Butyrophenone is again a major reaction product. The results of a typical experiment are given in Table V.

Table V. Reaction of Cyclopropyl Phenyl Ketone with DTBP and 2-Butanol at 130°

Reactant	mmoles	Product	mmole
Cyclopropyl phenyl	1.69	Acetone	0.41
DTBP	1.54	*t*-Butyl alcohol	2.50
2-Butanol	31.36	2-Butanone	1.89
		Butyrophenone	0.60
		Cyclopropylphenylcarbinol	0.26
		Cyclopropyl phenyl ketone (residual)	0.35

As in the case of cyclopropyl phenyl ketone, 2-methylcyclopropyl phenyl ketone, 2-butanol, and DTBP gives cyclopropane ring-opening rearrangement products. As with 2-methylcyclopropylphenylcarbinol, valerophenone predominates over isovalerophenone and the ratio is nearly the same, 9.19 ± 0.14 to 1. The results of a typical experiment are given in Table VI.

Table VI. Reaction of 2-Methylcyclopropyl Phenyl Ketone with 2-Butanol and DTBP

Reactant	mmole	Product	mmole
2-Methylcyclopropyl phenyl ketone	0.645	Isovalerophenone	0.010
DTBP	0.404	Valerophenone	0.091
2-Butanol	11.35	2-Methylcyclopropyl phenyl ketone (residue)	0.058
		2-Methylcyclopropylphenylcarbinol	0.181
		Acetone	0.126
		t-Butyl alcohol	0.673
		Methyl ethyl ketone	0.678

The relative rates of aryl alkyl ketone disappearance relative to the isobutyrophenone standard were measured by allowing DTBP to decompose in a 2-butanol solution containing the appropriate ketones. These results are reported in Table VII.

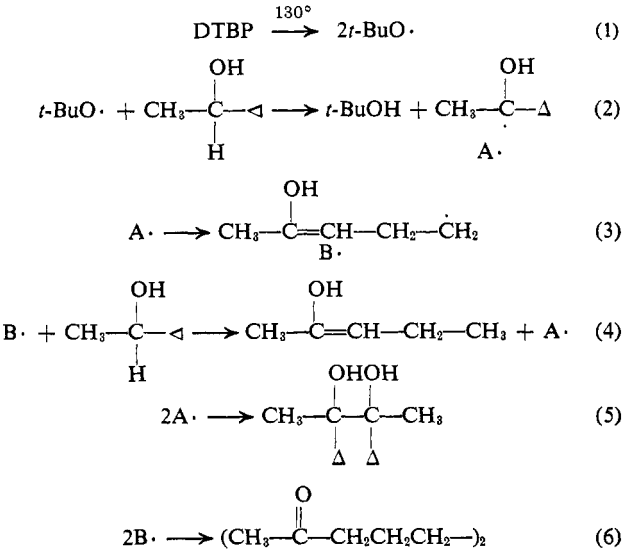
Table VII. Relative Reactivities of Aryl Alkyl Ketones toward Hydrogen Atom Addition

Ketone	k(aryl alkyl ketone)/k(isobutyrophenone)
Acetophenone	7.60 ± 0.80
Propiophenone	3.33 ± 0.20
Cyclopropyl phenyl ketone	36.00 ± 1.00
Cyclobutyl phenyl ketone	11.30 ± 1.20
Cyclopentyl phenyl ketone	1.84 ± 0.27
Cyclohexyl phenyl ketone	1.23 ± 0.10
Isobutyrophenone	1.00
Benzophenone	28.4 ± 0.8
2-Methylcyclopropyl phenyl ketone	70.3 ± 3.5
2-Phenylcyclopropyl phenyl ketone (*cis*)	515 ± 35
2-Phenylcyclopropyl phenyl ketone (*trans*)	450 ± 10
Isovalerophenone	3.16 ± 0.50

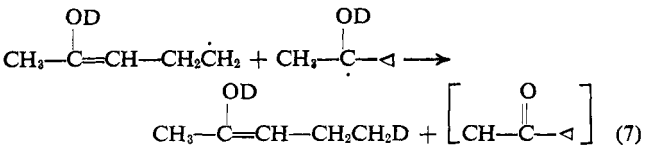
Ring-opened rearrangement products are isolated from the reactions of cyclopropyl phenyl ketone, cyclobutyl phenyl ketone, and cyclopentyl phenyl ketone with 2-butanol and DTBP; however, as the ring strain of the adjacent cyclic moiety decreases, smaller quantities of ring-opened products are obtained. Thus, only trace quantities of hexanophenone were isolated from the reaction of cyclopentyl phenyl ketone with 2-butanol and DTBP.

Discussion

The behavior of α-hydroxycyclopropylcarbinyl free radicals is characterized by a ring-opening rearrangement to an enolate radical. After chain transfer at a suitable hydrogen–carbon bond, the enol tautomerizes to the corresponding ketone. This mechanism is shown in eq 1–6 for the reaction of cyclopropylmethylcarbinol with di-*t*-butyl peroxide. That the reaction



occurs *via* the enolate radical and without disproportionation between two α-hydroxymethylcarbinyl radicals is shown by the fact that no methyl cyclopropyl ketone is found among the products. This result is contrasted to the experiments with cyclopropylphenylcarbinol and DTBP where cyclopropyl phenyl ketone is generally the predominant product. Undoubtedly the difference in resonance stability between the α-hydroxyphenylcyclopropylcarbinyl radical and the α-hydroxymethylcyclopropylcarbinyl radical influence the degree of ring opening. The experiments with cyclopropylmethylcarbinol-O-*d* confirm the fact that a keto–enol tautomerization is important and that the enolate radical plays a role in the reaction mechanism. Further, the fact that deuterium occurs exclusively in the 3-position of the 2-pentanone produced indicates that no 2-pentanone results by a disproportionation process.

