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.

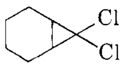
TABLE I

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

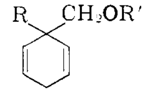
THE SOLVOLYSIS OF 1,4-DIHYDROBENZYL *p*-TOLUENESULFONATES

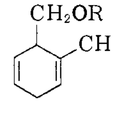
Sir:

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.

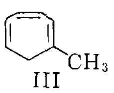
The alkylation[1a] of 1,4-dihydrobenzoic acid using potassium amide and methyl iodide in liquid ammonia afforded 1-methyl-1,4-dihydrobenzoic acid, m.p. 35–37°, which was reduced to 1-methyl-1,4-dihydrobenzyl alcohol (Ic), b.p. 105–110° (100 mm.). Conversion of the alcohol Ic to the *p*-toluenesulfonate 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^{EtOH}_{max} 269 mμ (ε 3,400) (*Anal.* Found for C_8H_{10}: C, 90.36; H, 9.47), 50% of 3-methylcycloheptatriene (V),[5] λ^{EtOH}_{max} 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.



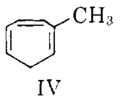


Ia, R = R′ = H
b, R = H; R′ = $SO_2C_6H_4CH_3$
c, R = CH_3; R′ = H
d, R = CH_3; R′ = $SO_2C_6H_4CH_3$

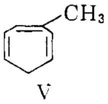
IIa, R = H
b, R = $SO_2C_6H_4CH_3$



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^{EtOH}_{max} 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.

We gratefully acknowledge support of this research in part from a Frederick Gardner Cottrell grant of the Research Corporation.

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RECEIVED AUGUST 6, 1959

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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.