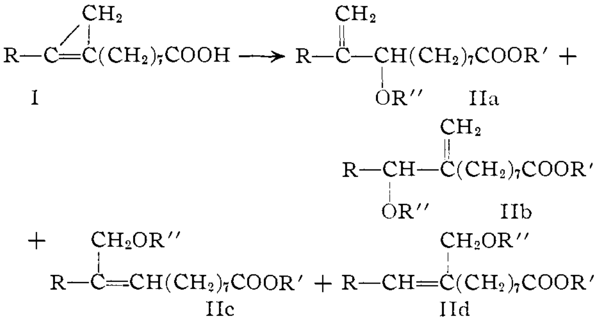

I, IIa-d, R = $CH_3(CH_2)_7$-

The polymer [*Anal.* Found: C, 77.63; H, 11.62] formed slowly at room temperature,[2,3,4b] rapidly at elevated temperature, gave no color with the Halphen reagent,[5,6] was insoluble in hot methanol. It showed no infrared absorption (CCl_4) at 1869 and 1010 cm.$^{-1}$ (cyclopropene)[3] but had bands at 1737 and 1169 cm.$^{-1}$ (ester),[7] 1712 and 960 cm.$^{-1}$ (end-group carboxyl),[7] 1648 and 901 cm.$^{-1}$ (*unsym.* disubstituted olefin).[7] The polymer was saponified to a mixture of the corresponding unsaturated hydroxy acids (IIa–d, R′ and R″ = H) [*Anal.* Found: C, 73.57; H, 11.57; N. eq., 318], infrared bands (CCl_4) at 3615 and 1281 cm.$^{-1}$ (hydroxyl),[7] 1707 and 935 cm.$^{-1}$, 1645 and 900 cm.$^{-1}$, which were acetylated to give the unsaturated acetoxy acids IIa–d (R′ = H; R″ = $COCH_3$)[8] [*Anal.* Found: C, 71.09; H, 10.91; N. eq., 354], with infrared bands (CCl_4) at 1735 and 1239 cm.$^{-1}$ (acetate),[7] 1707 and 945 cm.$^{-1}$, 1646 and 900 cm.$^{-1}$.

The unsaturated acetoxy acid mixture was oxidized by the periodate-permanganate procedure[9] to formaldehyde[10] (from IIa and IIb), determined with chromotropic acid,[9] together with the other products expected from structures IIa–d.

Pelargonic acid, m.p. 8–11°, (from IId) and azelaic acid, m.p. 105–107°, (from IIc) were identified by comparison with authentic samples, while 1-acetoxy-2-decanone, m.p. 55° [*Anal.* Found: C, 67.25; H, 10.23] (from IIc, R′ = H, R″ = $COCH_3$), was identical with a sample[11] prepared from nonanoyl chloride and diazomethane and subsequent acetolysis.[12]

The mixture of oxidation products from structures IIa and IIb (R′ = H, R″ = $COCH_3$), 9,10- and 10,9-acetoxyketoöctadecanoic acids [*Anal.* Found: C, 67.42; H, 10.42; N. eq., 352],[13] was saponified to a crude mixture of 9,10- and 10,9-hydroxyketoöctadecanoic acids,[13,14] melting 30–50°. The hydroxy keto acid mixture was further identified by chromic acid oxidation to 9,10-diketoöctadecanoic acid,[13,16] m.p. 82–83° (m.p. of authentic sample[14] 83–84°, lit.[16] m.p. 85–86°). The 2,4-dinitrophenylosazone,[15] prepared from the hydroxyketo acid mixture, had m.p. 147–147.5°, undepressed by mixture with an authentic sample, m.p. 148.5–149.5° (lit.[15] m.p. 146.5°), prepared from the oleic acid oxidation product.

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[5] G. Dijkstra and H. J. Duin, *Nature*, **176**, 71 (1955).

[6] P. K. Faure, *ibid.*, **178**, 372 (1956).

[7] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd. ed., John Wiley and Sons, Inc., New York, N. Y., 1958.

[8] This mixture (identical infrared spectrum) was prepared more simply by heating in acetic acid the acids isolated from saponification of *Sterculia foetida* seed oil, then isolating the unsaturated acetoxy acids (unadducted) by urea adduction and chromatography.

[9] R. U. Lemieux and E. von Rudloff, *Can. J. Chem.*, **33**, 1701, 1710 (1955).

[10] The yield of formaldehyde (43%) compares favorably with the 50% yield reported by Lemieux and von Rudloff[9] from the oxidation of allyl acetate under similar conditions and suggests that the major products of the polymerization-rearrangement are IIa and IIb.

[11] Prepared by D. A. Teets.