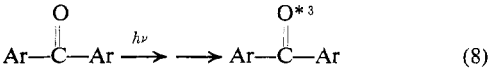


The reaction between aromatic ketones and α-hydroxyalkyl free radicals produced from di-*t*-butyl peroxide and 2-butanol has been reported by Huyser and Neckers.[13] The products obtained from this reaction are mixtures of the corresponding pinacol and alcohol from reduction of the aromatic ketone.

(13) E. S. Huyser and D. C. Neckers, *J. Am. Chem. Soc.*, **85**, 3641 (1963).

Control experiments conducted with phenyl cyclopropyl ketone under similar conditions to our peroxide-induced experiments indicate that the ketone is not rearranged to butyrophenone by either a polar process in 2-butanol or by *t*-butoxy radical induced hydrogen abstraction. Furthermore, under the conditions of our experiment, both cyclopropyl phenyl ketone and cyclopropylphenylcarbinol were shown to be stable. In a formal sense the reaction of α-hydroxyalkyl radicals with aromatic ketones resembles the latter stages of the photoreduction process of aryl ketones in alcohol solvents.

The mechanism for the photoreduction reaction (8–11) has been extensively studied and pieced together by a number of workers.[14–18]



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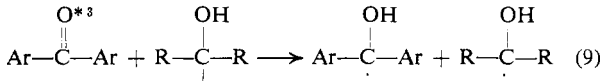

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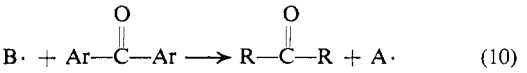

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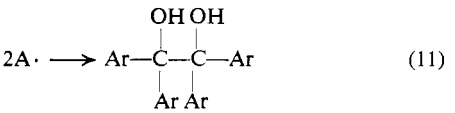
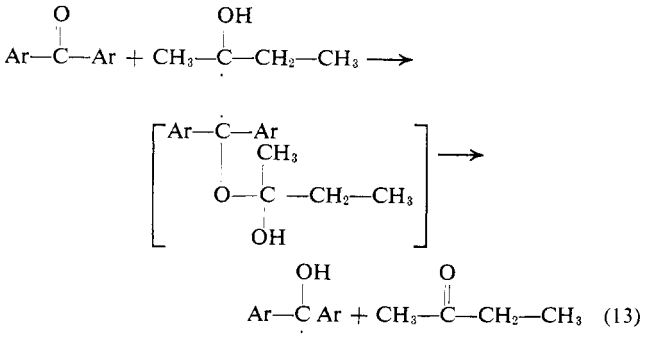


(11)

Some question still exists about the actual nature of step 10. A number of workers have suggested alternatives to the direct transfer of a hydrogen atom to an aryl ketone from an α-hydroxyalkyl radical. Franzen,[19] for example, has suggested on the basis of isotope data that electron transfer rather than hydrogen atom transfer occurs initially (eq 12). In the peroxide-induced reaction of 2-butanol with substituted acetophenones,[13] the radical-anion[20] postulate is supported by the observation that electron-withdrawing substituents accelerate the reaction. Others[21] have suggested that the reaction of an α-hydroxyalkyl radical with aryl or diaryl ketone takes place by initial addition of the α-hydroxyalkyl radical to the carbonyl oxygen of the ketone to form a hemiacetal radical. The hemiacetal radical then undergoes a collapse to the α-hydroxydiarylmethyl radical and an aliphatic ketone (eq 13). This process, initially suggested by Pitts to occur under conditions of high-intensity radiation, has sometimes been interpreted to be a generally occurring phenomenon.



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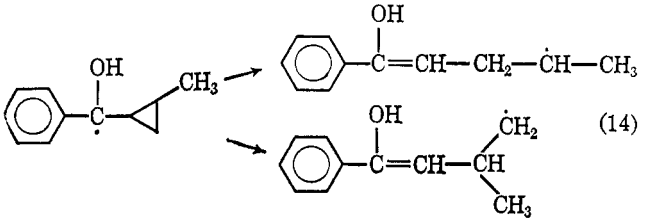
It is our opinion that, under normal circumstances, direct hydrogen atom transfer from an α-hydroxyalkyl radical to the aromatic ketone does occur. Our evidence is based on the observation that from an α-hydroxycyclopropylcarbinyl radical which possesses substituents on the cyclopropane ring, the ratio of the two possible ring-opened products is essentially the same regardless of whether the α-hydroxycyclopropylcarbinyl radical is generated by the known method, *t*-butoxy radical abstraction of the α-hydrogen from the carbinol,[22] or from the corresponding ketone, DTBP and 2-butanol. Thus, from the reaction of 2-methylcyclopropylphenylcarbinol with DTBP at 130°, we obtained three products: valerophenone, isovalerophenone, and 2-methylcyclopropyl phenyl ketone. The ratio of valerophenone to isovalerophenone was 9.33 ± 0.07 reflecting the stability imparted to the homoallylic radical by a methyl group (eq 14). On the other hand, from the ketone, 2-butanol and di-*t*-butyl peroxide, valerophenone predominated over isovalerophenone by a factor of 9.19 ± 0.14 to 1. Since the ketyl is presumed to see some contributions



