

(2) We next identify  $\nu_L$  as a methyl "rocking" mode<sup>11</sup> the only characteristic vibration capable of beginning the indicated motion, and choose  $-\nu_L^H = \nu^D = 925 \text{ cm.}^{-1}$  and  $-\nu_L^D = \nu^H = 765 \text{ cm.}^{-1}$ , using neopentane for a model.<sup>12</sup> Since the effective mass approximates that of a methyl group<sup>11a</sup> tunneling may be neglected. The calculated  $k_H/k_D$ , 1.74, may be compared with the observed value of  $1.71 \pm 0.06$ .

In view of this excellent agreement, it should be noted that the simple model specifies the energy, but not necessarily the structure, of the cyclopropane's immediate precursor. In particular, it does not exclude  $\alpha$ -lithium neopentyl chloride from this role nor are we aware of any evidence which does. It is hoped that related studies, now in progress, may shed more light on this matter.

(11) (a) W. T. King and B. Crawford, Jr., *J. Mol. Spectry.*, **5**, 421 (1960); **8**, 58 (1962); (b) J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, **19**, 117 (1963), and references cited therein.

(12) K. Simizu and H. Murata, *Bull. Chem. Soc. Japan*, **30**, 487 (1957).

(13) Taken from the M.S. dissertation of S. J. B., Cornell University, 1963. Partial support, provided by a Frederick Gardner Cottrell grant from Research Corporation, is acknowledged with gratitude.

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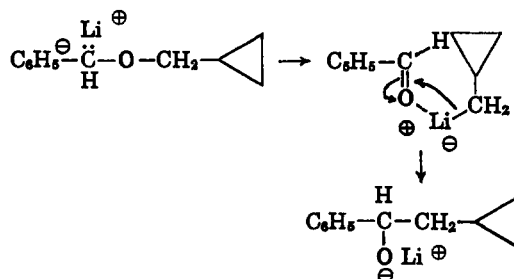
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RECEIVED APRIL 16, 1963

### Cyclopropylcarbinylithium

Sir:

Attempts to prepare the Grignard reagent from cyclopropylcarbinyl bromide and magnesium in the conventional manner have always resulted in the formation of products derivable from allylcarbinylmagnesium bromide.<sup>1</sup> Furthermore, the freshly prepared Grignard reagent itself has been shown to have the allylcarbinyl structure ( $\approx 99\%$ ) by n.m.r. spectroscopy.<sup>2</sup> We recently have carried out the Wittig rearrangement of cyclopropylcarbinyl benzyl ether and obtained the isomeric carbinol in which the cyclopropylcarbinyl group was largely unrearranged.<sup>3</sup> Although the above



pathway, involving an intermediate aldehyde-organolithium complex, seems to be reasonably established,<sup>3</sup> it was considered highly desirable to attempt to generate the cyclopropylcarbinyl anion by an independent and unambiguous route, in order to determine its stability with respect to the allylcarbinyl anion. We now wish to report the first preparation of cyclopropylcarbinylithium, using the low temperature metal-halogen exchange reaction<sup>4</sup> in diethyl ether, a solvent in which the carbon-lithium bond has appreciable ionic character.<sup>5</sup> This mode of generating carbanions avoids the possible complication of free radical intermediates, as may be the case in forming Grignard reagents.<sup>6</sup>

(1) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951).

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

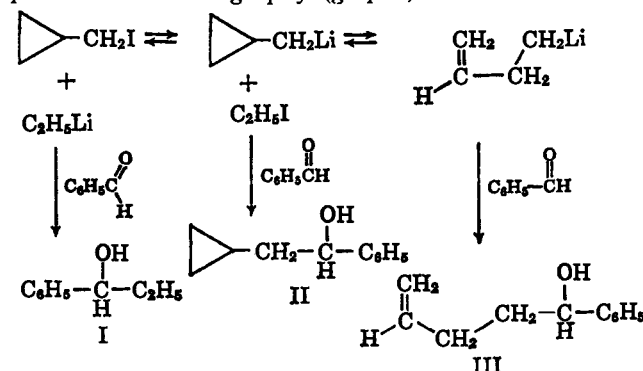
(3) P. T. Lansbury and V. A. Pattison, *ibid.*, **84**, 4295 (1962).

