1,1-Dimethylcyclopropane-2-d_1 (**XIX**) was not synthesized independently. The infrared spectrum of XIX from run 5 showed C–D bands at 2251 and 2269 cm.$^{-1}$ and C–H bands at 3059, 3021, 2994, 2941, 2924, 2880, and 2864 cm.$^{-1}$. The stronger C–D band (2251) is related to the 3021 C–H band by the approximate relationship $\nu_H = 1.35\nu_D$.[28] Both of these bands may arise from the ring $>C<^H_D$ system since the C–H band does not appear in the spectrum of 1,1-dimethylcyclopropane (C–H

bands at 3063, 2994, 2941, 2924, 2909, 2880, and 2864 cm.$^{-1}$; of these the peaks at 3063 and 2994 appear to be characteristic of cyclopropane compounds). The observed C–D bands are at sufficiently high frequencies to exclude saturated carbon atoms other than methylene in cyclopropane rings as a location for observed deuterium.

(28) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Am. Chem. Soc.*, **80**, 2326 (1958).
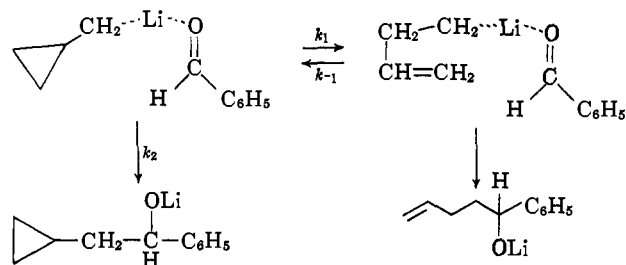

Preparation and Properties of Cyclopropylcarbinyllithium[1]

BY PETER T. LANSBURY,[2a] VICTOR A. PATTISON,[2b] WILLIAM A. CLEMENT,[2c] AND JACK D. SIDLER[2b]

The title compound has been prepared by the lithium–halogen exchange reaction at −70° and subjected to reaction with a number of electrophilic reagents. Cyclopropylcarbinyllithium-α,α-d_2 was also generated and found not to undergo isotopic scrambling.

In the course of studies on the organolithium-induced isomerization of benzyl alkyl ethers[3] (the Wittig rearrangement) we observed that benzyl cyclopropylcarbinyl ether underwent isomerization mainly to phenylcyclopropylcarbinylcarbinol. This result was of interest since the accepted mechanism[3,4] of the Wittig rearrangement involves cleavage and recombination, with the migrating group ejected as a carbanion (complexed by lithium ion with the benzaldehyde). Since attempts to generate the cyclopropylcarbinyl anion independent of electrophilic trapping reagents (see below) invariably lead to products of reaction containing the allylcarbinyl structure, we needed independent evidence that the unrearranged anion had at least sufficient stability to react intramolecularly with benzaldehyde in the Wittig intermediate at a rate somewhat faster than isomerization ($k_2 > k_1$). Since $k_1 \gg k_{-1}$, k_2 must be very large, for all indications suggest a very

suitable for rapid generation of cyclopropylcarbinyllithium and its reactions with various electrophilic species to give unrearranged cyclopropylcarbinyl-containing derivatives. In addition, experiments bearing on the question of isotope scrambling of the labeled anion have been carried out. This isomerization could be involved in the collapse of the Wittig intermediate from benzyl cyclopropylcarbinyl ether, by analogy with the formation of α-methylallyl products from the butenyl Grignard reagent.[6]
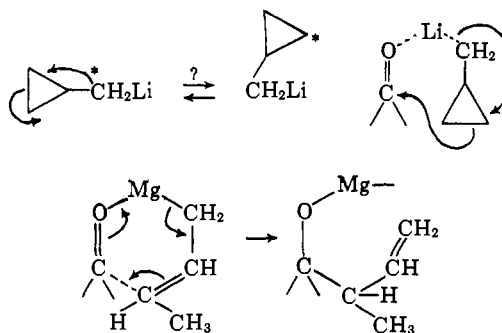
First, it is worthwhile to review previous studies of carbanionoid cyclopropylcarbinyl systems. Roberts and Mazur[7] found that products derived from the Grignard reagent of cyclopropylcarbinyl bromide had the allylcarbinyl structure; furthermore, n.m.r. studies of the freshly-prepared Grignard reagent[8] showed $\gtrsim 99\%$ of the rearranged reagent. Even when the Grignard reagent was generated in the presence of benzoic acid, to trap the initially-formed anion as soon as it is formed, only 6% of methylcyclopropane was isolated, as compared with 92% of 1-butene.[9] It is also of interest that the deamination of cyclopropylcarbinylamine by either difluoramine or the action of hydroxylamine-O-sulfonic acid in base on the p-toluenesulfonyl derivative (Nickon–Sinz reaction) gives exclusively 1-butene,[10] in spite of the fact that the latter procedure