(14)

from structures possessing a negative carbon (eq 15), a lower ratio of valerophenone to isovalerophenone would be expected if electron transfer were the occurring process.[23]

(14) (a) G. S. Hammond and W. M. Moore, *J. Am. Chem. Soc.*, **81**, 6334 (1959); (b) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Chem. Phys.*, **32**, 1594 (1960); (c) *J. Am. Chem. Soc.*, **83**, 2789 (1961); (d) G. S. Hammond, W. P. Baker, and W. M. Moore, *ibid.*, **83**, 2795 (1961); (e) H. L. Bächström, *The Svedberg*, **45** (1944); (f) H. L. Bächström, A. Steneryr, and P. Perlmann, *Acta Chem. Scand.*, **12**, 8 (1959); (g) H. L. Bächström and K. Sandros, *ibid.*, **14**, 48 (1960); (h) G. Porter and F. Wilkinson, *Trans. Faraday Soc.*, **57**, 1686 (1961); (i) W. M. Moore and M. Ketchum, *J. Am. Chem. Soc.*, **84**, 1368 (1962); (j) G. Porter and M. H. Windsor, *Proc. Chem. Soc.*, **A245**, 238 (1958); (k) D. McClure and P. L. Hanst, *J. Chem. Phys.*, **23**, 1772 (1955); (l) J. N. Pitts, H. W. Johnson, and T. Kuwana, *J. Phys. Chem.*, **66**, 2456 (1962).

(15) (a) E. L. Bowen and E. L. A. E. de la Praudiere, *J. Chem. Soc.*, 1503 (1934); (b) J. A. Bell and H. Linschitz, *J. Am. Chem. Soc.*, **85**, 528 (1963).

(16) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957.

(17) J. N. Pitts, R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Rechtenwald, and R. B. Martin, *J. Am. Chem. Soc.*, **81**, 1068 (1959).

(18) C. Weizmann, E. Bergmann, and Y. Hirschberg, *ibid.*, **60**, 1530 (1938).

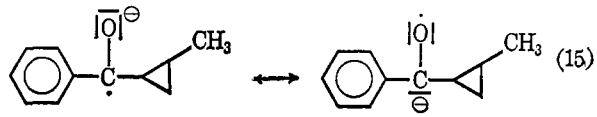
(19) V. Franzen, *Ann.*, **633**, 1 (1960).

(20) We refer to the radical anion (i) as a ketyl. Confusion has resulted in some instances because the α-hydroxydiarylmethyl radical (ii) was referred to as a ketyl.

(21) A. J. Testa, *J. Phys. Chem.*, **67**, 1341 (1963).

(22) (a) W. H. Urry, F. W. Stacey, O. O. Juveland, and C. H. McDonnell, *J. Am. Chem. Soc.*, **75**, 250 (1953); (b) W. H. Urry, F. W. Stacey, E. S. Huyser, and O. O. Juveland, *ibid.*, **76**, 450 (1954).

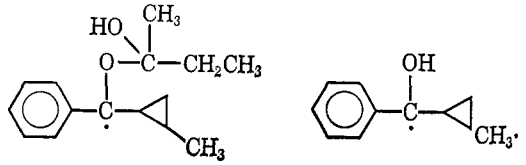
(23) It is recognized that proton transfer following the initial electron-transfer process might be extremely rapid. However, since the ring-opening process is intramolecular and may be concerted with radical formation, it is expected to occur more rapidly than proton transfer and the ketyl should be distinguishable.



(15)

To authentic the validity of the assumption that the ketyl would reflect some carbon negative character, we have actually generated the ketyl by the reaction of 2-methylcyclopropyl phenyl ketone with sodium at 130°. The ratio of valerophenone to isovalerophenone formed by this process was 0.577 ± 0.007.[24] *The ring-opened species possessing the radical on the primary carbon was actually the favored one.* Further, a series of relative reactivity measurements conducted in dioxane solution showed that a reaction intermediate far different from that developing in the reaction of α-hydroxyalkyl radicals with aromatic ketones was becoming important in the reactions of aromatic ketones with sodium.

As far as hemiacetal radical formation is concerned, the evidence for its formation is essentially that of Pitts.[17] That is, at high light intensity a yellow intermediate, thermally and photochemically unstable, is formed. This intermediate is destroyed by oxygen. Since our data indicate that the rearrangement products from 2-methylcyclopropyl phenyl ketone, 2-butanol, and di-*t*-butyl peroxide occur in exactly the same ratio as those from the 2-methylcyclopropylcarbinol and DTBP, we feel that the hemiacetal radical cannot be involved in our reactions. It would be coincidental indeed if I underwent elimination–rearrangement in

