

formation of an acid ester with sulphuric acid². The difference of behaviour in the two types of replacements has been fully confirmed. We developed more quantitatively the subject of replacements at the α -carbon atom and interpreted the relative difficulty of such reactions in terms of steric hindrance³. For example, adopting the conclusion of Cowdray, Hughes, Ingold, Masterman and Scott⁴, that the first stage in the formation of halides from alcohols by reagents such as hydrogen bromide, thionyl chloride and phosphorus trichloride is the production of intermediates such as ROH_2Br , $ROSOCl$ or $ROPCL_2$, we adduced evidence³ that all the routes by which such complexes could normally yield alkyl halides are very much restricted in the *neopentyl* system. Consequently, such intermediates should be easier to isolate in this system than in others. It is therefore very satisfactory that, while Whitmore and Rothrock had already isolated ROH_2Br in this system, Gerrard and Nechvatal have now isolated the esters $RO.SOCl$ and $RO.PCl_2$.

The points we wish to make are, therefore: (1) that the reactions which Gerrard and Nechvatal have realized belong to the class (substitution of hydroxylic hydrogen) of those which Whitmore and Rothrock, among others, found to be easy, not the class (substitution of hydroxyl) which they showed to be difficult; (2) that our interpretation³ of Whitmore's work involved the conclusion which Gerrard and Nechvatal's results support; and (3) that we did not conclude from Whitmore and Rothrock's paper that *neopentyl* alcohol does not react at all with the reagents specified above. Gerrard and Nechvatal quote as follows from Whitmore and Rothrock's paper: "The inactivity of *neopentyl* alcohol to heat and reagents has been demonstrated". However, this sentence is taken from the very brief final summary, and was clearly intended as a general and relative statement, not as contradicting part of the text of the paper.

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way⁴ some years ago. Bastiansen and Hassel find the following values for the distance and angle parameters:

$$\begin{aligned} C-H &= 1.08 \text{ \AA.}; & C-C &= 1.54 \text{ \AA.}; \\ \angle H-C-H &= 118.2^\circ; & \angle H-C-C &= 116.4^\circ. \end{aligned}$$

The uncertainty in the angles is quoted at $\pm 2^\circ$.

Spectroscopic studies by Smith⁵ have provided the value for one of the moments of inertia in cyclopropane ($I_B = 41.91 \times 10^{-40}$ gm./cm.²). The calculated moments of inertia of the Bastiansen-Hassel model are $I_A = 68.14 \times 10^{-40}$, $I_B = I_C = 42.68 \times 10^{-40}$. If the C—C distance in the proposed model is reduced from 1.54 \AA. to 1.52 \AA. , this alteration in itself is sufficient to give complete agreement with the experimental I_B . Bastiansen and Hassel do not quote the limits of error in the C—C distance determination, which, however, can scarcely be less than ± 0.02 \AA. Some justification for assuming that C—C may be slightly less than 1.54 \AA. follows from Pauling and Brockway's estimation of C—C = 1.53 ± 0.03 \AA. , and from O'Gorman and Schomaker's⁶ estimation of C—C = 1.52 ± 0.02 \AA. in monochlorocyclopropane.

Although the structural data are not yet complete, the 'most probable' cyclopropane structure would seem to agree with the assumption of near-trigonal bonding, at least in respect of the CH bond-length, force-constant and HCH angle. On the other hand, the C—C distance (~ 1.54 \AA.) corresponds with that of C—C found in the paraffin hydrocarbons, suggesting relatively little double-bond character in the C—C bonds. From the point of view of bond-length, it is satisfactory to represent the carbon-carbon bonding in cyclopropane by single C—C bonds: this representation, however, is not satisfactory in respect of the C—C bond-energy. The thermal data on cyclopropane indicate a marked *weakening* of the C—C bonds relative to C—C in diamond or ethane⁷. In regard to this latter point, it is perhaps significant that the assumption of trigonal bonding in cyclopropane nevertheless leaves a system in which the formation of σ or π C—C bonds occurs under conditions of angular strain.

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¹ Walsh, A. D., *Nature*, **159**, 165 and 712 (1947).

² Linnett, J. W., *Nature*, **160**, 162 (1947).

³ Bastiansen and Hassel, *Tids. Kjem. Bergvesen. Met.*, **6**, 71 (1946).

⁴ Pauling and Brockway, *J. Amer. Chem. Soc.*, **59**, 1223 (1937).

⁵ Smith, L. G., *Phys. Rev.*, **59**, 924 (1941).

⁶ O'Gorman and Schomaker, *J. Amer. Chem. Soc.*, **68**, 1138 (1946).

⁷ See, for example, Skinner, H. A., *Trans. Farad. Soc.*, **41**, 645 (1945).

Structure of Cyclopropane

DR. WALSH has defended his suggested structure¹ for the compounds ethylene oxide and cyclopropane in terms of a molecular orbitals picture based on the assumption that the carbon atoms are in the trigonal, or near-trigonal, state. The calculations by Linnett² of the CH-bond force-constants are consistent with trigonal bonding.

One would expect to find that the H—C—H angles in cyclopropane and ethylene oxide should lie close to 120° if the carbon atoms are indeed trigonally bonded. It is relevant, therefore, to direct attention to the results of a recent electron-diffraction study on cyclopropane, reported by Bastiansen and Hassel³. The photographs were obtained using a rotating-sector camera, and the results are probably more accurate than those obtained by Pauling and Brock-

I AM grateful to the Editors for affording me the opportunity of writing a final letter in this discussion. The fundamental idea underlying my earlier letter¹ was that the carbon atoms in cyclopropane and ethylene oxide were in a hybridization state close to that of the carbon atoms in ethylene. The evidence was then strong. Dr. J. W. Linnett has since pointed out that the CH stretching force-constant in these molecules is much closer to the ethylene than to the paraffinic CH_2 value. This developed a point already made, that the height of the strong Raman frequencies indicated the same conclusion. The Bastiansen-Hassel determination of the angle HCH in C_3H_6 as $118^\circ \pm 2$ provides further strong evidence for my fundamental point. (The smaller angle in the 1,1 dichloro derivative ($112^\circ \pm 4^\circ$) is expected since the angle ClCCl in the comparable 1,1 dichloro ethylene is