(0.6 g, 1.1%) was filtered. The organic layer of the filtrate was separated, and the aqueous layer was extracted with methylene chloride. The solvent from the combined organic solutions was distilled, and on cooling, the residue was solidified (45.3 g, 94%). Recrystallization three times from ethanol gave 15.8 g, (33%) of *p*-nitrostilbene oxide, mp 122–124.5°. The infrared spectrum was identical with that of the authentic sample (mp 125.5–126.5°) prepared according to the procedure of Bergmann and Hervey.[5]

Reaction of *p*-Nitrobenzyl Chloride with Acetone and Sodium Hydroxide.—A solution of *p*-nitrobenzyl chloride (34.3 g, 0.20 mole) in 50 ml of acetophenone was added to a stirred suspension of powdered sodium hydroxide (8.8 g, 0.22 mole) in 50 ml of acetophenone over a period of 30 min. The mixture was stirred at 100° for 3 hr, and, upon cooling, 100 ml of water was added. After acidification, 6.2 g (23%) of 1 was filtered. Infrared analysis of the syrup remaining after removing most of the acetophenone indicated the presence of mainly 1 in addition to acetophenone.

Reaction of *p*-Nitrobenzyl Chloride with Sodium Hydroxide in Cyclohexene.—A solution of *p*-nitrobenzyl chloride (34.3 g, 0.22 mole) in 400 ml of cyclohexene was added from a steam-heated funnel over a period of 20 min to a stirred suspension of powdered sodium hydroxide (8.8 g, 0.22 mole) in 100 ml of cyclohexane. After stirring at reflux for 4 hr and subsequent cooling, 100 ml of water was added and acidified. The remaining solid was filtered and extracted with hot cyclohexene to give 11.7 g (75% yield) of *trans* 1. The infrared spectrum was identical with that of the authentic sample. The organic layer of the filtrate was separated, and the aqueous layer was extracted with 50 ml of cyclohexene. The combined organic extracts, after drying over anhydrous calcium sulfate and distillation of the solvent, gave, on cooling, 25.1 g of crystals, mp 60–65°. Two recrystallizations from benzene–heptane gave 5.0 5 (15% recovery) of *p*-nitrobenzyl chloride. The infrared spectrum was identical with that of the authentic sample except for the presence of additional maxima at 12.61 and 13.23 μ (Nujol). From the combined mother liquors was obtained an additional 9.5 g of *p*-nitrobenzyl chloride. The total recovery of *p*-nitrobenzyl chloride was 14.5 g (42%).

Registry No.—**1,** 100-44-7; **3,** 104-83-6; **4,** 2362-18-7; **5,** 100-14-1; acetone, 67-64-1; benzaldehyde, 100-52-7; formaldehyde, 50-00-0; propionaldehyde, 123-38-6; acetophenone, 98-86-2; *trans-p,p*-dinitrostilbene 2501-02-2.

Carbene and Carbenoid Chemistry. IV. The Effect of Halide Ions on Chloro- and Bromocarbenoid Addition Reactions[1]

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Received May 12, 1967

cis- and *trans*-7-chloronorcaranes were the major cyclopropyl products from the reaction of cyclohexene with methylene chloride and methyllithium prepared from methyl chloride or bromide. Small amounts of *cis*- and *trans*-7-methylnorcaranes were also produced; use of methyl bromide gave small amounts of *cis*- and *trans*-7-bromonorcaranes. In contrast, methyllithium prepared from methyl iodide or from methyl chloride with lithium iodide added gave primarily the methylnorcaranes with smaller amounts of norcarane and the chloronorcaranes. 2,3-Dimethyl-2-butene gave 3-chloro-1,1,2,2-tetramethylcyclopropane and pentamethylcyclopropane on reaction with methylene chloride and methyllithium prepared from methyl iodide. The reaction of cyclohexene with methylene bromide and methyllithium prepared from either methyl bromide or iodide gave norcarane as the principal cyclopropyl product, accompanied by lesser amounts of the 7-bromo derivatives. The corresponding reaction with bromoform gave primarily 7,7-dibromonorcarane with smaller amounts of the 7-bromo derivatives. Methylene iodide was formed from the reaction of methylene bromide and methyllithium prepared from methyl iodide, but added lithium iodide was necessary for the formation of methylene iodide from methylene chloride and methyllithium. Probable reaction pathways are discussed to account for the above observations.

The reaction of methylene chloride with an alkyllithium in the presence of an olefin usually gives a chlorocyclopropane,[2] presumably *via* an intermediate carbenoid species.[2a,c,3] Recently several reports have appeared describing anomalies which result when this reaction is carried out with methyllithium prepared from methyl iodide. We reported earlier that the reaction of styrene, methylene chloride, and *n*-butyllithium prepared from *n*-butyl bromide gave the expected *cis*- and *trans*-1-chloro-2-phenylcyclopropanes.[4] However when the reaction was repeated with methyllithium which was prepared from methyl iodide, phenylcyclopropane and *cis*-1-methyl-2-phenylcyclopropane[5–7] were obtained, but no trace of the chlorophenylcyclopropanes was found.[4] Similarly, the reaction of cyclooctatetraene, methylene chloride, and methyl-

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[1] (a) Part III: W. L. Dilling and F. Y. Edamura, *Chem. Commun.*, 183 (1967). (b) Part II: W. L. Dilling and F. Y. Edamura, *Tetrahedron Letters*, 587 (1967). Preliminary accounts of this work have been reported in parts II and III.

[2] (a) J. Hine, "Divalent Carbon," The Ronald Press, New York, N. Y., 1964, pp 73–77; (b) W. Kirmse, *Progr. Org. Chem.*, **6**, 171 (1964); (c) W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, pp 188–193.

[3] (a) G. L. Closs and J. J. Coyle, *J. Am. Chem. Soc.*, **84**, 4350 (1962); (b) *ibid.*, **87**, 4270 (1965); (c) H. Heaney, *Organometal. Chem. Rev.*, **1**, 27 (1966); (d) G. Köbrich, *Angew. Chem. Intern. Ed. Engl.*, **6**, 41 (1967).

[4] W. L. Dilling, *J. Org. Chem.*, **29**, 960 (1964).

[5] In our original paper[4] the stereochemistry of the 1-methyl-2-phenylcyclopropane was not specified. Analysis of the nmr spectrum of this compound strongly suggests that it is the *cis* isomer.[6] The position of the methyl resonance (−0.82 ppm) is in good agreement with the data published for methyl groups *cis* to phenyl rings.[7] For example the *cis* (to phenyl) methyl resonance of 1,1-dimethyl-2-phenylcyclopropane occurs at −0.77 ppm while the *trans* methyl occurs at −1.20 ppm.[7] The singlet character of the phenyl resonance[4] is also in accord with the *cis* stereochemistry.[7] The phenyl resonance for *cis*-1-chloro-2-phenylcyclopropane is also a singlet while the *trans* isomer is a multiplet.[4] Finally the benzylic proton resonance supports the *cis* assignment; primary coupling constants of *ca.* 6.1, 8.5, and 8.5 cps.[4] The fact that none of the coupling constants is in the 3–5-cps range lends support to the proposal that this isomer is the *cis* isomer. One would expect the coupling constant between the benzylic proton and the proton on the methyl-bearing carbon to be in the 3–5-cps range for the *trans* isomer. From the published spectra[4] of the benzylic protons of the *cis*- and *trans*-1-chloro-2-phenylcyclopropanes it can be seen that the *cis* isomer has coupling constants of 7.7, 7.7, and 9.1 cps while the *trans* isomer has coupling constants of 3.3, 7.6, and 8.9 cps. The coupling constants involved in the benzylic proton of the methylphenylcyclopropane are closer in magnitude to those of the *cis*-chlorophenylcyclopropane than to the *trans* isomer. Apparently the coupling constant of the benzylic proton to the *trans* methylene proton in both of the chlorophenylcyclopropanes and the phenylmethylcyclopropane is larger than usual (in the range of 6.1–9.1 cps).

