

A detailed account of our experiments will appear in *Magyar Kémiai Folyóirat*. One of us (F. K.) is indebted to the Hungarian Academy of Science for grant.

K. GONDA-HUNWALD
G. GRÁF
F. KÖRÖSY

Körösy Laboratory,
Budapest.
Jan. 26.

¹ Hinshelwood, C. N., *J. Chem. Soc.*, 696 (1947).

² Weiss, J., *Ann. Rep. Chem. Soc.*, 44, 79 (1947).

³ Derbyshire, D. H., and Waters, W. A., *Nature*, 164, 446 (1949).

⁴ Melander, L., *Nature*, 163, 599 (1949).

⁵ Gillespie, R. J., Hughes, E. D., Ingold, C. K., Millen, D. J., and Reed, R. I., *Nature*, 163, 599 (1949).

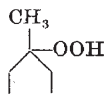
⁶ Bonner, T. G., James, M. E., Lowen, A. M., and Williams, G., *Nature*, 163, 955 (1949); see also their bibliography.

⁷ Uschakow, M. I., and Tchistow, W. O., *J. allgem. Chemie* (Russian), 1 (63), 1258 (1931); 4, 194 (1934); *Ber. deut. Chem. Ges.*, 68, 824 (1935).

⁸ Carlsohn, H., *Ber. deut. Chem. Ges.*, 68, 2209 (1935); *Z. angew. Chem.*, 46, 747 (1933).

Reaction of Methylcycloalkyl Hydroperoxides with Ferrous Sulphate

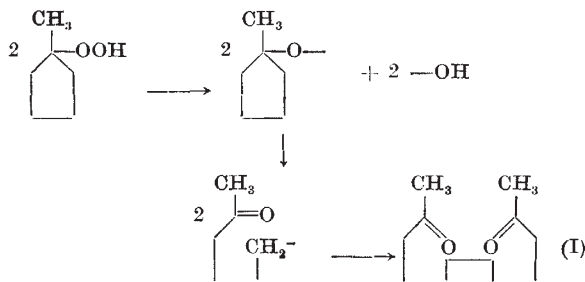
It has been found that when methylcyclopentyl hydroperoxide,



obtained from the oxidation products of the hydrocarbon¹, is treated with ferrous sulphate solution, the major product (c. 50 per cent) is a white solid of melting point 67.5–68.5° (I).

Analysis of this solid corresponds to the molecular formula $C_{12}H_{22}O_2$, and it has been identified as dodecanedione-2 : 11^{2,3} by the following evidence: (i) oxidation with sodium hypobromite yielded sebacic acid; (ii) treatment with methyl magnesium iodide provided the dicarbinol 2 : 11-dimethyldodecanediol-2 : 11, $C_{14}H_{32}O_2$ (m.p. 57–58.5°), identical with that formed from dimethyl sebacate by reaction with methyl magnesium iodide; (iii) reduction of the hydrazone by the Wolff-Kishner method⁴ gave *n*-dodecane, identified by its infra-red spectrum; (iv) dodecanedione-2 : 11 was afterwards synthesized by Dr. D. P. Young in these laboratories by reaction of dimethyl cadmium with sebacyl chloride, and proved to be identical with the product derived from the hydroperoxide decomposition.

The reaction proceeds very rapidly and evidently involves the dimerization of a free radical:



The other products of the reaction include methyl butyl ketone and carbinols.

Methylcyclohexyl hydroperoxide, on the other hand, reacts much more slowly with ferrous sulphate

solution, and the yield of the corresponding tetra-dodecanedione-2 : 13 (m.p. 76–77°⁵) is quite small (c. 10 per cent); the monoketones (including methyl amyl ketone) and alcohols are the main constituents of the product.

E. G. E. HAWKINS

Chemical Division,
Research and Development Department,
Distillers Company, Ltd.,
Great Burgh, Epsom.
Feb. 23.

¹ Union Oil Co., U.S.P.P. 2,430,864; 2,430,865.

² Cason and Prout, *J. Amer. Chem. Soc.*, 66, 46 (1944).

³ Bowden, Heilbron, Jones, Sargent and Sondheimer, *J. Chem. Soc.*, 1579 (1947).

⁴ Huang-Minton, *J. Amer. Chem. Soc.*, 68, 2487 (1946).

⁵ Work, *J. Chem. Soc.*, 1318 (1940).

Anomalous Thermal Expansion of the Short Intermolecular Bond in *para*-Nitro-aniline

A RECENT determination of the detailed crystal structure of *para*-nitro-aniline has revealed an unusually short distance of approach (2.66 Å.) between the oxygen atom of an NO_2 group of one molecule and one of the carbon atoms of the aromatic nucleus on a proximate molecule¹. This suggests special forces between these two atoms, the attraction of which appears to be intermediate between that in a covalent bond, and that due solely to Van der Waals' forces, and may be electrostatic in origin.

In analogous cases where special forces may contribute to the attraction, in short hydrogen bonds, anomalous thermal expansion of the bond has been observed in all the cases so far investigated²⁻⁶. This can be explained on the basis of exceptionally high anharmonicity of vibrations of such 'bonds'^{2,7}. Measurements of thermal expansion of *para*-nitro-aniline have now been carried out and have shown a similar anomaly.

The expansion ellipsoid for the total contraction over the temperature-range 288–90° K. has the axes $\alpha_{11} = 2.95 \times 10^{-2}$ at 55° to the *c* axis, α_{22} (along *b* axis, by crystal symmetry) = 0.24×10^{-2} , $\alpha_{33} = 0.45 \times 10^{-2}$.

This very large contraction along the α_{11} axis of the expansion ellipsoid coincides within 11° with the direction of the 'short intermolecular bond'. If the whole of the contraction on cooling were attributed solely to this bond, the short intermolecular bond would have a length of 2.46 Å. at 90° K. This gives an extreme value. Even if only the excess contraction over the average along the three axes is attributed to the bond, the length at 90° K. would be 2.53 Å.

This observation suggests a number of most interesting possibilities which are being further investigated.

(i) If the contraction maintains its anomalously large value along the bond direction below 90° K., the length of the short intermolecular bond at 0° K. must approximate to what might be expected for ionic contact, for example, as in the diagram (p. 70).

From the structure of sodium and potassium nitrites⁸, the ionic contact radius attributable to the oxygen atoms of O—N—O in the nitrite ion can be computed to be approximately 1.45 Å. Since the length of the short intermolecular bond at 0° K. must be less than 2.53 Å., this would leave a contact radius less than (2.53–1.45) Å., that is, less than 1.08 Å. for the positive carbonium ion. Such a value