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Carbenes from Alkyl Halides and Organolithium Compounds. IV.[1] Formation of Alkylcarbenes from Methylene Chloride and Alkyllithium Compounds[2]

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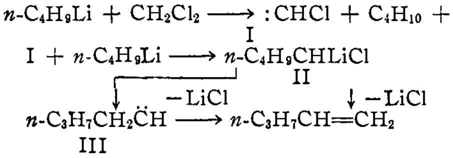
Reactions of alkyllithium compounds with methylene chloride yield olefins and cyclopropanes. Formation and distribution of products are interpreted in terms of a carbene mechanism. Chlorocarbene, generated from the organolithium compounds and methylene chloride, adds to a second molecule of the lithium reagent to form alkylchloromethyllithium. Elimination of lithium chloride from these intermediates leads to alkylcarbenes which rearrange to stable products by hydrogen or alkyl migration, respectively, and by intramolecular insertion.

Recently, we reported the formation of chlorocarbene from methylene chloride and alkyllithium compounds and its addition to olefins to yield chloro cyclopropanes.[3] Reactivity studies through competition experiments involving pairs of olefins of varying nucleophilicity demonstrated the expected electrophilic nature of the carbene.[4] In view of the strongly basic properties of alkyllithium compounds, a facile reaction of the carbene with the reagent used for its formation can be anticipated.[5] The occurrence of such a reaction is already indicated by the observation that the yields of chlorocyclopropanes obtainable in the above-mentioned synthesis are strongly dependent on the stationary concentration of the organolithium reagent.[3] Thus, highest yields were found on very slow addition of the lithium compound, whereas only traces of chlorocyclopropanes could be detected when methylene chloride was added to the mixture of olefin and alkyllithium. Similarly, olefins with a high degree of electron-releasing alkyl substitution compete more successfully with the lithium compound for the carbene, and therefore give better yields, than substrates with poorer nucleophilic properties.

As reported in a preliminary communication,[6] addition of methylene chloride to a solution of *n*-butyllithium in diethyl ether at −30° leads to the formation of 1-pentene in excellent yield. Although the preparative value of this reaction is greatly reduced by its stoichiometry, allowing only 50% of the alkyllithium compound to be incorporated into the terminal olefin, the elucidation of the mechanism seemed to be of sufficient interest to justify a more detailed investigation of the reaction.

At first sight it seems conceivable that pentene is the result of a simple displacement reaction leading to 1-chloropentane which might be converted to the olefin by subsequent elimination of hydrogen chloride. This reaction scheme was readily ruled untenable by demonstrating that a mixture of *n*-butyllithium and 1-chloropentane remained essentially unchanged over a period of one hour at −30°, the same temperature at which the reaction of methylene chloride with butyllithium is practically instantaneous.[7]

A more likely mechanism is represented in sequence 1: Chlorocarbene (I), generated from methylene chloride and *n*-butyllithium, is assumed to be the reactive intermediate. The addition of I to butyllithium can be expected to result in the formation of 1-chloro-*n*-amyllithium (II), or the corresponding ion pair, which is then converted to 1-pentene by loss of lithium chloride and rearrangement.



$$n\text{-}C_4H_9Li + CH_2Cl_2 \longrightarrow \underset{\text{I}}{:CHCl} + C_4H_{10} + LiCl$$

$$\text{I} + n\text{-}C_4H_9Li \longrightarrow \underset{\text{II}}{n\text{-}C_4H_9CHLiCl}$$

$$\underset{\text{III}}{n\text{-}C_3H_7CH_2\ddot{C}H} \xrightarrow{-LiCl} n\text{-}C_3H_7CH{=}CH_2 \qquad (1)$$

Although no direct evidence for the addition of chlorocarbene to *n*-butyllithium can be brought forth due to the expected instability of II, this reaction appears to be very probable in view of the above-mentioned electrophilicity of the carbene. The conversion of the hypothetical intermediate II to the terminal olefin may be either visualized as a one-step process involving loss of lithium chloride with a concerted hydrogen migration, or, may be thought to proceed through alkylcarbene III as a true intermediate. Experiments enabling one to decide between these alternatives are of interest in connection with a similar elimination, the rearrangement of 2,2-diarylvinylhalides with butyllithium resulting in the formation of diarylacetylenes. It has been demonstrated that in these cases of α-elimination from sp^2-hybridized carbon atoms the carbene is bypassed and migration occurs concerted with elimination.[8]