[6] See R. A. Moss, *J. Org. Chem.*, **30**, 3261 (1965).

[7] G. L. Closs and R. A. Moss, *J. Am. Chem. Soc.*, **86**, 4042 (1964).

Table I

Yields of Norcarane Derivatives and Methylene Iodide from Cyclohexene, Methylene Chloride, and Methyllithium[a]

Source of CH_3Li	1 *cis*-Cl	2 *trans*-Cl	3 *cis*-CH_3	4 *trans*-CH_3	5 *cis*-Br	6 *trans*-Br	7 H	CH_2I_2	Total yield
$CH_3Cl + Li$	28	13	1	1	. . .	. . .	. . .	. . .	42
$CH_3Br + Li$	26	12	3	2	1	1	. . .	. . .	44
$CH_3I + Li$	3–4	1–2	19	11–12	. . .	. . .	1	. . .	36
$CH_3Cl + Li$ (LiI added)[b]	4	2	8	5	. . .	. . .	1	15	35

[a] Yields (nearest per cent) of norcarane derivatives based on methyllithium assuming the reaction sequence shown in Scheme I; yield of methylene iodide based on lithium iodide. These data are slightly revised from those given in ref 1a. [b] One mole of lithium iodide per mole of methyllithium.

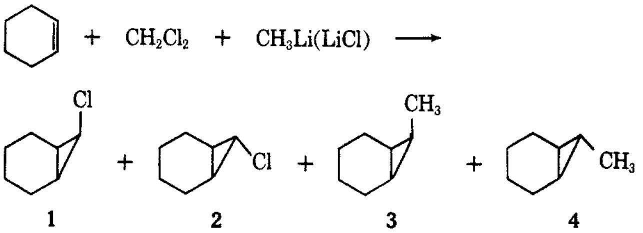
lithium prepared from methyl iodide gave *cis*-9-methylbicyclo[6.1.0]nonatriene as the only isolable product, whereas, when commercial methyllithium (prepared from methyl bromide) was employed, the product consisted of a mixture of *cis*- and *trans*-9-chlorobicyclo-[6.1.0]nonatrienes accompanied by small amounts of the 9-methyl derivative.[8] Three other related reactions in which the products depended on the presence of iodide ion in the methyllithium were the reaction with 7,7-dibromonorcarane,[9] and the formation of cyclopropane derivatives from benzal chloride[10] or dichloromethyl alkyl ethers[11] and olefins.

Bromocarbene (or bromocarbenoid) has not been studied as extensively as has the chloro analog.[2c] The bromo derivative has been postulated as an intermediate in the reaction of methylene bromide and potassium *t*-butoxide[12] and in the reaction of bromoform with metallic lithium.[13] Recently Closs and Coyle reported the preparation of free bromocarbene from thermolysis and photolysis of bromodiazomethane.[3b] The reaction of methyllithium (source unspecified) and methylene bromide evidently does not give bromocarbenoid but rather bromomethyllithium (carbenoid) by metal–halogen exchange;[14] in the presence of cyclohexene, norcarane was obtained.[15] Earlier we reported an analogous reaction in which phenylcyclopropane was obtained as the only isolable cyclopropyl derivative from styrene, methylene bromide, and methyllithium prepared from methyl iodide.[4]

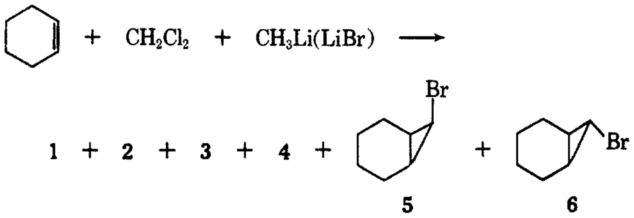
This paper presents our findings on the effect of halide ions (especially iodide) on some addition reactions of chloro- and bromocarbenoids, and the course of the reactions of methylene bromide and bromoform with methyllithium and cyclohexene.

Results

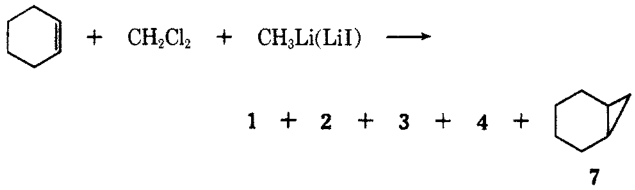
The reaction of cyclohexene, methylene chloride, and methyllithium, prepared from methyl chloride and lithium, in ether at 5–15° gave a 42% yield of norcarane derivatives consisting mainly of *cis*- (1) and *trans*-7-chloronorcarane (2) with minor amounts of *cis*- (3) and *trans*-7-methylnorcarane (4) (Table I) [$CH_3Li(LiCl)$ in the equation designates methyllithium generated from methyl chloride and lithium, not an equimolar complex of CH_3Li and LiCl].[16] The



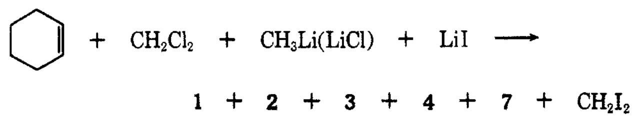
analogous reaction using methyl bromide as the methyllithium precursor gave similar results except for the production of small amounts of *cis*- (5) and *trans*-7-bromonorcaranes (6) (Table I). However with meth-



yllithium prepared from methyl iodide the distribution of the chloronorcaranes (1 and 2) and methylnorcaranes (3 and 4) was reversed and a small amount of norcarane (7) was formed (Table I). When meth-



yllithium, generated from methyl chloride, with added anhydrous lithium iodide, was used, the major volatile product was methylene iodide, with the methylnorcaranes (3 and 4) being obtained in slightly lower yields (Table I). By contrast no trace (<0.5%) of



methylene iodide was present in the reaction mentioned above using methyllithium prepared from methyl iodide. In separate control experiments,

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(8) T. J. Katz and P. J. Garratt, *J. Am. Chem. Soc.*, **86**, 4876 (1964).

(9) E. T. Marquis and P. D. Gardner, *Chem. Commun.*, 726 (1966).

(10) G. L. Closs and J. J. Coyle, *J. Org. Chem.*, **31**, 2759 (1966).

(11) U. Schöllkopf and J. Paust, *Angew. Chem. Intern. Ed. Engl.*, **2**, 397 (1963); *Chem. Ber.*, **98**, 2221 (1965).

(12) M. E. Volpin, D. N. Kursanov, and V. G. Dulova, *Tetrahedron*, **8**, 33 (1960).

(13) O. M. Nefedov, A. A. Ivashenko, M. N. Manakov, V. I. Shiryaev, and A. D. Petrov, *Izv. Akad. Nauk SSSR., Otd. Khim. Nauk*, 367 (1962); *Chem. Abstr.*, **57**, 11041 (1962).