low barrier for cyclopropylcarbinyl to allylcarbinyl interconversion (see below). We have succeeded in preparing cyclopropylcarbinyllithium (I) by the low temperature metal–halogen exchange reaction in ether,[1] thus confirming the stability of this species under sufficiently mild conditions, which are comparable to those under which optically-active 2-octyllithium undergoes extensive racemization.[5] Our initial observations have been extended and here we report conditions even more

(1) A preliminary communication on this subject has appeared: P. T. Lansbury and V. A. Pattison, *J. Am. Chem. Soc.*, **85**, 1886 (1963).

(2) (a) Alfred P. Sloan Foundation Fellow; (b) supported by a grant from the U. S. Army Research Office (Durham); (c) participant in NSF Research Participation Program for College Chemistry Teachers, summer, 1963.

(3) P. T. Lansbury and V. A. Pattison, *J. Am. Chem. Soc.*, **84**, 4295 (1962), and references cited therein.

(4) U. Schollkopf and W. Fabian, *Ann.*, **642**, 1 (1961).

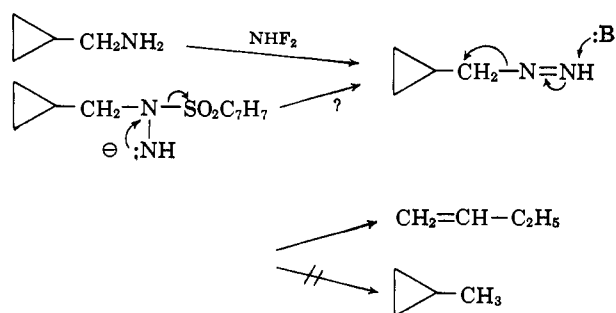(5) R. L. Letsinger, *J. Am. Chem. Soc.*, **72**, 4842 (1950).

(6) J. D. Roberts and W. G. Young, *ibid.*, **83**, 494 (1961).

(7) J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2509 (1951).

(8) M. S. Silver, P. R. Shafer, J. E. Nordlander, C. Ruchardt, and J. D. Roberts, *ibid.*, **82**, 2646 (1960).

(9) C. L. Hamilton, Ph.D. Thesis, California Institute of Technology, 1963.

(10) J. P. Freeman and C. L. Bumgardner, *J. Am. Chem. Soc.*, **85**, 97 (1963).

involves an aqueous medium. In the difluoramine reaction, ring opening is not surprising, since a high concentration of good proton donors is not present. The results of the Nickon deamination are novel, however, because the Wolff–Kishner reductions of cyclopropanecarboxaldehyde,[11] α-phenylcyclopropanecarboxaldehyde,[12] and methyl cyclopropyl ketone[12] all proceed without ring opening (although the corresponding deaminations with difluoramine give ring opening). In these cases, the carbanion arising from decomposition of the diimide apparently undergoes protonolysis faster than isomerization. Cyclopropylcarbinyl derivatives containing β-aryl groups, which stabilize the isomerized anion, undergo some ring opening even during Wolff–Kishner reduction.[12]
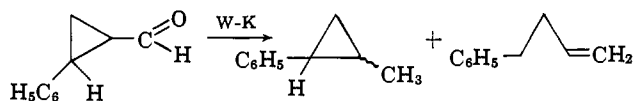
Finally, it should be noted that certain systems containing cyclopropylcarbinyl anions show unexpected stability, although for special reasons. For example, the Sommelet–Hauser rearrangement of dimethylbenzylcyclopropylcarbinylammonium ion proceeds without isomerization of the migrating group.[13] In this case,
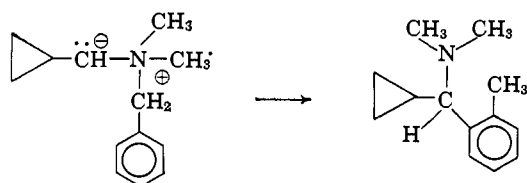
electrostatic attraction of the negative charge and the positive quaternary nitrogen apparently prevent facile ring opening. β-Phenyl groups on the cyclopropane ring, however, lead to ring-opened product.[12] Another example of a stable anion is in the lithium aluminum hydride reduction of the dibenzofulvene shown below,[14] where the negative charge is delocalized by cyclopentadienide resonance.
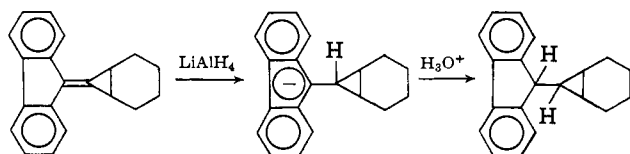
Very recently, cyclobutylcarbinyl organometallic reagents have been studied and found to undergo ring

