tube (Scientific Glass Apparatus, Bloomfield, N.J.). Temperature is believed to be accurate to within ±0.5°. Analysis of rate processes was achieved by line-shape fitting with computed spectra (Fortran IV coded program based on the Gutowsky–Holm equation).[26] In the case of the 6,1,2-hydride shift, a Fortran IV coded program based on the Gutowsky–Holm equations was used in conjunction with a Univac 1108 computer and a CalComp plotter. Spectra for determination of the 3,2-hydride shift rates were computed using Saunders multisite program as described previously.[4b]

Carbon-13 Nuclear Magnetic Resonance Spectra. [13]C spectra were obtained by irradiation of the 100-MHz proton spectrum with a

(26) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

swept 25.1-MHz frequency source (indor method). The detailed techniques employed have been described previously.[6] Modified instrumentation using a Monsanto 3300A digital frequency synthesizer as the 25.1 MHz frequency source were used for some of the most recent measurements. [13]C shifts were computed with respect to TMS as a reference and converted to the carbon disulfide standard by adding 194.6 ppm. Negative shifts thus correspond to resonances which are to low field of [13]CS_2.

Carbenoid Species from Methyl and Methylene Halides

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Abstract: Carbenoid species were generated by dehydrohalogenation of methyl halides with phenylsodium and dehalogenation of methylene halides with organolithium reagents. The reactive species *via* both modes of formation undergoes stereospecific addition to carbon–carbon double bonds. Relative rates of cyclopropane formation obtained *via* competition reactions and the absence of carbon–hydrogen insertion products indicate that a carbene complex is involved. Methylenation of olefins *via* methylene halides and organolithium reagents provides a simple route to cyclopropanes in moderate yield. Organolithium reagents, activated by tertiary amine chelating agents, were found to be excellent nucleophiles toward methyl chloride, and give the methylation products in high yield.

Depending on the precursor, mode of formation, and environment, methylene[2] exhibits a wide range of properties and reactivities.[3] In addition to the question of spin multiplicity there is the added problem of whether *free* carbenes or complexed carbenes (carbenoids) are the reactive intermediates. Free carbenes are undoubtedly produced by photolysis or thermolysis of diazo compounds (and ketenes). Carbenoids are the intermediates in most organometallic systems and metal (or metal ion) catalyzed decomposition of diazo compounds. The nature of the intermediate in *trans* methylenation (photolysis of oxiranes, thermolysis of methanocyclodecapentaene, etc.) is yet to be resolved. Carbenoids in general are much less reactive (more selective) than (corresponding)

carbenes and they usually do not insert into the C–H bond.

In addition to the more preparatively useful methylenation (*e.g.*, $CH_2/h\nu$, Δ, Cu^0, Cu^+; CH_2I_2/Zn, etc.) techniques,[3a] methylenation of cyclohexene with methyl chloride and phenylsodium was also shown to occur.[1a] It was of interest to extend this earlier work in light of the subtleties that have developed since, by reacting other methyl halides with phenylsodium and to attempt to characterize the nature of the intermediate *via* olefin competition studies.

Results and Discussion

1. Reactions of Methyl Halides with Phenylsodium. Products obtained from reaction of methyl halides with phenylsodium in the presence of cyclohexene are listed in Table I. Methyl iodide was not investigated, since extrapolation of the results indicated that α-elimination processes would at best be negligible. Cumene and *n*-propylbenzene reported as products earlier[1a] could not be detected.

Toluene is presumably formed *via* nucleophilic displacement of halide by phenylsodium, while methylene generated by dehydrohalogenation is trapped by cyclohexene to give norcarane (Scheme I). Conceivably, methylene could also insert into phenylsodium to give benzylsodium which would then react to give mainly ethylbenzene.[4] However, the data sup-

(1) (a) A portion of this work has appeared in preliminary form: L. Friedman and J. G. Berger, *J. Amer. Chem. Soc.*, **82**, 5758 (1960); (b) support in part by The National Science Foundation (Grant No. GP-3976) is gratefully acknowledged; (c) Allied Chemical Fellow, 1964–1966; (d) taken in part from the Ph.D. Thesis of R. J. H., Case Western Reserve University, 1970, and the Masters Dissertation of J. G. B., New York University, 1961.

(2) A definition of the term methylene is in order. By the term *methylene* or *carbene* we infer any formally divalent carbon species capable of transferring the :CH_2 group. The designation *carbenoid* refers specifically to complexed carbenes, α-halocarbanions, metal-complexed carbenes, etc.

(3) (a) For recent summaries of the structure and chemistry of carbenes and carbenoids, see W. Kirmse, "Carbenes, Carbenoids, and Carbene Analogs," Verlag Chemie GmbH., Weinheim/Bergstr., Germany, 1969; G. L. Closs in "Topics in Stereochemistry," Vol. 3, E. L. Eliel and N. L. Allinger, Ed., Interscience Publishers, New York, N. Y., 1968; W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964; J. Hine, "Divalent Carbon," The Ronald Press Co., New York, N. Y., 1964; (b) W. R. Moser, *J. Amer. Chem. Soc.*, **91**, 1135, 1141 (1969); (c) J. M. Mallan and R. L. Rebb, *Chem. Rev.*, **69**, 693 (1969); (d) R. A. Finnegan, *Ann. N. Y. Acad. Sci.*, **159**, 242 (1969).