Recently, it has been shown that alkylcarbenes, generated through base-catalyzed pyrolysis of tosylhydrazones in aprotic solvents, rearrange to olefins *via* hydrogen or alkyl migration, respectively. In addition, varying amounts of cyclopropanes are always formed by an intramolecular insertion of the carbenoid carbon into the γ-carbon–hydrogen bond.[9] Since this latter mode of stabilization is probably restricted to high-energy species, namely *free* alkylcarbenes, it was felt that a careful

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[1] Part III, G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **83**, 599 (1961).

[2] Presented in part at the 138th Meeting of the American Chemical Society, New York, N. Y., September, 1960.

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

[4] G. L. Closs and G. M. Schwartz, *ibid.*, **82**, 5729 (1960).

[5] A similar reaction is the addition of dihalocarbenes to alkoxide as described by P. S. Skell and I. Starer, *ibid.*, **81**, 4117 (1959).

[6] G. L. Closs and L. E. Closs, *ibid.*, **81**, 4996 (1959).

[7] About the relatively slow reaction of alkyllithium compounds with alkyl halides see: K. Ziegler and H. Colonius, *Ann.*, **479**, 135 (1930).

[8] D. Y. Curtin and E. W. Flynn, *J. Am. Chem. Soc.*, **81**, 4714 (1959); D. Y. Curtin, E. W. Flynn and R. F. Nystrom, *ibid.*, **80**, 4599 (1958); D. Y. Curtin, E. W. Flynn, R. F. Nystrom and W. H. Richardson, *Chemistry & Industry*, 1453 (1957).

[9] L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959); **82**, 1002 (1960); J. W. Powell and M. C. Whiting, *Tetrahedron*, **7**, 305 (1959).

TABLE I

REACTIONS OF ALKYLLITHIUM COMPOUNDS WITH METHYLENE CHLORIDE

$$2RLi + CH_2Cl_2 \longrightarrow 2LiCl + RH + \text{olefins} + \text{cyclopropanes}$$

	R	Solvent	Temp., °C.	Yield,[a] %	Products,[b] %		Cyclopropane Olefin
1	*n*-Amyl-	Diethyl ether	−30	96	1-Hexene	95	0.053
					n-Propylcyclopropane	5	
2	*n*-Amyl-	*n*-Pentane	30	41	1-Hexene	94	.064
					n-Propylcyclopropane	6	
3	Cyclohexyl-[c]	*n*-Pentane	30	37	Methylenecyclohexane	63	.59
					Bicyclo(4.1.0)heptane	37	
4	*s*-Butyl-	*n*-Heptane	25	42	2-Methyl-1-butene	59	.69
					Ethylcyclopropane	22	
					trans-Dimethylcyclopropane	17	
					cis-Dimethylcyclopropane	2	
5	*t*-Butyl-	*n*-Heptane	30	29	2-Methyl-1-butene	18	2.2
					2-Methyl-2-butene	13	
					1,1-Dimethylcyclopropane	69	

[a] Yields are based on two moles of alkyllithium compound. [b] Only products with composition RCH are listed. [c] One run, which was worked up under acidic conditions, gave 2% of 1-methylcyclohexene, probably due to isomerization of methylenecyclohexane (see ref. 2).

product analysis and extention of the reaction to secondary and tertiary alkyllithium compounds might provide evidence for or against the intermediacy of alkylcarbenes in the reaction under study.

The results of this investigation are summarized in Table I. The crude reaction mixtures were analyzed quantitatively by vapor phase chromatography (v.p.c.). Products were identified by v.p.c. retention times and, after separation by either fractional distillation or collection of the v.p.c. fractions, through comparison of their infrared spectra with those of authentic samples.