(11) E. Renk, P. R. Shafer, W. H. Graham, R. H. Mazur, and J. D. Roberts, J. Am. Chem. Soc., 83, 1987 (1961).
(12) C. L. Bumgardner and J. P. Freeman, Tetrahedron Letters, 737 (1964).
(13) C. L. Bumgardner, J. Am. Chem. Soc., 85, 73 (1963).
(14) D. Y. Curtin and B. O'Connor, private communication.

opening to pentenyl derivatives.[15] The equilibrium is slightly more favorable for the cyclobutylcarbinyl anion than the more strained cyclopropylcarbinyl system.

Results and Discussion

Preparation of Cyclopropylcarbinyllithium (I).—Although our first preparations of I were carried out in ether, we felt that the optimum conditions for preparing I, with a minimum of isomerization to allylcarbinyllithium (II), would be the use of a hydrocarbon solvent containing only a small amount of ether to permit the lithium–halogen exchange to proceed at a reasonable rate. Since optically-active lithium reagents possess greater optical stability in solvents such as hexane[16] than in ether, isomerization of I to II should also be suppressed in the former medium. Furthermore, sec-butyllithium was used in the present work, rather than ethyllithium, since the desired equilibrium is much more favorable using a secondary alkyllithium reagent.[15,17] These changes resulted in: (1) more complete and rapid conversion of cyclopropylcarbinyl iodide to I; (2) greater stability of I; and (3) less need to keep reaction conditions carefully regulated during reaction of I with electrophiles (as was the case when ether was the solvent[1]). The table presents first our earlier studies with ethyllithium in ether,[1] then our most recent data with sec-butyllithium in petroleum ether containing ca. 10% ether. The ratios of I to II were obtained by quenching the mixture of lithium reagents with benzaldehyde, a reaction previously shown to be irreversible under the conditions used.[3] Details are given in the Experimental section. The results in Table I clearly show that cyclopropylcarbinyl iodide undergoes rapid and essentially quantitative exchange with sec-butyllithium at −70°. Addition of benzaldehyde, as well as other electrophiles (see below), at −70° shortly after the exchange reaction results in the formation of nearly pure cyclopropylcarbinyl derivatives (cf. runs 5–7), but isomerization of I to II becomes appreciable within an hour (runs 8–10). That rearrangement of I to II is slow relative to carbonyl addition is seen by comparing runs 6 and 7 and runs 9 and 10, which show that the ratio of V to VI is not affected by whether quenching is very rapid or slow. It is important to note that the total organolithium concentration decreases with time, apparently due to side reactions with the sec-butyl iodide formed (e.g., β-elimination, coupling, etc.), so that for optimum yields in synthesis, compound I should be used as soon as possible after the exchange reaction. Finally, run 11 shows that tetrahydrofuran is less desirable than ether for catalyzing the exchange, causing greater isomerization of I to II, just as it is better for racemizing optically-active organolithium compounds.[16]

A detailed study of the effect of exchange temperature on the stability of I has not been made. However, an exchange of sec-butyllithium and cyclopropylcarbinyl iodide, carried out like runs 5–7 except that the temperature was −21°, yielded only VI and no V when quenched with benzaldehyde only 3 min. after exchange.

(15) E. A. Hill, H. G. Richey. Jr., and T. C. Rees, J. Org. Chem., 28, 2161 (1963).
(16) D. Y. Curtin and W. J. Koehl, Jr., J. Am. Chem. Soc., 84, 1967 (1962).
(17) D. E. Applequist and D. F. O'Brien, ibid., 85, 743 (1963).

