

632. *Surface Isomerisation. Part I. The Surface-catalysed Racemisation of 2-Phenylbutane.*

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Optically active 2-phenylbutane recovered after adsorption on carbon has been found to have undergone partial racemisation, the degree of racemisation depending on the time and temperature of residence on the carbon. A tentative explanation of this phenomenon is given in terms of homolytic fission of the hydrocarbon on the surface of the adsorbent.

It has been postulated that one of the functions of a heterogeneous catalyst may in some cases be to disrupt reacting molecules into free radicals on adsorption, the distance between adsorption sites and the structure of the adsorbate molecule being among the factors which determine the position of fission in the adsorbed molecule (Waters, "The Chemistry of Free Radicals," 2nd Edn., Oxford Univ. Press, 1948, pp. 214—221; Melville, *Ann. Reports*, 1938, **35**, 71—77). In this paper we give further evidence for the occurrence of homolysis produced by surface adsorption, based on measurements of optical activity of a substance before and after adsorption on carbon surfaces.

Carbon was chosen as a suitable adsorbent because of its high specific surface area, which was necessary for the convenient adsorption of a sufficient quantity of material for use in measurements of optical activity.

In choosing a suitable compound for study, attention was given to the following points : (1) In order to minimise the possibility of heterolytic (ionic) fission occurring on adsorption, use of a hydrocarbon appeared preferable. (2) The hydrocarbon chosen must be capable of resolution, a fact which drastically limits the available choice. (3) The hydrocarbon must be of the type which is likely to undergo homolysis at the asymmetric centre. Homolytic fission normally occurs readily at a tertiary hydrogen atom; choice was thus directed to compounds of the type $CR^1R^2R^3H$. (4) In order that the radical shall be fairly readily formed at moderate temperatures, it is preferable that one of the groups R^1 , R^2 , or R^3 should be a phenyl group, so that the radical formed is resonance stabilised. Since 2-phenylbutane fulfils all these requirements and has been previously resolved (Harrison, Kenyon, and Shepherd, *J.*, 1926, 658), it was chosen for these studies. That 2-phenylbutane can undergo homolysis at the asymmetric centre of the molecule is indicated by its autoxidation to form 2-phenyl-2-butyl hydroperoxide (Hawkins, *J.*, 1949, 2076), and by the fact that this reaction is catalysed by ultra-violet light (Ivanov, Savinova, and Zhakhovskaya, *Doklady Akad. Nauk. S.S.S.R.*, 1948, **59**, 905). Similar, more comprehensive evidence exists for the free-radical reactions of 2-phenylpropane (Hock and Lang, *Ber.*, 1944, **77**, 257; Kharasch, McBay, and Urey, *J. Org. Chem.*, 1945, **10**, 401; Farmer and Moore, *J.*, 1951, 131).

Two widely differing specimens of carbon were used in the experiments : (A) "Norit" and (B) a granular animal charcoal. Adsorption was brought about by passing a stream of nitrogen saturated with the hydrocarbon vapour over the carbon, or by admitting the vapour to the thoroughly evacuated adsorbent. The carbon carrying the adsorbed material was then heated to *ca.* 200° for varying lengths of time, in order to determine the effect of different residence conditions. In the early experiments attempts were made to desorb the hydrocarbon by passing over it a stream of pure nitrogen while keeping the carbon at a temperature well above the normal boiling point of the hydrocarbon (172°). This was found to remove only a small fraction of the total adsorbate, and the hydrocarbon recovered by this method, which was probably only capillary-adsorbed, had undiminished rotation. The carbon carrying the remainder of the hydrocarbon, which was probably held by chemisorption and van der Waals forces, was a dry powder with no trace of the characteristic smell of the hydrocarbon. This strongly adsorbed material could be partly recovered from the carbon by heating it under a high vacuum and high temperature, or completely by extracting it with hot benzene, and the hydrocarbon thus obtained had a diminished

rotation, the degree of loss of activity depending on its treatment while on the adsorbent. The results of typical experiments are summarised in the table.

Expt.	Specimen of carbon	Heating :		Activity of hydrocarbon, α_D ($l = 0.5$):		Loss of activity, %
		time, hrs.	temp., etc.	initial	final	
1	B	—	—	-1.00 ^o	-0.92 ^o	8
2	A	1	100 ^o /25 mm.	+1.50	+1.41	6
3	B	1	190	-1.02	-0.86	16
4	B	1	200	+1.47	+1.28	13
5 (i) } (ii) }	B [*]	ca. 2 } ca. 5 }	200/10 ⁻⁴ mm.	+0.38	+0.31* +0.20†	18 47

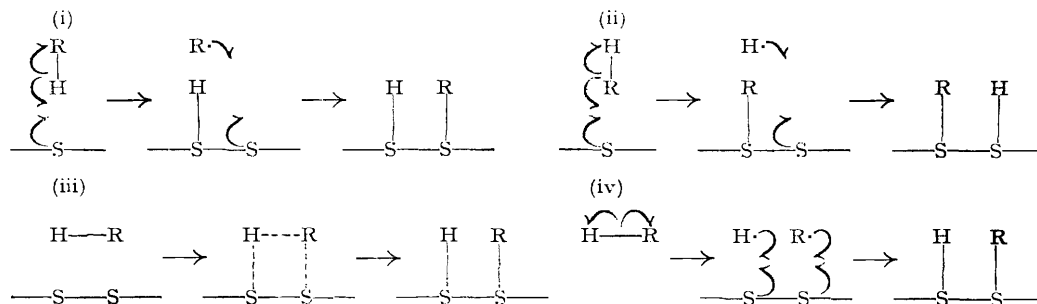
* Pumped off at 10⁻⁴ mm.