(4) (a) It was suggested by a referee that ethylbenzene might be a result of methylene insertion on toluene.[5] Since no other carboninsertion products (*e.g.*, with cyclohexane) were observed in the system, it is highly unlikely, although it cannot be completely excluded; (b)

Table I. Relative Yields of Products Obtained in the Reaction of Phenylsodium with Methyl Halides in Cyclohexene

Run no.	Halide	Temp, °C	△ (cyclohexane)	◯–CH₃	◯–CH₂CH₃	% Conversion[b]
1	CH₃Cl	25–30	4.1	95.9	Trace	75
2	CH₃Cl	25–30	4.4	95.6	Trace	75
3	CH₃Cl	25–30	4.7	95.3	Trace	83
4	CH₃Cl	25–30	6.2	93.8	Trace	26[c]
5	CH₃Cl	45–50	7.0	90.9	2.1	88
6	CH₃Cl	45–50	5.8	92.1	2.1	95
7	CH₃F	25–30	1.5	97.8	0.7	76
8	CH₃F	25–30	1.3	98.2	0.5	80
9	CH₃Br	25–30	1.2	98.8	Trace	~100
10	CH₃Br	25–30	1.2	98.8	Trace	~100

Column heading for hydrocarbons reads: —Mole % hydrocarbons[a]—, with sub-columns CH₃ and CH₂CH₃.

[a] Determined via glpc. [b] Based on phenylsodium employed. [c] This reaction was deliberately quenched at low conversion.

port a third mechanism: direct metallation of toluene, since benzylsodium if formed via methylene insertion would be expected to correlate (*i.e.*, ethylbenzene) with that of norcarane; this is not the case (*cf.* runs 7 and 8 with 1–3). It was found that phenylsodium *does* met-

Scheme I
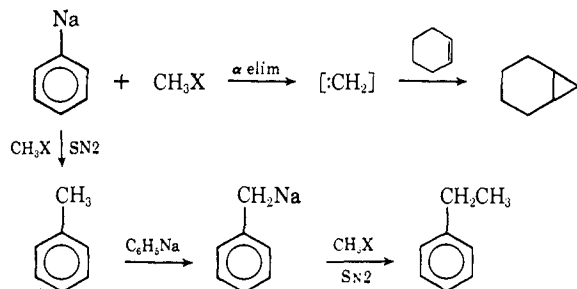
allate toluene (see Experimental Section) under comparable reaction conditions; higher temperatures and/or extended reaction periods[6] would be expected to give more metallation, as was observed.

It is interesting that a higher yield of norcarane is obtained when total conversion to products is low (run 4), indicating that the nature of the phenylsodium surface in the heterogeneous system is an important factor in influencing the reaction pathways. Thus, the extent of specific reaction mechanisms must vary as the reaction proceeds.

The observed order of dehydrohalogenation based on relative yields of norcarane[7] is CH₃Cl > CH₃F ~ CH₃Br and is best explained as the result of a combination of halide substituent effects: inductive (F > Cl > Br > I), carbanion stabilization (I ~ Br > Cl > F),[8]

in addition, there is compelling evidence that reactions of phenyllithium (and sodium) with alkyl chlorides proceed with almost complete inversion. A. Streitwieser, J. R. Wolfe, and W. D. Schaeffer, *Tetrahedron*, **6**, 338 (1959); R. L. Letsinger, *J. Amer. Chem. Soc.*, **70**, 406 (1948).

(5) *Cf.* insertion of dichlorocarbene in benzylic C–H of cumene, ethylbenzene, etc: E. K. Fields, *ibid.*, **84**, 1744 (1962).

(6) The reaction of phenylsodium with methyl chloride and methyl bromide required 15–30 min for completion, while methyl fluoride required approximately 1 hr. This extended reaction period undoubtedly results in increased metallation[3c,d] of toluene and hence higher yields of ethylbenzene via the fluoride.

(7) Although differences in the relative yields of norcarane are small, they are quite reproducible.

(8) (a) J. Hine, R. C. Peek, Jr., and B. D. Oakes, *J. Amer. Chem. Soc.*, **76**, 827 (1954); (b) J. Hine and N. W. Berske, *ibid.*, **78**, 3337 (1956); (c) J. Hine, N. W. Berske, H. Hines, and P. B. Langford, *ibid.*, **79**, 1406

etc., and the competitive SN2 process, which would be expected to be most facile with methyl bromide.