The reaction of the primary alkyllithium compound, *n*-amyllithium,[10] with methylene chloride in ether at −30° produced an almost quantitative yield of C_6-hydrocarbons consisting of 95% 1-hexene and 5% *n*-propylcyclopropane. Since secondary and tertiary alkyllithium compounds are known to be unstable in diethyl ether,[11] reactions of the latter compounds had to be conducted in hydrocarbon solvents. To obtain comparable results throughout the series the reaction of amyllithium with methylene chloride was repeated using pentane as a solvent. No significant change in the ratio of olefin to cyclopropane was noted; however, the total yield of C_6-compounds was considerably reduced. Also, the temperature had to be raised to 30° to obtain a smooth reaction rate. The reduced velocity is undoubtedly due to the retarded rate of the lithium–hydrogen interchange on methylene chloride, the first step in the chlorocarbene formation.[3] It is well established that metalation reactions are strongly accelerated by polar solvents.[12] The reduction in total yield must be attributed to side reactions such as coupling of methylene chloride with the lithium compound since a considerable amount of 1-chlorohexane was also formed.

As to be expected from statistical considerations' the relative yields of cyclopropanes increase with a higher degree of substitution of the α-carbon of the lithium compound. The availability of only one β-hydrogen and the larger number of γ-carbon–hydrogen bonds favors intramolecular insertion of the hypothetical intermediates derived from cyclohexyl and *sec*-butyllithium, respectively. Finally, *t*-butyllithium reacts with methylene chloride to give predominantly the insertion product, 1,1-dimethylcyclopropane. Carbon skeleton rearrangements, which do not occur to any detectable extent in the reactions of the secondary lithium compounds, lead to 2-methyl-2-butene and 2-methyl-1-butene as minor products.

TABLE II

CARBENOID DECOMPOSITION OF ALDEHYDE TOSYLHYDRAZONES

$$RCH{=}NNHTs + CH_3ONa \longrightarrow R\ddot{C}H + N_2 + NaTs + CH_3OH$$

$$R\ddot{C}H \longrightarrow \text{olefins} + \text{cyclopropanes}$$

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	R	Temp., °C.	Products, %		Cyclopropanes Olefins
1[a]	*n*-Propyl-	180	1-Butene	92	0.048
			trans-2-Butene	2.3	
			cis-2-Butene	1.2	
			Methylcyclopropane	4.6	
2[a]	*i*-Propyl-	180	2-Methylpropene	61	.64
			Methylcyclopropane	39	
3	*s*-Butyl-	160	2-Methyl-1-butene	63	.59
			Ethylcyclopropane	20	
			trans-Dimethylcyclopropane	12	
			cis-Dimethylcyclopropane	5	
4[a]	*t*-Butyl-	180	2-Methyl-2-butene	7	11.5
			2-Methyl-1-butene	1	
			1,1-Dimethylcyclopropane	92	

[a] Data are taken from Friedman and Shechter, ref. 9.

The fact that cyclopropanes are formed in the reactions of alkyllithium compounds with methylene chloride indicates the intermediacy of alkylcarbenes. This conclusion is strongly supported by a comparison of the product distributions found in these reactions with those obtained from the car-

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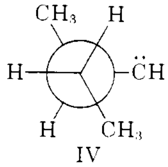
[10] *n*-Amyllithium was chosen for the quantitative experiment because the products resulting from its reaction were easier to separate from the solvent than those obtained from the previously studied *n*-butyllithium.

[11] H. Gilman, A. H. Haubein and H. Hartzfeld, *J. Org. Chem.*, **19**, 1034 (1954).

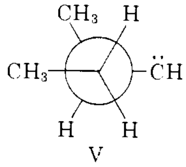
[12] H. Gilman, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., Vol. VIII, p. 258.

benoid pyrolysis of tosylhydrazones of suitable aldehydes (Table II). In both reactions hydrogen migration is the most likely mode of stabilization followed by intramolecular insertion. The slowest process, carbon skeleton rearrangement, can only be observed when hydrogen migration is impossible for structural reasons. Considering that the two reactions are carried out at temperatures differing by 150° the agreement of the product ratios is remarkably good for those cases in which primary (1 and 2, Table I *versus* 1, Table II) and secondary (3 and 4, Table I *versus* 2 and 3, Table II) alkylcarbenes are assumed to be intermediates. A much less favorable comparison is obtained between the two reactions which should proceed through *t*-butylcarbene (5, Table I *versus* 4, Table II). Here, the tosylhydrazone method produces considerably less olefins than the reaction of *t*-butyllithium with methylene chloride. Particularly, the formation of relatively large amounts of 2-methyl-1-butene cannot be explained by a carbene mechanism. It is suggested that the latter product arises from a rearrangement of either 1,1-dimethylcyclopropane or 2-methyl-2-butene, although no evidence can be cited supporting this speculation.

