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CYCLOPROPANES FROM 1°-ALKYL CHLORIDES BY α-ELIMINATION

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Abstract—The reaction of appropriate primary alkyl chlorides with sodium or potassium gives cyclopropanes, in addition to previously observed hydrocarbons. Through the use of tritium and deuterium, it was proved that isobutyl chloride produces methylcyclopropane by a mechanism involving α-elimination to a carbene and insertion into a carbon–hydrogen bond. Isobutylene is formed by α- and β-elimination. No α-elimination (as reflected by cyclopropane production) is found with s-butyl chloride, methyl isobutyl ether or with methyl isobutyl sulfide.

1,1-DIMETHYLCYCLOPROPANE is the major product of the treatment of neopentyl chloride with sodium[1,2] or sodium alkyls.[3] This unique reaction is the more striking in that no cyclopropane derivatives are reported in the Wurtz reaction[4] or in the reaction of 1-chlorohexane with sodium ethyl.[3] Now, thanks to the higher analytical power of gas liquid partition chromatography (g.l.p.c.), cyclopropane derivatives are found to be minor products in the reaction of other primary chlorides with sodium or potassium.

Thus, the reaction of sodium in cyclohexane with n-propyl chloride gives cyclopropane (4 per cent of the C_nH_{2n} fraction) and propylene (96 per cent), in addition to propane and hexane. n-Butyl chloride, under the same conditions, gives methylcyclopropane (7 per cent), 1-butene (86 per cent), *trans*-2-butene (4 per cent) and *cis*-2-butene (3 per cent). The latter products are probably formed by the isomerization of 1-butene.[5] Isobutyl chloride yields methylcyclopropane in significantly larger amount (35 per cent of the C_4H_8 fraction). These values are to be compared with those for neopentyl chloride which gives dimethylcyclopropane exclusively as the C_5H_{10} product.[2] It is significant that isobutyl *bromide* gives only a trace of methylcyclopropane (3 per cent of the C_4H_8 fraction), while methyl isobutyl ether and methyl isobutyl sulfide react with sodium and n-propyl chloride to give isobutylene and no methylcyclopropane. While both sodium and potassium produce methylcyclopropane from isobutyl chloride, lithium gives none, a point to which we shall return later. The secondary chloride, 2-chlorobutane, gives no methylcyclopropane under any conditions, as shown in Table 1. In summary, primary chlorides with γ-hydrogen can now be expected to give varying amounts of cyclopropanes when treated with sodium or potassium or their corresponding alkyl derivatives.

The mechanism of the production of the cyclopropanes has been formulated as a γ-elimination by Whitmore. His first proposal, involving homolytic elimination by way of an α,γ-diradical, was followed by an ionic elimination involving removal of a γ-proton by sodium alkyl and an intramolecular ring closure of the displacement

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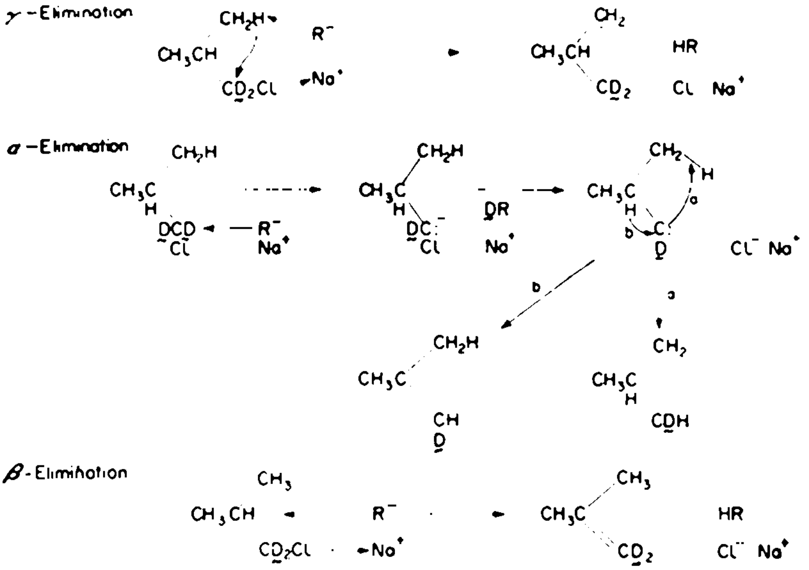
[1] F. C. Whitmore, A. H. Popkin and J. R. Pfister, *J. Amer. Chem. Soc.* **61**, 1616 (1939).

