CCCXL.—*The Mobility of Symmetrical Triad (Prototropic*) Systems. Part III. Three-carbon Prototropy in an αγ-Diphenylallyl Ether.*

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IN a recent communication (Burton and Ingold, this vol., p. 908, footnote), it was suggested that the transformation of α-arylated allyl alcohols to saturated ketones in the presence of alcoholic alkali

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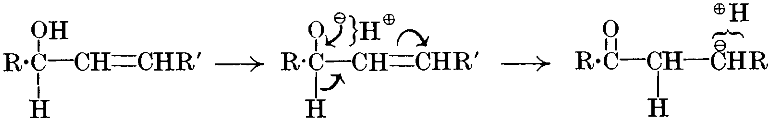
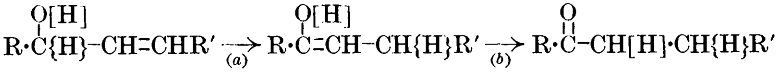
* This word has been added to the serial title to indicate the exclusion of triad *anionotropic* systems which are being concurrently investigated in these laboratories.

(Tiffeneau, *Bull. Soc. chim.*, 1907, **1**, 1209; Nomura, *ibid.*, 1925, **37**, 1245) occurred through the pinacolic electron displacement :



Alternatively, the change may be regarded as proceeding by three-carbon prototropy (*a*) succeeded by ketonisation (*b*) :



$$\overset{O[H]}{R\cdot C}\{H\}\text{-}CH{=}CHR' \xrightarrow[(a)]{} \overset{O[H]}{R\cdot C}{=}CH\text{-}CH\{H\}R' \xrightarrow[(b)]{} R\cdot\overset{O}{\overset{\|}{C}}\text{-}CH[H]\cdot CH\{H\}R'$$

In a paper (Ingold, Shoppee, and Thorpe, J., 1926, 1480) dealing with the mechanism of tautomerism in the so-called three-carbon system CH·C:C·C:O (which, according to the view there advanced, is not a symmetrical triad system but a pentad keto-enol complex; see also Ingold, *Ann. Report*, 1927, **24**, 114), it was shown that hydroxyl, and still better ethoxyl, ions should be extremely powerful catalysts for the αβ-βγ change. When the theoretical reason for this is examined, it is seen to apply not only to this special case, but to the whole of prototropy, and thus, having regard to the experimental conditions of the reaction considered by Burton and Ingold, it seemed possible that the mobility of a truly triad three-carbon system was under observation. Since this condition has not previously been established, except for systems involved in a ring (*e.g.*, indene; Ingold and Piggott, J., 1923, **123**, 1469; compare Goss and Ingold, this vol., p. 1268), the mechanism of the reaction referred to appeared worthy of study.

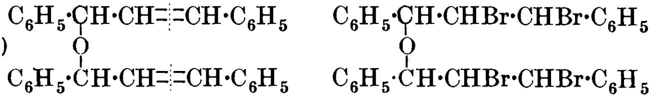
An attempt is now described to differentiate between the mechanisms formulated above by investigating an ether of type (I). Here pinacolic electron displacement cannot occur, for there can be no ionisation of the alkyl group R, with consequent formation of an electron source to constitute the driving force of the rearrangement. On the other hand, three-carbon prototropy can take place with

(I.) $R'\cdot CH(OR)\cdot CH{:}CHR''$ $R'\cdot C(OR){:}CH\cdot CH_2R''$ (II.)

production of the isomeride (II), corresponding with process (*a*) above, but the substituent R will prevent further change [process (*b*) above]. Thus, if pinacolic electron displacement is the mechanism underlying the first-mentioned transformation, an ether of type (I) will be unaffected by treatment with alcoholic sodium ethoxide; but if the rearrangement can take place by a three-carbon prototropic change, equilibration of the ethers (I) and (II) is to be anticipated.