[12] The second oxidation product from structure IId (R′ = H, R″ = $COCH_3$), 10-acetoxy-9-ketodecanoic acid, has not yet been isolated from the chromatographed products.

[13] The infrared spectra of these compounds were identical with those of authentic samples prepared *via* permanganate oxidation of oleic acid.[15,16]

[14] Authentic samples prepared by D. A. Davenport.

[15] G. King, *J. Chem. Soc.*, 1788 (1936).

[16] R. T. Holman, W. O. Lundberg, W. M. Lauer and G. O. Burr, THIS JOURNAL, **67**, 1285 (1945).

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RECEIVED JULY 14, 1959

REACTIONS OF ALKYLLITHIUMS WITH POLYHALIDES

Sir:

We wish to report the reaction of alkyllithiums with polyhalogen compounds and olefins to produce cyclopropanes. Our results support the conclusion that methylenes or carbenes are formed as reaction intermediates.

In attempting the preparation of trifluoromethyllithium from trifluoromethyl iodide by halogen–metal interconversion with methyllithium at −45°, Pierce, McBee and Judd observed the formation of tetrafluoroethylene in 43% yield. No evidence for the presence of the desired trifluoromethyllithium was obtained by hydrolysis of the reaction mixture.[1] This result suggests a possible intermediate formation of difluorocarbene by decomposition of trifluoromethyllithium[2] and has led us to investigate the reactions of alkyllithiums with polyhalogen compounds.

We find that when a variety of polyhalogenated methanes[5] are treated with methyl- or *n*-butyllithium in the presence of excess cyclohexene in ether solution at from −60° to room temperature olefin–carbene addition products are formed. Immediate precipitation of lithium halide takes place and

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[1] O. R. Pierce, E. T. McBee and G. F. Judd, THIS JOURNAL, **76**, 474 (1954).

[2] This interpretation was first made in connection with unsuccessful attempts to prepare halofluoromethylzinc iodides.[3] We also note the possible formation of methylene by decomposition of iodomethylzinc iodide, although recent evidence appears to favor the direct reaction of iodomethylzinc iodide with olefins to form cyclopropanes.[4]

[3] W. T. Miller, Jr., E. Bergman and A. H. Fainberg, THIS JOURNAL, **79**, 4159 (1957).

[4] H. E. Simmons and R. D. Smith, *ibid.*, **80**, 5323 (1958); Abstracts of Papers, 120th Meeting, Amer. Chem. Soc., Boston, Mass., April, 1959, p. 51-O.

[5] Methane derivatives of the type RCX_2R' in which the R's may be organic groups as well as hydrogen or halogen are considered of possible application.

yields of norcarane derivatives ranging from eight to ninety per cent. have been isolated, Table I. Other products appear to arise primarily from reactions which involve carbon–carbon bond formation as the initial step. Our results are consistent with the type reaction sequence shown, illustrated with bromotrichloromethane which is postulated to yield dichlorocarbene.

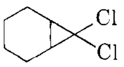
TABLE I

Reactants	Moles RLi/CX$_4$	Temp., °C.	Yield, %
CH_3Li, CCl_4	0.26	−60	8[a]
n-BuLi, CCl_4	1.0	−60	50[a]
CH_3Li, $CBrCl_3$	1.3	−60	67[a]
n-BuLi, $CBrCl_3$	1.3	−30	91[a]
CH_3Li, CCl_3I	1.5	+ 5	71[a]
n-BuLi, CBr_4	1.1	−50	11[b]
CH_3Li, CH_2Br_2	0.87	−20	14[c]

[a] Dichloronorcarane, b.p. 80.0–81.0° (15 mm.), n^{23}D 1.5012. Reported: b.p. 78–79° (15 mm.), n^{23}D 1.5014.[6] The identity of all products was also supported by infrared spectra. [b] Dibromonorcarane, b.p. 100.0–101.0° (8 mm.), n^{22}D 1.5575. Reported: b.p. 100° (8 mm.), n^{22}D 1.5578.[6] [c] Norcarane, b.p. 114.5° (uncor.), n^{25}D 1.4549. Reported: b.p. 116°, n^{25}D 1.4550.[6]

$$CBrCl_3 + n\text{-}BuLi \longrightarrow CCl_3Li + BuBr \qquad (1)$$

$$CCl_3Li \longrightarrow CCl_2 + LiCl \qquad (2)$$

$CCl_2 + C_6H_{10} \longrightarrow$  (3)

The presence of trichloromethyllithium in reaction mixtures could not be shown by hydrolysis at −60° in the absence of olefin and reactions (1) and (2) may therefore consist of a single concerted process.