Relative Olefin Reactivity. The formation of *cis*-1,2-dimethylcyclopropane as the sole cyclic product from *cis*-2-butene and methyl chloride with phenylsodium[1a] is consistent with properties reported for singlet carbene and/or an organometallic carbenoid species.[9] To determine the discriminating ability of methylene, generated in this manner, with regard to olefin addition, a competition study with tetramethylethylene, isobutylene, and cyclohexene was undertaken. The results are reproducible with great precision and were independent of temperature over the range studied, reagent concentrations, etc. (Table II).[10] Methylene

Table II. Olefin Relative Reactivities with Methylene Generated from Methyl Chloride and Phenylsodium

Olefin	T, °C	Relative reactivity[a,b]
⟩=⟨	5–10	0.86 (0.86)[c]
	25–30	0.85, 0.85[d]
⟩=	5–10	1.33, 1.30[d]
◯	5–10	1.00

[a] Determined via glpc. Reactants and products stable to phenylsodium under the reaction conditions employed. [b] In competition with cyclohexene, unless otherwise specified. [c] Measured in competition with isobutylene. [d] The internal consistency of the olefin relativity reactivity is demonstrated by at least duplicate experiments.

generated in this manner is clearly less electrophilic and (not unexpectedly) less discriminating[11] than mono- and dichlorocarbene[12] (Table III).

However, its decreased ease of addition to tetramethylene is *a priori* unexpected. Similar behavior has only been observed with other carbenes[15a] and carbenoids[3b,15b,c] when the overall steric bulk of the divalent carbon intermediate becomes important (Table III). Thus, from these data, a demonstrable steric effect, the absence of C–H insertion, and stereospecific addition, it is concluded that the methylene transfer agent from methyl chloride and phenylsodium is a carbenoid. Since the system is heterogeneous, a surface reaction is proposed, and the carbenoid can be depicted as a base–methyl halide complex (1) or an α-halocarbanion (2).

(1957); (d) J. Hine and P. B. Langford, *ibid.*, **79**, 5497 (1957); (e) J. Hine, R. Butterworth, and P. B. Langford, *ibid.*, **80**, 819 (1958).

(9) (a) H. E. Simmons and R. D. Smith, *ibid.*, **80**, 5323 (1958); (b) G. L. Closs and L. E. Closs, *Angew. Chem.*, **74**, 431 (1962).

(10) Initially, some difficulty in obtaining consistent cyclopropane ratios was encountered. This problem was solved by refluxing the olefinic starting materials over calcium hydride and distillation through an efficient column.

(11) P. S. Skell and M. S. Cholod, *J. Amer. Chem. Soc.*, **91**, 7131 (1969).

(12) The higher selectivities exhibited have been attributed to resonance stabilization by halogen.[13] However, this is not the complete answer, since the reactive intermediate generated from methylene chloride and alkyllithium[1ab] is a carbenoid and the free chlorocarbene is formed from the corresponding diazo compound,[14] which is as expected less selective in its addition to olefins, and moreover is capable of C–H insertion.

(13) (a) P. S. Skell and A. Y. Garner, *J. Amer. Chem. Soc.*, **78**, 5430 (1956); (b) G. L. Closs and G. M. Schwartz, **82**, 5729 (1960).

(14) G. L. Closs and J. J. Coyle, *ibid.*, **87**, 4270 (1965).

(15) For example, (a) see Table III, footnote *f*; (b) E. P. Blanchard and H. E. Simmons, *J. Amer. Chem. Soc.*, **86**, 1337 (1964); (c) W. R. Moore and H.R. Ward, *J. Org. Chem.*, **25**, 2073 (1960); W. R. Moore, H. R. Ward, and R. F. Merritt, *J. Amer. Chem. Soc.*, **83**, 2019 (1961).

**Table III.** Olefin Relative Reactivities with Various Carbenes and Carbenoids

Olefin	:CH₂ (CH₃Cl/C₆H₅Na)	:CCl₂ (HCCl₃/B⁻)[b]	:CHCl (CH₂Cl₂/RLi)[c]	:CHCl (RN₂/Δ)[d]	:CH₂ (ICH₂ZnI)[e]	⟨C₆H₅ / C₆H₅⟩ (RN₂/Δ)[f]
)=(	0.86	53.7	4.68	2.00	1.29	0.33
)=	1.33	8.34	1.67	1.67	2.53	0.81
◯	1.00	1.00	1.00		1.00	1.00

[a] Taken from Table II. [b] W. v. E. Doering and W. A. Henderson, *J. Amer. Chem. Soc.*, **80**, 5274 (1958); relative addition rates of chlorofluorocarbene to olefins (R. A. Moss and R. Gerstl, *J. Org. Chem.*, **32**, 2268 (1967)) and difluorocarbene (R. A. Mitsch, *J. Amer. Chem. Soc.*, **87**, 758 (1965)) have been determined. Both appear to be more selective than dichlorocarbene. [c] Reference 13b. [d] Reference 14. [e] Reference 9a. [f] W. M. Jones, M. H. Grasley, and W. S. Brey, Jr., *J. Amer. Chem. Soc.*, **85**, 2754 (1963).