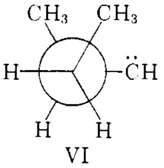
Of particular interest is the reaction of *sec*-butyllithium with methylene chloride. The resulting *sec*-butylcarbene can form stable products by either hydrogen migration, or, by three different modes of γ-insertions which lead to ethylcyclopropane and *cis*- and *trans*-dimethylcyclopropane, respectively. Again, 2-methyl-1-butene, formed by hydrogen migration, is the major product. Furthermore, it is found that insertion into the methyl group yielding ethylcyclopropane is only slightly favored over attack on the methylene group. However, there is a significant difference in the yields of *cis*- and *trans*-dimethylcyclopropane. The predominance of the latter can be attributed to conformational factors. If one assumes that the steric requirements of the divalent carbon atom are less than those of a methyl group, structures IV, V and VI will represent the conformations of *sec*-butylcarbene in sequence of increasing energy.



IV



V



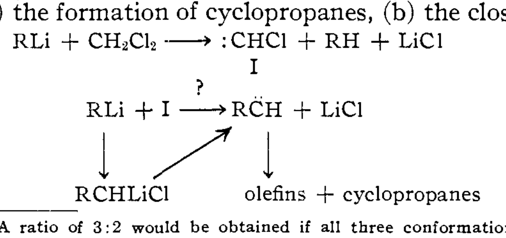
VI

Conformation IV can only give *trans*-dimethylcyclopropane, whereas V may be a precursor for *trans* and *cis* product as well. However, the transition state derived from V leading to *trans*-dimethylcyclopropane will be more favored because of lessening of non-bonded interactions between the methyl groups, while the formation of the *cis* product causes an increase of these repulsions. Conformation VI yields only *cis*-dimethylcyclopropane, but, due to unfavorable energetics, its relative concentration is probably insignificant. All three conformations are equally suited to give the methyl insertion product.

Whether or not insertion into the secondary carbon-hydrogen bond is favored intrinsically is difficult to assess since the above-mentioned conformational effects prevent statistical corrections to be applied rigorously. Nevertheless, there appears to be a slight preference for reaction with the methylene group because the product ratio of ethylcyclopropane to dimethylcyclopropanes should be greater, or at least equal to, 3:2 if attack on both groups would occur without discrimination.[13] Methylene, the most reactive carbene, is known to insert into primary and secondary carbon-hydrogen bonds with equal rate.[14] Alkylcarbenes should be somewhat less reactive species because the electron-deficient carbon atom is stabilized by inductive and hyperconjugative effects of the alkyl group. The finding of some preference for insertion into secondary carbon-hydrogen bonds of alkyl substituted methylenes is therefore in line with expectations.[15]

When *sec*-butylcarbene was generated by base-catalyzed decomposition of the tosylhydrazone of 2-methylbutyraldehyde at 160°, a very similar product distribution was found. The only significant difference is the larger *cis*→*trans* ratio of dimethylcyclopropane. This observation is readily understood by considering the effect of a temperature raise of 130° on the conformational equilibrium IV-VI. Particularly, the increased relative concentration of conformation VI will be responsible for an enhancement of the formation of the *cis* product.

The conclusions derived from this study can be summarized by stating that the reaction of alkyllithium compounds with methylene chloride appears to proceed *via* the primary formation of chlorocarbene (I) followed by combination of the latter with the lithium compound to give alkylcarbenes. It cannot be decided whether this second reaction is a one-step displacement of chloride ion from chlorocarbene or whether it is better formulated as addition-elimination reaction in which alkyl chloromethyllithium is an intermediate. The authors favor the second alternative (sequence 2) since certain α-chlorocarbanions have been shown to have a finite lifetime.[16] However, the intermediacy of free alkylcarbenes is strongly indicated by (a) the formation of cyclopropanes, (b) the close



$$RLi + CH_2Cl_2 \longrightarrow \underset{\text{I}}{:CHCl} + RH + LiCl$$

$$\begin{tikzcd} RLi + I \arrow[r, "?"] \arrow[d] & R\ddot{C}H + LiCl \arrow[d] \\ RCHLiCl \arrow[ur] & \text{olefins} + \text{cyclopropanes} \end{tikzcd}$$

(2)

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[13] A ratio of 3:2 would be obtained if all three conformations were of equal energy and if formation of *cis*- and *trans*-dimethylcyclopropane from V would require the same activation energy. Factors favoring a larger ratio are (a) predominance of IV in the conformational equilibrium and (b) the additional activation energy required to transform V into *cis*-dimethylcyclopropane due to interactions of the methyl groups in the transition state.