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(6) W. von E. Doering and A. K. Hoffmann, THIS JOURNAL, **76**, 6162 (1954).

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RECEIVED JULY 10, 1959

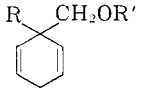
THE SOLVOLYSIS OF 1,4-DIHYDROBENZYL *p*-TOLUENESULFONATES

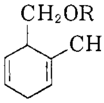
Sir:

We wish to report a convenient synthesis of cycloheptatrienes from 1,4-dihydrobenzoic acids.[1] The chemical conversion consists of (1) lithium aluminum hydride reduction of the dihydro acid to a 1,4-dihydrobenzyl alcohol, (2) preparation of the corresponding *p*-toluenesulfonate derivative and (3) solvolysis of the sulfonate in acetic acid at 90° for about 36 hours in the presence of sodium dihydrogen phosphate monohydrate.[2] The syntheses of cycloheptatriene and three of the four possible methylcycloheptatrienes are described below as illustrations of the method.

Reduction of 1,4-dihydrobenzoic acid[1b] gave 1,4-dihydrobenzyl alcohol (Ia), b.p. 95–97° (20 mm.), from which the corresponding tosylate Ib was prepared. Solvolysis of Ib gave a 70% yield of a mixture of hydrocarbons which was shown by gas chromatography[3a] to consist of 88% cycloheptatriene and 12% toluene. The products were identified by comparison of their infrared spectra with those of authentic samples.

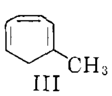
The alkylation[1a] of 1,4-dihydrobenzoic acid using potassium amide and methyl iodide in liquid ammonia afforded 1-methyl-1,4-dihydrobenzoic acid, m.p. 35–37°, which was reduced to 1-methyl-1,4-dihydrobenzyl alcohol (Ic), b.p. 105–110° (100 mm.). Conversion of the alcohol Ic to the *p*-toluenesulfonate derivative Id and solvolysis of the latter compound gave a 73% yield of hydrocarbons, b.p. 136–138°, shown by gas chromatography[3b] to consist of 48% of 1-methylcycloheptatriene (III),[4] λ_{max}^{EtOH} 269 mμ (ϵ 3,400) (*Anal.* Found for C_8H_{10}: C, 90.36; H, 9.47), 50% of 3-methylcycloheptatriene (V),[5] λ_{max}^{EtOH} 260 mμ (ϵ 3,880) (*Anal.* Found for C_8H_{10}: C, 90.50; H, 9.35) and 2% of a material which was not identified.



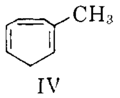


Ia, R = R′ = H
b, R = H; R′ = $SO_2C_6H_4CH_3$
c, R = CH_3; R′ = H
d, R = CH_3; R′ = $SO_2C_6H_4CH_3$

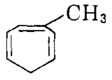
IIa, R = H
b, R = $SO_2C_6H_4CH_3$



III



IV



V

In a similar series of reactions, 1,4-dihydro-*o*-toluic acid[1a] was reduced to 1,4-dihydro-2-methylbenzyl alcohol (IIa), b.p. 109° (26 mm.), which was converted to the *p*-toluenesulfonate derivative IIb, m.p. 42–43°. Solvolysis of IIb gave 73% of a mixture of hydrocarbons shown by gas chromatography[3b] to consist of 54% of 1-methylcycloheptatriene (III), 31% of 2-methylcycloheptatriene (IV), λ_{max}^{EtOH} 258 mμ (ϵ 2,600) (*Anal.* Found for C_8H_{10}: C, 90.46; H, 9.46), 7% of 3-methylcycloheptatriene (V) and 8% *o*-xylene. A mechanistic interpretation for this solvolysis leads one to predict the formation of 2-methylcycloheptatriene in higher yield and no formation of 3-methylcycloheptatriene. This ambiguity was resolved when it was found that 2-methylcycloheptatriene was converted in part to the other two methylcycloheptatrienes (III and V) under the conditions of the solvolysis.

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(1) (a) A. J. Birch, *J. Chem. Soc.*, 1551 (1950); (b) H. Plieninger and G. Ege, *Angew. Chemie*, **70**, 505 (1958).

(2) *Cf.* H. L. Dryden, Jr., THIS JOURNAL, **77**, 5633 (1955).

(3) Using a column at 70° containing 30% by weight of (a) a solution of silver nitrate (30–40% by weight) in polyethylene glycol or (b) 3-methyl-3-nitropimelonitrile on 48–80 mesh firebrick support.

(4) The structure of III is based on its unique proton resonance spectrum.

(5) The proton resonance spectrum of this material is consistent for either IV or V; however, a consideration of the mechanism of the rearrangement leads to the assignment of structure V for the product.