[2] F. C. Whitmore, A. H. Popkin, H. I. Bernstein and J. P. Wilkins, *J. Amer. Chem. Soc.* **63**, 124 (1941).

[3] F. C. Whitmore and H. D. Zook, *J. Amer. Chem. Soc.* **64**, 1783 (1942).

[4] Cf. W. Hückel, A. Krämer and F. Thiele, *J. Prakt. Chem.* **142**, 207 (1935).

[5] W. O. Haag and H. Pines, *J. Amer. Chem. Soc.* **82**, 387 (1960).



type. Since removal of protons by sodium alkyl from hydrocarbons is an unknown reaction,[6] one would consider a concerted version of proton removal and displacement as energetically more attractive.

TABLE 1. C_4H_8 PRODUCTS FROM 2-CHLOROBUTANE AND ALKALI METALS

	Li	Na	K
1-Butene	66	68	60
trnas-Butene	24	17	28
cis-Butene	10	15	12
Methylcyclopropane	—	—	—

Another mechanism involves α-elimination by abstraction of an α-proton, loss of chloride ion and intramolecular insertion of the resulting carbene into the γ-carbon hydrogen bond. The credibility of the first step is not demonstrated by directly analogous reactions, but rather by extrapolations from related reactions. Removal of α-proton is very easy with chloroform where three chlorine atoms stabilize the resulting carbanion;[7] in methylene chloride with only two chlorine atoms to stabilize the resulting carbanion, the proton can still be removed, albeit only by the action of the stronger bases of the alkyl lithium type;[8] in alkyl chlorides, even stronger bases would be required, since the resulting carbanion would now be stabilized by only a single chlorine atom. Indeed, Hill *et al.* find some α-elimination in the conversion of n-octyl bromide to octene-1 with sodium amide in liquid ammonia and employ α-elimination with terminal step b (Chart 1) as explanation.[9] The second step, the loss of chloride

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[6] See, however, A. I. Shatenshtein, L. N. Vasil'eva, N. M. Dykhno and E. A. Izraelevich, *Dokl. Akad. Nauk SSSR.* **85**, 381 (1952).

[7] J. Horiuti and Y. Sakamoto, *Bull. Chem. Soc. Japan* **11**, 627 (1936).

[8] G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.* **81**, 4996 (1959).

[9] D. G. Hill, W. A. Judge, P. S. Skell, S. W. Kantor and C. R. Hauser, *J. Amer. Chem. Soc.* **74**, 5599 (1952); S. M. Luck, D. G. Hill, A. T. Stewart, Jr. and C. R. Hauser, *J. Amer. Chem. Soc.* **81**, 2784 (1959). See also U. Schöllkopf and M. Eistert, *Agnew. Chem.* **72**, 349 (1960).

ion, is exemplified by the intermediacy of dichlorocarbene[10] and chlorocarbene.[8] The third step, the insertion of the alkylcarbene into the γ-carbon-hydrogen bond, is the typical reaction of carbenes, more commonly observed, however, as the intermolecular[11] rather than the intramolecular reaction.[12–15]

To define the mechanism, the fate of deuterium in the reaction of 1-chloro-1,1-dideutero-2-methylpropane (the labeled isobutyl chloride of Chart 1) with sodium was determined. This mode of attack on the mechanistic problem follows that used by Hill *et al.* in their investigation of α-elimination.[9] The labeled isobutyl chloride was prepared by a two-step sequence involving reduction of ethyl isobutyrate with lithium aluminum deuteride and treatment of the resulting 1,1-dideutero-2-methylpropanol-1 with thionyl chloride. It was isolated in pure form by preparative g.l.p.c. and was found by mass spectrographic analysis to consist of $\sim$90 per cent dideuterated material. When this chloride was treated with sodium metal, monodeuterated methylcyclopropane was produced, containing less than 1 per cent of dideuterated material. Since γ-elimination would lead exclusively to dideuterated material and α-elimination followed by insertion (terminal step *a* of Chart 1) would lead exclusively to monodeuterated methylcyclopropane, only the α-elimination-insertion path is compatible with the experimental results. Quantitatively, it can be asserted confidently that less than 2 per cent of the methylcyclopropane is formed by γ-elimination.