(4) Cf. (a) R. L. Letsinger, *ibid.*, **72**, 4842 (1950); (b) D. E. Applequist and D. F. O'Brien, *ibid.*, **85**, 743 (1963).

(5) D. Y. Curtin and W. J. Koehl, Jr., *ibid.*, **84**, 1967 (1962).

(6) H. M. Walborsky, *Rec. Chem. Progr.*, **23**, 75 (1962).

The generation of cyclopropylcarbinylithium involved the exchange reaction of ethyllithium and cyclopropylcarbinyl iodide in ether at  $-70^\circ$ ; the reaction mixture was quenched by reaction with excess benzaldehyde at  $-70^\circ$  to yield the corresponding phenylcarbinols which are known<sup>8</sup> and separable by gas-liquid partition chromatography (g.l.p.c.).



The results of several experiments are summarized in Table I.

TABLE I

No.	mmoles		T, °C.	Exchange time, min.	%		
	C <sub>2</sub> H <sub>5</sub> Li	C <sub>3</sub> H <sub>7</sub> I			I	II	III
1	1.0	1.0	-70	5	35	49	16
2	1.0	1.0	-70	30	11	51	38
3	1.0	1.0	-70	120	3	17	80
4	10.0	10.0	-70	5	54	18	10
5	10.0	10.0	-18	15	14	0	57

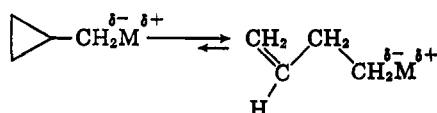
Cyclopropylcarbinyl iodide was prepared from cyclopropylcarbinyl chloride<sup>7</sup> by bimolecular displacement with sodium iodide in dry acetone. The iodide had b.p.  $88-90^\circ$  (150 mm.) and analyzed correctly (Calcd. for C<sub>4</sub>H<sub>7</sub>I: C, 26.39; H, 3.88. Found: C, 26.56; H, 3.72); its n.m.r. spectrum<sup>8</sup> showed a broad multiplet at 0.2-1.5 p.p.m. (cyclopropyl protons<sup>7</sup>) and a sharp doublet ( $J \sim 8$  c.p.s.) at 3.15 p.p.m. ( $-\text{CH}_2-\text{I}$ ). Less than 1% of cyclobutyl and allylcarbinyl iodides were present, as shown by the extremely weak signals at 4.5, 2.1 and 2.65 p.p.m. (due to cyclobutyl iodide<sup>4b</sup>) and at 5.2 p.p.m. (due to vinyl protons), even at high spectrum amplitude. In a typical experiment, such as entry 1, the iodide and benzaldehyde (2 mmoles) were placed in separate ampoules, each attached to a separate rod for breaking it, and suspended through a rubber serum cap into the ethyllithium solution (*ca.* 5 ml.) contained in a test tube. The entire assembly was cooled in a Dry Ice-acetone bath for 30 min. and the ampoule containing the iodide then was broken by pressing the rod through the serum cap. After the appropriate exchange time, the benzaldehyde was introduced similarly and the reaction mixture kept at  $-70^\circ$  for 30 min. more, then hydrolyzed and worked up in the usual manner.<sup>3</sup> The product mixtures were analyzed by g.l.p.c., on a 5-ft. 30% "Tide" on Chromosorb P column at  $135^\circ$ , using synthetic mixtures of authentic samples<sup>8</sup> for calibration. Products isolated from preparative g.l.p.c. were checked with standards by infrared spectroscopy. The carbinol yields reported in runs 1-3 are normalized to 100% but in larger scale runs (4 and 5) the actual yield of the three carbinols was 70-80% of theory.<sup>9</sup>

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

(8) Recorded on a Varian A-60 spectrometer with tetramethylsilane as internal standard and carbon tetrachloride solvent.

(9) In some of the runs small amounts (less than 10%) of benzyl alcohol also were found; this undoubtedly arises from some reduction of benzaldehyde by the organolithium reagents. In most cases, however, benzyl alcohol was not present in greater than trace quantities.