TABLE I

PREPARATION OF I BY METAL–HALOGEN EXCHANGE AT $-70°$

Run	mmoles RLi	mmoles C_4H_7I	Exchange time, min.	% III (IV)	% V	% VI	% alcohols
		A. RLi = ethyllithium in ether[a]					
1	1.0	1.0	5	35	49	16	..
2	1.0	1.0	30	11	51	38	..
3	1.0	1.0	120	3	17	80	..
4	10.0	10.0	5	66	22	12	82
		B. RLi = sec-butyllithium in 10:1 petroleum ether–ether					
5	1.0	1.2	2	1	95	4	89
6[b]	1.0	1.2	2	1	93	6	83
7[c]	1.0	1.2	2	<1	94	6	82
8	1.0	1.2	60	0	84	16	60
9	1.0	1.2	240	0	55	45	33
10[d]	1.0	1.2	240	0	53	47	41
11[e]	1.0	1.2	2	0.5	71	28.5	

[a] Yields of III, IV, V, and VI are normalized to 100%. The last column (% alcohols) reports the *actual* yields of all carbinols present (determined by v.p.c. using internal standards). [b] Rapid quenching with pure benzaldehyde in 1–2 sec. [c] Benzaldehyde in petroleum ether solution slowly added during 3 min. [d] Quenched as in footnote c, during 10 min. [e] 10% tetrahydrofuran instead of ether.

This result parallels the earlier observations in pure ether solvent.[1]

Reactions of I with Other Electrophiles.—We have not undertaken an exhaustive study of cyclopropylcarbinyllithium reactions with electrophilic reagents. However, freshly-prepared I reacted in high yield with benzophenone and benzoyl chloride to give tertiary alcohols VII and VIII, with phenyl isocyanate to give the anilide IX, and with bromine to give mainly cyclopropylcarbinyl bromide. The above reactions were carried out at $-70°$; analytical data, physical properties, and yields are given in the Experimental section.
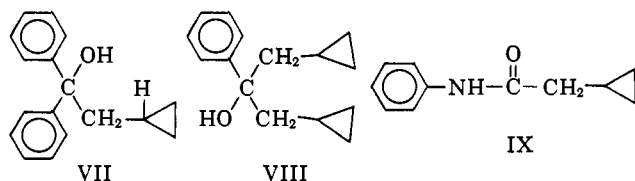
The n.m.r. spectra of the above products support the proposed structures in all cases. Moreover, carbinol VIII showed the expected magnetic nonequivalence of the methylene protons adjacent to the cyclopropane rings, there being the predicted eight-line multiplet (AB part of ABX spectrum) centered at 1.73 p.p.m.[18] with $\delta_{AB} = 0.53$ p.p.m. and $J_{AB} = 14.2$ c.p.s. An interesting feature of the octet is the fact that the vicinal coupling constants J_{ax} and J_{bx} are different, as seen in Fig. 1. A reasonable explanation for the unequal

(18) All chemical shifts are reported in parts per million (p.p.m.) downfield from the internal standard, tetramethylsilane (δ = 0.0 p.p.m.).
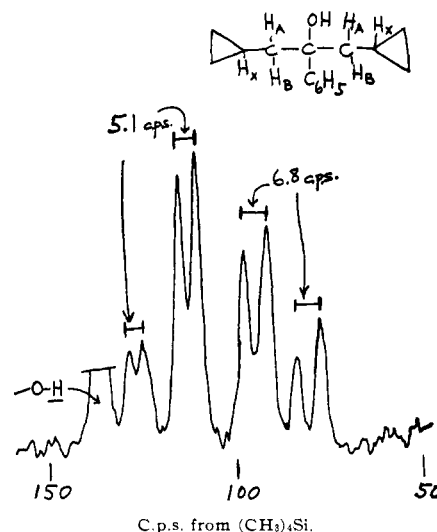

Fig. 1.—Partial n.m.r. spectrum (60 Mc.) of bis(cyclopropylcarbinyl)phenylcarbinol (VIII), showing the multiplet arising from the magnetically nonequivalent methylene protons.

coupling of H_x with the adjacent nonequivalent methylene protons H_a and H_b is that preferred conformations a and b (below) are unequally populated, due to the asymmetric nature of R. Thus δ_{AB} would be expected to be large because of the preferential shielding of
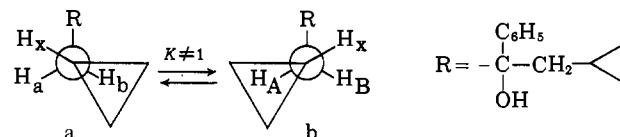
either H_A or H_B by the cyclopropane ring.[19] Furthermore, it can be seen that the more highly shielded methylene proton would be essentially *trans* to H_x (on a time-average basis), whereas the less shielded proton is essentially *gauche*. This should result in the high field proton having a larger vicinal coupling constant[20] exactly as is observed (see Fig. 1).