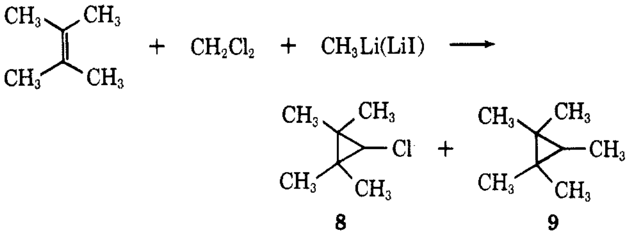
(14) W. Kirmse and B. v. Wedel, *Ann.*, **666**, 1 (1963).

(15) W. T. Miller, Jr., and C. S. Y. Kim, *J. Am. Chem. Soc.*, **81**, 5008 (1959).

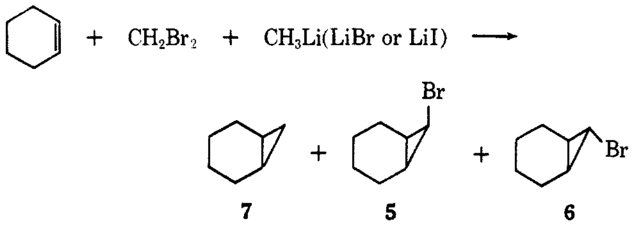
(16) See (a) K. Ziegler, K. Nagel, and M. Patheiger, *Z. Anorg. Allgem. Chem.*, **282**, 345 (1955); (b) T. V. Talalaeva, A. N. Rodionov, and K. A. Kocheshkov, *Dokl. Akad. Nauk SSSR*, **140**, 847 (1961) (Engl. trans. p 985); *Chem. Abstr.* **56**, 5989 (1962).

methylene iodide in 10% yield was obtained from the reaction of methylene chloride, methyllithium prepared from methyl chloride, and lithium iodide. However no trace (<0.5%) of methylene iodide was obtained from the reaction of methylene chloride and lithium iodide in the absence of methyllithium, nor from the reaction of methylene chloride and methyllithium prepared from methyl iodide (<0.1%).

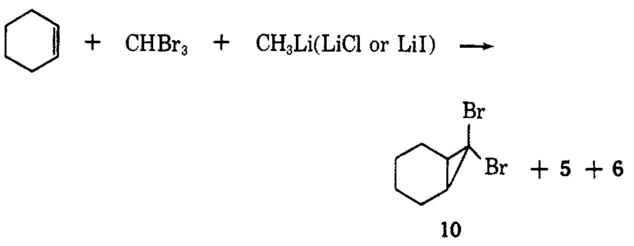
The reaction of methylene chloride and methyllithium prepared from methyl iodide, in the presence of 2,3-dimethyl-2-butene, gave 3-chloro-1,1,2,2-tetramethylcyclopropane (**8**) and pentamethylcyclopropane (**9**) (14% total yield) in a ratio of 3:2 respectively. The reaction mixture also contained small amounts of several iodinated species including chloroiodomethane, but no trace of 1,1,2,2-tetramethylcyclopropane or methylene iodide was evident. Chloro (**8**) (67% yield) was the only product reported when *n*-butyllithium prepared from the chloride was used.[17]



The reaction of cyclohexene with methylene bromide and ethereal methyllithium prepared from methyl bromide gave a 5% yield (based on methyllithium) of norcarane derivatives which consisted of norcarane (**7**) (75–93%), *cis*- (**5**) (4–14%) and *trans*- (**6**) (3–11%) bromonorcarane. In contrast to the reaction of methylene chloride described above the reaction of cyclohexene with methylene bromide and methyllithium prepared from methyl iodide gave a similar yield and distribution of the norcaranes (**5**–**7**). Also, methylene iodide was found in the latter reaction. In separate control experiments, methylene iodide was shown to result from the reaction of methylene bromide, methyllithium prepared from methyl chloride, and lithium iodide, but not from the reaction of methylene bromide and lithium iodide in the absence of methyllithium. No deuterium incorporation (<2%) was observed in the norcarane (**7**) obtained when the reaction of cyclohexene, methylene bromide, and methyllithium prepared from methyl bromide was carried out with deuterium oxide work-up. The recovered methylene bromide also showed no trace of deuterium incorporation (<1%).



The reaction of cyclohexene with bromoform and methyllithium prepared from methyl chloride or iodide gave an *ca.* 8% yield of norcarane products consisting of 7,7-dibromonorcarane (**10**) (86–91%) and the monobromo derivatives (**5**) (7–9%) and (**6**) (2–5%).

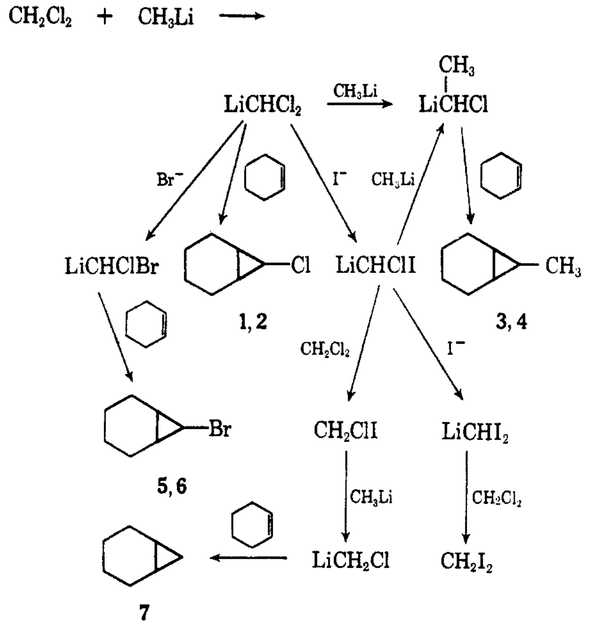


All of the products of the above reactions except *cis*-7-methylnorcarane (**3**) and pentamethylcyclopropane (**9**) have been characterized in the literature. Identifications were made by comparing spectral properties of samples collected by preparative gas chromatography (gc) with data from the literature. Mass spectral analyses corroborated the assigned structures. The two unreported cyclopropanes (**3** and **9**) gave infrared, nuclear magnetic resonance (nmr), and mass spectra which were consistent with the assigned structures (see Experimental Section). The *cis*-methyl derivative (**3**) exhibited spectra which were only slightly different from those of the known *trans* isomer (**4**) an observation which suggested that this compound had a similar structure and differed only in the stereochemistry at the 7 position. The assignment of the *cis* configuration for this compound is supported by its higher boiling point, longer gc retention time, and higher refractive index (von Auwers-Skita rule).[18]

Discussion

Scheme I illustrates a number of possible reaction pathways to account for the observed products from the reaction of methylene chloride and methyllithium in the presence of cyclohexene. The reactions are depicted as proceeding through α-haloorganolithium intermediates, although the concept of carbene–lith-

SCHEME I



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(17) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **82**, 5723 (1960).