[14] W. v. E. Doering, R. G. Buttery, R. G. Laughlin and N. Chaudhuri, *J. Am. Chem. Soc.*, **78**, 3224 (1956); W. v. E. Doering and H. Prinzbach, *Tetrahedron*, **6**, 24 (1959).

[15] W. v. E. Doering and W. Kirmse, *ibid.*, **11**, 272 (1960), reported the formation of *trans*-dimethylcyclopropane and ethylcyclopropane in the reaction of 1-chloro-2-methylbutane with sodium at 150° in a 23.5:16.5 ratio. The authors demonstrated that *sec*-butylcarbene is the precursor of the cyclopropanes.

[16] C. R. Hauser, W. R. Brasen, P. S. Skell, S. W. Kantor and A. E. Brodhag, *J. Am. Chem. Soc.*, **78**, 1653 (1956).

correspondence of product ratios with those obtained from the base-catalyzed decomposition of tosylhydrazones in which identical or similar carbenes are intermediates and (c) the relatively small discriminating ability of the intermediate as demonstrated by the competitative insertion into primary and secondary carbon–hydrogen bonds.[17]

Experimental

General.—All reactions were carried out under an atmosphere of dry argon. Separations by distillation were carried out over a 2-ft. column packed with Heli-Pak 3180, Tantalum, by Podbielniak. Boiling points are uncorrected. Vapor phase chromatograms were carried out with a Fisher–Gulf partitioner, equipped with automatic integrator. Separations were effected on a 12-ft. column charged with 30% tricresyl phosphate on firebrick. Quantitative analyses of the reaction mixtures were obtained by calibrating the sensitivity of the detector with known mixtures of the compounds to be analyzed. Peak areas, as determined by the integrator, were used as measures of concentrations. Trapping of the v.p.c. fractions for further identification was carried out by the usual U-tube method using 0.05-ml. samples on the analytical column. When necessary, several such runs were combined to obtain a sufficiently large sample for infrared analysis. The infrared spectra were determined either as neat liquids or in carbon tetrachloride solutions with a Perkin–Elmer model 21 spectrophotometer.

Reaction of *n*-Butyllithium with Methylene Chloride in Diethyl Ether.—Methylene chloride (5.0 g., 0.06 mole) in ether (20 ml.) was added to a solution of *n*-butyllithium (0.1 mole) in ether (75 ml.) at −30° within 1 hour. Immediate precipitation of lithium chloride was noticed upon addition. The reaction mixture was allowed to warm to room temperature and the volatile components were distilled into a cooled receiver. 1-Pentene was identified as its dibromide by adding bromine (8.0 g., 0.05 mole) at −30° to the distillate. The solution was washed with sodium bicarbonate, dried, and the solvent was distilled off. The residue was distilled once over a short Vigreux column at reduced pressure. 1,2-Dibromopentane (9.44 g., 0.041 mole, 82%) was collected at 91–91.5° (41 mm.), $n^{20}\text{D}$ 1.5072. The infrared spectrum was found to be identical with the spectrum of a sample prepared from authentic 1-pentene.

Reaction of *n*-Amyllithium with Methylene Chloride. (a) In Diethyl Ether.—Methylene chloride (25 g., 0.30 mole) was added to a well stirred solution of *n*-amyllithium (0.50 mole) in diethyl ether (320 ml.) at −30° over a period of 1 hour. The reaction mixture was washed with water and analyzed by v.p.c.. 1-Hexene (ret. time at 55°, 50 ml. helium/min., 5.85 min.) and *n*-propylcyclopropane (ret. time, 6.60 min.) was present in a 95:5 ratio.

