The Solvolytic Reactions of 2 : 2-*Dimethyl*-1-*phenylpropyl Bromide.*

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The solvolysis of 2 : 2-dimethyl-1-phenylpropyl bromide (CMe_3·CHPhBr) in various solvents has been studied. No rearrangement was found in various aqueous and alcoholic solvents, whereas from the product of solvolysis in moist formic acid a small proportion of 2-methyl-3-phenylbut-2-ene containing a rearranged carbon skeleton was isolated. The rôle of the solvent in this rearrangement is discussed. No evidence for the participation of the migrating group in the solvolytic reaction was found.

In connection with the study of the rôle of neighbouring groups in displacement reactions, Winstein and Morse (*J. Amer. Chem. Soc.*, 1952, **74**, 1133) have discussed the solvolytic reactions of optically active 2 : 2-dimethyl-1-phenylpropyl chloride (CMe_3·CHPhCl) and toluene-*p*-sulphonate. Acetolysis of both these compounds yielded 2 : 2-dimethyl-1-phenylpropyl acetate with an optical activity indicating a small preponderance of inversion in the course of reaction. In addition, in the acetolysis of the optically active chloride a maximum of 4% of inactive rearranged product is formed. From these results they conclude that a bridged structure of the carbonium ion in this rearrangement is improbable.

In the course of an investigation into the mechanism of rearrangements in the *neo*-pentyl system we had examined the solvolysis of 2 : 2-dimethyl-1-phenylpropyl bromide. Winstein and Morse's conclusions are in essential agreement with our own, but a number of points emerge from the additional data presented below which merit further discussion.

The solvolysis of this bromide in aqueous silver nitrate was first examined by Skell and Hauser (*ibid.*, 1942, **64**, 2633), who obtained as products 2 : 2-dimethyl-1-phenylpropanol containing a proportion of an impurity which they assumed to be 2-methyl-3-phenylbutan-2-ol formed by rearrangement. From the depression of the freezing point of the alcohol, they estimated the extent of rearrangement to be not more than 30%. Winstein and Morse (*loc. cit.*) repeated this work, using a purer bromide, and concluded from the small depression of the freezing point of the resulting alcohol that only very little rearrangement had occurred. In the same reaction, using very pure bromide, we have isolated this impurity from the products and identified it as the nitrate of the unrearranged alcohol. In the solvolysis in aqueous silver nitrate no products other than the unrearranged alcohol and its nitrate were found.

No solvolysis could be detected in a pure water suspension of the bromide even after 24 hours' refluxing, presumably owing to the very limited solubility. Solvolysis in aqueous dioxan mixtures of varying proportions (containing a suspension of potassium carbonate) and in 40% aqueous ethanol yielded the unrearranged alcohol only. Solvolysis in 80% aqueous ethanol gave a mixture of the unrearranged alcohol and its ethyl ether.

In moist formic acid containing approximately 1% of water, a mixture of unrearranged alcohol and up to 10% of an olefin, 2-methyl-3-phenylbut-2-ene, containing a rearranged carbon skeleton was obtained. The rate of formation of this olefin was found to be slower than that of liberation of bromide ion.

In order to eliminate the possibilty that the olefin observed in the solvolysis of the bromide in formic acid is due to the action of the acid on the unrearranged alcohol, the action of formic acid, of acidified dioxan, and of acidified 40% ethanol on 2 : 2-dimethyl-1-phenylpropanol was investigated. It was found that, even under conditions more extreme than those obtaining in the solvolysis reactions, no olefin was produced. On the other hand, the rearranged alcohol, 2-methyl-3-phenylbutan-2-ol, in formic acid at 40° yields this olefin at a rate comparable to that found in the solvolysis of 2 : 2-dimethyl-1-phenylpropyl bromide. It thus appears, that the olefin obtained in the formolysis of this bromide results from the loss of water from the rearranged alcohol or from its formate formed in the course of the reaction. Since the solvolytic reaction is unimolecular, it would seem that in formic acid, at least, both unrearranged and rearranged carbonium ions are capable of separate existence.