The ether examined was *bis-αγ-diphenylallyl ether* (III), an unsaturated crystalline solid which yields a *tetrabromide* (IV), and on fission with ozone gives benzaldehyde and benzoic acid.

(III.)

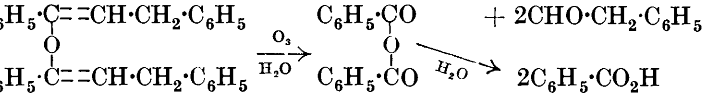


$$\begin{array}{cc}C_6H_5{\cdot}\underset{|}{C}H{\cdot}CH{=}CH{\cdot}C_6H_5 & C_6H_5{\cdot}\underset{|}{C}H{\cdot}CHBr{\cdot}CHBr{\cdot}C_6H_5\\ O & O\\ C_6H_5{\cdot}\overset{|}{C}H{\cdot}CH{=}CH{\cdot}C_6H_5 & C_6H_5{\cdot}\overset{|}{C}H{\cdot}CHBr{\cdot}CHBr{\cdot}C_6H_5\end{array}$$

(IV.)

This ether was heated with alcoholic sodium ethoxide, and the absence of an appreciable amount of phenyl β-phenylethyl ketone, which would be formed if hydrolysis of the ether linking occurred, was shown by treatment with semicarbazide. The product was a liquid isomeric with the ether (III); it was shown to consist essentially of the ether (V), since on fission with ozone it yielded the products, phenylacetaldehyde and benzoic acid, to be expected from a compound of this constitution.

(V.)



$$\begin{array}{lcl}C_6H_5{\cdot}\underset{|}{C}{=}CH{\cdot}CH_2{\cdot}C_6H_5 & & C_6H_5{\cdot}\underset{|}{C}O \qquad + 2CHO{\cdot}CH_2{\cdot}C_6H_5\\ O & \xrightarrow[H_2O]{O_3} & O\\ C_6H_5{\cdot}\overset{|}{C}{=}CH{\cdot}CH_2{\cdot}C_6H_5 & & C_6H_5{\cdot}\overset{|}{C}O \xrightarrow{H_2O} 2C_6H_5{\cdot}CO_2H\end{array}$$

Treatment with bromine confirmed this structure, four atoms being absorbed; the product, however, was not a saturated tetrabromide (VI) isomeric with (IV), but an unsaturated dibromide (VII), evidently formed from (VI) as a consequence of the well-known instability of halogens in α-halogeno-ethers $(\text{—}\overset{\curvearrowright}{O}\text{—}C\text{—}\overset{\curvearrowright}{Br})$:

$$\text{(VI.)}\ (CH_2Ph{\cdot}CHBr{\cdot}CBrPh)_2O \xrightarrow{-2HBr} (CH_2Ph{\cdot}CBr{:}CPh)_2O\ \text{(VII.)}$$

The position of equilibrium in hot alcoholic sodium ethoxide favours the isomeride (V) very largely, and it thus appears that the combined electronic affinities (inductive effect) represented in $\begin{smallmatrix}Ph\searrow\\ RO\nearrow\end{smallmatrix}C(H){\cdot}C{:}C$ are sufficient to produce (under the catalytic conditions mentioned) tautomeric mobility in a three-carbon system which is of a particularly simple type, since it is not implicated in a "developed" keto-enol complex.

Whether the reaction discussed by Burton and Ingold is to be represented by the first or the second of the mechanisms formulated at the outset cannot yet be decided, but the possibility of the second mechanism is clearly established by the example herein described.

EXPERIMENTAL.

Bis-αγ-diphenylallyl Ether (III).—αγ-Diphenylallyl alcohol was prepared from cinnamaldehyde and phenyl magnesium bromide and had m. p. 58° after crystallisation from ligroin (b. p. 40—60°).