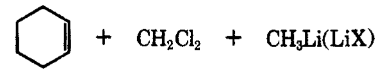
(18) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 216.

ium halide complexes could also be advanced. The initial step is the formation of dichloromethyllithium (chlorocarbenoid). Dichloromethyllithium has been prepared in solution at low temperature and trapped with benzophenone and mercuric chloride.[19] In the absence of iodide ion (*i.e.*, with methyllithium prepared from methyl chloride or bromide), the major portion of the dichloromethyllithium reacts with cyclohexene to give the chloro derivatives (**1** and **2**). However a small amount of the intermediate must also react with methyllithium to account for the methyl derivatives (**3** and **4**) formed.[20] In the presence of bromide ion a small portion of the intermediate is converted to bromochloromethyllithium (bromocarbenoid) which leads to the bromo derivatives (**5** and **6**). The formation of bromocyclopropanes in a similar reaction has been reported previously.[21]

In the presence of iodide ion, which is a good nucleophile, most of the intermediate reacts to give chloroiodomethyllithium. Evidence for this step has been found by Closs and co-workers who obtained chloroiodomethane (12% yield) when the reaction of methylene chloride and methyllithium, prepared from methyl iodide, was carried out at −70° in tetrahydrofuran and then quenched with water.[22] We also observed the formation of small amounts of chloroiodomethane in an experiment involving methyllithium prepared from methyl iodide. Reaction of chloroiodomethyllithium with another mole of methyllithium would give α-chloroethyllithium (methylcarbenoid) which could give the relatively large amount of the methyl derivatives (**3** and **4**). A possible alternate source of the methylnorcaranes (**3** and **4**) *via* reaction of the chloro derivatives (**1** and **2**) with methyllithium has been ruled out by Magid and Welch who showed that **1** and **2** were inert to the action of methyllithium.[23a] Similarly Nefedov and co-workers[20e] showed that 7-chloronorcarane is essentially unaffected by treatment with phenyllithium, and Katz and Garratt[8] were unable to obtain any 9-methylbicyclo[6.1.0]nonatriene by treatment of the corresponding 9-chloro compound with methyllithium. However, Magid and Welch have isolated small amounts of *cis*- and *trans*-7-iodonorcaranes from the reaction under consideration.[23a] They showed that the *cis*-iodo compound gave the *cis*-methyl derivative (**3**) and norcarane (**7**) on treatment with methyllithium, while the *trans*-iodo compound gave the *trans*-methyl derivative (**4**) and norcarane (**7**) under the same conditions.[23a] These workers also showed that treatment of the chloronorcaranes (**1** and **2**) with anhydrous lithium iodide in ether did not yield the iodo compounds. We did not detect any iodonorcaranes under our reaction and analytical conditions, possibly owing to the thermal instability of the iodo compounds.[23b] The iodonorcaranes would be logical products of the interception of either chloroiodomethyllithium or diiodomethyllithium (Scheme I) by cyclohexene. Since some of the methyl compounds (**3** and **4**) are formed in the reactions of methyllithium prepared from methyl chloride or methyl bromide and since iodide ion is a better leaving group than chloride or bromide ion, it seems reasonable that some of the methyl derivatives (**3** and **4**) would be formed *via* the route shown in Scheme I. Possibly both routes are operative.

The data in Table II show the dramatic effect of the halide ion on the methylcyclopropyl–chlorocyclopropyl product ratios. Closs and Coyle[10] have shown a similar effect in the analogous reactions of benzal chloride.

TABLE II
DEPENDENCE OF METHYLNORCARANES (**3** AND **4**) TO CHLORONORCARANE (**1** AND **2**) RATIO ON SOURCE OF METHYLLITHIUM[a]



Source of CH_3Li	(**3** + **4**):(**1** + **2**)
CH_3Cl + Li	0.02
CH_3Br + Li	0.05
CH_3I + Li	2.8–3.5
CH_3Cl + Li (LiI added)	1.0

[a] These ratios (molar ratios, not yield ratios) could be determined more accurately than the absolute yields shown in Table I.

The relative amounts of the chloro derivatives (**1** and **2**) and the methyl derivatives (**3** and **4**) obtained with different olefins (Table III) are in accord with the competition of iodide ion and the olefin for the dichloromethyllithium. The relative amount of the chlorocyclopropanes with respect to the methylcyclopropanes increases as the nucleophilicity of the olefin increases.[24,25] Thus the more nucleophilic olefins compete more effectively with iodide ion for the dichloromethyllithium than do the less nucleophilic olefins.

TABLE III
RELATIVE DISTRIBUTION OF CYCLOPROPANE DERIVATIVES FROM VARIOUS OLEFINS[a]

Olefin	":CHCl" addn products	":CHCH$_3$" addn products	":CH$_2$" addn product
Styrene[b]	0[c]	1.0	0.5
Cyclohexene	0.3–0.4	1.0	0.03
2,3-Dimethyl-2-butene	1.5	1.0	0[c]

[a] Methyllithium prepared from methyl iodide and lithium. [b] Data from ref 4. [c] None detectable by gc analysis.

The slightly increased amount of the methyl derivatives from methyl bromide compared with methyl chloride indicates a higher reactivity of bromochloromethyllithium than dichloromethyllithium toward methyllithium (not shown in Scheme I).

The anion-displacement reactions on the haloalkyl-

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(19) (a) G. Köbrich, K. Flory, and W. Drischel, *Angew. Chem. Intern. Ed. Engl.*, **3**, 513 (1964); (b) G. Köbrich, H. Trapp, K. Flory, and W. Drischel, *Chem. Ber.*, **99**, 689 (1966); (c) G. Köbrich and H. R. Merkle, *ibid.*, **99**, 1782 (1966).

(20) For analogies to this step, see (a) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **81**, 4996 (1959); (b) G. L. Closs and L. E. Closs, *Tetrahedron Letters*, No. 10, 38 (1960); (c) W. Kirmse and B.-G. v. Bülow, *Chem. Ber.*, **96**, 3316, 3323 (1963); (d) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **85**, 99 (1963); (e) O. M. Nefedov, V. I. Shiryaev, and A. S. Khachaturov, *J. Gen. Chem. USSR*, **35**, 509 (1965).

(21) C. W. Jefford and R. Medary, *Tetrahedron Letters*, 2069, 2792, 6317 (1966).

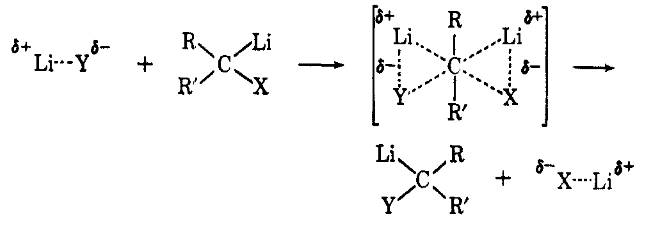
(22) We wish to thank Professor G. L. Closs for this information.

(23) (a) R. M. Magid and J. G. Welch, *Chem. Commun.*, 518 (1967). We wish to thank Professor Magid for a preprint of this paper. (b) R. M. Magid and J. G. Welch, private communication.

(24) See E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart, and Winston, Inc., New York, N. Y., 1959, pp 534–535.

(25) For discussions and data on the electrophilicity of haloalkyllithium reagents, see (a) G. L. Closs and G. M. Schwartz, *J. Am. Chem. Soc.*, **82**, 5729 (1960); (b) W. T. Miller, Jr., and D. M. Whalen, *ibid.*, **86**, 2089 (1964); (c) D. F. Hoeg, D. I. Lusk, and A. L. Crumbliss, *ibid.*, **87**, 4147 (1965); (d) G. Köbrich, K. Flory, and R. H. Fischer, *Chem. Ber.*, **99**, 1793 (1966).

lithiums are probably quite complicated since the lithium reagents are undoubtedly aggregated in ether solution. By analogy with the proposed mechanism for the reaction of olefins with α-haloalkyl metal compounds,[25c,26] these displacements could be looked upon as partial dissociation of the lithium halide from the carbene in the transition state, thus rendering the carbon more electrophilic.