Further evidence is obtained by a comparison of the rates of solvolysis of the bromide in 40% aqueous ethanol and in moist formic acid, solvents of almost equal ionizing power. Although no rearrangement was found in the first solvent and up to 10% in the second, the rates were almost identical. Thus no acceleration due to rearrangement could be found such as is evident in the rearrangement of 2 : 2 : 2-triphenylethyl chloride (Brown, Hughes, Ingold, and Smith, *Nature*, 1951, **168**, 65). This would indicate the absence of any neighbouring-group effect and of a synartetic ion in the rearrangement of the 1-phenyl-substituted *neo*pentyl system. A similar conclusion was reached by Winstein and Morse (*loc. cit.*) from their study of the acetolysis of the optically active chloride.

In the absence of neighbouring-group effects, the extent of rearrangement occurring in a solvolytic reaction may be expected to depend on the length of life of the carbonium ion in the particular solvent used as compared with the time required for establishment of equilibrium between the various possible forms of the ion. Although the ionizing power of the solvent has a marked effect on the rate of formation of the carbonium ion, it has relatively little effect on the length of its life, as is shown by the difference in extent of rearrangement in solvents of nearly identical ionizing power, such as moist formic acid and 40% ethanol.

On the other hand, the extent of rearrangement increases in the order of the acidity of the solvent: 40% aqueous ethanol $<$ AcOH $<$ $H{\cdot}CO_2H$, *i.e.*, in the inverse order of their nucleophilic power. It seems that the latter property is the controlling factor in the length of life of the carbonium ion. In the rearrangement of 2 : 2-dimethyl-1-phenylpropyl bromide it would appear that the nucleophilic attack by the water in aqueous alcohol on the unrearranged carbonium ion occurs before the latter has an opportunity to undergo rearrangement. As the nucleophilic power of the solvent is decreased (in acetic and formic acids) the span of life of the carbonium ion is increased, and with it the opportunity to rearrange.

As has been pointed out by various authors (Skell and Hauser, *loc. cit.*; Eliphimoff-Felkin and Tchoubar, *Compt. rend.*, 1950, **231**, 1314), the unrearranged carbonium ion may by stabilized by the accession of electrons from a 1-phenyl group to the positive carbon atom. In those cases where the rearranging group participates in the solvolytic reaction, these electrons may be provided by the nucleophilic action of this group, thereby reducing the stabilizing influence of a 1-phenyl group. This is probably the cause of the considerable rearrangement of 1 : 2 : 2 : 2-tetraphenylethanol to tetraphenylethylene when treated with hydrogen bromide (Skell and Hauser, *loc. cit.*), whereas no rearrangement can be detected with 2 : 2-dimethyl-1-phenylpropanol under the same conditions.

Thus, whilst the body of evidence both kinetic and stereochemical is for the participation of a migrating phenyl group in solvolysis reactions, there are strong indications that when a methyl group migrates, as for example in the *neo*pentyl system, no such mechanism is in operation and both rearranged and unrearranged carbonium ions can exist.

EXPERIMENTAL

All m. p.s are uncorrected.

2 : 2-Dimethyl-1-phenylpropanol, prepared from *tert.*-butylmagnesium chloride and benzaldehyde, and purified *via* its crystalline hydrogen phthalate (m. p. 140—141°), had m. p. 45·0°. The bromide, prepared by the treatment of this alcohol in ether with gaseous hydrogen bromide at 0° and worked up in the usual way, had b. p. 85—86°/3 mm. No rearrangement occurred in the course of preparation, as is shown by the constant first-order rate coefficients obtained for the solvolysis in 80% aqueous ethanol.

2 : 2-*Dimethyl*-1-*phenylpropyl ethyl ether*, prepared from the bromide and sodium ethoxide in absolute alcohol, had b. p. 98—100°/1 mm. (Found: C, 80·7; H, 10·2; OEt, 23·4. $C_{13}H_{20}O$ requires C, 81·2; H, 10·4; OEt, 23·4%).