For further identification the mixture was fractionally distilled. The C_6-hydrocarbons (22.2 g.) were collected at 62–70° and were determined by v.p.c. to be 91% pure (96%). After three additional distillations pure 1-hexene (b.p. 63.5°) and 83% pure *n*-propylcyclopropane (b.p. 68–68.5°) were obtained. The final purification of *n*-propylcyclopropane was accomplished by v.p.c. The infrared spectra of both compounds were identical with those of authentic samples (for a convenient preparation of *n*-propylcyclopropane, see ref. 3).

(b) In Pentane.—Methylene chloride (25 g., 0.30 mole) was added to a solution of *n*-amyllithium (0.50 mole), prepared from 1-chloropentane (64 g., 0.60 mole) and lithium wire (10 g., 1.4 g. atoms) in pentane (300 ml.), over a period of 65 min. at 30°. The reaction mixture was washed with water and analyzed by v.p.c. 1-Hexene and *n*-propylcyclopropane were found to be present in a 94:6 ratio. Fractional distillation of the reaction mixture yielded a mixture of 1-hexene and *n*-propylcyclopropane (11.8 g.) boiling between 60 and 71° which was found to be 73% pure by v.p.c. (41%). 1-Chlorohexane (8.1 g., 0.067 mole, 13.5%) was collected at 132–134°.

Reaction of Cyclohexyllithium with Methylene Chloride.—Cyclohexyllithium was prepared from cyclohexyl chloride (120 g., 1.0 mole) and lithium dispersion (containing 20 g. lithium by titration of aliquot) in pentane (1000 ml.). Titration of the resulting solution established the yield (48%). The solution was decanted from the excess lithium dispersion and lithium chloride and treated with methylene chloride (34 g., 0.4 mole) over a period of 1 hour at 30°. After the modestly exothermic reaction had subsided the mixture was washed with water and analyzed by v.p.c. Identified by retention times were the following compounds: Cyclohexane (ret. time at 65°, 80 ml. helium/min., 7.1 min.), cyclohexene (ret. time, 10.2 min.; shown to be present in cyclohexyllithium solution in same concentration by hydrolysis of aliquot and v.p.c. analysis), methylene cyclohexane (ret. time, 16.3 min.) and bicyclo[4.1.0]-heptane (ret. time, 28.3 min.). The latter two compounds were present in a 63:37 ratio.

For further identification the reaction mixture was fractionally distilled. First, the C_7-hydrocarbons were collected between 98 and 120° (10.4 g.). This fraction was analyzed by v.p.c. and shown to contain 82% of a mixture of methylene cyclohexane and bicyclo[4.1.0]heptane, corresponding to a 37% yield of C_7-hydrocarbons. Further fractionation of this mixture yielded pure methylenecyclohexane (b.p. 102–103°). The final purification of bicyclo[4.1.0]heptane was carried out by v.p.c. The infrared spectra of both compounds were found to be identical with those obtained from authentic samples.[3,18]

Other compounds isolated by fractionation of the reaction mixture and identified by their infrared spectra include: chlorocyclohexane (142–144°) and chloromethylcyclohexane (164–166°).

Reaction of *sec*-Butyllithium with Methylene Chloride.—*sec*-Butyllithium was prepared from *sec*-butyl chloride (14 g., 0.15 mole) and lithium dispersion (containing 3.5 g., 0.5 g.-atom lithium) in 100 ml. heptane at 35–38°. After decanting the solution from the excess lithium and salts the yield was established by titration of an aliquot (0.085 mole in 70 ml., 57%). To this solution was added methylene chloride (5.0 g., 0.06 mole) at 25°. A Dry Ice condenser prevented the escape of low-boiling compounds. After addition was complete (90 min.) the reaction mixture was washed with ice-water and analyzed by v.p.c. In addition to butane, small amounts of 1-butene and *cis*- and *trans*-butene-2 (were shown to be present in the *sec*-butyllithium solution). The following compounds were identified by their retention times: *trans*-dimethylcyclopropane (ret. time at 26°, 35 ml. helium/min., 12.80 min.), 2-methyl-1-butene (ret. time, 14.56 min.), ethylcyclopropane (ret. time, 17.88 min.)and *cis*-dimethylcyclopropane (ret. time, 18.66 min.). The relative concentrations were found to be 17:59:22:2. *cis*-Dimethylcyclopropane was separated only incompletely and appeared as a shoulder on the peak of ethylcyclopropane. The concentration of this compound was determined by comparison of the envelop of the curve with those of synthetic mixtures of *cis*-dimethylcyclopropane and ethylcyclopropane. All compounds were further identified by their infrared spectra after separation had been achieved by v.p.c., with the exception of *cis*-dimethylcyclopropane which was enriched to only 35% by v.p.c. An infrared spectrum of this mixture showed all the absorption peaks of *cis*-dimethylcyclopropane.[19]