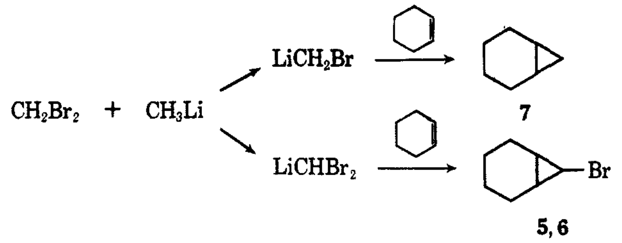


One possible route to the small amount of norcarane (**7**) found is shown in Scheme I. Halogen–metal exchange on chloroiodomethane would give chloromethyllithium (carbenoid) which would be expected to give norcarane (**7**). The reason for the decrease in the amount of ":CH_2" addition product (Table III) with respect to the methylcyclopropyl product as the olefin nucleophilicity increases is not immediately apparent. The alternate route to norcarane (**7**) of halogen-metal exchange on 7-iodonorcarane followed by metalation or "hydrolysis" has been noted above.[23]

The formation of methylene iodide necessarily involves two iodide ions (Scheme I) while the formation of the methylcyclopropanes (**3** and **4**) and norcarane (**7**) requires only one. In order to rationalize the formation of methylene iodide in the presence of methyllithium, prepared from methyl chloride and lithium, with added lithium iodide (Table I), and its absence in the presence of methyllithium prepared from methyl iodide and lithium, we suggest that the methyllithium reagents are different in the two reactions. Talalaeva and co-workers[16b] isolated a 1:1 complex of methyllithium and lithium iodide ($CH_3Li{\cdot}LiI{\cdot}2Et_2O$) from the reaction of methyl iodide and lithium in ether. This material was tetrameric in ether solution ($(CH_3Li{\cdot}LiI)_2$).[27] When an excess of lithium iodide was added to a solution of methyllithium (known to contain only 2–10 mole % lithium chloride),[16] prepared from methyl chloride and lithium only $LiI{\cdot}2Et_2O$ was isolated; no $CH_3Li{\cdot}LiI{\cdot}2Et_2O$ was found. However one should note that these conditions are not exactly comparable since an excess of lithium iodide was used instead of 1 molar equiv. If one assumes that all of the lithium iodide is tied up as a 1:1 complex (or 2:2) with methyllithium when generated from methyl iodide, the absence of methylene iodide is explainable since for each molecule of methyllithium which reacts with methylene chloride, only one iodide ion is available for displacement of chloride (Scheme I). In the presence of added lithium iodide, "free" iodide is present and can carry out the second displacement of chloride ion leading to methylene iodide. The yield of methylene iodide in the fourth entry of Table I approximately accounts for the difference in yields of the methylnorcaranes (**3** and **4**) in the third and fourth entries. This reasoning is only a partial explanation for these results, and more experimental work will be required to achieve a complete picture of these reactions.[28]

The reactions shown in Scheme II are consistent with the observed cyclopropyl products in the reaction of methylene bromide with methyllithium. Halogen–metal exchange on methylene bromide would lead to norcarane (**7**) (*via* $LiCH_2Br$), whereas proton removal (metalation) would lead to the isomeric 7-bromonorcaranes (**5** and **6**). An alternate route to norcarane by metal–halogen exchange of **5** or **6** followed by "hydrolysis" is theoretically possible since some cyclopropyl bromides are known to undergo metal–halogen exchange with alkyllithiums.[29] However this route is very unlikely in this case since deuterium oxide work-up gave no deuterated norcarane. Although slow "hydrolysis" of 7-lithionorcarane by methylene bromide or by ether, before deuterium oxide work-up, could account for nonquantitative deuteration,[29] the complete lack of deuterium incorporation suggests that this is not a significant route to norcarane under our reaction conditions.[30]

SCHEME II



The predominance of norcarane (**7**) over the monobromonorcaranes (**5** and **6**) might suggest that more methylene bromide reacts by halogen–metal exchange than by metalation, but the relatively large amount of methylene iodide formed in the presence of iodide ion indicates that a significant portion of methylene bromide must be reacting by metalation (since methylene iodide cannot be formed by halogen–metal exchange, and direct iodide displacement on methylene bromide has been ruled out). The presence of iodide ion in the methyllithium appears to have little effect on the methylene bromide reactions leading to cyclopropyl derivatives, except to cause methylene iodide formation.

An interesting observation is that methylene iodide is formed from methylene bromide and methyllithium prepared from methyl iodide, whereas the analogous reaction of methylene chloride and methyllithium requires externally added lithium iodide. It is possible that a mechanism, similar to that proposed above for the reaction of methylene chloride, is also operative in the case of methylene bromide. In this case it is necessary to postulate that the displacement of both bromines in $LiCHBr_2$ (to form LiCHBrI and then

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(26) (a) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959); (b) H. E. Simmons, E. P. Blanchard, and R. D. Smith, *ibid.*, **86**, 1347 (1964).

(27) T. V. Talalaeva, A. N. Rodionov, and K. A. Kocheshkov, *Dokl. Akad. Nauk SSSR*, **154**, 174 (1964) (Engl. trans. p 47); *Chem. Abstr.*, **60**, 11425 (1964).

(28) See, *e.g.*, L. M. Seitz and T. L. Brown, *J. Am. Chem. Soc.*, **88**, 2174 (1966).

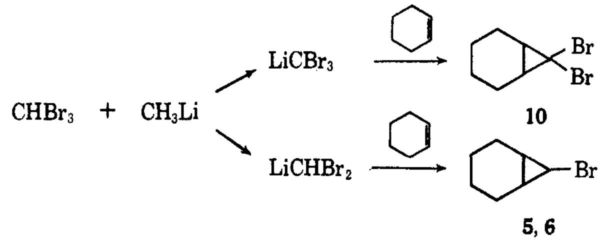
(29) (a) H. M. Walborsky, *Record Chem. Progr.*, **23**, 75 (1962); (b) H. M. Walborsky, F. J. Impastato, and A. E. Young, *J. Am. Chem. Soc.*, **86**, 3283 (1964).

(30) H. M. Walborsky, private communication.

$LiCHI_2$) is possible with methyllithium prepared from methyl iodide. Further work is necessary in order to obtain a clearer understanding of this difference in the reactivity of methylene bromide compared to methylene chloride.

The formation of 7,7-dibromonorcarane from the reaction of bromoform with methyllithium in the presence of cyclohexene indicates that $LiCBr_3$ is being formed by metalation (Scheme III). The isolation of small amounts of the bromonorcaranes (**5** and **6**) suggests that some of the bromoform also reacts by halogen–metal exchange to give $LiCHBr_2$ as an intermediate. Although *gem*-dibromocyclopropanes are known to react with methyllithium,[31] the products are usually not the monobromocyclopropanes, and furthermore this reaction is not likely to be significant in the presence of a large excess of bromoform. The increased acidity of the proton in bromoform accounts for the greater tendency of this compound to undergo metalation as compared to methylene bromide. Since essentially the same results were obtained in the reaction of bromoform with methyllithium prepared from either methyl chloride or iodide, it appears that the presence of iodide ion does not affect the course of these reactions.

