

LETTERS TO THE EDITORS

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Trifluoromethyl Derivatives of Phosphorus, Arsenic and Sulphur

THE synthesis of iodotrifluoromethane and iodo-pentafluoroethane¹ has opened up a route to the synthesis of organo-metallic compounds containing perfluoroalkyl groups. The mercurials CF_3HgI and $\text{CF}_3\text{CF}_2\text{HgI}$ have been prepared by the reaction of the fluoroiodides with mercury in the absence of a solvent², and these may readily be converted into the corresponding dimercurials (for example, $\text{Hg}(\text{CF}_3)_2$)³. The reactions of iodotrifluoromethane with phosphorus, arsenic and sulphur have now been investigated and are found to yield organometallic compounds.

The interaction of yellow phosphorus and iodotrifluoromethane in sealed tubes at 220° is almost complete and leads to the formation of a mixture of $\text{P}(\text{CF}_3)_3$, $\text{P}(\text{CF}_3)_2\text{I}$ and $\text{P}(\text{CF}_3)\text{I}_2$. These compounds have been fully characterized and have boiling points 17.3°/760 mm., 73°/755 mm. and 133°/413 mm. respectively. Phosphorus tris trifluoromethyl burns in air, and, like the iodo compounds, is quantitatively hydrolysed to fluoroform by dilute alkali; this constitutes a convenient method of analysis.

The combination of arsenic with iodotrifluoromethane takes place smoothly at 220°, and similarly yields $\text{As}(\text{CF}_3)_3$ (b.p. 33.3°); $\text{As}(\text{CF}_3)_2\text{I}$ (b.p. 14°/54 mm.) and probably $\text{As}(\text{CF}_3)\text{I}_2$. These compounds are also readily hydrolysed to CF_3H .

The reaction with sulphur occurs at temperatures above 200°. One of the main products is thiocarbonyl fluoride, CSF_2 , and in this respect there is a parallel with the reaction between iodotrifluoromethane and oxygen, which leads to the formation of carbonyl fluoride. The amount of thiocarbonyl fluoride present in the product increases with increase in reaction temperature. With a temperature of 205°, other products can be isolated, one of which has the molecular formula $\text{C}_2\text{S}_2\text{F}_6$ (b.p. 34.5°). It probably has the structural formula $\text{CF}_3\text{—S—S—CF}_3$, and is hydrolysed by alkali without the formation of fluoroform. The compound $\text{CF}_3\text{—S—CF}_3$ is also believed to be present in the reaction product.

The chemistry of these new organometallic compounds is being investigated in detail, and the study is being extended to include the corresponding pentafluoroethyl derivatives. The reactions of iodotrifluoromethane and iodo-pentafluoroethane with other non-metals and metals will be described in subsequent communications.

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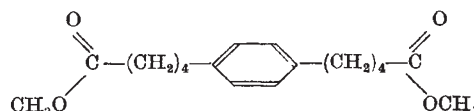
¹ Banks, Emeléus, Haszeldine and Kerrigan, *J. Chem. Soc.*, 2188 (1948).

² Emeléus and Haszeldine, *J. Chem. Soc.*, 2948 (1949).

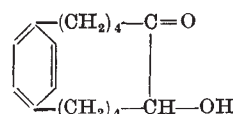
³ Emeléus and Haszeldine, *J. Chem. Soc.*, 2953 (1949).

Synthesis of a Benzene Ring with a Ten-Membered Para-Bridge

WE have recently investigated the synthesis of para-bridged benzene rings by dehydrogenation of maleic anhydride adducts of large ring dienes¹. As this method is very laborious, we decided to find the lowest possible number of carbon atoms necessary to form a para-bridge starting from a preformed benzene ring, and then to use our dehydrogenation method systematically only for smaller bridges, which cannot be synthesized by ring closure. We have used the acyloin ring closure as described by Prelog and collaborators², and cyclized the diester



prepared according to Ruzicka and collaborators³ from pure *p*-xylene. Surprisingly, we obtained the acyloin



in 70 per cent yield (b.p. 150–160°, 0.3 mm. mercury). After standing in the icebox, it solidified to a very low-melting crystalline solid (found: C, 78.07; H, 8.93; calculated for $\text{C}_{16}\text{H}_{22}\text{O}_2$; C, 78.01; H, 9.00 per cent). In alcohol with platinum oxide, this compound took up one mole of hydrogen and the corresponding diol was obtained (m.p. 102–103°; found: C, 77.39; H, 9.73 per cent; calculated for $\text{C}_{16}\text{H}_{24}\text{O}_2$; C, 77.37; H, 9.74 per cent). The diol consumed the theoretical amount of periodic acid. The high yield of the pure acyloin is interesting, as under identical conditions the cyclization reaction gives a yield of only 58 per cent *cyclotetradecoin*. It seems that the shortest para-bridge will have less than ten and more than six carbons, which is the length of the shortest bridge in the meta-position.

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¹ *Canad. J. Res.* (in the press).

² Prelog, Frenkiel, Kobelt and Barman, *Helv. Chim. Acta*, **30**, 1741 (1947).

³ Ruzicka, Buijs and Stoll, *Helv. Chim. Acta*, **15**, 1220 (1932).

⁴ Prelog, Wiesner, Ingold and Hafiger, *Helv. Chim. Acta*, **31**, 1325 (1948).

Quantitative Paper Chromatography on Mixed Solutions of Nickel and Cobalt, and Determination of both Elements

THE chromatographic procedure used in this work is as follows: Whatman paper No. 1 cut into 25 cm. × 1 cm. strips. Solutions to be determined (50 per cent by vol. hydrochloric acid) are taken from automatic horizontal burettes¹. The solutions contain the desired amount (γ) of each cation in 0.01 ml. This volume of solution is deposited on the paper strip at 3.5 cm. distance from its top, and the drop is rapidly dried at 35–40° C.