The above results provide positive evidence for the existence of cyclopropylcarbinyllithium at low temperatures but clearly reveal the facile isomerization of this species to allylcarbinyllithium. This was dramatically illustrated when rapid removal of some of an exchange mixture, which had been kept at  $-70^\circ$  for 5 min., by a hypodermic syringe already containing an uncooled ethereal solution of benzaldehyde in the barrel resulted in a ratio of III/II of *ca.* 20! This observation shows that conditions must be controlled carefully in order to get reproducible data and explains any apparent anomalies in product ratios reported above. Our experiments are in accord with the results of Roberts, *et al.*,<sup>2</sup> who showed that the cyclopropylcarbinyl Grignard reagent is an unstable intermediate in the equilibration of C<sub>1</sub>- and C<sub>2</sub>-labeled allylcarbinylmagnesium bromide at room temperature.



The present work demonstrates that cyclopropylcarbinyllithium is definitely accessible under appropriate conditions and makes this reagent available for synthetic work.

Further studies on the generation and properties of cyclopropylcarbinyllithium are underway and will be reported at a later date.

**Acknowledgment.**—We are grateful to the U. S. Army Research Office (Durham) for generous support of this work.

(10) National Aniline Research Fellow, 1962–1963.

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RECEIVED APRIL 11, 1963

### A General Synthesis of Tetraphenylcyclobutadiene-Metal Complexes by Ligand-Transfer

Sir:

Although a number of cyclobutadiene-metal complexes, particularly those of tetraphenylcyclobutadiene<sup>1–4</sup>, have now been synthesized, all the syntheses are unique for the particular compounds prepared and are not readily extended to others. We report here a synthesis of tetraphenylcyclobutadiene-metal complexes which appears to have general applicability to transition metals which form carbonyls. Thus, reaction of tetraphenylcyclobutadiene palladium bromide<sup>5</sup> (I, M = PdBr<sub>2</sub>) with iron pentacarbonyl or nickel tetracarbonyl gives tetraphenylcyclobutadiene iron tricarbonyl [I, M = Fe(CO)<sub>3</sub>] and tetraphenylcyclobutadiene nickel bromide (I, M = NiBr<sub>2</sub>), respectively. This is the first example of the conversion of one hydrocarbon-transition metal complex into another by direct ligand transfer and also of a reaction involving cyclobutadienes in which the cyclobutadiene group remains intact.

Tetraphenylcyclobutadiene palladium bromide (1.6 mmoles) and a large excess (25 mmoles) of iron penta-

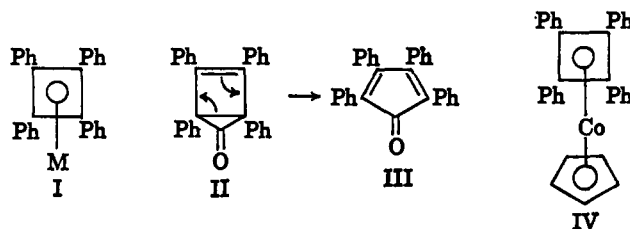
(1) R. Criegee and G. Schröder, *Ann.*, **623**, 1 (1959); R. Criegee, *Angew. Chem. Intern. Ed. English*, **1**, 519 (1962).

(2) H. H. Freedman, *J. Am. Chem. Soc.*, **83**, 2194, 2195 (1961).

(3) W. Hübel, E. H. Braye, A. Clauss, E. Weiss, U. Krueker, D. A. Brown, G. S. D. King and C. Hoogzand, *J. Inorg. Nucl. Chem.*, **9**, 205 (1959); cf. R. P. Dodge and V. Schomaker, *Nature*, **186**, 798 (1960).

(4) A. T. Blomquist and P. M. Maitlis, *J. Am. Chem. Soc.*, **84**, 2329 (1962).