SCHEME III



In general all of the carbenoid addition reactions studied (":CHCl," ":CHBr," and ":$CHCH_3$") show a preference for *cis* addition although the ratio is not constant for any given carbenoid generated from different sources (Table IV). Closs and Closs[17] reported a variation in the *cis*:*trans* ratio in the 1-chloro-2-propylcyclopropanes obtained from 1-pentene and chlorocarbenoid: 3.4 with butyllithium at −40 to −35°, 1.8 with methyllithium at 30°. Our data are in general agreement with previous findings that the *cis* isomer usually predominates.[6,17,32]

TABLE IV

cis:*trans* RATIOS IN THE ADDITION OF CARBENOIDS TO CYCLOHEXENE[a]

Carbenoid source		*cis*-Cl (**1**): *trans*-Cl (**2**)	*cis*-Br (**5**): *trans*-Br (**6**)	*cis*-CH_3 (**3**): *trans*-CH_3 (**4**)
$CH_2Cl_2 + CH_3Li$	(CH_3Cl + Li)	2.1[b]	...	~1.0
	(CH_3Br + Li)	2.2	~1.1	~1.7
	(CH_3I + Li)	2.0–2.3	...	1.6–1.8
	(CH_3Cl + Li) + LiI	2.5	...	~1.8
$CH_2Br_2 + CH_3Li$	(CH_3Br + Li)	...	1.2–1.4	...
$CHBr_3 + CH_3Li$	(CH_3Cl + Li)	...	2.0	...
	(CH_3I + Li)	...	~2.9	...

[a] Data could be determined more accurately than that shown in Table I. [b] Closs and Closs[17] reported a ratio of 3.2 using *n*-butyllithium at −40 to −35°.

The low yields of the cyclopropyl products observed in the above reactions are probably due to side reactions of the highly reactive α-haloalkyllithiums and possibly other reactions between the polyhalomethanes and methyllithium, such as alkylation. We have not examined these side reactions in the present study except for the formation of methylene iodide. We did observe a number of components which had shorter gas chromatographic retention times than the cyclopropanes. Most of these components were also formed in control experiments in the absence of the olefins. In an earlier paper we reported the formation of a large number of alkanes, alkenes, and alkyl halides from the reactions of methylene chloride and bromide with methyllithium under similar reaction conditions.[4]

Experimental Section

General Techniques.—Elemental microanalyses were determined by Mr. L. E. Swim and co-workers. Infrared spectra were recorded by Mr. F. L. Beman and co-workers with a Perkin-Elmer Model 337 double-grating spectrometer. Nmr spectra were obtained in carbon tetrachloride solution by Mr. Beman and co-workers with a Varian A-60 spectrometer. Chemical shifts are reported as δ in parts per million from tetramethylsilane, which was used as an internal standard. Coupling constants are reported in cycles per second. Mass spectral analyses were performed by Mrs. W. L. Dilling and co-workers with a magnetically scanning 90° sector spectrometer using an electron ionizing voltage of 75 ev. High-resolution mass spectra were obtained by Dr. L. A. Shadoff with a Consolidated Electrodynamics Corp. Model 21-110B spectrometer. Gc analyses were determined with a F & M Model 500 instrument equipped with 0.25 in. × 20 ft columns containing 20% 410 gum rubber on 60–80 mesh Chromosorb P (column A) or 20% Apiezon L on 60–80 mesh Chromosorb W (column B). Helium flow rates were *ca.* 50 ml/min. The relative peak areas were nearly equal to mole per cent for a number of hydrocarbons and halogenated hydrocarbons (toluene, tetrachloroethylene, chlorobenzene, *o*-dichlorobenzene, and bromoform). Yield data were obtained by gas chromatography using one of the above compounds as an internal standard. All glassware was dried in an oven at 125–130° for several hours. In addition, reaction flasks were flame dried in a stream of helium before use. Transfers were made with dried syringes. All reactions were carried out under a static helium atmosphere. Anhydrous ether (Mallinckrodt analytical reagent) and methylene chloride (Fisher certified reagent) were used without further treatment. Methylene bromide, bromoform, cyclohexene (Matheson Coleman and Bell), and 2,3-dimethyl-2-butene (Columbia Organic Chemicals) were freshly distilled before use.

Reaction of Cyclohexene with Methylene Chloride and Methyllithium Prepared from Methyl Bromide.—A solution of methyllithium in ether was prepared by passing excess methyl bromide into a rapidly stirred mixture of anhydrous ether (350 ml) and lithium metal (5 g). Acid titration of an aliquot, after hydrolysis, indicated a methyllithium concentration of 0.98 *M*. This methyllithium solution (40 ml, 0.04 mole) was added dropwise to a stirred solution of cyclohexene (9.9 g, 0.12 mole) and methylene chloride (6.8 g, 0.08 mole) at 5–15°. An additional 15 ml of anhydrous ether was then added. The reaction mixture was stirred for an additional 2 hr at room temperature, then water (*ca.* 30 ml) was added. The aqueous layer was separated and extracted with methylene chloride. The combined organic portions were washed with water, dried (Drierite), and concentrated to a volume of *ca.* 12 ml. Gc analysis (A, 125°) indicated a 44% yield (based on methyllithium) of products listed in Table I. The isomeric 7-chloronorcaranes (**1** and **2**) were isolated by preparative gc: *cis*-(**1**), ν_{max}^{neat} 2940, 2860, 1450, 1290, 728, 690, and 646 cm^{-1}; *trans*-(**2**)

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(31) (a) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960); (b) W. R. Moore and H. R. Ward, *Chem. Ind.* (London), 594 (1961); (c) E. T. Marquis and P. D. Gardner, *Tetrahedron Letters*, 2793 (1966); (d) L. Vo-Quang, and Y. Vo-Quang, *Compt. Rend.*, **263**, 640 (1966).

(32) G. L. Closs, R. A. Moss, and J. J. Coyle, *J. Am. Chem. Soc.*, **84**, 4985 (1962).

$\nu_{\max}^{\text{neat}}$ 2935, 2865, 1455, 1250, 1016, and 740 cm^{-1}. The nmr data for **1** and **2** were in agreement with those reported in the literature.[17,32,33] The mass spectra of the two isomers were quite similar; they showed molecular ions at *m/e* 130, and the ratio of the chlorine isotopes showed the presence of one chlorine atom.

Reaction of Cyclohexene with Methylene Chloride and Methyllithium Prepared from Methyl Chloride.—The preceding experiment was repeated with commercial methyllithium in ether (Foote Mineral Co., prepared from methyl chloride, 1.7 *M*). Gas chromatographic analysis (A, 125°; B, 175°) gave the results shown in Table I. No trace (<0.1%) of norcarane (**7**) was detected.

Reaction of Cyclohexene with Methylene Chloride and Methyllithium Prepared from Methyl Iodide.—A solution of methyllithium in ether (1.05 *M*) was prepared from lithium (7.7 g) and methyl iodide (71 g) in 250 ml of anhydrous ether, according to the procedure of Gilman, Zoellner, and Selby.[34] The preceding experiment was repeated with this methyllithium solution (40 ml, 0.04 mole). The product distribution is given in Table I. No trace (<0.5% yield, based on methyllithium) of methylene iodide was detected.

The reaction was repeated on a larger scale (0.5 mole of methyllithium, 1.5 moles of cyclohexene, and 1.0 mole of methylene chloride). The product distribution was essentially the same as in the smaller run. Preparative gc (B, 150°) of appropriate distillation fractions gave samples of norcarane (**7**) and the 7-methylnorcaranes (**3** and **4**). The first component eluted was identified as norcarane (**7**). The mass spectrum exhibited a molecular ion (*m/e* 96) and a cracking pattern consistent with the proposed structure. The infrared and nmr spectra were in agreement with the spectra reported in the literature.[35]

The second component eluted was identified as *trans*-7-methylnorcarane (**4**): $n^{24.5}_{\mathrm{D}}$ 1.4503, lit.[36] n^{26}_{D} 1.4496; $\nu_{\max}^{\text{neat}}$ 3010, 2930, 2860, 1470, 1460, 1390, 1078, 960, 940, and 765 cm^{-1}. The infrared and nmr spectral data agreed with those reported by LaLonde and Tobias.[36] The mass spectrum was consistent with the proposed structure.