Reaction of *t*-Butyllithium with Methylene Chloride—*t*-Butyllithium was prepared from highly purified *t*-butyl chloride (92 g., 1.0 mole) and lithium dispersion (containing 20 g., 2.9 g.-atoms of lithium) in heptane (500 ml.) at 35–40°. After decanting from excess lithium and salts the solution was assayed by titration (0.47 mole, 47%). Methylene chloride (34 g., 0.4 mole) was added over a period of 1 hour at 30°. A Dry Ice condenser prevented the escape of low boiling compounds. The reaction mixture was then washed with ice-water and analyzed by v.p.c. The following compounds were identified by their retention times: Isobutane (ret. time at 28°, 60 ml. helium/min., 2.8 min.), isobutylene (ret. time, 4.4 min.; shown to be present in *t*-butyllithium solution in same concentration), 1,1-di-

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(17) Recently, a number of reactions have been demonstrated to proceed through alkylcarbenes, *e.g.*, W. Kirmse and W. v. E. Doering, *Tetrahedron*, **11**, 266 (1960); L. Friedman and J. G. Berger, *J. Am. Chem. Soc.*, **83**, 492, 500 (1961); P. S. Skell and A. P. Krapcho, *ibid.*, **83**, 754 (1961).

(18) G. Wittig and U. Schöllkopf, *Ber.*, **87**, 1318 (1954).

(19) All three cyclopropanes were prepared for comparison from the corresponding chlorocyclopropanes by reduction with sodium and methanol in tetrahydrofuran as described in ref. 3.

methylcyclopropane (ret. time, 7.8 min.), 2-methyl-1-butene (ret. time, 11.6 min.) and 2-methyl-2-butene (ret. time, 14.6 min.). The latter three compounds were present in ratios of 69:18:13.

For further identification the reaction mixture was fractionated. After three distillations 1,1-dimethylcyclopropane was obtained 94% pure (b.p. 20–20.5°) and showed an infrared spectrum identical to that of an authentic sample (prepared from 1-chloro-2,2-dimethylcyclopropane by reduction with sodium and methanol in tetrahydrofuran[8]. The two methylbutenes could not be separated by distillation and were trapped from the vapor phase chromatogram. Identification was achieved by their infrared spectra. The total yield of C_5-hydrocarbons was determined by v.p.c. of the various distillation fractions to be 29%.

2-Methylbutan *p*-Toluenesulfonylhydrazone.—To a solution of 2-methylbutanal[20] (5.0 g., 0.058 mole) in methanol (20 ml.) was added a solution of *p*-toluenesulfonylhydrazide (16.5 g., 0.058 mole) in 60° methanol (40 ml.). The mixture was cooled at once with an ice-bath and the product was allowed to crystallize at −20° for 2 hours. The precipitate was filtered off and washed with cold (−20°) methanol and dried *in vacuo* (9.2 g., 45%). A sample, recrystallized from methanol for analysis, melted at 73–74°.

Anal. Calcd. for $C_{12}H_{18}N_2O_2S$ (354.8): C, 40.62; H, 5.11. Found: C, 40.36; H, 5.26.