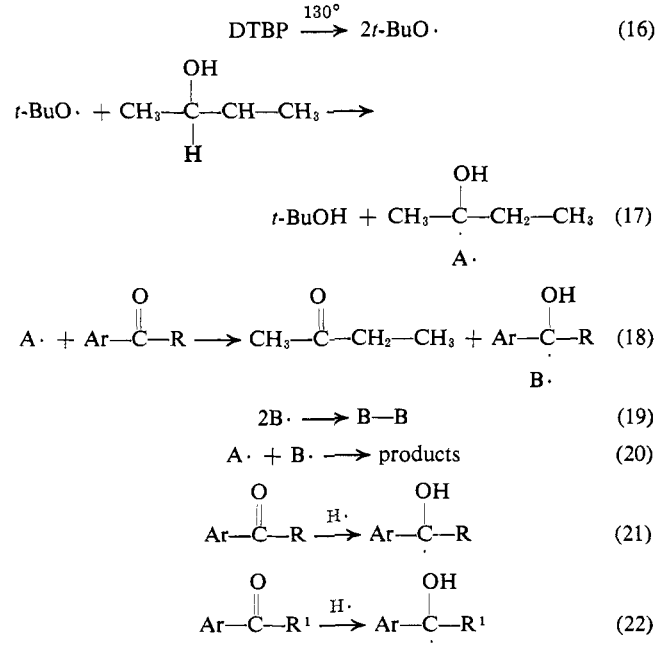


I

II

an exactly similar fashion to II. It is our conclusion that, in the photochemical reduction of diaryl ketones with alcohols, formation of a hemiacetal radical occurs only under conditions of high intensity. This conclusion is further supported by the observations that photoreduction of benzophenone in ethers produces no acetals[13,25] and, in hydrocarbons, no ethers.[14d,26] In both the photochemical reaction and the peroxide-induced reaction, a direct hydrogen transfer from the α-hydroxyalkyl radical to the aromatic ketone does occur. The mechanism for the reaction of di-*t*-butyl peroxide, 2-butanol, and an aromatic ketone is shown in eq 16–20.

Now considering the relative reactivity data of Table VII, the relative reactivities evaluated therein give a measure of the hydrogen atom addition process (eq 21–22). This process is undoubtedly favored by the increase in resonance stability of the α-hydroxybenzyl radical as compared to the α-hydroxyalkyl radical and is highly irreversible[17] in spite of some reports to the contrary.[27] The data clearly indicate that substituents



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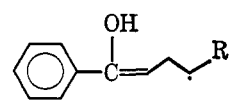
on the cyclopropane ring affect the rate of cyclopropylcarbinyl radical formation. As the substituents on the cyclopropane ring become more capable of stabilizing a radical on the carbon to which they are attached, the rate of cyclopropylcarbinyl radical formation is increased.[28] Thus 2-methylcyclopropyl phenyl ketone and both *cis*- and *trans*-2-phenylcyclopropyl phenyl ketone are more reactive than the unsubstituted material. Furthermore these substituents on the cyclopropane ring influence the direction of ring opening greatly.

Even though the cyclopropylcarbinyl free radical appears to recognize the fact that it is going to undergo a ring-opening reaction upon formation, it is also apparent that formation of the cyclopropylcarbinyl radical is a significantly different process from the analogous cyclopropylcarbinyl carbonium ion formation. First, the degree of ring-opening rearrangement appears to be highly dependent upon radical lifetime, a fact untenable with a single resonance hybrid. Second, in the corresponding carbonium ion, substituents on the cyclopropane ring have little or no effect on the rate of carbonium ion formation,[29] while the cyclopropylcarbinyl radical is markedly influenced. Third, cyclobutyl products are generally not observed from the cyclopropylcarbinyl radical. Our experiments with cyclopropane-substituted cyclopropyl phenyl ketones suggest that the reaction is affected by the nature of the ring-opened, homoallylic species III.



III

The other relative reactivity results are as expected. Since electron-withdrawing groups favor the reaction

(24) To show that this number is a valid indicator of the ring-opened product ratio, a control experiment was conducted which measured the reactivity of valerophenone and isovalerophenone toward sodium. They were similarly reactive. These data will be presented in a later communication.

(25) (a) G. Ciamician and P. Silber, *Ber.*, **44**, 1554 (1911); (b) E. Bergmann and S. Fugise, *Ann.*, **483**, 65 (1930); (c) S. G. Cohen and S. Aktipas, *Tetrahedron Letters*, 579 (1965).

(26) (a) E. J. Bowen and A. T. Horton, *J. Chem. Soc.*, 1685 (1936); (b) C. Walling and M. J. Gibian, *J. Am. Chem. Soc.*, **87**, 3361 (1965).

(27) A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 276 (1943).

(28) An alternative explanation for the effect of substituents on the cyclopropane ring on the rate formation of cyclopropylcarbinyl radical formation would be that the substituent effects are purely inductive. See, for example, J. A. Landgrebe and D. E. Applequist, *J. Am. Chem. Soc.*, **86**, 1536 (1964). Our data do not allow us to differentiate between the alternatives.

(29) R. A. Sneen, K. Lewandowski, I. Taha, and B. Smith, *ibid.*, **83**, 4843 (1961).

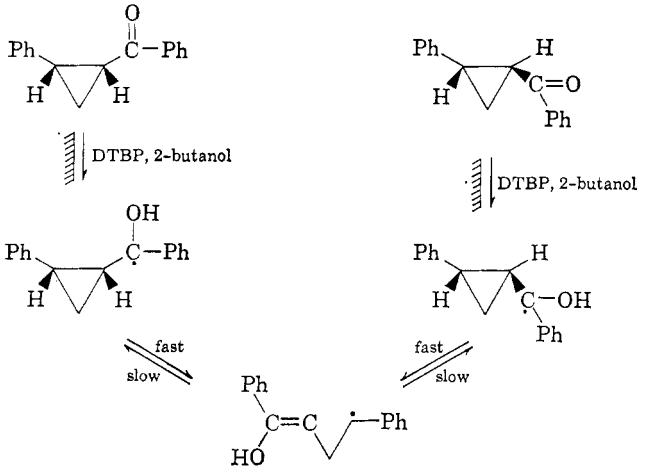
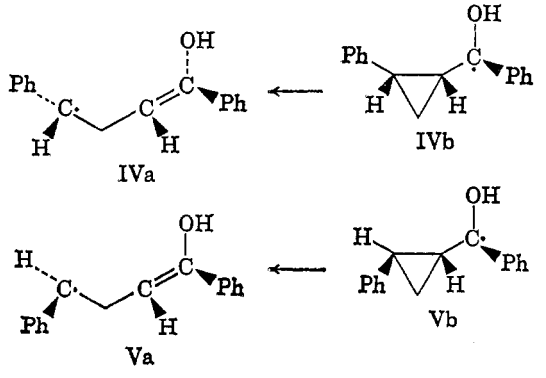


Figure 2.