The brominolysis reaction is of interest since addition of bromine at $-70°$ 3 min. after exchange gives the same product ratio, 91% cyclopropylcarbinyl bromide and 9% allylcarbinyl bromide, that benzaldehyde does (within experimental error). In fact, when the exchange mixture containing I and II was kept for 4 hr. at $-70°$, brominolysis gave 58% cyclopropylcarbinyl bromide and 42% allylcarbinyl bromide which again parallels the benzaldehyde results (Table I, run 9). Now Applequist and Peterson[21] found that *cis*- and *trans*-2-methylcyclopropyllithium reacted stereospecifically with carbon dioxide to give the respective *cis*- and *trans*-2-methylcyclopropanecarboxylic acids, but that brominolysis was not stereospecific.[22] This sug-

(19) (a) K. B. Wiberg and R. P. Ciula, *J. Am. Chem. Soc.*, **81**, 5261 (1959). (b) Moreover, cooling should increase the population of the more stable conformer and give a greater δ_{AB}. In accord with this expectation, δ_{AB} increases from 31 to 39 c.p.s. when the temperature is lowered from +40 to $-20°$.

(20) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

(21) D. E. Applequist and A. H. Peterson, *J. Am. Chem. Soc.*, **83**, 862 (1961).

(22) Walborsky and co-workers (*Record Chem. Progr.*, **23**, 75 (1962)), on the other hand, report that brominolysis and iodinolysis of optically active 1-methyl-2,2-diphenylcyclopropyllithium proceed with 95 and 100% retention of configuration, respectively. Therefore it appears that racemization during brominolysis of cyclopropyllithiums is not necessarily a general phenomenom. However, assuming Applequist's results (ref. 21) to be valid, one must consider the possible role of radical intermediates in such reactions, although heterolytic electrophilic substitution may well be the major mechanistic pathway.
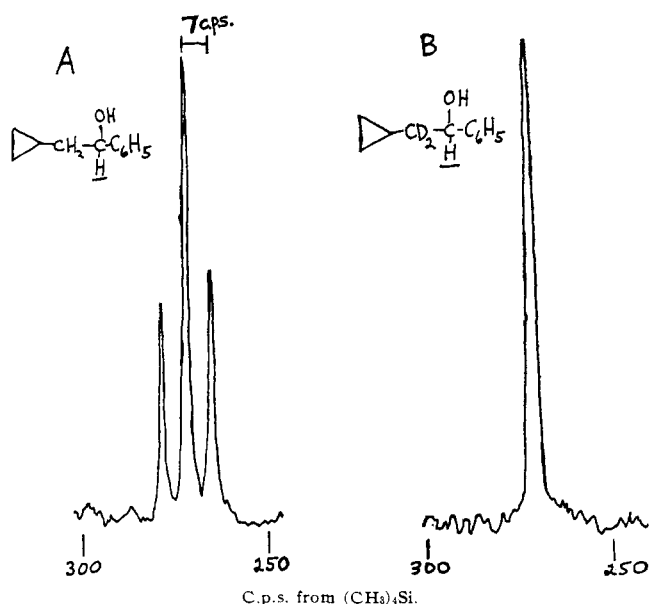
Fig. 2.— The carbinol proton region of the n.m.r. spectra of cyclopropylcarbinylphenylcarbinol (V) prepared from I (in A) and I-α,α-d_2 (in B).

gested that, at least in part, the brominolysis must involve either radical or carbonium ion intermediates. That the carbonium ion pathway is not of importance is clearly shown by the absence of cyclobutyl bromide in our brominolysis product,[23] as well as the formation of only cyclobutyl iodide from cyclobutyllithium and iodine[17]; thus, no typical cyclobutyl–cyclopropylcarbinyl cationic interconversion products are formed. The alternative radical mechanism for brominolysis thus remains to account for the nonstereospecific brominolysis of cis- and trans-2-methylcyclopropyllithium.[21] However, our product distribution is similar to that from carbanion reactions, rather than that which might be expected from the cyclopropylcarbinyl radical, which gives largely ring opened products in many cases.[24] This apparent inconsistency is resolvable if one postulates a "cage" reaction of bromine with cyclopropylcarbinyllithium wherein radical combination[21] occurs faster than prior radical ring opening ($k_1 > k_2$).
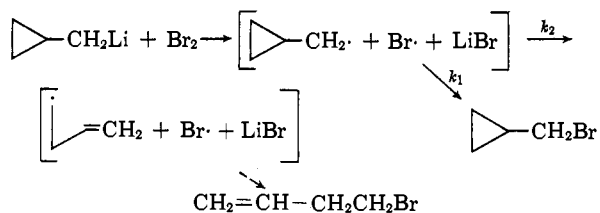
Isotope Position Rearrangement in I.—Although isotopic labels undergo scrambling in the cyclopropylcarbinyl cation,[23] supposedly via nonclassical "bicyclobutonium" ions, no analogous rearrangement occurs in the radical.[24a] It was therefore of interest to see if any


isotope position rearrangement occurs in the anion. For this purpose, cyclopropylcarbinyl-α,α-d_2 iodide was

