

The product obtained after crystallising twice from water melted at  $213^\circ$ ; mixed melting point with a genuine sample of *trans*-caronic acid remained undepressed. The acid obtained from the mother liquor on treatment with acetic anhydride at  $220^\circ$  in the usual manner gave *cis*-caronic acid m.p.  $175^\circ$ . It is interesting to note that ethyl maleate also gives *trans*-caronic acid under identical conditions; evidently the *cis*-variety is unstable under the conditions of the experiment (cf. Formation of *trans*-caronic acid from  $\Delta^3$ -carene by oxidation).<sup>5</sup>

Dimethyldiazomethane reacts similarly with diethyl glutaconate to yield finally homocaronic acid which has been recently synthesised by Owen and Simonsen<sup>6</sup> from ethyl  $\Delta\beta$ -isohexenoate.

The action of dimethyldiazomethane is being tried with a number of other suitable unsaturated compounds with a view to synthesising carane and other compounds of the carane group.

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1 Soc. 1899 75 56-57

<sup>2</sup> *J. pr. Chem.*, 1907 (2) 75, 501.

<sup>3</sup> *J. C. S.*, 1921, 119, 1322.

<sup>4</sup> Proc. Ind. Sci. Cong., Presidential Address (Chemistry Section), 1930, p. 146; Philips, Ramage and Simonsen, J. C. S., 1936, 828; Ryton, J. C. S., 1936, 829; Ranganathan, J. Ind. Chem. Soc., 1936, **13**, 619.

<sup>5</sup> Gib-on and Simonsen, *J. C. S.*, 1929, 305.

<sup>6</sup> *J. C. S.*, 1933, 1225.

dicarboxylic acid), the ultimate degradation product of a number of naturally occurring bicyclic compounds, e.g., carone,  $\Delta^3$ - and  $\Delta^4$ -carene has been synthesised by Perkin and Thorpe<sup>1</sup> from ethyl *a*-bromo- $\beta\beta$ -dimethyl-glutarate, by Kotz<sup>2</sup> from ethyl *iso*-propylidene dimalonate and by Kon and others<sup>3</sup> from Guareschi-imide.

Although diazomethane and diazoacetic ester have found application in the synthesis of some monocyclic and bicyclic derivatives of compounds of the thujane group,<sup>4</sup> no synthetic investigation seems to be on record in which dimethyl-diazomethane has been used for such synthesis.

Dimethyldiazomethane has now been found to react with ethyl fumarate and maleate at a temperature of about  $-18^{\circ}\text{C}$ . to give the pyrazolone derivative (I) which when heated to about  $240-50^{\circ}$  loses nitrogen yielding ethyl *trans*-caronate (b.p.  $240^{\circ}$ ) as the primary product. This ester yields *trans*-caronic acid (II) on hydrolysis with 5% KOH on water-bath.