2 : 2-*Dimethyl*-1-*phenylpropyl nitrate* was prepared from the bromide and silver nitrate in anhydrous ether by Lucas and Hammett's method (*J. Amer. Chem. Soc.*, 1942, **64**, 1928); it had b. p. 83—86°/3 mm., n_D^{20} 1·5160 (Found: C, 62·9; H, 7·0. $C_{11}H_{15}O_3N$ requires C, 63·0; H, 7·2%).

2-Methyl-3-phenylbutan-2-ol, prepared from methylmagnesium iodide and ethyl hydratropate, had b. p. 92—93°/3 mm., m. p. 19°, n_D^{20} 1·5156. When this was refluxed with anhydrous oxalic acid it afforded 2-methyl-3-phenylbut-2-ene (phenyltrimethylethylene), b. p. 190°.

Solvolysis Experiments.—(a) *In aqueous dioxan* (10%, 50%, *and* 90% *by vol.*). In a typical experiment 2 : 2-dimethyl-1-phenylpropyl bromide (2·5 g.) was dissolved in sufficient aqueous dioxan in which potassium carbonate (2 g.) was suspended. After 36 hr.' refluxing the solution was diluted with water and extracted with ether. On drying and distillation of solvents, the product was found to consist entirely of 2 : 2-dimethyl-1-phenylpropanol, m. p. 45°.

(b) *In aqueous ethanol.* In a number of experiments the bromide was dissolved in aqueous ethanol and kept in a thermostat at 25·1° until the reaction was completed. The solution was then diluted with water and extracted with ether, and the ethereal layer dried and fractionally distilled. The products of solvolysis in 40% aqueous ethanol consisted entirely of 2 : 2-dimethyl-1-phenylpropanol, m. p. 45°, but in 80% aqueous ethanol two fractions were obtained: (i) b. p. 99—102°/20 mm., consisting mainly of 2 : 2-dimethyl-1-phenylpropyl ethyl ether (2—3% of the total) (Found: OEt, 20·3%); (ii) b. p. 90—93°/4 mm., consisting of unrearranged alcohol, m. p. 44·5—45°.

(c) *In aqueous silver nitrate.* In a typical experiment the bromide (23 g., 0·11 mole) was shaken overnight at room temperature with a silver nitrate solution (30 g., 0·17 mole, in 100 ml. of distilled water). After separation of precipitated silver bromide, the aqueous solution was extracted with ether, and the extract washed with cold water and dried (Na_2SO_4). After removal of ether, the residue was fractionally distilled. The product had an m. p. varying from 39° to 42° which could not be changed by further fractionation. The crude product was treated with phthalic anhydride and pyridine in a manner essentially similar to that now described by Winstein and Morse (*loc. cit.*), and the hydrogen phthalate of the unrearranged alcohol extracted from the benzene solution with aqueous sodium carbonate. After acidification of the aqueous carbonate layer, the hydrogen phthalate was extracted, dried, and recrystallized from acetic acid. The purified ester was hydrolysed and steam-distilled, yielding pure 2 : 2-dimethyl-1-phenylpropanol, m. p. 45°.

On removal of the solvent from the benzene layer, a residue melting at approximately 25° was obtained which was re-treated (twice) with phthalic anhydride and pyridine. In the final step a mere trace of hydrogen phthalate was extracted. The residue, b. p. 98—100°/4 mm. (Found : C, 63·6; H, 7·1%), had an infra-red spectrum identical with that of 2 : 2-dimethyl-1-phenylpropyl nitrate, prepared as described above.