(5) Synthesized by an analogous route to that for the chloride<sup>4</sup>; preliminary results, however, suggest that there is little difference in the reactivities of the different halides.



carbonyl were refluxed in xylene until evolution of carbon monoxide had nearly ceased (20 min.). Filtration from the insoluble material gave a yellow solution which yielded 88% of tetraphenylcyclobutadiene iron tricarbonyl [I, M = Fe(CO)<sub>3</sub>],<sup>3</sup> m.p. after crystallization from cyclohexane 232° (uncorr.), identical with an authentic sample<sup>6</sup> (mixture melting point and infrared spectrum).

Tetraphenylcyclobutadiene palladium bromide (1.6 mmoles) was treated with 11 mmoles of nickel carbonyl in benzene under nitrogen. Reaction began slowly at room temperature and was complete after 2.5 hr. of refluxing. Filtration gave a purple solution which yielded 17% tetraphenylcyclopentadienone (III).<sup>7</sup> Extraction of the benzene-insoluble residue with boiling chloroform gave a 47% yield of tetraphenylcyclobutadiene nickel bromide (I, M = NiBr<sub>2</sub>).<sup>8</sup>

These reactions are not unexpected since it has been shown previously that the halogens attached to palladium in tetraphenylcyclobutadiene palladium chloride (I, M = PdCl<sub>2</sub>) are not strongly bound and that thermal decomposition, for example, gave 1,4-dichloro-1,2,3,4-tetraphenylbutadiene. It has also been shown that a highly colored and paramagnetic species, probably tetraphenylcyclobutadiene, is obtained transiently in decomposition reactions of tetraphenylcyclobutadiene palladium complexes<sup>9</sup> and related systems<sup>2</sup> in solution. Since metal carbonyls are known to react with some covalently-bound halogens<sup>10</sup> the first step in the first reaction must be formation of iron tetracarbonyl bromide.<sup>11</sup> Removal of the bromine from the palladium complex causes total decomposition and releases the tetraphenylcyclobutadiene which then reacts with excess iron pentacarbonyl present by ligand displacement to give I [M = Fe(CO)<sub>3</sub>] in the usual manner for reactions of metal carbonyls and polyolefins.<sup>13</sup> The nickel reaction is more complex and the nature of the product is probably determined by the greater stability of the nickel bromide complex I (M = NiBr<sub>2</sub>) compared with that of the unknown carbonyl I [M = Ni(CO)<sub>2</sub>]. In neither of these reactions was any of the tetraphenylcyclobutadiene dimer (octaphenylcubane<sup>9</sup>) or tolan detected.

These reactions are very solvent-sensitive and only proceed in aromatic hydrocarbons; no product was obtained using saturated hydrocarbons such as cyclohexane or decalin or ethers such as diglyme. This is

(6) Kindly supplied by Dr. W. Hübel.

(7) Tetraphenylcyclopentadienone (III) is not an unreasonable product from this reaction and is probably formed by insertion of carbon monoxide into a cyclobutadiene ring *via* an intermediate (II).

(8) Identified by comparison with an authentic sample kindly supplied by Dr. H. H. Freedman; the infrared and visible spectra were identical and both samples showed a fairly sharp decomposition point (dark green to light brown) at 316° (uncorr.) in an evacuated tube. Both I [M = Fe(CO)<sub>3</sub>] and I (M = NiBr<sub>2</sub>) gave satisfactory analyses.

(9) P. M. Maitlis and F. G. A. Stone, *Proc. Chem. Soc.*, 330 (1962); H. H. Freedman and D. R. Petersen, *J. Am. Chem. Soc.*, **84**, 3837 (1962).

(10) U. S. Patent 2524833 (1950) [Chem. Abstr., **45**, 1618a (1951)]; E. Coffey, *J. Am. Chem. Soc.*, **83**, 1623 (1961); E. O. Fischer and G. Bürger, *Z. Naturforsch.*, **16b**, 77 (1961).

(11) The xylene-insoluble residue from this reaction contained palladium and a compound similar in character and infrared spectrum to that obtained by heating iron tetracarbonyl bromide<sup>12</sup> in xylene for 30 min.

(12) W. Hieber and G. Bader, *Ber.*, **81**, 1717 (1928).

(13) E. O. Fischer and H. Werner, *Angew. Chem. Intern. Ed. English*, **2**, 85 (1963).