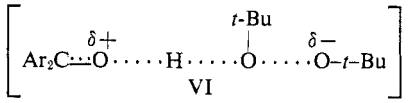
of α-hydroxyalkyl free radicals with substituted acetophenones, the α-hydroxyalkyl radical is maintaining its usual polar role of an electron donor in free-radical reactions and sites of lower electron density are attacked preferentially. Thus, in the alkyl aryl ketone series, as the alkyl group is increased in size from methyl to ethyl to isopropyl to *t*-butyl, the rate of reaction with 2-hydroxybutyl radicals decreases in a regular fashion. In the cycloalkyl series, the rates decrease smoothly as the size of the adjacent ring increases, a fact that probably indicates that radical formation provides the small ring with an excuse for relief of strain. It is significant to note that adjacent cyclopropyl gives driving force to the radical-formation process so as to make formation of the α-hydroxycyclopropylcarbinyl free radical preferable to formation of the α-hydroxydiphenylmethyl free radical.

The *cis*- and *trans*-2-phenylcyclopropyl phenyl ketone systems differ in reactivity probably because of a greater steric repulsion in the ground state of the *cis* isomer. There is little reason to favor, *a priori*, the intermediacy of radical IVb over radical Vb. Similar observations were made by Walborsky in analogous carbonium ion systems.[30]



It is of interest that neither *cis*-2-phenylcyclopropyl phenyl ketone nor *trans*-2-phenylcyclopropyl phenyl ketone was isomerized under the conditions of our experiments to the other isomer. This result, shown in Figure 2, suggests that either the ring-opening rearrangement of α-hydroxycyclopropylcarbinyl radicals is extremely rapid and nearly irreversible or that the reconversion of the α-hydroxycyclopropylcarbinyl free radical to the starting ketones does not occur, or, if it does occur, does so stereospecifically. We favor the former explanation and suggest that with at least our 2-phenylcyclopropylcarbinyl radical–homoallylcarbinyl radical conversion, little tendency toward ring reclosure is observed. This result also is in direct contrast with analogous carbonium ion intermediates where conversion of allylcarbinyl to cyclopropylcarbinyl occurs regardless of the species' stabilities.

Finally our results with substituted cyclopropylphenylcarbinols and di-*t*-butyl peroxide indicate that, at very low concentrations of peroxide, the ring-opening process is slowed down by electron-donating substituents on the aromatic nucleus. Since it is doubtful that these substituents have any effect on the ring-opened free radical, either they are serving to stabilize the closed species with regard to ring opening or they are increasing its rate of disappearance. If the induced decomposition of the peroxide is the primary process necessary for arylcyclopropyl ketone production and a transition state such as VI is reasonable for the induced decomposition, then electron-donating substituents would increase the rate of such a process.



Experimental Section[31]

Materials. Cyclopropyl phenyl ketone, cyclopropylphenylcarbinol, cyclopropylmethylcarbinol, cyclopropyl methyl ketone, cyclopropyl-4-fluorophenylcarbinol, cyclopropyl 4-fluorophenyl ketone, cyclopropyl-4-methylphenylcarbinol, cyclopropyl 4-methylphenyl ketone, cyclopropyl-4-methoxyphenylcarbinol, 4-fluorobutyrophenone, and 4-methylbutyrophenone were purchased from Aldrich Chemical Co. Propiophenone, butyrophenone, acetophenone, isobutyrophenone, valerophenone, isovalerophenone, 2-butanol, and benzophenone were purchased from Eastman Chemical Co. Di-*t*-butyl peroxide was purchased from Lucidol. The preparations of cyclobutyl phenyl ketone, cyclopentyl phenyl ketone, and cyclohexyl phenyl ketone have been described previously.[1]

All materials were purified by conventional methods when vapor phase chromatography indicated their purity to be less than 99.5%. *p*-Methoxybutyrophenone (bp 110° (1 mm); lit.[32] 116–120° (2 mm)) was prepared from anisole and butyryl chloride using conventional Friedel–Crafts techniques. Cyclopropyl *m*-trifluoromethyl ketone was prepared from cyclopropanoyl chloride and *m*-trifluoromethylphenylcadmium after the method of Vogel.[33] Cyclopropyl-*m*-trifluoromethylphenylcarbinol was (bp 78–82° (1 mm)) prepared by sodium borohydride reduction of cyclopropyl *m*-trifluoromethylphenyl ketone.

Anal. Calcd for $C_{11}H_{11}F_3O$: C, 61.09; H, 5.26; F, 26.43. Found: C, 61.12; H, 5.10; F, 26.39.