† Extracted with benzene after further desorption by pumping became impossible.

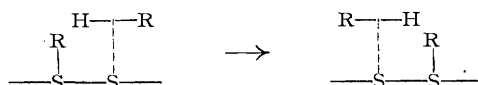
A control experiment in which the hydrocarbon was heated to 200° for 1 hour in a sealed tube produced no racemisation; therefore it seems safe to conclude that the racemisation observed in our experiments is the result of the adsorption-desorption process. Chemisorption or strong van der Waals adsorption appears necessary for the racemisation, since the loosely held hydrocarbon, which was probably capillary-condensed, was recovered with unchanged rotation.

Discussion.—This racemisation of the hydrocarbon might have taken place (a) during the process of adsorption, (b) while adsorbed on the carbon surface, or (c) during the desorption process.

(a) *The adsorption process.* At least four possible mechanisms of chemisorption may be considered, viz., (i)—(iv). Mechanism (i) would involve formation of a planar free radical with consequent racemisation; (ii) might involve inversion of configuration in the group R; (iii) is unlikely to produce racemisation; and (iv) would involve complete racemisation even in the absence of a surface, and our control experiment has shown that this does not occur.



(b) *Reaction in the adsorbed layer.* Two types of mechanism are usually postulated to account for reaction on a catalyst surface (Eley, *Quart. Reviews*, 1949, 3, 209). (i) Reaction between adjacent molecules or radicals chemisorbed on the surface. This might lead to the formation of R-H, or R-R and H-H. If R-H is produced, desorption would probably occur and racemisation might then be brought about by re-adsorption by any of the above mechanisms. Appreciable formation of dehydro-dimer (R-R), and corresponding amounts of hydrogen, is excluded since almost quantitative recovery of the original hydrocarbon is made experimentally. (ii) The reaction between molecules or radicals in the chemisorbed layer with molecules in the van der Waals adsorbed layer:



This would probably involve extensive racemisation.

(c) *The desorption process.* Any of the four postulated adsorption mechanisms may function in reverse, although the reverse of reactions (i) and (iv) seems rather improbable. The fact that, as shown in the table, the time and temperature of residence on the carbon

markedly affect the degree of racemisation of the hydrocarbon indicates that at least a large portion of this racemisation must occur during stage (b). Of the two possible mechanisms given above, (b, ii) is the one normally recognised as being effective at moderate temperatures such as those employed in our experiments.

The results of experiments (1) and (2) indicate that only a small degree of racemisation is obtained if the hydrocarbon is desorbed immediately after adsorption, or after only a small amount of heating on the surface. This would suggest that racemisation during processes (a) and (c), if occurring at all, is of relatively small importance.

In view of the above results, it would appear to be of value to study other cases in which surface homolysis may lead to isomerisation. Studies of the surface-catalysed geometrical isomerisation of maleic and fumaric acids are in progress in this laboratory, and it is hoped to extend the investigation to other substances, *e.g.*, *cis*- and *trans*-decahydronaphthalene.

EXPERIMENTAL

Materials.—Carbon *A*, a commercial specimen of finely-divided "Norit," was shaken with dilute sulphuric acid, washed, shaken with dilute sodium hydroxide, thoroughly washed, and dried at 120°. It was then refluxed for a prolonged period with absolute alcohol, then with pure benzene, and dried at 120° under vacuum. Carbon *B*, a granular animal charcoal, was similarly purified.

2-Phenylbutane, prepared by Hawkins's method (*J.*, 1949, 2076), was resolved by Harrison, Kenyon, and Shepherd's method (*loc. cit.*). The various specimens were distilled directly before use (b. p. 171—172°).

Optical Activities.—These were measured on the pure liquid at room temperature in a 5-cm. tube, sodium-*D* light being used.

Adsorption and Desorption.—Two methods of adsorption were used: (i) A slow stream of pure dry nitrogen was passed through the hydrocarbon (*ca.* 1.5 g.) kept at about 60°, and the resulting vapour led up a column packed with the adsorbent (*ca.* 30 g.) kept at a slightly higher temperature to prevent mechanical condensation. (ii) About 60 g. of the carbon were evacuated at 10⁻⁴ mm. and 200° for a prolonged period, after which the outgassed hydrocarbon was allowed to distil on to it at room temperature from a side arm. The carbon carrying the adsorbed hydrocarbon was then heated *in situ* for varying periods, a thermostatically controlled electric heating jacket being used. Desorption was brought about by pumping at 10⁻⁴ mm. and 200° into a trap at -80°, or by repeated refluxing with benzene. It was never possible to remove all the adsorbed material by the former method. The recovered hydrocarbon was distilled, and its boiling point and refractive index were taken as criteria of purity.