Anal. Calcd for C_8H_{14}: C, 87.19; H, 12.81; mol wt, 110. Found: C, 87.4; H, 12.6; mol wt, 110 (mass spectrometry).

The final component collected was identified as *cis*-7-methylnorcarane (**3**): $n^{24.5}_{\mathrm{D}}$ 1.4640, $\nu_{\max}^{\text{neat}}$ 3015, 2935, 2860, 1475, 1455, 750, and 720 cm^{-1}; nmr spectrum unsymmetrical methyl doublet centered at −0.95 ppm (J = 4.2 cps) superimposed on a broad multiplet at −2.0 to −0.3 ppm with major peaks at −1.24 and −0.77 ppm. The mass spectrum was very similar to that of the *trans* isomer (**4**), showing a base peak at *m/e* 81 ($C_6H_9^+$).

Anal. Calcd for C_8H_{14}: C, 87.19; H, 12.81; mol wt, 110. Found: C, 87.1, 87.3; H, 12.8, 12.6; mol wt, 110 (mass spectrometry).

Marquis and Gardner[31c] have recently reported (without giving details) that the methyl resonance for the *trans*-7-methyl isomer (**4**) was a doublet while *cis* isomer (**3**) showed a broadened singlet for the methyl group.

Reaction of Cyclohexene with Methylene Chloride, Methyllithium Prepared from Methyl Chloride, and Lithium Iodide.—Anhydrous lithium iodide (5.4 g, 0.04 mole, prepared from lithium hydride and iodine according to the procedure of Taylor and Grant[37]) was carefully added to a solution of methyllithium in ether (25 ml of 1.7 *M* solution, 0.04 mole, prepared from methyl chloride) in a drybox. The resulting slurry of methyllithium and lithium iodide was then added to a mixture of cyclohexene (0.12 mole) and methylene chloride (0.08 mole) as described above. Gc analysis showed the product distribution in Table I. A sample of the methylene iodide was collected by preparative gc; its infrared, nmr, and mass spectra, and gc retention time were identical with those of an authentic sample. Several minor unidentified components with short gc retention times were also present.

Control Reactions of Methylene Chloride.—A solution of anhydrous lithium iodide (1.34 g, 0.01 mole) in anhydrous ether (6 ml) was added to methylene chloride (1.7 g, 0.02 mole) at room temperature and stirred overnight. Gc analysis (B, 175°) showed no detectable amount of methylene iodide (estimated <0.5% yield) after the usual work-up procedure.

A solution of methyllithium in ether (7.9 ml of 1.27 M solution, 0.01 mole, prepared from methyl iodide) was added to methylene chloride (1.7 g, 0.02 mole) at 5-15° and stirred overnight at room temperature. Gc analysis showed no trace of methylene iodide (estimated <0.1% yield). However, several unidentified components of shorter retention time were present.

Anhydrous lithium iodide (1.34 g, 0.01 mole) was added to a solution of methyllithium in ether (6 ml of 1.67 *M* solution, 0.01 mole, prepared from methyl chloride) and the resulting slurry was slowly added to methylene chloride (1.7 g, 0.02 mole) at 5-15°. The reaction mixture was stirred overnight at room temperature. Gc analysis indicated the presence of methylene iodide in 10% yield (based on lithium iodide).

Reaction of 2,3-Dimethyl-2-butene with Methylene Chloride and Methyllithium Prepared from Methyl Iodide.—A solution of methyllithium in ether (280 ml of 1.25 *M* solution, 0.35 mole, prepared from methyl iodide) was added dropwise over a period of 2 hr to a stirred solution of 2,3-dimethyl-2-butene (59 g, 0.70 mole) and methylene chloride (59 g, 0.70 mole) at 10-15°. The reaction mixture was stirred overnight at room temperature and worked up as in the reaction with cyclohexene above. Preparative gc (A, 120°; B, 85°) of appropriate distillation fractions gave the two cyclopropane derivatives (**8** and **9**). The first component collected was identified as pentamethylcyclopropane (**9**): $\nu_{\max}^{\text{neat}}$ 2990, 2940, 2875, 1470, 1395, 1300, 950, 770, and 660 cm^{-1}; nmr spectrum, a singlet at −1.04 ppm (relative area 6.3, two CH_3 groups), a doublet centered at −0.90 (J = 6.2 cps, $CHC\mathit{H}_3$), a singlet at −0.88 ppm (two CH_3 groups) (total relative area 8.7), and a quartet centered at −0.17 ppm (J = 6.2 cps, $C\mathit{H}CH_3$, relative area 1.0).

Anal. Calcd for C_8H_{16}: nuclidic mass, 112.1252. Found: nuclidic mass, 112.1249.

The second component collected was identified as 3-chloro-1,1,2,2-tetramethylcyclopropane (**8**): $\nu_{\max}^{\text{neat}}$ 2995, 2960, 2880, 1465, 1395, 1277, 1034, 940, and 770 cm^{-1}. The nmr spectrum agreed with that given in the literature for **8**.[17] Mass spectral analysis was in agreement with the assigned structure, showing a molecular ion at *m/e* 132 with the correct isotopic ratio for one chlorine atom.

The total yield of cyclopropane derivatives was 14%; the ratio of **8**:**9** was 3:2.

Mass spectral examination of other fractions indicated the presence of much smaller amounts of several iodinated compounds: *m/e* 168 (C_3H_5I), *m/e* 170 (C_3H_7I), and *m/e* 176 (CH_2ClI). The C^{13}:C^{12} and Cl^{37}:Cl^{35} ratios were correct for the assigned formulas. A careful examination of the reaction mixture showed no trace of 1,1,2,2-tetramethylcyclopropane. However it is possible that a small amount of this material might not have been detected.

Reaction of Cyclohexene with Methylene Bromide and Methyllithium Prepared from Methyl Bromide.—A solution of methyllithium in ether (48 ml of 0.83 *M* solution, 0.04 mole, prepared from methyl bromide and lithium) was added dropwise over a period of 45 min to a stirred solution of cyclohexene (9.9 g, 0.12 mole) and methylene bromide (13.9 g, 0.08 mole) at 5-15°. The reaction mixture was stirred overnight at room temperature, then worked up as described above. Gc (A, 125°; B, 175°) of the product showed the presence of norcarane derivatives (estimated yield *ca.* 5%, based on methyllithium) consisting of 75% norcarane (**7**) and 14% *cis*- (**5**) and 11% *trans*-7-bromonorcarane (**6**) (see below). No trace (<2%) of the methyl derivatives (**3** and **4**) could be detected.

This experiment was repeated using D_2O (99.8 mole % D) for the work-up instead of water, and a total reaction time before hydrolysis of 1.25 hr. Gc analysis showed a 4% yield of norcarane derivatives consisting of 93% **7**, 4% **5**, and 3% **6**. Mass spectral analysis of a sample of norcarane (**7**) isolated by preparative gc, showed no evidence (<2%) of deuterionorcarane. Mass spectral analysis of methylene bromide recovered from the reaction showed no trace (<1%) of deuteriomethylene bromide.

Reaction of Cyclohexene with Methylene Bromide and Methyllithium Prepared from Methyl Iodide.—The preceding experiment was repeated with methyllithium prepared from

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(33) D. Seyferth, H. Yamazaki, and D. L. Alleston, *J. Org. Chem.*, **28**, 703 (1963).