Preparation of 2-Methylcyclopropanecarbonitrile. β-Methyl-γ-chlorobutyronitrile was prepared by method of Applequist[34] (bp 88° (17 mm) (lit.[34] 83.0–85.5 (15 mm). A mixture of 60 g (0.74 mole) of β-methyl-γ-chlorobutyronitrile and 10.6 g (0.192 mole) of powdered potassium hydroxide was stirred and heated on a steam bath for 4 hr. After the addition of 125 ml of water, stirring and

(30) H. W. Walborsky and L. Plonsker, *J. Am. Chem. Soc.*, **83**, 2138 (1961).

(31) Melting points are uncorrected. Microanalysis were performed by Galbraith Analytical Laboratories, Knoxville, Tenn. Vapor phase chromatographic analyses were performed using either a Wilkens Model A-90-P gas chromatograph equipped with thermal conductivity detectors and using helium as a carrier gas or an F & M Model 609 with hydrogen flame detector and using helium as a carrier gas. A Beckman Model IR-8 was used for infrared analysis.

(32) S. Yoshida and S. Akagi, *J. Pharm. Soc. Japan*, 72, 317 (1952).

(33) A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., London, 1956, p 937.

(34) D. E. Applequist and A. H. Peterson, *J. Am. Chem. Soc.*, **82**, 2374 (1960).

heating were continued for an additional 30 min. After cooling, the solution was extracted with ether; the ether solution was washed with 5% HCl and water and dried over magnesium sulfate; the ether was removed by distillation. Continued distillation gave 30 g (50%) of the desired 2-methylcyclopropanecarbonitrile, bp 145°; lit.[35] 144.5–145.5°.

Preparation of 2-Methylcyclopropyl Phenyl Ketone. To a 500-ml round-bottom flask equipped with dropping funnel, stirrer, and condenser and containing 49.7 g (0.274 mole) of phenylmagnesium bromide in 300 ml of anhydrous ether was added dropwise 20.3 g (0.25 mole) of 2-methylcyclopropanecarbonitrile in 125 ml of ether. A precipitate formed almost immediately. After 6 hr of refluxing, the mixture was cooled, and 150 g of ice and 50 ml of concentrated HCl were added with stirring. The ether was removed by distillation and the mixture heated gently with stirring for 1 hr to hydrolyze the ketimine. The cooled solution was extracted with four successive 150-ml portions of ether, and the ether extracts were combined, washed with water, and dried over magnesium sulfate; the ether was removed under aspirator pressure. The residue was fractionally distilled giving 6 g of 2-methylcyclopropyl phenyl ketone, bp 69° (35 mm).

Anal. Calcd for $C_{11}H_{12}O$: C, 82.60; H, 7.56. Found: C, 82.60; H, 7.56.

Preparation of 2-Methylcyclopropylphenylcarbinol. To a 250-ml round-bottom flask equipped with a reflux condenser was added 3.0 g (0.019 mole) of 2-methylcyclopropyl phenyl ketone in 75 ml of methanol. After cooling the solution to 0°, 4.5 g (0.12 mole) of sodium borohydride was added in small portions with continuous magnetic stirring. After the addition of all the sodium borohydride, the solution was allowed to warm to room temperature and the stirring continued for 5 hr. Water (20 ml) was added and the stirring continued for an additional hour after which the solution was extracted with three 50-ml portions of ether. The ether extract was washed with water and dried over anhydrous magnesium sulfate. After removal of the ether, 2.0 g of 2-methylcyclopropylphenylcarbinol, bp 84° (0.75 mm), was obtained. Further purification was affected by preparative vapor phase chromotography using a 2-ft column packed with 2% Carbowax 20M at 125° and 15 psi of helium.

Anal. Calcd for $C_{11}H_{14}O$: C, 81.45; H, 8.70. Found: C, 81.40; H, 8.70.

Reaction of Cyclopropylarylcarbinols with DTBP at 130°. Cyclopropylarylcarbinol (1.0 mmole) and 0.1 mmole of DTBP were placed in test tubes, sealed, and heated for 24 hr in an oil bath thermostated at 130°. After this period the tubes were removed and opened and the products, butyrophenone and cyclopropyl phenyl ketone, analyzed on a 5-ft 10% Carbowax 1500 column at temperatures between 125 and 145° and using 15 psi of helium as a carrier.

For experiments requiring variable concentrations of peroxide, a similar method was used except that the molar quantity of DTBP was altered from 0.1 to 10 mmole per mmole of carbinol.

Reaction of Cyclopropylphenylcarbinol with DTBP at 130°. Cyclopropylphenylcarbinol (1.03 g, 6.94 mmoles) and DTBP (0.107 g, 0.73 mmole) were sealed in a Pyrex tube and heated to 130° for 12 hr. At the end of this period, the tube was cooled and opened. A weighed portion of acetophenone was added, and cyclopropyl phenyl ketone, residual cyclopropylcarbinol, and butyrophenone were analyzed by vapor phase chromatography at 125° and 15 psi of helium using the Carbowax 1500 column already described. Acetone, residual DTBP, and *t*-butyl alcohol were analyzed against *n*-butyl acetate as an internal standard using either the Carbowax 1500 column described above at 40° and 5 psi of helium or a 10-ft 15% Carbowax 4000 column at 60° and 7 psi.

Reaction of Cyclopropyl Phenyl Ketone with DTBP and 2-Butanol at 130°. Cyclopropyl phenyl ketone (0.245 g, 1.69 mmoles), DTBP (0.225 g, 1.54 mmoles), and 2-butanol (2.34 g, 31.36 mmoles) were sealed in a Pyrex tube and heated to 130° for 12 hr. At the end of this period, the tube was opened and cyclopropyl phenyl ketone residue, cyclopropylphenylcarbinol, and butyrophenone were analyzed using the Carbowax 1500 column mentioned previously with acetophenone as the internal standard, while methyl ethyl ketone, *t*-butyl alcohol, DTBP residue, and acetone were analyzed using *n*-butyl acetate as the internal standard and the Carbowax 4000 column mentioned earlier.