The distribution of deuterium in the isobutylene produced along with the methylcyclopropane fixes the ratio of α- to β-elimination. Isobutylene formed by α-elimination-rearrangement (terminal step *b* of Chart 1) will retain only one deuterium atom, whereas isobutylene formed by conventional β-elimination will retain both deuterium atoms. In this experiment, α-elimination-rearrangement predominated (67 per cent) over β-elimination (33 per cent). Distribution of rearrangement and insertion within the α-elimination path cannot be determined with much assurance, because of the high probability that isobutylene reacts further with isobutyl sodium. In this connection, it has been found that the addition of cyclohexane strongly inhibits the production of isobutylene and methylcyclopropane without eliminating isobutane.

The argument for the intervention of a carbene is strengthened by noting (Table 2) how closely the product distribution in the reaction of primary chlorides with sodium parallels that observed by Friedman and Schechter in the decomposition of *p*-toluenesulfonylhydrazones of the related aldehydes.[12]

An estimation of the magnitude of the isotope effect has been obtained from experiments using tritium-labeled isobutyl chloride. The results are shown in Table 3. From the identity of the activities of the isobutane and isobutene in the lithium reaction, it is clear that no α-elimination is involved. The increased radioactivity in isobutane (and the decreased activity in isobutene) is a reflection of the extent to which α-elimination is a component of the reaction. By this criterion potassium leads to more α-elimination than sodium. On the assumptions that the ratio of the activity of methylcyclopropane to that of isobutane from the lithium reaction (taken as a measure of the activity of the isobutyl chloride) is proportional to the rate of α-elimination of

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[10] J. Hine, *J. Amer. Chem. Soc.* **72**, 2438 (1950).

[11] W. von E. Doering and H. Prinzbach, *Tetrahedron* **6**, 24 (1959).

[12] L. Friedman and H. Schechter, *J. Amer. Chem. Soc.* **81**, 5512 (1959).

[13] H. Meerwein and K. van Emster, *Ber. Dtsch. Chem. Ges.* **53**, 1815 (1920).

[14] L. Friedman and H. Schechter, *J. Amer. Chem. Soc.* **82**, 1002 (1960).

[15] J. W. Powell and M. C. Whiting, *Tetrahedron* **7**, 305 (1959).

hydrogen, and that the possibility of a difference in the ratio of β- to α-elimination in isobutyl chloride and tritium-labeled isobutyl chloride may be ignored, a simple calculation leads to $k_H/k_D = 1{\cdot}6$. A more refined calculation involving a correction for the second assumption leads to a value of 1·9. This isotope effect is surprisingly small and may be compared with a value of 15·5 for β-elimination in isopropyl bromide (calculated from the observed k_H/k_D ratio of 6·7[16] by the method of Swain *et al.*[17]).

TABLE 2. COMPARISON OF THE SODIUM-ALKYL CHLORIDE REACTION WITH THE ALKALINE DECOMPOSITION OF ALDEHYDE TOSYLHYDRAZONES[12]

Hypothetical carbenes	Products in %	RCl·Na	R = NNHTs
$CH_3CH_2\ddot{C}H$	cyclopropane	4	2
	propene	96	98
$CH_3CH_2CH_2\ddot{C}H$	methylcyclopropane	7	5
	butene-1	86	92
	cis-butene	3	1
	trans-butene	4	2
$(CH_3)_2CH\ddot{C}H$	methylcyclopropane	35	45
	isobutene	65	55
$(CH_3)_3C\ddot{C}H$	1,1-dimethyl-cyclopropane	~95[3]	~92

TABLE 3. RELATIVE RADIOACTIVITIES[a] IN PRODUCTS FROM THE REACTION OF 1-CHLORO-2-METHYLPROPANE-1-^{3}H[b]

	Li	Na	K
isobutane	1·00	1·10	1·29
isobutene	1·04	0·79	0·70
methylcyclopropane		0·64	0·63

[a] The average of the activities of isobutane from the lithium reaction are taken as 1·00. [b] All reactions were run on the same sample of labeled isobutyl chloride.

