[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

MOLECULAR REARRANGEMENTS INVOLVING OPTICALLY ACTIVE RADICALS. VI. THE DISPLACEMENT OF HYDROXYL BY CHLORINE IN OPTICALLY ACTIVE 2-METHYL-2-PHENYLBUTANOL-1*

EVERETT S. WALLIS AND PHILIP I. BOWMAN†

Received October 5, 1936

From earlier work carried out in this laboratory[1] the fact has emerged that in certain molecular rearrangements involving optically active radicals, notably of the Curtius, Lossen, and Hofmann types, the optically active group maintains an asymmetric configuration during rearrangement, and undergoes no appreciable racemization during the process. The mechanism of these rearrangements has been the subject of much discussion, and the electronic nature of the migrating group has been variously interpreted.[2] But in certain previous discussions[3] of the views which have been expressed it has been pointed out that the optical stability of such molecules during rearrangement is most easily explained by an electronic mechanism involving the shift of a group with its pair of electrons, and that at no time is the asymmetric carbon atom without its complete octet of electrons. That this electronic viewpoint has certain distinct advantages over the older ionic mechanisms has been shown by certain in-

---

* Some of the experimental results herein described were discussed in a paper read at the Fifth Organic Chemistry Symposium at Ithaca, New York, December 28–30, 1933. See also Communication to the Editor, *J. Am. Chem. Soc.*, **56**, 491 (1934).

† This paper is based upon a thesis submitted by Philip I. Bowman, Harvard Fellow in Chemistry, to the faculty of Princeton University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[1] JONES AND WALLIS, *J. Am. Chem. Soc.*, **48**, 169 (1926); WALLIS AND NAGEL, *ibid.*, **53**, 2787 (1931); WALLIS AND DRIPPS, *ibid.*, **55**, 1701 (1933); WALLIS AND ADAMS, *ibid.*, **55**, 3838 (1933).

[2] STIEGLITZ, *Am. Chem. J.*, **29**, 57 (1903); *J. Am. Chem. Soc.*, **36**, 288 (1914); HESSE, STIEGLITZ, *Am. Chem. J.*, **29**, 56 (1903); JONES, *ibid.*, **50**, 441 (1913); JONES AND WALLIS, ref. 1; WHITMORE, *J. Am. Chem. Soc.*, **54**, 3274 (1932).

[3] WALLIS AND MOYER, *J. Am. Chem. Soc.*, **54**, 3426 (1932); WALLIS AND BOWMAN, *ibid.*, **56**, 491 (1934); WALLIS AND WHITMORE, *ibid.*, **56**, 1427 (1934); SPRUNG AND WALLIS, *ibid.*, **56**, 1715 (1934).

vestigations carried out in this laboratory[4] on an optically active amide (*d*-3,5-dinitro-6-α-naphthylbenzamide), of a sterically hindered biphenyl derivative.

The results of these experiments raised the question as to whether in any rearrangements involving optically active molecules the optical stability of the tercovalent group during the rearrangement is dependent upon its electronic nature. If the migrating group is never completely free, either as a negative, positive or neutral fragment but in some way is always within the influence of the forces within the molecule during the rearrangement process, then it might happen that regardless of the type of rearrangement studied the reaction would take place with no racemization, and the products formed would be always optically active. Facts previously recorded[5] indicate that this is not the case.

In an attempt to obtain further evidence which would throw light on this question Sprung and Wallis[6] made a detailed study of the rearrangements of certain optically active alkyl phenyl ethers. The results of their investigations strongly indicated that a particular electronic arrangement of the migrating group was of fundamental importance in maintaining asymmetry. However, in the discussion of their results they pointed out that a second explanation involving a bimolecular process had to be considered, and that it was possible that the alkyl phenols were not produced from the alkyl phenyl ethers by rearrangement, but by a metathetical reaction involving two molecules of the ether. Evidence that such bimolecular processes have to be considered had already been reported.[7] It seemed necessary, therefore, to continue further our studies in this series in order to obtain added evidence that the electronic arrangement about a group plays a vital rôle in producing optical stability sufficient to maintain an asymmetric configuration during rearrangement processes.