Reaction of 2-Methylcyclopropylphenylcarbinol with DTBP at 130°. A procedure similar to that described earlier was used. Analysis was accomplished using the previously described Carbowax 1500 and Carbowax 4000 columns against acetophenone and *n*-butyl acetate at 125 and 40°, respectively.

Reaction of 2-Methylcyclopropyl Phenyl Ketone with 2-Butanol and DTBP at 130°. A procedure exactly analogous to that described earlier was used. Analysis was accomplished using the techniques described for the reaction of DTBP with 2-methylcyclopropylphenylcarbinol.

Reaction of Cyclopropylmethylcarbinol-O-*d* with DTBP at 130°. Cyclopropylmethylcarbinol-O-*d* was prepared by three successive exchanges with 50% excess D_2O. Distillation of the exchanged carbinol gave cyclopropylmethylcarbinol-O-*d* (purity >95%). Cyclopropylmethylcarbinol-O-*d* (0.409 g, 6.48 mmoles) and 0.163 g (0.110 mmole) of DTBP were sealed in a Pyrex tube and heated to 130° for 4 hr. The 2-pentanone product was collected using the 15% Carbowax 4000 column described earlier as was the residual cyclopropylmethylcarbinol. A carbon–deuterium stretching frequency at 4.67 μ appeared in the infrared spectrum of the 2-pentanone, and the mass spectrum of the product showed enrichment of the acetone fragment with deuterium to the extent that 56.3% of all the 2-pentanone molecules possessed one deuterium atom at the 3-position. No enrichment was observed at the 1-position (methyl fragment) or in the 4- and 5-positions (ethylene fragment). The infrared spectrum of the residual cyclopropylmethylcarbinol still showed some O-deuteration (4.03 μ, O–D stretch), but no carbon–deuterium stretch was observed.

Relative Reactivities of Cycloalkyl Aryl Ketones with DTBP and 2-Butanol. Weighed quantities of the 2-ketones totaling 1 mmole, DTBP (0.5 mmole), and 2-butanol (30 mmoles) were sealed in Pyrex tubes and heated to 125° in a constant temperature bath. After 6–12 hr the sample tubes were opened, and a weighed quantity of an appropriate aryl alkyl ketone was added as an internal standard. Analysis for residual cycloalkyl aryl ketone was accomplished using the 5-ft 10% Carbowax 4000 column at temperatures from 125 to 150° and 15 psi of helium. Relative reactivities were calculated from $k/k_0 = (\log A_0/A)/(\log B_0/B)$, where A_0 and A are initial and final concentrations of cycloalkyl aryl ketone A, and B_0 and B are initial and final concentrations of isobutyrophenone.

Attempted Isomerization of *cis*-2-Phenylcyclopropyl Phenyl Ketone with 2-Butanol and DTBP at 130°. *cis*-2-Phenylcyclopropyl phenyl ketone (0.100 g, 0.045 mmole), DTBP (0.050 g, 0.034 mmole), and 2-butanol (1.0 g, 13.5 mmoles) were sealed in a Pyrex tube and heated to 130° for 2.5 hr. After this period, the tube was opened and the contents analyzed by vapor phase chromatography using a 3-ft 5% GE SE-30 column thermostated at 165° using 40 psi of helium as a carrier gas. No evidence existed for the appearance of *trans*-2-phenylcyclopropyl phenyl ketone.

Reaction of *trans*-2-Phenylcyclopropyl Phenyl Ketone as the DTBP and 2-Butanol. Experimental conditions similar to the above were used. Although several new products appeared, no evidence for formation of *cis*-2-phenylcyclopropyl phenyl ketone existed.

Reaction of Cyclopropyl Phenyl Ketone with DTBP at 160°. Cyclopropyl phenyl ketone (0.711 g, 4.88 mmoles) and DTBP (0.243 g, 1.67 mmoles) were sealed in a Pyrex tube and heated to 160° for 5 hr. No butyrophenone was observed among the products.

Attempted Thermal Rearrangement of Cyclopropylphenylcarbinol at 130°. Approximately 1 g of cyclopropylphenylcarbinol was sealed in a Pyrex tube and heated to 130° for 24 hr. At 130° there was no significant disappearance of the carbinol and no butyrophenone or cyclopropyl phenyl ketone was observed *via* vapor phase chromatography as before.

Reaction of 2-Methylcyclopropyl Phenyl Ketone with Sodium in Dioxane at 130°. To a Pyrex test tube containing 0.187 g (1.17 mmoles) of 2-methylcyclopropyl phenyl ketone in 1 ml of dioxane was added 0.024 g (1.05 mmoles) of sodium. After sealing, the tube and contents were heated to 130° in an oil bath for 12 hr. At the end of this period the tube was cooled and opened, and 2 ml of 5% hydrochloric acid was added. The contents was stirred for 10 min and then extracted with ether. Vapor phase chromatographic analysis of the ether extract was accomplished using the Carbowax 1500 column mentioned earlier at 125°, using 15 psi of helium as the carrier gas. The relative valerophenone to isovalerophenone ratio was obtained by comparing the peak areas with those of known standards.