1 2
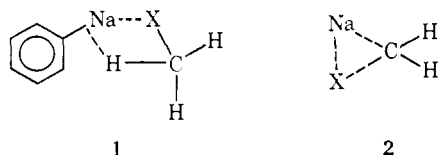
Since phenyllithium– and butyllithium–N,N,N′,N′-tetramethylenediamine (TMEDA) complexes[16] were found to promote extensive α-dehydrohalogenation[1d] with several primary alkyl chlorides whereas the uncomplexed lithioorganics do not,[17a] similar reactions with methyl chloride were investigated. Unfortunately, norcarane was not obtained; instead, the products were toluene (the small amount of ethylbenzene is formed from benzyllithium, a metallation product[16a,d,f]) and n-pentane, respectively, which presumably arise by direct SN2 displacement[4b,17b] (Scheme II). Pentane (and toluene) could conceivably arise

Scheme II
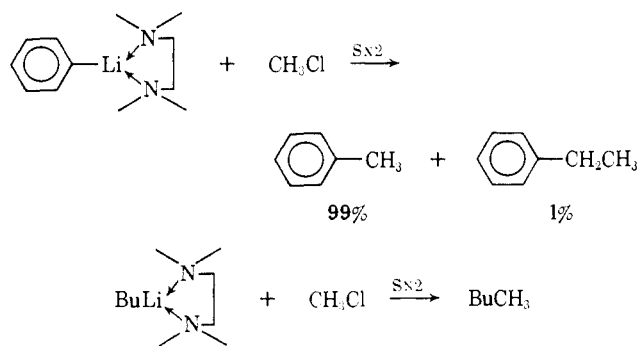
via insertion of methylene into the C–Li bond of butyllithium (or phenyllithium) followed by protonation. That this is not the case was determined by quenching with deuterium oxide; the pentane (and toluene[19]) had not incorporated deuterium (analyzed

(16) (a) G. C. Eberhardt and W. A. Butte, *J. Org. Chem.*, **29**, 2928 (1964); (b) C. G. Screttas and J. F. Eastham, *J. Amer. Chem. Soc.*, **87**, 3276 (1965); (c) A. W. Langer, *Trans. N. Y. Acad. Sci.*, **27**, 741 (1965); (d) *Polym. Preprints*, **7** (1), 132 (1966); (e) U. S. Patent 3,451,988 (1969); (f) U. S. Patent 3,458,586 (1969).

(17) (a) In light of the hyperbasicity of menthyllithium (W. H. Glaze and C. H. Freeman, *J. Amer. Chem. Soc.*, **91**, 7198 (1969), and references contained therein), it would be of interest to elucidate its reaction pathway with methyl chloride; (b) reactions of TMEDA complexed organolithium reagents with alkyl chlorides (not bromides or iodides) do not proceed by homolytic processes.[1d,18]

(18) For an example of such a homolytic reaction, see H. R. Ward, R. G. Lawler, and H. Y. Loken, *J. Amer. Chem. Soc.*, **90**, 7359 (1968).

(19) Toluene was composed of approximately 99% d_0 and 1% d_1 which parallels the amount of ethylbenzene obtained. The common intermediate, benzyllithium, is a result of metallation of toluene with the phenyllithium–TMEDA complex.[16]

via mass spectroscopy). Moreover, no hexane was formed. This leaves no doubt that carbene mechanisms are not involved.

2. Reactions of Methylene Halides with Organolithium Reagents. The second reaction sequence studied was the formation of methylene via halogen–metal exchange between alkyllithium and methylene bromohalides[20] (Scheme III). In the presence of cyclo-

Scheme III
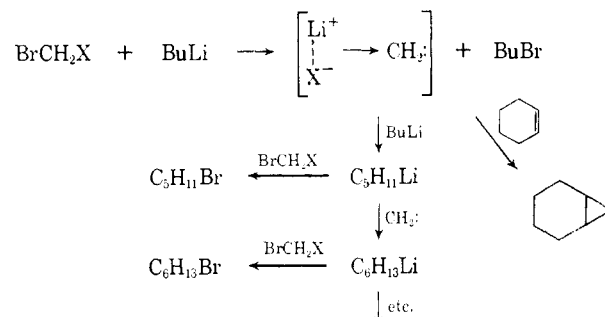
hexene, methylene generated in this manner adds to the double bond to form norcarane and also undergoes carbon–lithium bond insertion reactions, producing amyl- and hexyllithium, which react further with the methylene bromohalide to give methylene and amyl and hexyl bromide, respectively. Under optimum conditions, where yields of 31% norcarane, 24% amyl bromide, and 7.5% hexyl bromide are obtained, the alkyllithium reagent is added to a solution of methylene chlorobromide and excess cyclohexene maintained at 0 to −20°. The use of higher or lower reaction temperatures, ether as a solvent, TMEDA[16] as a catalyst, or methylene bromide, resulted in lower yields of norcarane (Table IV).

Other cyclopropanes were prepared in moderate yield by this technique (Table V). This procedure has merit in that it is rapid and convenient (especially for the preparation of low boiling cyclopropanes). The divalent carbon species generated in this manner adds to cis- and trans-2-butene stereospecifically, a characteristic of a singlet carbene, while the absence of carbon–hydrogen insertion products is indicative of a complexed species, a carbenoid rather than free methylene.

Since butyllithium is polymeric (hexamer) in hydrocarbon solvents, the initial reaction might be expected

(20) W. T. Miller, Jr., and C. S. Kim, *J. Amer. Chem. Soc.*, **81**, 5008 (1959).