In this paper we wish to describe certain experiments which we have made in a study of a reaction process which, essentially, is closely allied to a Wagner rearrangement, and to discuss the results so obtained in the light of certain views which have been expressed with regard to the mechanism of this rearrangement. It is well known that tertiary butyl compounds are often produced in metathetical reactions involving isobutyl alcohol, and that nitrous acid reacts with tertiary-butyl-methylamine to produce

---

[4] WALLIS AND MOYER, ref. 5. See also FRANK BELL, *J. Chem. Soc.*, **1934,** 835.

[5] MCKENZIE, ROGERS AND WILLS, *J. Chem. Soc.*, **129,** 779 (1926); MCKENZIE AND DENNLER, *Ber.*, **60,** 220 (1927); ROGER AND MCKENZIE, *ibid.*, **62,** 272 (1929); KENYON AND PHILIPS, *J. Chem. Soc.*, **133,** 1677 (1930); WALLIS AND ADAMS, ref. 3.

[6] SPRUNG AND WALLIS, ref. 5.

[7] SHORT AND STEWART, *J. Chem. Soc.*, **1929,** 553; SOWA, HINTON, AND NIEUWLAND, *J. Am. Chem. Soc.*, **54,** 2019, 3694 (1932); **55,** 3402, (1933); LAUER AND SPIELMAN, *ibid.*, **55,** 4923 (1933).

dimethylethylcarbinol. Many other reactions of this type are known. The dehydration of isobutyl alcohol to give normal butylene may serve as another example. Applying an electronic mechanism for intramolecular rearrangements first enunciated by Jones[8] and by Stieglitz[8] for rearrangements of organic nitrogen compounds, Whitmore[8] has successfully put many types of rearrangements on a common basis, and has shown how in reactions involving molecules of the type, $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{A}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{B}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{X}}:$, the products formed may be (1) normal, (2) abnormal, (3) olefinic. In the light of what has been written above it is of interest to know the nature of the products formed when a substitution reaction is carried out on this type of molecule in which atom "A" is asymmetric. Such knowledge would give us a more definite answer to the question of the optical stability of tercovalent groups during rearrangement processes; for in this type of compound the migration of a group attached to "A" with its electron pair leaves the asymmetric carbon atom, "A", with only a sextet of electrons, as contrasted with other rearrangements of the Hofmann type, studied in this laboratory, in which the asymmetric carbon atom appears to be at no time during the rearrangement process without its octet of electrons.

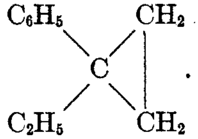
Accordingly we prepared *l*-2-methyl-2-phenylbutanol-1, $CH_3CH_2C(CH_3)(C_6H_5)CH_2OH$, ($[\alpha]^{19}_{5893} = -4.90$, without solvent). A study was made of the products formed when this compound was allowed to react with thionyl chloride. It was expected on the basis of the conceptions of molecular rearrangements outlined above that the replacement of the hydroxyl group by chlorine would lead to both (a) "abnormal" products resulting from rearrangement and (b) to olefine compounds, inasmuch as it is well known that the tendency to rearrange increases with the number of carbon atoms directly attached to "A". This was found to be the case. No detectable amount of the primary chloride, *l*-1-chloro-2-methyl-2-phenylbutane, $C_2H_5C(CH_3)(C_6H_5)CH_2Cl$, was found in the reaction products. The unsaturated hydrocarbon which was produced was identified as 1-phenyl-2-methylbutene-1, $C_2H_5C(CH_3){=}CHC_6H_5$, showing that rearrangement took place with migration of the phenyl group. The halide formed was a tertiary chloride, $C_2H_5C(CH_3)(CH_2C_6H_5)Cl$. The corresponding tertiary carbinol, 1-phenyl-2-methylbutanol-2, was produced in small amounts as a result of partial hydrolysis which occurred in working up the products of the reaction. A quantitative analysis of the products showed no primary chloride, 31.3 per cent. tertiary chloride, 59.1 per cent. unsaturated hydrocarbon, and 9.6 per cent. tertiary carbinol (by difference). Both the tertiary chloride, and the corresponding carbinol pos-

---

[8] JONES, ref. 4; STIEGLITZ, ref. 4; WHITMORE, ref. 4.

sessed optical activity, although partial racemization occurred during the reaction. It was also observed that an inversion in sign of the rotatory power took place during the rearrangement since the lævorotatory alcohol, α^{19}_{5893} −4.90 (without solvent, 1-dm. tube), yielded a dextrorotatory rearrangement product, α^{18}_{5893} +0.63 (without solvent, 1-dm. tube). Conversion of a portion of the chloride obtained in the reaction to the carbinol by hydrolysis with aqueous silver nitrate increased the positive rotatory power of the material, α^{19}_{5893} +0.88 (without solvent, 1-dm. tube); the presence of any primary chloride would have decreased this value by yielding lævorotatory primary alcohol.