(d) *In moist formic acid.* The bromide (2·2 g., 0·01 mole) was dissolved in 98% formic acid (10 c.c.) and kept at 25·1° for 20 hr. The solution was then poured into 500 ml. of water and extracted with ether. The extract was washed with sodium carbonate solution and dried (Na_2SO_4). On removal of ether and fractional distillation of the residue, two fractions were obtained: (i) B. p. 187—188°/758 mm., consisting of 2-methyl-3-phenylbut-2-ene (0·15 g.), n_D^{20} 1·5180; oxidation with 5% potassium permanganate solution, steam-distillation, extraction with ether, and fractional distillation afforded acetophenone (2 : 4-dinitrophenylhydrazone, m. p. 249°). (ii) The residue, consisting of 2 : 2-dimethyl-1-phenylpropanol and its formate, was hydrolysed with 0·1N-sodium hydroxide, extracted with ether, and fractionally distilled. Only unchanged alcohol, m. p. 45°, was obtained.

The rate of formation of olefin was estimated from a number of solvolysis experiments conducted at 39·9°. The amount of olefin was determined either by fractional distillation and weighing or by bromine-number determination on the crude product (A.S.T.M. Standards on Petroleum Products, 1950, p. 677).

In the solvolysis of the bromide (0·1M-solution) in 98% formic acid, the evolution of bromide ions was complete in 5 hr., but only a trace of olefin was detected in the mixture after 6 hr. and less than 10% after 24 hr. Under similar conditions, a solution of 2 : 2-dimethyl-1-phenylpropanol gave no olefin fraction even after 36 hr., whilst a solution of 2-methyl-3-phenylbutan-2-ol gave about half the equivalent amount of olefin in the same time. No olefin was detected in the products of the action of 50% aqueous dioxan, 0·12N in perchloric acid, at 100° for 12 hr. on 2 : 2-dimethyl-1-phenylpropanol; pure alcohol (m. p. 44—48°) was recovered unchanged in over 97% yield, care being taken that at no stage in the recovery could fractionation of alcohol and olefin occur. The time of reaction used in this experiment is calculated to be at least 1000 times longer than the time required for the solvolysis of the bromide under the same conditions. No olefin was detected in the action of 40% aqueous ethanol 0·1N in perchloric acid at 25° for 14 hr. on the unrearranged alcohol.

Kinetic Measurements.—Materials. 2 : 2-Dimethyl-1-phenylpropyl bromide was prepared as above. 40% Aqueous ethanol was obtained by mixing 40 vol. of dry ethanol (distilled from CaO) and 60 vol. of distilled water. Formic acid, 98—100% (Baker & Adamson C.P.), was recrystallised four times; the product had m. p. 7·0°, indicating approx. 1% of water.

Measurements. The rate of solvolysis was determined by a conductivity method. Cells were made of Pyrex glass of approximately 8—10 ml. capacity, in the sides of which smooth platinum electrodes were sealed. Solvent was added to a level about 1 cm. above the electrodes, and the cell closed with a ground-glass stopper and immersed for 30 min. in a water-filled thermostat at 25·10° ± 0·03°.

A drop of the bromide was added from a capillary and dissolved by shaking. At measured times the conductivity was determined with a bridge assembly of the type described by Jones and Josephs (*J. Amer. Chem. Soc.*, 1928, **50**, 1049), with a 1300-cycles phase shift audio-oscillator, a peaked audio-amplifier, and head-phones. At the high dilutions used (0·001—0·0001M) it may be assumed that conductivity is proportional to concentration. The first-order rate constants were therefore calculated directly from the conductivities of each run by means of the relation $k_1 = (2{\cdot}3/t) \log (k_\infty - k_0)/(k_\infty - k_t)$, where k_0, k_t, and k_∞ are the reciprocals of resistance at time zero, t, and infinity, respectively.

Satisfactory results were obtained for the solvolysis in 40% aqueous ethanol but a slight upward drift towards the end of the reaction was apparent in formic acid. A similar but larger trend is reported by Evans and Hamann (*Trans. Faraday Soc.*, 1951, **47**, 28). The results are summarized below:

Solvent	" Y " Factor *	$k_1 \times 10^4$ at 25·1°
40% Aqueous ethanol	2·151	5·42
Formic acid	2·08	5·15

* Grunwald and Winstein, *J. Amer. Chem. Soc.*, 1948, **70**, 846.

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