Table IV. Products from the Reaction of Butyllithium, Methylene Chlorobromide and Bromide, and Cyclohexene[a]

| Halide	T, °C		AmBr	HexBr
CH₂ClBr[c]	+30	17	23	18
CH₂ClBr[c]	−20	31	24	15
CH₂ClBr[c]	−60	17	20	14
CH₂Br₂	+30	11	29	28
CH₂Br₂	−20	24	31	26
CH₂Br₂	−60	14	27	28

[a] *n*-Hexane was reaction solvent. [b] *Via* glpc, based on methylene halide consumed, *i.e.*, HexBr requires 2 equiv of CH₂X₂ for its formation. [c] At −20°, MeLi and C₆H₅Li (in Et₂O) give low yields (≲3%) of norcarane, Et and Pr bromides, and bromobenzene and benzyl bromide, respectively.

Table V. Cyclopropanes from Methylene Chlorobromide–*n*-Butyllithium and Olefins

| Olefin	Product	Yield,[a] %
Cyclohexene	Norcarane	31
Isobutylene	1,1-Dimethylcyclopropane	38
cis-2-Butene	*cis*-Dimethylcyclopropane	33
trans-2-Butene	*trans*-Dimethylcyclopropane	37
2,3-Dimethyl-2-butene	1,1,2,2-Tetramethylcyclopropane	34

[a] *Via* glpc. Isolated yields were a few per cent lower.

to be the formation of a new alkyllithium polymer, with this species acting as the methylene transfer agent.[21]

$$(BuLi)_6 + CH_2ClBr \longrightarrow [(BuLi)_5CH_2LiCl] + BuBr$$
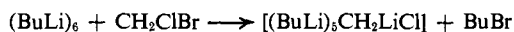
The bulky intermediate would be expected to undergo olefin addition or collapse, giving higher alkyllithium analogs. Dilution of the alkyllithium reagent does not decrease the alkyl bromide–cyclopropane ratio (Table VI). This is to be expected if the complexed carbene

Table VI. Reaction of Butyllithium and Methylene Chlorobromide in Cyclohexene. Independence of Product Yield as a Function of Butyllithium Concentration

| BuLi[a] concn, M		C₅H₁₁Br	C₆H₁₃Br
2.2	31	24	15
1.1	30	26	16
0.5	26	24	17

[a] 0.11 mol of BuLi in *n*-heptane was added to a solution of 0.10 mol of bromochloromethane and 25 ml of cyclohexene, with efficient stirring, maintaining the temperature at −15 to −25°. [b] Yield based on the consumption of methylene halide.

can react *internally* to give the carbon–lithium insertion products.

Ether, which breaks down the polymer, and TMEDA, which forms a chelated monomer, gave lower yields of norcarane. Although smaller aggregates of butyllithium might be expected to give rise to less carbon–lithium insertion products (and therefore more cyclopropane) the nature of carbenoids is altered considerably in Lewis base media[22] and the net effect is lower

(21) Evidence in support of the involvement of organolithium aggregates in chemical reactions was presented by T. L. Brown, Fourth International Conference on Organometallic Chemistry, Bristol, England, 1969.

yields of cyclopropanes. In addition, the strongly basic TMEDA complex might be expected to undergo either nucleophilic displacement of bromide or initiate α-dehydrohalogenation of the dihalomethane to give a halo carbene, which could be trapped by the olefinic solvent (Scheme IV). However, none of these products

Scheme IV
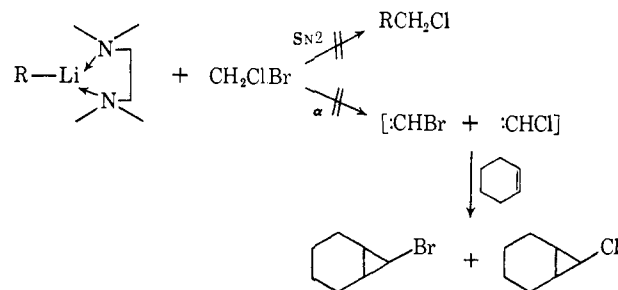
were detected. Instead, the yields of amyl and hexyl bromides were slightly increased (to 26 and 22%, respectively) in ether which is consistent with the enhanced reactivity of the Lewis base complexed alkyllithium, *i.e.*, nucleophilic capture[24] of the carbenoid by alkyllithium, is more favorable than olefin addition, under these circumstances.[25] However, BuLi–TMEDA gave much less amyl and hexyl bromides (4.7 and 2.8%, respectively). This is probably a result of either ylide formation followed by a Stevens rearrangement, or direct insertion to give a methylenated TMEDA.

Olefin Relative Reactivities. To study the discriminating ability of the methylene transfer agent (and the importance of aggregate base), methylene chlorobromide, methylene bromide, and methylene iodide were treated with *n*-butyl- or neopentyllithium in the presence of olefin mixtures (Table VII).

