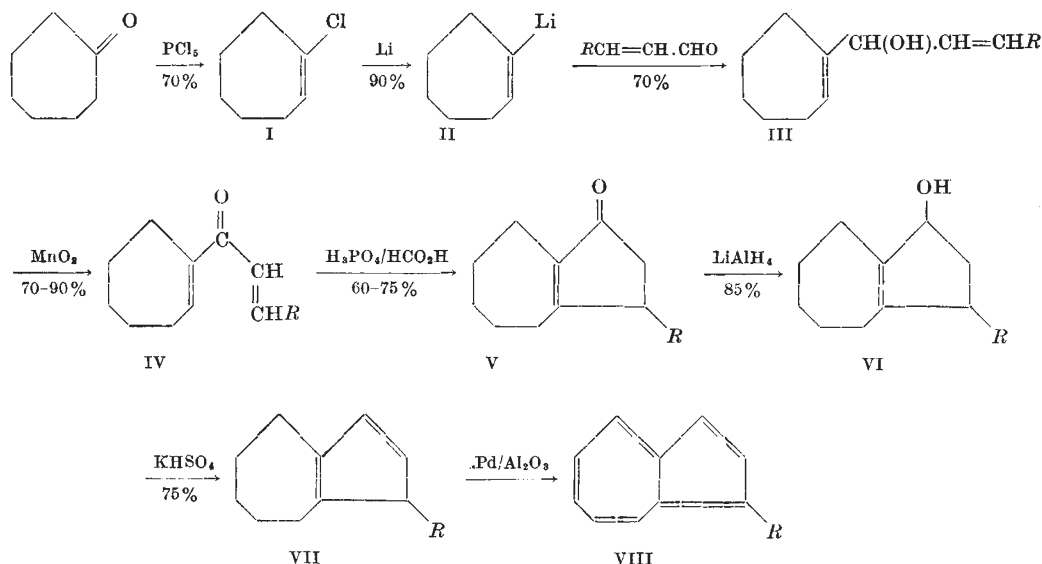


### A New Route to Azulenes

ALTHOUGH several syntheses of azulene (VIII;  $R=H$ ) and azulene derivatives have been described<sup>1</sup>, investigations on the chemistry of this non-benzenoid aromatic system have been hampered by the fact that the procedures hitherto available do not readily lend themselves to the preparation of azulenes on more than a relatively small scale. We have recently developed a new synthesis, based on the method of

$C_{11}H_{10}O$  requires C, 79.5; H, 10.8 per cent), 3:5-dinitrobenzoate (m.p. 87°). Dehydration of the alcohols (VI) by distillation from potassium bisulphate and dehydrogenation of the resulting dienes (VII) with a palladium-alumina catalyst<sup>9</sup> afforded azulene (VIII,  $R=H$ ) and 1-methylazulene (VIII,  $R=Me$ ). The latter gave an *s*-trinitrobenzene adduct (m.p. 155°, undepressed on admixture with an authentic specimen kindly provided by Prof. Pl. A. Plattner<sup>7</sup>).



alkenylation with lithium alkenyls<sup>2</sup>, which offers some advantages in this respect.