(23) R. Breslow in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp. 259–265.

(24) (a) Reference 23, pp. 291–293; (b) E. S. Huyser and J. D. Taliaferro, J. Org. Chem., **28**, 3442 (1963).

prepared by the sequence of reactions used to prepare the undeuterated iodide. Cyclopropylcarbinyl-α,α-d_2 iodide (X) had the same n.m.r. spectrum as the undeuterated compound[1] except that the doublet at 3.15 p.p.m. (–CH$_2$–I) was almost completely gone (less than 6% –CH$_2$–I present). When X was exchanged with sec-butyllithium for 2 min., then the mixture quenched with benzaldehyde (as in run 5, Table I), 92% of the carbinol fraction was V. This product was purified by preparative gas chromatography and examined by n.m.r. The spectrum showed the carbinol proton as a clean singlet at 5.5 p.p.m. (whereas a triplet with $J \sim 7$ c.p.s. would have appeared if any vicinal protons were present[4]) and integration of the cyclopropyl hydrogen multiplet (0.1 to 0.7 p.p.m.) indicated no measurable deuterium incorporation. Thus, within the limits of detection, no scrambling occurs. A second experiment with X involved a 2-hr. exchange to allow a greater
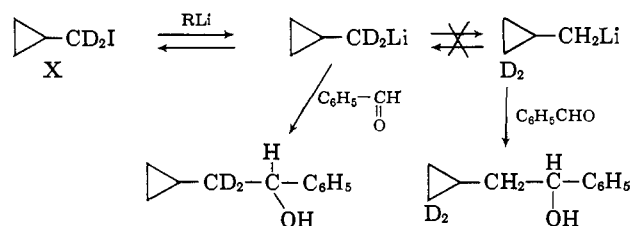
opportunity for scrambling of the label. The ratio of V to VI was 53:47 this time; again isolation of pure V by preparative v.p.c. and n.m.r. analysis (Fig. 2) revealed that no rearrangement of I-d_2 had occurred. Finally, we have prepared benzyl cyclopropylcarbinyl-α,α-d_2 ether, rearranged it in the usual manner[3] and found that no deuterium scrambling had occurred in the formation of the isomeric carbinol V.

From the above studies, we conclude that the cyclopropylcarbinyl anion has little, if any, "nonclassical" character, in agreement with the molecular orbital calculations of Howden and Roberts.[25]

Experimental[26]

Cyclopropylcarbinyl Iodide.—A solution of 20 g. (0.22 mole) of cyclopropylcarbinyl chloride[27] and 33 g. (0.22 mole) of sodium iodide in 150 ml. of reagent grade acetone was gently refluxed overnight. The solution was then decanted from the inorganic residue; the latter was extracted with petroleum ether and the extract added to the main solution. Solvent was removed by distillation through a 10-in. helices-packed column and the product then vacuum distilled at ca. 30°, trapping the distillate in a Dry Ice–acetone cooled flask. Careful distillation of the crude iodide gave 22 g. (55%) of cyclopropylcarbinyl iodide, b.p. 88–90° (150 mm.). The n.m.r. spectrum (neat) showed a doublet ($J = 8$ c.p.s.) at 3.15 p.p.m. (–CH$_2$–I) and a multiplet at 0.2–1.5 p.p.m. (cyclopropyl protons) in the ratio of 2 to 5. At high spectrum amplitude, a weak quintet centered at 4.5 p.p.m. due to cyclobutyl iodide[17] and a weak signal at 5.2 p.p.m. (vinyl protons) due to allylcarbinyl iodide were present. The intensity of these peaks was so low that integration was not possible and the total impurities were estimated to be $\leq 2\%$.

(25) M. E. H. Howden and J. D. Roberts, Tetrahedron Suppl., **2**, 403 (1963).