These facts are pertinent when viewed in the light of certain theories which have been proposed to explain the mechanism of this type of rearrangement. They are not in agreement with the hypothesis upheld by Ruzicka[9] to explain the mechanism of the rearrangement which takes place in the dehydration of tertiary alkyl carbinols. This hypothesis postulates the intermediate closure of a cyclopropane ring, and then its rupture in a different position so that the radical which supplies the hydrogen for elimination as water, or in this case as hydrogen chloride, is the radical which migrates to the adjoining carbon atom. In the reaction under discussion it is the phenyl group which migrates, and not one of the alkyl groups. The fact that the products of the rearrangement possess optical activity also precludes the intermediate formation of cyclopropane rings of the type,



Ionic hypotheses[10] are not excluded by the above facts if we assume that carbonium ions can have an independent existence without loss of optical activity. This assumption has been made by McKenzie, Roger and Wills[11] to explain the retention of optical activity during the "semipinacolenic deamination of certain amino alcohols." It was also discussed as a possible explanation of the results obtained in the early work in this laboratory[12] on molecular rearrangements involving optically active radicals. However, in the light of more recent experimental studies on the

---

[9] Ruzicka, *Helv. Chim. Acta*, **6**, 267 (1923).

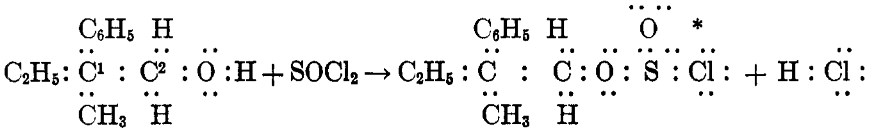
[10] Meerwein and Wortmen, *Ann.*, **435**, 190 (1924).

[11] McKenzie, Roger, and Wills, ref. 7.

[12] Jones and Wallis, ref. 3.

spatial configuration of the valences in tercovalent compounds[13] it seems very doubtful that one is dealing with true carbonium ions. Application of the newer theoretical methods[14] of considering such systems also leads to the conclusion that such ions are not likely to be formed. It is imperative that one take into account the energy required to break the bonds in these molecules. In molecular rearrangements which proceed at room temperature it is improbable that the molecules are sufficiently "energy-rich" to allow dissociation into either ions or radicals. Therefore it seems reasonable to regard them as intramolecular processes.

It seems to us that in the particular reaction under discussion the facts may be easily explained on the basis of an electronic mechanism of intramolecular rearrangements involving the essential ideas put forward by Whitmore[15] for reactions involving molecules of the type $:\overset{..}{\underset{..}{A}}:\overset{..}{\underset{..}{B}}:\overset{..}{\underset{..}{X}}:$. With the aid of this concept the reaction may be formulated as follows:

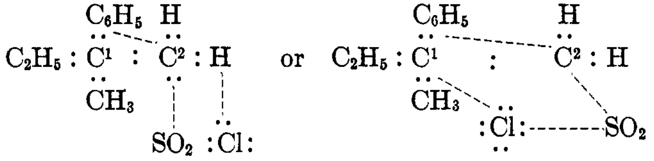


$$C_2H_5:\overset{C_6H_5}{\underset{CH_3}{C^1}}:\overset{H}{\underset{H}{C^2}}:\overset{..}{\underset{..}{O}}:H + SOCl_2 \rightarrow C_2H_5:\overset{C_6H_5}{\underset{CH_3}{C}}:\overset{H}{\underset{H}{C}}:\overset{..}{\underset{..}{O}}:\overset{O}{S}:\overset{..}{\underset{..}{Cl}}: + H:\overset{..}{\underset{..}{Cl}}:$$

*

II

Compound II undergoes decomposition and rearrangement. At the moment when sulfur dioxide begins to be removed from the molecule the approximate picture of the system must be much like that indicated in one of the following diagrams, depending on the position of the chlorine atom.