The alcohol (15 g.), dissolved in glacial acetic acid, was treated with 75 g. of a 30% solution of hydrogen bromide in glacial acetic acid in the cold, and the mixture stirred for 2 hours. Pouring on ice, extraction with ether, washing (sodium hydrogen carbonate), drying, and evaporation of the ethereal extract yielded an oil which soon crystallised. After rubbing with a mixture of ether and ligroin, the *ether* was collected. It crystallised from ligroin (b. p. 60—80°), or from a large volume of methyl alcohol, in fine, rhombic prisms, m. p. 98—99° (Found: C, 89·5, 89·7; H, 6·6, 6·7. $C_{30}H_{26}O$ requires C, 89·5; H, 6·5%); yield, 13 g.

Bis-βγ-dibromo-αγ-diphenylpropyl Ether (IV).—The above ether (1·0 g.), dissolved in chloroform, was treated with a chloroform solution of bromine; absorption of 2 mols. took place readily, and removal of the solvent yielded a pale yellow oil (Found: C, 50·1; H, 3·9. $C_{30}H_{26}OBr_4$ requires C, 49·9; H, 3·6%).

Ozonolysis of the Ether (III).—A solution of the ether (2·0 g.) in glacial acetic acid was treated with ozonised oxygen, and after decomposition of the ozonides, the product was separated into neutral and acid fractions. The former had the characteristic odour of benzaldehyde, which was identified as the phenylhydrazone, m. p. 156°; the yield was small, but the acid fraction, which consisted entirely of benzoic acid, was correspondingly large.

Bis-αγ-diphenylpropenyl Ether (V).—The ether (III) (2·0 g.) was added to a solution of sodium (2·0 g.) in 99·5% ethyl alcohol (25 c.c.), and the mixture boiled under reflux for 2 hours on a sand-bath. The product was poured into much water and extracted with ether, and the dried extract evaporated. The yellow oil obtained (Found: C, 88·5; H, 6·5. $C_{30}H_{26}O$ requires C, 89·5; H, 6·5%) decomposed on distillation in a vacuum; it was treated with alcoholic semicarbazide acetate solution for a week, but no semicarbazone separated, and the oil was recovered by pouring the solution into water and extraction with ether.

Bis-β-bromo-αγ-diphenylpropenyl Ether (VII).—The crude ether (V) was treated with 2·5 mols. of bromine in chloroform solution. Addition took place at first, but hydrogen bromide was soon evolved. Hydrogen bromide and chloroform were removed by evaporation on the steam-bath; the oil obtained, which did not solidify when kept over potash in a vacuum, was dissolved in ether, and the solution filtered and evaporated. Analysis indicates that, although not quite pure, the product consists essentially of the dibromo-compound (VII) (Found: C, 62·0; H, 4·1. $C_{30}H_{24}OBr_2$ requires C, 64·3; H, 4·3%). It quickly decolorises an alkaline solution of permanganate in aqueous acetone.

Ozonolysis of the Ether (V).—The ether (2·0 g.), dissolved in glacial acetic acid, was treated with ozonised oxygen. After decomposition of the ozonides, the product was separated into neutral and acid fractions. The former on treatment with alcoholic semicarbazide acetate solution yielded a fluffy precipitate after several days (absence of benzaldehyde); this was filtered off, and after two crystallisations from methyl alcohol, separated in needles, m. p. 153°, identified as phenylacetaldehydesemicarbazone. The acid fraction was systematically crystallised from ligroin; benzoic acid was obtained, but no trace of phenylacetic acid could be detected.

Phenyl β-Phenylethyl Ketone Semicarbazone.—The ketone, m. p. 72—73°, prepared by the method of Perkin and Stenhouse (J., 1891, **59**, 1007), was treated with alcoholic semicarbazide acetate solution, and the *semicarbazone* crystallised out during 24 hours; it separated from dilute alcohol in needles, m. p. 144° (Found: C, 72·0; H, 6·4. $C_{16}H_{17}ON_3$ requires C, 71·9; H, 6·4%).

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