The selectivities exhibited are highly dependent upon the alkyllithium and the mode of addition of reagents. The conclusion which may be drawn from these data is that the carbenoid is complexed with the alkyllithium and is not a "free" or aggregate carbenoid species. Although the electronic effects of a carbenoid complexed with neopentyllithium might be expected to differ from a carbenoid complexed with butyllithium, these differences would be expected to be small. The variation in the discriminating ability of the carbenoids generated from methylene chlorobromide, methylene bromide, and methylene iodide by changing the alkyllithium reagent are characteristic of a steric effect of the carbenoid–alkyllithium aggregate, indicating that steric hindrance can play a large part in determining the selectivity of a carbenoid toward addition to olefins. Obviously, the neopentyllithium–carbenoid complex would be expected to exert a larger steric effect and the data support this. Olefin reactivities from the butyllithium–carbenoid complex infer a more elec-

(22) The carbanion character of carbenoids is greatly enhanced in ether solvent and presumably also in the presence of tertiary amines.[16,23] This would undoubtedly affect the ability of the carbenoid to undergo olefin addition.

(23) (a) G. Kobrich, K. Flory, and W. Drischel, *Angew. Chem.*, **74**, 536 (1964); G. Kobrich, H. R. Merkle, and H. Trapp, *Tetrahedron Lett.*, **15**, 969 (1965); G. Kobrich and H. R. Merke, *Chem. Ber.*, **99**, 1782 (1966); G. Kobrich and R. H. Fischer, *Tetrahedron*, **24**, 4343 (1968); D. F. Hoeg, D. I. Lusk, and A. L. Crumbliss, *J. Amer. Chem. Soc.*, **87**, 4147 (1965).

(24) Homolytic reaction of the amine complexed lithium alkyl with the methylene halide cannot be ruled out.[18]

(25) *Cf.*, however, ref 13b.

Table VII. Olefin Relative Reactivities toward Methylene Generated from Methylene Halides and Lithium Alkyls[a,b]

| Olefin | Methylene precursor | | | | | |
| | CH₂ClBr | | CH₂Br₂ | | CH₂I₂ | |
	n-BuLi	neo-C₅Li	n-BuLi	neo-C₅Li	n-BuLi	neo-C₅Li
⟩⟨	0.44	0.07 (0.07)[c]	1.28	0.09 (0.08)[c]	0.00	0.00
⟩=	1.81 (0.71)[d]	0.13	3.48 (0.37)[d]	0.16	0.00	0.00
◯	1.00	1.00	1.00	1.00	1.00	0.00

[a] Determined by glpc. Reactant olefins and cyclopropane unchanged under reaction conditions. [b] Alkyllithium added to a solution of the methylene halide and olefins unless otherwise specified. Measurements were made in competition with cyclohexene unless otherwise specified. [c] Measured in competition with isobutylene. [d] Inverse addition; methylene halide added to a large excess of alkyllithium and olefins.

trophilic species, where relative rates of addition to olefins are governed to a greater extent by electronic effects. However, the anomalous behavior of tetramethylethylene (its low reactivity) may still be a result of a steric effect of the butyllithium–carbenoid complex (cf. CH₃Cl/C₆H₅Na) which, although it would be smaller in magnitude than the neopentyllithium–carbenoid complex, is still to be reckoned with.

Bromomethyllithium–butyllithium complex generated from methylene bromide and butyllithium was found to be more electrophilic than chloromethyllithium complex. Similar results have been found with aryl halocarbenoids.[26] This has been explained in terms of increasing electron deficiency on the carbenoid carbon, reflecting greater carbon–halogen bond breaking in the transition state with increasing atomic weight of the halide ion. It is interesting that from its discriminating ability, iodomethyllithium is not more electrophilic than bromoethyllithium, but rather demonstrates an overwhelming steric effect, presumably as a direct consequence of the size of iodine.

It should be pointed out that the "normal" mode of addition of reagents is to add slowly the alkyllithium into a solution of the methylene halide and the olefin mixture. In doing so, the steric effects observed should be a result of the individual steric effects of the various carbenoid–alkyllithium oligomers (butyllithium hexamer → dimer). To test this hypothesis, competitive studies were carried out utilizing inverse addition procedures, with butyllithium in large (threefold) excess. The relative reactivities of cyclohexene and isobutylene change dramatically (Table VII). The trend seems to be toward greater steric control (on the relative rates of methylenation) with bromoethyllithium demonstrating a greater steric requirement than chloromethyllithium. Here we are undoubtedly observing (the reactivity of) still higher aggregates of the butyllithium–carbenoid complex.

Conclusions

The divalent carbon species generated by the action of phenylsodium on methyl halides and lithium alkyls on methylene halides are undoubtedly carbenoids. The reactivity of these complexed carbenes with respect to olefin addition is a function of electronic and steric effects. When generated from an alkyllithium reagent, the carbenoid is incorporated into the organometallic aggregate, with the state of aggregation dependent upon the relative concentrations of reagents. Thus,

(26) S. H. Goh, L. E. Closs, and G. L. Closs, J. Org. Chem., **34**, 25 (1969).

the concept of steric effects in addition of carbenes and carbenoids to olefins should not be underestimated.