The failure of lithium to give methylcyclopropane can be ascribed either to the inability of lithium alkyl to remove α-hydrogen or to the inability of the resultant lithium chloroalkyl to lose chloride ion and to form the carbene. The reaction of lithium isopropyl with methylene chloride according to Closs[8] leads to isobutylene (79 per cent) and methylcyclopropane (21 per cent). It is apparent that lithium alkyl has added to chlorocarbene forming lithium 1-chloroisobutyl which has then lost chloride ion to form the carbene and thence methylcyclopropane. The failure of lithium in the reaction of isobutyl chloride is thus due to the inability of lithium isobutyl to remove α-hydrogen.*

EXPERIMENTAL

Reactions of alkyl chlorides with alkali metals. Reactions were carried out in a 50 ml, three-necked flask equipped with a gas inlet tube, reflux condenser and dropping funnel. The top of the reflux condenser was connected to a dry-ice trap. The alkali metals were cut into small pieces under mineral

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* *Note added in proof:* G. L. Closs, Abstracts of papers presented at the 138th Meeting of the American Chemical Society, September, 1960, p. 9P and *Chem. Enging. News* **38**, No. 38, 54 (1960), as also obtained cyclopropane derivatives in the reaction of alkly lithium with methylene chloride.

[16] V. J. Shiner, Jr., *J. Amer. Chem. Soc.* **74**, 5285 (1952).

[17] C. G. Swain, E. C. Shivers, J. F. Reuwer, Jr. and L. J. Schaad, *J. Amer. Chem. Soc.* **80**, 5885 (1958).

TABLE 4. MASS SPECTRA OF ISOBUTYL CHLORIDE

m/e	unlabeled	labeled
41	44·8	25·0
42	52·6	50·0
43	100	100
44	3·3	4·5
45	0·1	0·4
75	0·50	—
76	0·41	0·21
77	3·02	0·33
78	0·30	0·25
79	1·04	2·67
80	—	0·17
81		0·88

TABLE 5. MASS SPECTRA OF PRODUCTS FROM 1-CHLORO-2-METHYLPROPANE-1,1-^{2}H

	Methylcyclopropane		Isobutylene	
m/e	Unlabeled	Labeled[a]	Unlabeled	Labeled[a]
27	6·7	7·3		
28	20·9	19·9		
29	30·3	31·9		
30	14·2	26·3		
31		11·7		
38	3·9	3·1	6·32	5·4
39	39·0	23·0	44·9	33·5
40	6·7	22·8	10·2	33·5
41	90·0	43·1	100·0	64·6
42	3·9	82·3	3·65	100·0
43	2·8	3·3		28·1
44		0·7		1·3
50	5·5	3·5		
51	4·7	4·0		
52	1·2	2·6		
53	8·3	3·0		
54	3·5	6·3		
55	25·6	4·9	16·0	5·4
56	100·0	24·6	44·5	22·5
57	4·3	100·0	1·98	63·3
58		4·4		28·3
				1·8

[a] From the reaction described here.

oil, washed with solvent and transferred to the flask. After sweeping with nitrogen and heating to reflux, the alkyl halide with more solvent was added from the dropping funnel. A slow stream of nitrogen was passed through the mixture during the reaction. In most runs, 20 mmoles of alkali metal and alkyl halide in 10 ml cyclohexane were used. When the liquid in the dry-ice trap did not increase any more (ca. 3 hr with lithium and sodium; 0·5-1 hr with potassium) the trap was disconnected and any excess of alkali metal decomposed with methanol. Water was added and the organic layer washed several times with water. The Wurtz hydrocarbons $(C_nH_{2n-1})_2$, the only products remaining in the solvent were separated by g.l.p.c. on a 2 m OX column (Perkin-Elmer) or a 4 m silicone column.