$$C_2H_5:\overset{C_6H_5}{\underset{CH_3}{C^1}}:\overset{H}{\underset{SO_2}{C^2}}:\underset{:\ddot{Cl}:}{H} \quad \text{or} \quad C_2H_5:\overset{C_6H_5}{\underset{CH_3}{C^1}}:\overset{H}{C^2}:H \quad :\underset{..}{\overset{..}{Cl}}:\text{-------}SO_2$$

Dotted lines indicate the more important partial valences which influence the rearrangement. Electronically this corresponds to the system $:\overset{..}{\underset{..}{A}}:\overset{..}{\underset{..}{B}}:$ discussed by Whitmore. With the removal of sulfur dioxide there is a simultaneous migration of an electron pair with its attached phenyl group

---

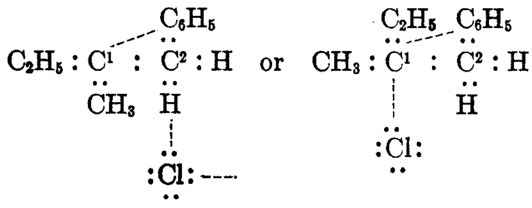
[13] Wallis and Adams, ref. 3.

[14] Eyring, *J. Chem. Phys.*, **3**, 107 (1934); Wallis and Moyer, ref. 5.

[15] Whitmore, ref. 4.

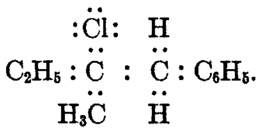
* In some reactions of thionyl chloride on alcohols, compounds of this type have actually been isolated.

from carbon atom (1) to carbon atom (2). In this process the phenyl group does not leave the molecule's sphere of influence. No ions are formed. The system may now be illustrated as:



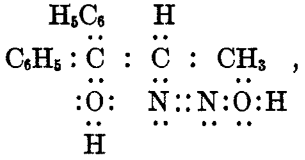
$$\begin{array}{ccccccc} & & & & \mathrm{C_6H_5} & & \\ & & & & \cdot\cdot & & \\ \mathrm{C_2H_5} & : & \mathrm{C^1} & : & \mathrm{C^2} & : & \mathrm{H} \\ & & \cdot\cdot & & \cdot\cdot & & \\ & & \mathrm{CH_3} & & \mathrm{H} & & \\ & & & & \vdots & & \\ & & & & :\ddot{\mathrm{Cl}}:--- & & \end{array} \quad \text{or} \quad \begin{array}{ccccccc} & & \mathrm{C_2H_5} & & \mathrm{C_6H_5} & & \\ & & \cdot\cdot & & \cdot\cdot & & \\ \mathrm{CH_3} & : & \mathrm{C^1} & : & \mathrm{C^2} & : & \mathrm{H} \\ & & \vdots & & \cdot\cdot & & \\ & & \vdots & & \mathrm{H} & & \\ & & :\ddot{\mathrm{Cl}}: & & & & \end{array}$$

with the remaining partial valence of the chlorine taken up by the departing molecule of sulfur dioxide. Electronically this is essentially $:\ddot{\mathrm{A}}:\underset{\cdot\cdot}{\ddot{\mathrm{B}}}:$, and can stabilize itself, with loss of a proton, to yield 1-phenyl-2-methylbutene-1, $\mathrm{C_2H_5}:\underset{\mathrm{H_3C}}{\underset{\cdot\cdot}{\mathrm{C}}}::\underset{\mathrm{H}}{\underset{\cdot\cdot}{\mathrm{C}}}:\mathrm{C_6H_5}$, or by addition of an electron pair from the adjacent chlorine to give, 1-phenyl-2-chloro-2-methylbutane,



$$\begin{array}{ccccccc} & & :\ddot{\mathrm{Cl}}: & & \mathrm{H} & & \\ & & \cdot\cdot & & \cdot\cdot & & \\ \mathrm{C_2H_5} & : & \mathrm{C} & : & \mathrm{C} & : & \mathrm{C_6H_5}. \\ & & \cdot\cdot & & \cdot\cdot & & \\ & & \mathrm{H_3C} & & \mathrm{H} & & \end{array}$$