The new synthesis is illustrated here for azulene itself and for 1-methylazulene. 1-Chlorocycloheptene (I), prepared by treating cycloheptanone with phosphorus pentachloride<sup>3</sup>, is readily converted into 1-cycloheptenyl lithium (II) by reaction with lithium metal in ether suspension<sup>4</sup>. The lithium alkenyl undergoes the usual addition reaction with acrolein or crotonaldehyde, to give the dialkenylcarbinols (III;  $R=H$  or Me)<sup>4</sup>. Oxidation of the latter with manganese dioxide in petrol suspension<sup>5</sup> affords the dialkenyl ketones (IV;  $R=H$ ) (b.p. 61°/0.5 mm.,  $n_D^{21}$  1.5138; found: C, 80.4; H, 9.7;  $C_{10}H_{14}O$  requires C, 80.0; H, 9.4 per cent), 2:4-dinitrophenylhydrazone (m.p. 198°), and (IV,  $R=Me$ ) (b.p. 84°/0.4 mm.,  $n_D^{25}$  1.5166; found: C, 80.6; H, 10.1;  $C_{11}H_{16}O$  requires C, 80.4; H, 9.8 per cent), 2:4-dinitrophenylhydrazone ( $\alpha$ -form, m.p. 118°;  $\beta$ -form, m.p. 129°). Treatment of the ketones (IV) with a mixture of phosphoric and formic acids<sup>6</sup> at 90° resulted in smooth cyclization to the octahydroketoazulenes (V,  $R=H$ ),  $\lambda_{max}$  2410 ( $\epsilon$  12,300) and 2910 Å. ( $\epsilon$  85) in ethanol; semicarbazone, m.p. 238° (reported<sup>7,8</sup> m.p. 238° and 235–236°) and (V,  $R=Me$ ) (b.p. 77°/0.4 mm.;  $n_D^{23}$  1.5118;  $\lambda_{max}$  2440 ( $\epsilon$  9200) and 3000 Å. ( $\epsilon$  65) in ethanol; found: C, 80.4; H, 9.8;  $C_{11}H_{16}O$  requires C, 80.4; H, 9.8 per cent), 2:4-dinitrophenylhydrazone (m.p. 236°). Reduction of the octahydroketoazulenes with lithium aluminium hydride in ether at 0° gave the hydroxyoctahydroazulenes (VI,  $R=H$ ) (b.p. 64°/0.1 mm.,  $n_D^{20}$  1.5132; found: C, 79.1; H, 10.9;  $C_{10}H_{16}O$  requires C, 78.9; H, 10.6 per cent) and (VI,  $R=Me$ ) (b.p. 80°/0.4 mm.,  $n_D^{21}$  1.5058; found: C, 79.5; H, 10.9;

Other methods of effecting the last step are under investigation, and details of this work will be published elsewhere in due course.

E. A. BRAUDE  
W. F. FORBES

Imperial College of Science and Technology,  
South Kensington,  
London, S.W.7.  
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<sup>1</sup> For references, cf. Pommer, *Angew. Chem.*, **62**, 281 (1950).

<sup>2</sup> Braude, Coles and Timmons, *Nature*, **166**, 58 (1950); *J. Chem. Soc.*, 2006, 2007, 2012, 2014 (1950); 2078 (1951). Braude and Forbes, *J. Chem. Soc.*, 1755 (1951).

<sup>3</sup> Favorskii and Domnin, *J. Gen. Chem. U.S.S.R.*, **6**, 727 (1936).

<sup>4</sup> Braude and Forbes, *J. Chem. Soc.* (forthcoming paper).

<sup>5</sup> Ball, Goodwin and Morton, *Biochem. J.*, **42**, 516 (1948); Wendler, Slates and Tishler, *J. Amer. Chem. Soc.*, **71**, 3267 (1949).

<sup>6</sup> Nazarov et al., *Bull. Acad. Sci. U.S.S.R., Cl. Sci. Chim.*, 633 (1946); 205 (1947); *J. Gen. Chem. U.S.S.R.*, **20**, 1441 (1950).

<sup>7</sup> Plattner and Büchi, *Helv. Chim. Acta*, **29**, 1608 (1946).

<sup>8</sup> Cook, Philip and Somerville, *J. Chem. Soc.*, 164 (1948).

<sup>9</sup> Anderson and Nelson, *J. Amer. Chem. Soc.*, **73**, 232 (1951).

### Some Trithiocarbonate Derivatives of Carbohydrates

ETHYLENE oxide (I) and its simple analogues react with carbon disulphide and potassium hydroxide in methyl alcoholic solution to give cyclic compounds, containing three atoms of sulphur, which are termed trithiocarbonates. Culvenor, Davies and Pausacker<sup>1</sup> described the transformation of ethylene oxide into ethylene trithiocarbonate (II), and of cyclohexene oxide into cyclohexene trithiocarbonate. Furthermore, although this transformation has not yet been carried out, these compounds should readily undergo reductive desulphurization