The contents of the dry-ice trap were analyzed by g.l.p.c. at room temperature on a 1/4″, 6 m column consisting of a polyether $[CH_3(OCH_2CH_2)_4OCH_3]$ on firebrick. Samples of the liquid condensate were drawn directly into a syringe, in order to avoid fractionation. Cyclopropanes and other unknown substances were identified by their mass spectra. It has been shown that, for a wide range of hydrocarbons, peak areas represent the composition within the error of determination.[18] In a typical run, from 1·84 g isobutyl chloride (20 mmoles) and 0·46 g sodium (20 mmoles), 0·78 g (56%) volatile products were obtained, consisting of isobutane (57%), isobutene (29%) and methylcyclopropane (14%). Other results may be found in Tables 1 and 2.

1-Chloro-2-methylpropane-1,1-^{2}H. Methyl isobutyrate (6·1 g, 60 mmoles) was reduced with 1·1 g (25 mmoles) of lithium aluminum deuteride (95·6%, Metal Hydrides, Inc.) in refluxing ether (50 ml). A small excess of ester was used in order to assure complete utilization of the hydride. The crude isobutyl alcohol obtained by distillation was converted to the chloride with thionyl chloride in pyridine. Pure isobutyl chloride was isolated by g.l.p.c. at 35° in a Perkin-Elmer, 1″ preparative column packed with didecylphthalate on firebrick. From the mass spectrum in Table 4, the sample contained 90% of the d_2 compound. The peaks corresponding to the C_3 ions show the absence of deuterium quite clearly. The group of peaks of mass 75-81 corresponds to the parent minus methyl. The parent peaks themselves are too weak to be of use.

This material (1 mmole) was treated with 1 mmole sodium in 0·5 ml cyclohexane in a sealed, evacuated tube (1 hr at 80°). The volatile contents of the tube were transferred to a bypass system on a vacuum line and subjected to g.l.p.c. on the 6 m polyether column. The mass spectra of the isolated methylcyclopropane and isobutene are shown in Table 5.

1-Chloro-2-methylpropane-1-^{3}H. An ethereal solution (150 ml) of diazoisobutane was prepared from 15 g N-nitroso-isobutylurea according to the directions of Bruchhausen[19].

Tritiated hydrogen chloride, generated by dropping tritiated water (10 mC/g) on phosphorus pentachloride was swept into the cooled diazoisobutane solution by a slow stream of nitrogen. Decoloration was effected by using 0·5 ml water. The ethereal solution was dried, neutralized by shaking with 2 g anhydrous potassium carbonate for 0·5 hr, diluted with 10 ml toluene and distilled through a 20 cm helix-packed column giving fractions of b.p. 55-64° (0·7 g), 64-69° (3·6 g, 40%) and 69-90° (1·3 g). The main fraction was almost pure isobutyl chloride. Analysis by g.l.p.c. showed the main impurities to be ether and traces of olefins, which were removed by shaking with an equal volume of conc. sulfuric acid. The final product contained less than 2% of isomeric butyl chlorides.

The labelled isobutyl chloride (5 mmoles) reacted with 5 mmoles of sodium in 5 ml of refluxing cyclohexane. The volatile products were analyzed on the 6 m polyether column which was part of a g.l.p.c.-flow counter system.[20] All runs were made at the same flow rate, and relative activities were measured in counts/mm^2 peak area on the mass track. The results are shown in Table 3.

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[18] E. M. Fredericks and F. R. Brooks, *Analyt. Chem.* **28**, 297 (1956).

[19] F. v. Bruchhausen and H. Hoffmann *Ber. Dtsch. Chem. Ges.* **75**, 1593 (1941).

[20] R. Wolfgang and R. S. Rowland, *Analyt. Chem.* **30**, 903 (1958); W. von E. Doering and H. Prinzbach, *Tetrahedron* **6**, 24 (1959).