Such a concept can be applied equally well to the deamination of amino alcohols. In this it is the compound,



$$\begin{array}{ccccccc} & & \mathrm{H_5C_6} & & \mathrm{H} & & \\ & & \cdot\cdot & & \cdot\cdot & & \\ \mathrm{C_6H_5} & : & \mathrm{C} & : & \mathrm{C} & : & \mathrm{CH_3}\ , \\ & & \cdot\cdot & & \cdot\cdot & & \\ & & :\mathrm{O}: & & \mathrm{N}::\mathrm{N}:\ddot{\mathrm{O}}:\mathrm{H} & & \\ & & \cdot\cdot & & & & \\ & & \mathrm{H} & & & & \end{array}$$

which undergoes decomposition and intramolecular rearrangement. It is of special interest to note that in both instances the process is accompanied by partial racemization, and by an inversion in the sign of the rotatory power. It can be stated, therefore, that regardless of the mechanism by means of which the rearrangement takes place the action of thionyl chloride on *l*-2-methyl-2-phenylbutanol-1 constitutes added evidence that in rearrangements involving optically active molecules the stability of the asymmetric tercovalent group during the process is dependent on its electronic nature, and that in rearrangements of the above type the asymmetric group possesses a stability far less rigid than in rearrangements of the Hofmann, Curtius, Lossen type, in which the process takes place with no detectable racemization and with no inversion in sign.

In conclusion we wish to state that the facts obtained in the study of this reaction also have an important bearing in all investigations on the study of configurational relationships of organic compounds. It can no longer be taken for granted that in substitution reactions of the above type the products formed are configurationally related to the original material. The asymmetric carbon atom may very well become involved in such reactions, and although the products are optically active this in itself is no criterion that the molecule has not undergone a complete structural change.

EXPERIMENTAL PART

Preparation of the Methyl Ether of 2-Phenylbutanol-2, C_2H_5-$C(CH_3)(C_6H_5)(OCH_3)$.—Methylethylphenylcarbinol was prepared by the action of ethylmagnesium bromide on acetophenone; yield of carbinol, 88.06 per cent. theoretical; b. p., 85–88° at 2–3 mm.* A solution of 61.20 g. of the carbinol in 100 ml. of ethyl alcohol, and 3.6 ml. of concentrated sulfuric acid was allowed to stand overnight. It separated into two layers upon addition of water. The product of the reaction was dissolved in ether, and the ether extract was washed with sodium carbonate solution. The dried solution was evaporated, and the residue was distilled under diminished pressure; yield, 53 g. (79.21 per cent. theoretical yield); b. p. 63–65° at 2–3 mm.

Preparation of 2-Methyl-2-phenylbutanoic Acid, C_2H_5-$C(CH_3)(C_6H_5)COOH$.—This acid was prepared from the above ether according to a method described by Conant and Carlson[16] for the preparation of 2-methyl-2-phenyl-*n*-caproic acid. Fifty grams of the ether gave 23.4 g. of an acid (43.12 per cent. theoretical) of b. p. 136–137° at 2–3 mm.; m.p. 57–58°.† A study of the nature of the by-products was made in another experiment on the preparation of this acid. 2-Phenylbutane was isolated, b.p. 173–174° at 760 mm.‡ This compound is formed whenever any moisture is present to react with the red potassium alkyl.

Resolution of 2-Methyl-2-phenylbutanoic Acid.—The acid was resolved by fractional crystallization of its quinine salt. One hundred ten grams of the acid and 203.5 g. of quinine were dissolved in 700 ml. of hot alcohol and filtered. Sufficient water was added to the filtrate to cause a turbidity, which was dispelled by the addition of alcohol. Three crystallizations gave a salt which, upon decomposition with 10 per cent hydrochloric acid at 0° yielded an acid of the following specific rotation in benzene: $[\alpha]^{20}_{D}$ $-$ 23.28. Neutralization equivalent calculated for $C_{11}H_{14}O_2$, 178.11; found, 178.39.

Preparation of l-*2-Methyl-2-phenylbutyramide,* $C_2H_5C(CH_3)(C_6H_5)CONH_2$.—Twenty-one grams of the above acid dissolved in 40 ml. of benzene was treated with 55.6 g. of thionyl chloride. The mixture was refluxed on the water bath for one hour. Excess thionyl chloride was removed at reduced pressure. The acid chloride

---

* TIFFENEAU, *Ann. chim. phys.*, [8], **10**, 362, gives b. p. 103–104° at 16 mm.; INGLIS, *J. Chem. Soc.*, **99**, 540, (1911), reports b. p. 106.5° at 15 mm.