(26) Melting points, taken in a Mel-temp capillary apparatus, and boiling points are uncorrected. Elemental analyses were by Dr. Alfred Bernhardt, Mulheim, Germany. Infrared spectra were obtained on a Beckman IR-5 spectrometer and n.m.r. spectra on a Varian A-60 spectrometer, using carbon tetrachloride or deuteriochloroform as solvent with tetramethylsilane as internal standard. Chemical shifts are reported in p.p.m. downfield from TMS. Gas chromatography analyses were performed on a F and M Model 300 apparatus. All petroleum ether used for chromatography and as reaction solvent had b.p. 30–60° and was olefin free.

(27) M. S. Caserio, W. H. Graham, and J. D. Roberts, Tetrahedron, **11**, 171 (1960).

Anal. Calcd. for C_4H_7I: C, 26.39; H, 3.88. Found: C, 26.56; H, 3.72.

Similarly, using cyclopropylcarbinyl-α,α-d_2 chloride,[26] the deuterated iodide X, b.p. 84–86° (140 mm.), was prepared in 48% yield by displacement with sodium iodide in acetone. The n.m.r. spectrum showed a *weak* doublet at 3.15 p.p.m. (corresponding to <6% –CH_2I contamination), indicating almost complete deuteration of the α-carbon atom, and only traces of other impurities (as above).

General Procedure for Preparation and Reactions of Cyclopropylcarbinyllithium.—All reactions were run in one-neck round-bottom flasks with side arms fitted with a rubber septum. After the desired amount of *sec*-butyllithium solution (obtained from the Foote Mineral Co. as a 1.2 *M* solution in hexane) was added to the nitrogen-flushed flask, which also contained a magnetic stirring bar, a Nujol bubbler was placed in the neck and *all* subsequent additions made through the rubber septum by means of a hypodermic syringe. The reaction flask was cooled to −69 ± 2° (internal temperature) by a Dry Ice–acetone bath throughout the exchange reaction and subsequent quenching. For several reactions at −20°, a Dry Ice–ethanol–water bath was used.

In a typical run, 0.01 mole of *sec*-butyllithium (*ca.* 9 ml.) was added to a 200-ml. flask and diluted to 50 ml. with petroleum ether. After cooling to −70° for 30 min., a solution of 0.012 mole of cyclopropylcarbinyl iodide in 5 ml. of ether was added during 1 min., with magnetic stirring. After an additional 2 min. at −70°, a solution of 0.02 mole of benzaldehyde in 2 ml. of ether was added dropwise (*ca.* 1 min.) with stirring and the solution kept at −70° for at least 15 more min. As shown in Table I, the exact time required to add the benzaldehyde did not affect the product distribution, contrary to the case when pure ether was the solvent.[1] The procedure was the same when other reagents were allowed to react with I. In all cases, the cyclopropylcarbinyl iodide was employed in *ca.* 20% excess so as to drive the initial exchange equilibrium essentially completely to completion and avoid the presence of *sec*-butylphenylcarbinol and related compounds in the product mixture.

The reaction mixtures were hydrolyzed by adding ammonium chloride solution or water at low temperature, then working up, after warming to room temperature, by procedures developed earlier.[1,4] Product mixtures from I and benzaldehyde were analyzed[1,4] on v.p.c. columns consisting of Tide on Chromosorb P; in those cases where absolute yields were obtained (runs 5–10, Table I) α-phenylethyl alcohol was used as internal standard. For n.m.r. examination of samples of V prepared from I and I-α,α-d_2, the pure carbinols were isolated by preparative v.p.c. and their spectra taken in CCl_4 solution.

Reaction of I with Other Electrophiles. With Phenyl Isocyanate.—A solution containing *ca.* 10 mmoles of I was prepared from 10 mmoles of *sec*-butyllithium in 50 ml. of petroleum ether to which was added 2.2 g. (12 mmoles) of cyclopropylcarbinyl iodide in 5 ml. of ether during 1 min. at −70°. After additional 2 min., 1.19 g. (10 mmoles) of phenyl isocyanate was slowly added (syringe). After 15 min. more at −70°, the reaction mixture was hydrolyzed with water and worked up as above. Evaporation of the ether solution of product left 1.27 g. (73%) of the amide IX, m.p. 98–99° (reported[7] 98.8–99.6°) after several recrystallizations from benzene–petroleum ether.

Anal. Calcd. for $C_{11}H_{13}NO$: C, 75.40; H, 7.48. Found: C, 75.33; H, 7.37.