Relative Reactivities of Aryl Alkyl Ketones with Sodium in Dioxane at 130°. Weighed quantities of the two ketones under study totaling 2.4 mmoles were added to a Pyrex test tube containing 2

(35) M. T. Rogers, *J. Am. Chem. Soc.*, **69**, 2544 (1947).

ml of dioxane. Sodium (1.2 g-atoms) was added and the tube sealed. The tube and contents were heated to 130° in an oil bath for 12 hr. At the end of this period the tube was cooled and opened, and remaining concentrations of ketone were determined against an internal standard using the Carbowax 1500 column at 125° and 15 psi of helium. Several experiments at different relative concentrations of sodium to ketones indicated that the results were reproducible. Relative reactivities were calculated as before.

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Nuclear Magnetic Resonance Investigation of α-C^{13}-Phenylmethyllithiums

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Contribution from the Dow Chemical Company, Eastern Research Laboratory, Wayland, Massachusetts. *Received October 8, 1965*

Abstract: The α-C^{13} nuclear magnetic resonance spectra of triphenylmethyllithium, diphenylmethyllithium, and benzyllithium indicate these species are substantially sp^2 hybridized in tetrahydrofuran solution. The chemical shift of the α-H of diphenylmethyllithium is downfield from that of diphenylmethane, whereas α-H of benzyllithium is upfield from toluene. The Li^7 resonances of these arylmethyllithiums are upfield from inorganic lithium, in contrast to those of alkyllithium compounds.

The long wavelength electronic absorption spectra[1] of the odd alternate "carbanions" triphenylmethyllithium, diphenylmethyllithium, and benzyllithium and the proton magnetic resonance spectra of these[2] and similar arylmethyllithiums[3] are indicative of extensive delocalization of the carbon–lithium bond electrons throughout the π system. Although for maximum overlap, it is supposed that the central carbon atom should be coplanar and sp^2 hybridized, the extent of sp^2 hybridization required for substantial electron delocalization is not known. Recently it was reported that in N-phenyl-substituted cyclic imines, which are isoelectronic with organolithium compounds, π–sp^3 conjugation is as effective as π–sp^2 conjugation.[4] Studies of rigid amines has also shown that "resonance is present to a remarkable degree even when N is pyrimidal," again illustrating the effectiveness of π–sp^3 conjugation.[5] The nuclear magnetic resonance of α-C^{13}-triphenylmethyl cation, in the highly polar sulfuric acid, has been interpreted as indicative of sp^2 hybridization of the central carbon atom.[6] Nevertheless sp^2 hybridization of organolithium compounds in a low dielectric medium, *e.g.*, tetrahydrofuran (THF), might be opposed by anion–cation coordination.

We wish to report evidence that the α-carbon atoms of triphenylmethyllithium, diphenylmethyllithium, and benzyllithium are substantially sp^2 hybridized, indicating that the electron pair is in an orbital having predominantly p character. The orbital occupied by the electron pair in benzyllithium may, however, have more s character than in the others. This conclusion is based on the α-C^{13} nuclear magnetic resonance spectra of these arylmethyllithium compounds in which the α-carbon atom is enriched with ~58% C^{13}. Also, as a result of C^{13}–H splittings in the proton spectra, it is possible to locate the α hydrogens on benzyllithium and diphenylmethyllithium which were not previously detected.

Experimental Section

The nuclear magnetic resonance spectra were observed on 0.9–1.2 *M* 100% THF solutions of the respective organolithium compound in sealed 0.25-in. o.d. thin wall tubes at ambient probe temperature. A modification of the high-resolution nmr spectrometer of Baker and Burd[7] was used for recording the spectra.

Benzyllithium was prepared from 2,2′-di-α-C^{13}-dibenzylmercury (obtained from Merck Sharp and Dohme Ltd. with ~58% C^{13} labeling) by reaction with lithium in THF.[1] After 3 hr of reaction at room temperature, a clear benzyllithium solution was obtained by centrifuging. In this and in the following preparations ultraviolet and visible spectral readings were used to determine complete reaction.

Diphenylmethyllithium was prepared from α-C^{13}-diphenylmethylchloride (obtained from Merck Sharp and Dohme Ltd. with ~58% C^{13}) by reaction with lithium in THF[1] at room temperature.

Triphenylmethyllithium was prepared from α-C^{13}-triphenylmethane by reaction with *n*-butyllithium in ~85:15 hexane–THF solution at room temperature. The precipitated triphenylmethyllithium was washed twice with hexane. The solid triphenylmethyllithium was pumped to dryness under high vacuum and made up to volume with THF. To prepare α-C^{13}-triphenylmethane 1.2 g of triphenyl-C^{13}-methanol (58% C^{13}, from Merck Sharp and Dohme Ltd.) was refluxed in 30 ml of 98–100% formic acid for 2 hr. The yellow solution (only partially dissolved when cold) first turned highly colored, then colorless on refluxing. On cooling, colorless

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(3) R. Waack and M. A. Doran, *ibid.*, **85**, 4042 (1963).
(4) A. T. Bottini and C. P. Nash, *ibid.*, **84**, 734 (1962).
(5) "Progress in Stereochemistry," W. Klyne and P.B.D. de la Mare, Ed., Vol. 2, 1957, 122.
(6) G. A. Olah, E. B. Baker, and M. B. Comisarow, *J. Am. Chem. Soc.*, 86, 1265 (1964).
(7) E. B. Baker and L. W. Burd, *Rev. Sci. Instr.*, **28**, 313 (1957); **34**, 238 (1963).