[16] CONANT AND CARLSON, *J. Am. Chem. Soc.*, **54**, 4054 (1932).

† BLONDEAU, *Compt. rend.*, **174**, 1424–26 (1922), reports m.p. 60° for this acid prepared by a different method.

‡ KLAGES, *Ber.*, **35**, 3509 (1902), reports b.p. 173–174° at 760 mm.

so formed was added slowly to 200 ml. of concentrated ammonium hydroxide solution at 0°. The precipitated amide was purified in the usual manner. Two recrystallizations from petroleum ether (60–65°) gave a product which melted at 64.0–64.6°,* and had the following specific rotation in benzene solution: $[\alpha]_{5893}^{20} - 14.90$.

Preparation of l-*2-Methyl-2-phenylbutanol-1*, $C_2H_5C(CH_3)(C_6H_5)CH_2OH$.—Six grams of *l*-methylphenylbutyramide was thoroughly desiccated in a vacuum over phosphorous pentoxide for 24 hours. Absolute ethyl alcohol (58.9 g.), prepared from ordinary absolute alcohol (99.5–99.8 per cent.) by refluxing with one-twentieth of its weight of sodium metal for one hour, was distilled directly from the sodium ethylate into a 500-ml. Pyrex three-necked flask containing the dry amide. The flask was fitted with a large water-cooled condenser (106 cm. long, with 16 mm. internal diameter condenser tube) and a thermometer. With the temperature of the reaction mixture at 80° (oil bath), 9.3 g. (three times theoretical equivalent) of carefully cleaned sodium metal was added all at once through the top of the condenser. During the violent reaction the temperature rose to 95°. Throughout the following half-hour period it was maintained at 100–103°. Excess sodium was decomposed at 95° by addition of alcohol. To the cooled reaction mixture was added sufficient water to dissolve the sodium ethylate. The ethyl alcohol was removed by distillation. The product was extracted from the remaining alkaline water solution with ether, and was freed from amines by washing, first with dilute hydrochloric acid, and then with sodium carbonate solution. The ether extract was dried over sodium sulfate, and the ether was removed at reduced pressure. Distillation of the residue gave 3.80 g. (68.4 per cent. theoretical yield) of product of the following physical properties: b.p. 123–125° at 12–13 mm.; m.p. of benzoyl derivative, 46–46.2°; observed rotation in 1 dm. tube at 19°, without solvent:† $\alpha_{6563} - 4.20°$; $\alpha_{5893} - 4.90°$; $\alpha_{5463} - 5.78$; $\alpha_{4861} - 7.35$; $\alpha_{4358} - 9.6$.

Experiments on the Action of Thionyl Chloride on l-*2-Methyl-2-phenylbutanol-1*.—(*A*) Formation of 2-methyl-1-phenylbutene-1, $C_2H_5C(CH_3){=}CHC_6H_5$: A qualitative study of this reaction indicated that an unsaturated hydrocarbon was produced as one of the products. The following experiment was made to determine its structure. Ten grams of thionyl chloride was added at 0° over a period of twenty minutes to 5.4 g. of *l*-2-methyl-2-phenylbutanol-1. The mixture was allowed to stand overnight, and then refluxed for thirty minutes. On cooling, it was poured on ice. The product was extracted with ether and washed. The dried ether solution was evaporated. Qualitative experiments showed that the residue contained halides and unsaturated compounds. It was also found that the halide gave an immediate precipitate with either aqueous or alcoholic silver nitrate solution, that it was hydrolyzed by dilute sodium carbonate solution, and that it lost hydrogen chloride either on heating at atmospheric pressure or on refluxing with pyridine.

Distillation of the residue at reduced pressure gave (*a*) 2.7 g. of material, b.p. 87–89° at 13 mm., and (*b*) 1.1 g., b.p. 90–95° at 13 mm. Fraction (*a*) was refluxed with five times its weight of pyridine for one hour. The product was poured on ice, and after acidifying with hydrochloric acid was extracted with ether. The hydro-

---

* RAMART AND AMAGAT, *Ann. chim.*, [10], **8**, 276 (1927), report m.p. 85–86° for the racemic amide.