Experimental Section

Analytical. Infrared and mass spectra were obtained on a Beckman IR 8 spectrophotometer and a General Electric Analytical (GE 1-28508B) spectrometer, respectively. Gas chromatographic data were obtained on an Aerograph Hy-Fi Model 600-D or when preparative glpc was required, on an instrument equipped with gold-plated tungsten filaments. The columns utilized are: (1) 12 ft 20% Apiezon L on Chromosorb W 30–60 at 90°, He 80 ml/min; for the resolution of toluene, norcarane, and ethylbenzene; (2) 15 ft 30% Dowtherm A (mixture of biphenyl and diphenyl ether) on Chromosorb P 60–80 at room temperature, He 60 ml/min for the detection of 1,1-dimethyl-, trans-1,2-dimethyl, and cis-1,2-dimethylcyclopropanes and pentane; (3) 12 ft 25% bis-2-ethylhexyl azelate (UCC Z-88 Plasticizer) on Chromosorb P 60–80 at 70°, He 40 ml/min for the resolution of 1,1,2,2-tetramethylcyclopropane. The analysis of methylcyclohexenes (the 3 and 4 isomers could not be separated) was effected at 100° and He 60 ml/min. The resolution of n-butyl bromide, norcarane, n-amyl bromide, and n-hexyl bromide was effected at 130° and He 40 ml/min.

All glpc product yields were based on peak areas relative to those of internal standards, corrected for differences in thermal conductivity. Products were identified by comparisons of gas chromatographic retentions and infrared or mass spectra with those of known samples or spectra.

Materials. Pure grade (99 mol % min) cyclohexene, cis-butene-2, and trans-butene-2 were obtained from the Phillips Petroleum Co. 2,3-Dimethylbutene-2 was a product of the Chemical Samples Co. and isobutylene (99% min) was obtained from the Matheson Co., Inc. The liquid olefins were distilled over calcium hydride and fractionated through an efficient column. Gaseous olefins were passed through a train of potassium hydroxide and Drierite. When analyzed by gas chromatography, all the olefins were found to be >99% pure. Methyl chloride and bromide were purchased from the Matheson Co., Inc. and the methyl fluoride was a product of the Hynes Chemical Research Corp. Methylene bromide and chlorobromide were products of the Dow Chemical Co. and methylene iodide was obtained from the National Biochemical Co. N,N,N',N'-Tetramethylethylenediamine, obtained from Matheson Coleman and Bell, was purified by distillation over calcium hydride. Butyllithium in n-pentane was synthesized and methyllithium in diethyl ether was a product of the Lithium Corporation of America. Commercial phenyllithium in benzene–ether (Foote Mineral Co.) and the reagent prepared from bromobenzene and lithium gave comparable results.

Phenylsodium.[27] Sodium (45.8 g, 2 g-atoms) was dispersed in 100 ml of n-decane (distilled over calcium hydride) in a 1-l. three-necked flask equipped with a 3000-rpm motor and a perforated stainless steel paddle stirrer, thermometer, nitrogen inlet tube, and venting tube. A stable dispersion was obtained by stirring for 10–15 min at 105–110° and then allowing the mixture to cool to room temperature without stirring. The entire operation was conducted under a nitrogen atmosphere.

When the dispersion had cooled to room temperature, 20 ml of a solution of chlorobenzene (115 g, 1.02 mol) in n-decane (110 ml)

(27) M. Schlosser in "Newer Methods of Preparative Organic Chemistry," Vol. 5, W. Foerst, Ed., Verlag Chemie GmbH, Weinheim/Bergstr., Germany, and Academic Press, New York, N. Y., 1968, p 300.

was added with stirring (stirrer motor used from this point on was the Wilkens-Anderson, Inc. Waco motor; slow speed shaft). Usually there was an induction period. Commencement of the reaction was evidenced by a temperature increase and intense purple coloration of the dispersion. The balance of the chlorobenzene solution was added slowly and the reaction mixture maintained between 25 and 35° by intermittent cooling with a Dry Ice–acetone bath. During the course of the addition the reaction mixture usually becomes too viscous to permit adequate stirring. Additional solvent is then added as needed to decrease the viscosity. After the addition was complete, stirring was continued for a few hours. Under no circumstances was the reaction mixture allowed to exceed 40° (biphenyl formation). Prepared in this manner, the mixture was free of sodium and had no tendency to ignite on contact with water or air. The dispersion of phenylsodium has a tendency to settle out, but can be uniformly dispersed with adequate shaking and safely transferred with wide bore pipets, syringes, etc. It was conveniently standardized by reaction with a dilute solution of dimethyl sulfate in benzene (approximately 0.020 mol of dimethyl sulfate per 25 ml of dry benzene), followed by quantitative analysis of the toluene product by glpc. Heptane, octane, and hexadecane were also used as solvents.