(34) H. Gilman, E. A. Zoellner, and W. M. Selby, *J. Am. Chem. Soc.*, **55**, 1252 (1933).

(35) (a) H. E. Simmons, E. P. Blanchard, and H. D. Hartzler, *J. Org. Chem.*, **31**, 295 (1966); (b) R. T. LaLonde and M. A. Tobias, *J. Am. Chem. Soc.*, **85**, 3771 (1963).

(36) R. T. LaLonde and M. A. Tobias, *ibid.*, **86**, 4068 (1964).

(37) M. D. Taylor and L. R. Grant, *ibid.*, **77**, 1507 (1955).

methyl iodide. Gc analysis (A, 125°; B, 175°) showed the principal products to be norcarane (**7**) and methylene iodide in a ratio of *ca.* 1:3. The bromonorcaranes (**5** and **6**) were each present in trace amounts. No trace of the 7-methylnorcaranes was present (estimated <5% relative to norcarane). The actual yield of norcarane was *ca.* the same as that in the preceding experiment.

Control Reactions of Methylene Bromide.—A solution of anhydrous lithium iodide (1.34 g, 0.01 mole) and methylene bromide (3.5 g, 0.02 mole) in anhydrous ether (6 ml) was stirred for 3 hr at room temperature, then processed in the usual manner. Gc analysis (B, 175°) showed no trace of methylene iodide (<1% yield).

Anhydrous lithium iodide (1.34 g, 0.01 mole) was added to a solution of methyllithium in ether (6 ml of 1.67 *M* solution, 0.01 mole, prepared from methyl chloride), and the resulting slurry was slowly added to methylene bromide (3.5 g, 0.02 mole) at *ca.* 10–30°. The reaction mixture was stirred for 3 hr at room temperature, then processed as above. Gc analysis indicated a 40% yield (based on lithium iodide) of methylene iodide.

Reaction of Cyclohexene with Bromoform and Methyllithium Prepared from Methyl Chloride.—A solution of methyllithium in ether (24 ml of 1.67 *M* solution, 0.04 mole, prepared from methyl chloride) was added dropwise over a period of 45 min to a stirred solution of cyclohexene (9.9 g, 0.12 mole) and bromoform (20.3 g, 0.08 mole) at 5–15°. An additional 5 ml of ether was then added. The reaction mixture was stirred for an additional 2 hrs at room temperature, then worked up as described above. Gc analysis (A, 150°) indicated an *ca.* 8% yield (based on methyllithium) of products in the following relative proportions: 86% 7,7-dibromonorcarane (**10**) and 9% *cis*- (**5**) and 5% *trans*-7-bromonorcarane (**6**). In addition a large number of unidentified components of short retention time were obtained. However a separate control reaction of bromoform and methyllithium prepared from methyl chloride showed that all of these components resulted from reactions which did not involve cyclohexene. There was no evidence of any norcarane (**7**) or the methylnorcaranes (**3** and **4**) (limit of detectability *ca.* 5%). The three bromo derivatives were isolated by preparative gc (A, 175°; B, 160°). The first two components eluted were identified as the *cis*- (**5**) and *trans*-bromo- (**6**) isomers: mass spectrum, *m/e* 174 (M^+, one bromine atom per molecule). The nmr spectra were in agreement with data reported in the literature[38].

The third component eluted was the dibromo derivative (**10**): mass spectrum, *m/e* 252 (M^+, two bromine atoms per molecule); nmr spectrum, a broad multiplet at −2.4 to −1.1 ppm with major peaks at −1.83 and −1.33 having an area ratio of ~6:4. The infrared spectrum was identical with that reported.[38]

Reaction of Cyclohexene with Bromoform and Methyllithium Prepared from Methyl Iodide.—The preceding experiment was repeated using methyllithium prepared from methyl iodide. Gc analysis of the product after work-up indicated an 8% yield (based on methyllithium) of norcarane derivatives in the following proportions: 91% **10**, 7% **5**, and 2% **6**. In addition a large number of unidentified components of short retention time were also obtained. A control reaction of bromoform and methyllithium prepared from methyl iodide, in the absence of cyclohexene, also gave these unidentified products. Norcarane (**7**) and the methylnorcaranes (**3** and **4**) were not evident, but their presence in relative amounts up to *ca.* 10% could not be ruled out because of the interference of the unidentified compounds mentioned above.

Registry No.—**1**, 1121-42-2; **2**, 1121-43-3; **3**, 14154-00-8; **4**, 14123-39-8; **5**, 1121-40-0; **6**, 1121-41-1; **7**, 286-08-8; **8**, 14123-41-2; **9**, 14172-83-9; **10**, 2415-79-4; cyclohexene, 110-83-8; methylene chloride, 75-09-2; methyllithium, 917-54-4; 2,3-dimethyl-2-butene, 563-79-1; methylene bromide, 74-95-3; bromoform, 75-25-2; methylene iodide, 75-11-6.

Acknowledgment.—We wish to thank Dr. J. C. Little, and Professors G. L. Closs, R. M. Magid, M. Stiles, and H. M. Walborsky for many helpful comments.

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[38] W. v. E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

Group Migrations to Carbene Centers. Pyrolysis of the Sodium Salts of α-Arylisobutyrophenone Tosylhydrazones

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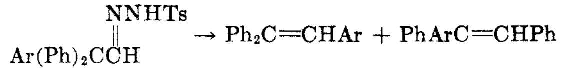
Received May 17, 1967

Tosylhydrazones **1** of several α-arylisobutyrophenones have been synthesized, converted to the corresponding dry sodium salts, and thermally decomposed to give a mixture of aryl migration products **2** and carbon–hydrogen insertion products **4**, but no products of methyl migration. Protic decomposition of **1** resulted in the formation of **2**. The syntheses of all possible reaction products are described. Migratory aptitudes for the aryl groups follow: *m*-chlorophenyl, 0.67; phenyl, 1.0; *p*-tolyl, 1.90. The data followed σ^+ with $\rho = -0.68$.

The facile migration of hydrogen and aryl groups to carbene sites generated in several systems has long been recognized,[2] but relatively little systematic information on the detailed nature of the transition state for migration as a function, both of electronic interactions by substituents on the migrating group and substituents directly attached to the divalent carbon atom, is available.

In a recent study by Sargeant and Shechter,[3] the thermal decompositions of several 2,2-diphenyl-2-arylacetaldehyde tosylhydrazones were carried out in the presence of excess sodium methoxide in diethyl carbitol at 90° to give a mixture of products from which the migratory aptitudes for the aryl groups were calculated. The data fitted a Hammett plot (σ^+) with $\rho = -0.28$



$$\mathrm{Ar(Ph)_2C\overset{\overset{\displaystyle NNHTs}{\|}}{C}H} \rightarrow \mathrm{Ph_2C{=}CHAr + PhArC{=}CHPh}$$

In the present study, the dry salts of several tosylhydrazones **1** have been prepared and thermally decomposed both in the absence of solvent and in ethylene glycol solution. The only expected products

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[1] Taken from the Ph.D. Dissertation of A. G. K., University of Kansas, 1966. Partial support from National Science Foundation Grant Gp-3519 is hereby acknowledged.

[2] (a) W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964; (b) J. Hine, "Divalent Carbon," Ronald Press, Inc., New York, N. Y., 1964.

[3] P. B. Sargeant and H. Shechter, *Tetrahedron Letters*, 3957 (1964).