† BLONDEAU, *Compt. rend.*, **174**, 1424 (1922), reports b.p. 138° at 23 mm; m.p. of benzoyl derivative 46° for the racemic modification.

carbon obtained from the ether extracts boiled at 205° (corr.).* Its nitrosyl chloride derivative was prepared by dissolving the unsaturated hydrocarbon in ethyl nitrite and adding an equivalent amount of acetyl chloride at −10°. The mixture was allowed to stand for thirty minutes. On addition of alcohol a crystalline powder separated; this was filtered and washed with absolute ether. Recrystallization gave a product which melted at 105.7–106°.†

Anal. Calc'd for $C_{11}H_{14}ClNO$: C, 62.43; H, 6.62.
Found: C, 62.42; H, 6.81.

(*B*) Quantitative determination of the course of the rearrangement: Three and a half grams of *l*-2-methyl-2-phenylbutanol-1 was treated at 0° over a period of one-half hour with 7.0 g. of thionyl chloride. The mixture was held at room temperature for thirty minutes, then warmed to 80–85° for an equal period, and finally held at room temperature for another half-hour period. The reaction product was poured on ice, extracted with ether, washed with 10-ml. portions of 5 per cent. sodium bicarbonate solution and of water. It was dried over sodium sulfate, filtered through animal charcoal, and the ether was removed at reduced pressure. The residue gave the following rotation at 18° without solvent in a 1-dm. tube: α_{6563} + 0.49; α_{5893} + 0.63; α_{5463} + 0.75. A quantitative analysis was made of this material.

(*1*) Analysis for tertiary chlorides: Two methods of analysis were used for the determination of the total amount of chlorine present. The results obtained were as follows: Carius method, 6.16 per cent.; Schultz method, 6.15 per cent.[17] The amount of chlorine present as tertiary halide was determined by precipitation with aqueous silver nitrate at room temperature; 0.3006 g. of sample gave 0.0724 g. of AgCl, or 5.96 per cent. chlorine as tertiary halide. Therefore, within the experimental error all the chlorine was present as tertiary halide. This corresponds to 31.3 per cent. 1-phenyl-2-chloro-2-methylbutane.

(*2*) Determination of the percentage of unsaturated hydrocarbons: A method of analysis previously described by McIlhiney[18] was used in these analyses. The analytical results were as follows: titration with bromine in carbon tetrachloride (0.3 *N*), addition of potassium bromate, then potassium iodide, and back-titration with sodium thiosulfate (0.08820 *N*) gave, as an average of three determinations, 59.10 per cent. unsaturated hydrocarbon.

In our qualitative experiments described in (*A*), it was found that the halide present was hydrolyzed by sodium bicarbonate solution. In working up the products of the reaction in (*B*), it was necessary to wash the material thoroughly with 5 per cent. bicarbonate solution and water. Partial hydrolysis of the halide took place at this point. The analytical data described above indicate that the percentage of carbinol so formed (obtained by difference) was approximately 10 per cent.

(*C*) Change in value of the optical rotatory power with hydrolysis of 1-phenyl-2-chloro-2-methylbutane to the corresponding carbinol: A sample of material obtained in (*B*), α^{18}_{5893} + 0.63, was dissolved in acetone and hydrolyzed with aqueous silver nitrate. On working up the material a product was obtained which gave the following rotation at 19° in a 1-dm. tube without solvent: α_{5893} + 0.88.

---

* Franke and Stern, *Monatsh.*, **49**, 21–6 (1928), report b.p. 205–206° for 2-methyl-1-phenylbutene-1 (prepared by another method).

† This shows that the hydrocarbon was not 3-phenylpentene-2. Klages, *Ber.*, **36**, 3692 (1903), reports that this hydrocarbon boils at 197–8° at 753 mm., but that it gives a nitrosyl chloride derivative which melts at 117°.

[17] Schultz, *Ber.* **17**, 1695 (1884); see also Cohen *et al.*, *J. Chem. Soc.*, **97**, 1625 (1910).

[18] McIlhiney, *J. Am. Chem. Soc.*, **21**, 1084 (1899).

CONCLUSIONS

The reaction of thionyl chloride with *l*-2-methyl-2-phenylbutanol-1 has been studied quantitatively.

Unsaturated and rearrangement products have been identified.

Optical activity is maintained during rearrangement, but with partial racemization and inversion in sign.

An interpretation of the experimental results based on modern electronic theories of intramolecular rearrangements is advanced.

The bearing of these results on studies of configurational relationships is indicated.