Methyl Halides with Phenylsodium. A round-bottomed three-necked flask, equipped with a stainless steel mechanical stirrer, thermometer, and Dry Ice–acetone condenser, was thoroughly flushed with nitrogen and charged with 0.053 mol of phenylsodium in 33 ml of n-decane and 50 ml of cyclohexene. The methyl halide was then bubbled into the stirred suspension at such a rate that the reaction temperature (25–30°) could be easily controlled by means of an ice–water bath. When the reaction was carried out at a higher temperature (45–50°), the temperature of the reactants was raised by means of a heating mantle, and then maintained by the exothermicity of the reaction. Addition of the methyl halide was discontinued when the exothermicity of the reaction ceased (about 15–30 min for methyl bromide and chloride and 1 hr for methyl fluoride). The reaction mixture was then cooled to 0° and hydrolyzed with ethanol and water. A measured quantity of internal standard was then added, the organic layer washed with water, dried over anhydrous potassium carbonate, and analyzed by glpc (Table I).

Metallation of Toluene. Toluene (1.23 g, 0.013 mol) in 10 ml of benzene was allowed to react with 10 ml of C_6H_5Na (0.013 mol) in n-decane for 1 hr under a nitrogen atmosphere. The reaction vessel was then cooled to 0° and quenched with dimethyl sulfate (2.52 g, 0.020 mol) in 25 ml of benzene, maintaining the temperature below 30°. The reaction mixture was then washed with water and dried over potassium carbonate. Glpc indicated 3.5% ethylbenzene, corresponding to 3.5% metallation of toluene.

Phenyllithium–TMEDA with Methyl Chloride. A reaction flask was charged with 0.12 mol of phenyllithium in ether or benzene–ether, 0.10 mol of TMEDA, and 100 ml of cyclohexene. During the addition of methyl chloride, the reaction temperature was maintained at 40–50°. The reaction mixture was then cooled to 0°, hydrolyzed with water, and the internal standard added. The ethereal solution was extracted with dilute hydrochloric acid, washed with water, and dried over anhydrous calcium chloride. Low-boiling solvent was removed by fractionation through an 18-in. glass-helices-packed column before gas chromatographic analysis.

A 91% yield of products was obtained, composed of 99% toluene and 1% ethylbenzene. Norcarane could not be detected.

Butyllithium–TMEDA with Methyl Chloride. The organolithium amine complex was prepared by adding TMEDA (34.8 g, 0.30 mol) slowly to 0.30 mol of butyllithium in n-heptane. This solution was slowly added into cyclohexene (24.6 g, 0.30 mol) and methyl chloride (10.0 g, 0.20 mol) with stirring at 0°. After quenching the reaction mixture with deuterium oxide, the organic layer was worked up as described above. Fractional distillation gave a few grams of material with bp 30–36°, the major component of which was isolated by preparative gas chromatography. Mass spectral and glpc analysis of the compound showed it to be n-pentane, and it contained no species of mass P + 1 above the normal isotopic abundance. The pot residue (bp >40°) did not contain norcarane or n-hexane.

Organolithium Reagents with Methylene Halides. The organolithium reagents (0.11 mol of butyllithium, in n-heptane, phenyllithium, and methyllithium in ether) were slowly added to a well-stirred solution of 0.10 mol of the methylene halide chlorobromide or dibromide and 25 ml of cyclohexene. After the addition was complete, the reaction was quenched with ethanol and water, and worked up in the usual way and analyzed by glpc. These reactions were carried out at various temperatures (Table IV).

The yields of cyclopropanes obtained under the optimum conditions (n-butyllithium at 0–20°) with various olefins (cyclohexene, isobutylene, cis- and trans-2-butene) are listed in Table V. The methylene transfer agent adds stereospecifically to olefins as evidenced by the exclusive formation of >99.5% cis 1,2-dimethylcyclopropane and trans-1,2-dimethylcyclopropane from the corresponding olefins.

Competitive Addition of Methylene to Olefins. (1) Methyl chloride was bubbled into a well-stirred suspension of 0.033 mol of phenylsodium in 25 ml of n-decane and equimolar (approximately 0.05 mol each) quantities of the olefin pairs in a three-necked flask fitted with Dry Ice–acetone condenser, thermometer, and stainless steel mechanical stirrer. Competitive experiments were carried out at 5–10 and 25–30° to demonstrate the insensitivity of the competition[28] to temperature. Relative rates were calculated utilizing the equation

$$K/K_0 = P/P_0 \times O_0/O$$

where P/P_0 is the mole ratio of product cyclopropanes and O/O_0 is the initial mole ratio of olefin reactants. No greater than 1% of the total olefin was consumed in these reactions.

(2) In *normal* addition, 0.021 mol of butyllithium (or neopentyllithium) in n-pentane was added to a well-stirred solution of 0.020 mol of methylene halide and 0.050 mol each of two or three olefins, maintaining the temperature at −20 ± 5°. The reaction mixture was then quenched and analyzed *via* glpc. For *inverse* addition, 0.020 mol of the methylene halide was slowly added to a solution of 0.060 mol of butyllithium in n-pentane and 0.050 mol each of the olefin pairs; the temperature was maintained at −20 ± 5°.

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(28) Cyclopropane ratios were independent of temperature over the range studied; however, the total absolute yield of cyclopropanes diminished as the temperature was decreased. See, however, ref 11.