The infrared spectrum of IX (Nujol mull) showed amide carbonyl absorption at 6.07, the cyclopropyl ring stretch[28] at 9.8, phenyl C–H out-of-plane deformations at 14.5, and N–H stretching at 3.1 μ. The n.m.r. spectrum was run first without tetramethylsilane (TMS), in order to allow integration of the entire cyclopropyl proton multiplet, and then with TMS to provide the chemical shift values: multiplet at 0.1–0.8 p.p.m. (cyclopropyl, area 4.9), doublet at 2.23 p.p.m. (*J* = 6.7 c.p.s., –C(=O)CH_2—,

area 1.9), multiplet at 7.0–7.7 p.p.m. (aryl protons, area 5.0); no signals appeared in the vinyl proton region (4–6 p.p.m.).

With Benzoyl Chloride.—A solution containing 10 mmoles of I was prepared exactly as above and treated with 0.56 g. (4 mmole) of benzoyl chloride in 1 ml. of ether. After 30 min. more stirring at −70°, the reaction mixture was hydrolyzed and worked up. The crude oily product mixture, whose infrared spectrum was free of carbonyl absorption, was chromatographed over 30 g. of alumina and eluted with 40% ether–60% petroleum ether, providing 0.743 g. (86%) of VIII as an uncrystallizable oil. Significant bands in the infrared spectrum (neat) were at 2.8 (O–H stretching), 9.8 (cyclopropyl ring stretch), and 14.3 μ (phenyl). The n.m.r. spectrum (CCl_4 solvent) showed a multiplet at 0.0–0.8 due to cyclopropyl protons, an octet centered at 1.73 due to the methylene protons (see Discussion), the O–H signal at 2.27, and the aromatic protons at 7.0–7.5 p.p.m., all in the expected ratios of areas. A weak multiplet at *ca.* 6 p.p.m. was due to vinyl protons, but integration indicated <5% impurity (allylcarbinyl-containing structures).

Anal. Calcd. for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.39; H, 9.24.

With Benzophenone.—A solution containing 10 mmoles of I (as above) was treated with 1.82 g. (10 mmoles) of benzophenone in 2 ml. of ether at −70°, 2 min. after the exchange reaction was completed. After stirring for an additional 0.5 hr., the reaction mixture was hydrolyzed and worked up as above. The crude oily product, which showed both hydroxyl and carbonyl absorption in the infrared, was chromatographed over 50 g. of alumina. Elution with 30% ether–70% petroleum ether provided 1.65 g. (70%) of pure carbinol VII as an oil, which resisted crystallization and did not form solid derivatives. The infrared spectrum of VII (neat) showed O–H stretching at 2.80 and 2.85, cyclopropyl ring stretching[27] at 9.8 μ, and a strong band, due to phenyl groups, at 14.3 μ. The n.m.r. spectrum showed signals (area and assignment) at: multiplet at 7.0–7.5 (10 phenyl protons), singlet at 2.47 (1 O–H), doublet at 2.13, *J* = 6.0 c.p.s. (1.97 –CH_2– protons), and −0.1 to +0.7 p.p.m. (multiplet, 5.03 cyclopropane protons). No vinyl protons were detected.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.63; H, 7.56.

With Bromine.—Typical reaction conditions were used and, in addition, light was kept out of the reaction flask. In the first run, 1.0 mmole of I was treated at −70°, 3 min. after exchange, with 0.16 g. (1 mmole) of bromine in 0.5 ml. of petroleum ether. After hydrolyzing with water, the ether solution was washed with cold sodium bisulfite solution, 5% sodium bicarbonate, ice water, and then dried over sodium sulfate in the cold room. The ether solution was carefully concentrated and analyzed by v.p.c., using a 7-ft., 20% Tide on Chromosorb P column at 55° with a helium flow rate of 60 cc./min. The allylcarbinyl bromide (9%) and cyclopropylcarbinyl bromide (91%) peaks were trapped out and their infrared spectra taken. These corresponded with the reported spectra[7]; moreover, cyclobutyl bromide[29] was shown to be absent by noting that the infrared spectrum of the cyclopropylcarbinyl bromide showed no absorption in the regions where authentic cyclobutyl bromide had strong bands (these two bromides were not separated by v.p.c. using the above and other columns).

A second run, in which the solution of I was kept for 4 hr. at −70° before addition of bromine, resulted in cyclopropylcarbinyl bromide and allylcarbinyl bromide being formed in the relative yields of 58 and 42%, respectively.

(28) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed. John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 29–30.

(29) Kindly donated by Professor D. E. Applequist.