Decomposition of 2-Methylbutanal *p*-Toluenesulfonylhydrazone with Sodium Methoxide.—A three-neck flask was equipped with stirrer, dropping funnel, thermometer and a 1-ft. uninsulated Vigreux column which was connected with a receiving flask cooled to −70°. Sodium methoxide (2.7 g., 0.05 mole) was suspended in diethylene glycol dimethyl ether (50 ml.). The mixture was heated to 160° and a solution of 2-methylbutanal *p*-toluenesulfonylhydrazone (8.0 g., 0.022 mole) in diethylene glycol dimethyl ether (75 ml.) was added dropwise. The heating of the mixture was regulated so as to permit the olefins, cyclopropanes and the methanol to distill into the receiving flask. After addition was complete (70 min.) the apparatus was flushed with nitrogen for 10 min. to drive all the volatile products into the receiver. To the contents of the receiver heptane (20 ml.) was added and the mixture was washed with ice-water to remove the methanol; v.p.c. analysis established the composition. The following compounds were identified by their retention times: *trans*-dimethylcyclopropane (ret. time at 24°, 35 ml. helium/min., 14.08 min.) 2-methyl-1-butene (ret. time, 16.02 min.) ethylcyclopropane (ret. time, 19.65 min.) and *cis*-dimethylcyclopropane (ret. time, 20.52 min.). The compounds were present in concentration ratios of 12:63:20:5. The peak of *cis*-dimethylcyclopropane was separated only incompletely from ethylcyclopropane. The concentration ratio of these compounds was determined by comparison of the shape of the curve with those of synthetic mixtures of the two cyclopropanes. All compounds were further identified by their infrared spectra after trapping the fractions from the vapor phase chromatogram.

Distillation of the product mixture over a short Vigreux column separated the C_5-hydrocarbons from higher boiling (mainly small amounts of diethylene glycol dimethyl ether). The fraction distilling from 30 to 40° (1.25 g., 0.18 mole, 82%) was collected and consisted entirely of the above-mentioned C_5H_{10} hydrocarbons.

Stability of *n*-Butyllithium in the Presence of 1-Chloropentane.—To a solution of *n*-butyllithium (0.053 mole) in diethyl ether (100 ml.) at −30° was added 1-chloropentane (6.2 g., 0.058 mole). After 1 hour an aliquot was withdrawn and and the concentration of *n*-butyllithium was determined by the double titration method[21] (0.047 mole, 89%).

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The Reaction of Dichlorocarbene with 2,3-Chromene and 3,4-Chromene[1]

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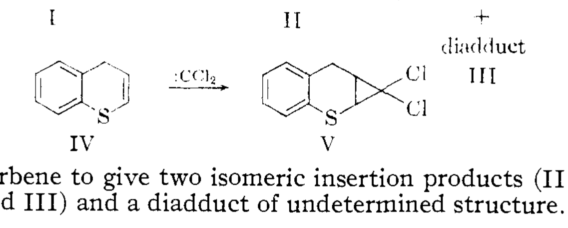
The reaction of dichlorocarbene with 2,3- and 3,4-chromene affords cyclopropyl adducts in high yield. No insertion products, as found for the analogous 2,3-thiochromene, were evident. The derived cyclopropyl adducts are thermally quite stable and unlike 2-oxa-7,7-dichloronorcarane, which readily loses hydrogen chloride to give 3-chloro-dihydroöxepine, they do not afford derivatives of benzoxepine when decomposed in the presence of hot quinoline.

A previous study[2] of the reaction of dichlorocarbene with the thiochromenes I and IV established that the course of reactions was dependent upon the position of the double bond in the olefin. Thus, 3,4-thiochromene (I) reacted with dichlorocarbene to give two isomeric insertion products (II and III) and a diadduct of undetermined structure.



However, none of the dichlorocyclopropane adduct was formed. By contrast, 2,3-thiochromene (IV) reacted with dichlorocarbene to give only a high yield of 1,1-dichlorocyclopropa(b)(1)thiobenzopyran (V). In view of these results, it was considered of particular interest to determine the course of reaction of the corresponding oxygen analogs (XIII and XVII) with dichlorocarbene.

Interest in the chromenes was also stimulated by the possibility that the derived cyclopropane adducts might serve as starting material for the preparation of chlorobenzoxepines, since it had been shown[3] that the dichlorocyclopropane adduct of dihydropyran could be readily converted to 2,3-dihydro-6-chloroöxepine by pyrolysis in quinoline at 140°. The b and c isomers of 1,1-dichlorocylopropa(1)benzopyran (VI and VII, respectively) might, therefore, be expected to form 3- and 4-chlorobenzoxepine (VIII and IX, respectively) by a similar reaction.

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