THE COMMON BASIS OF INTRAMOLECULAR REARRANGEMENTS[1]

BY FRANK C. WHITMORE

The failure of organic reactions to give yields approaching the theoretical is well known. Processes which deviate most from the theoretical involve either an apparent metathesis or the elimination of an inorganic molecule such as water, halide acid or nitrogen. These reactions are also the chief source of the rearrangements which have become so common in organic chemistry. In the years since Fittig discovered the pinacolone rearrangement,[2] countless other rearrangements have been found and many explanations have been evolved.[3] These explanations have assumed intermediates including cyclopropane rings, ethylene oxide rings, olefins, univalent nitrogen, bivalent carbon, ordinary ions, bipolar ions and chelate compounds.

The purpose of this paper is to show that rearrangements and the peculiarities of organic "metathetical" reactions have a common mechanism based on the very nature of the "bonds" in organic compounds as contrasted to the ionic attachments in inorganic molecules. All the essentials of the mechanism proposed in this paper are old and are implicit in conceptions of atoms and molecules introduced during the last twenty years by G. N. Lewis, Arthur Michael, Julius Stieglitz, Lauder W. Jones, W. A. Noyes, Hans Meerwein, H. J. Lucas and Charles Prévost. In each

[1] An abstract of a paper presented at the Fourth Symposium on Organic Chemistry of the American Chemical Society, New Haven, Conn., Dec. 30, 1931. See pp. 3431–3454.

[2] Fittig, *Ann.*, 114, 56 (1860).

[3] The following give the more recent work in this field: "Chem. Soc. Ann. Rep.," 1923, p. 115; 1924, p. 96; 1925, p. 116; 1927. pp. 115, 133; 1928, p. 133; 1930, pp. 114–124. Meerwein and co-workers, *Ann.*, 435, 190 (1924); 453, 32 (1927); 455, 227 (1927); Michael, THIS JOURNAL, 42, 787 (1920); Tiffeneau and co-workers, *Bull. soc. chim.*, [4] 27, 459, 782 (1920); Lévy. *ibid.*, [4] 29, 865 (1921); Stieglitz, THIS JOURNAL, 44, 1294 (1922); Robinson (Ingold), *J. Chem. Soc.*, 123, 1706 (1923); Ruzicka, *Helv. Chim. Acta*, 6, 276 (1923); Lucas, Simpson and Carter, THIS JOURNAL, 47, 1465 (1925); McKenzie, and co-workers, *J. Chem. Soc.*, 779 (1926); Stewart and Aston. THIS JOURNAL, 49, 1718 (1927); Shoppee, *Brit. Chem. Abstracts*, [A] 1135 (1928); Porter. "Molecular Rearrangements," A. C. S. Monograph, The Chemical Catalog Co., New York, 1928; Ramart-Lucas, *Bull. soc. chim.*, [4] 45, 718 (1928); Latimer. THIS JOURNAL, 51, 3185 (1929); Hückel, *Ann.*, 477, 156 (1930); Prévost and Kirrmann, *Bull. soc. chim.*, [4] 49, 212, 240 (1931); Bergmann and Schuchardt, *Ann.*, 487, 225 (1931); Hückel, "Theoretische Grundlagen der organischen Chemie," Leipzig, 1931, Vol. I, pp. 205–251; Tiffeneau and co-workers. *Bull. soc. chim.*, [4] 49, 1595–1874 (1931); Ramart-Lucas and Amagat, *ibid.*, [4] 51, 108 (1932); Bachmann. THIS JOURNAL, 54, 1124, 2112 (1932).

case circumstances limited the application of these conceptions. The time has arrived, however, when the multitude of explanations of organic rearrangements can be discarded and the fact must be realized that these interesting reactions are not merely freaks to be expected from certain complex compounds but are dependent on properties inherent in even the simplest organic molecules.   As soon as this important fact is recognized, it will be possible to focus attention on the fundamental changes taking place in all rearrangements instead of considering each type of rearrangement as an isolated exception.   Even such simple processes as the formation of tertiary butyl halides from isobutyl alcohol will be found to follow the same course as the pinacolone rearrangement.[4]

The first recognition of the true cause of an intramolecular rearrangement was achieved independently by Julius Stieglitz and Lauder W. Jones about 1913 in connection with the rearrangements of organic nitrogen compounds.[5]   Jones says of the Hofmann conversion of N-bromoamides to isocyanates and amines: "The present mode of viewing the rearrangement would speak of the potency of the carbon atom to lose negative electrons and of the nitrogen atom to acquire them, and would look upon the free valences of univalent nitrogen as the stage setting required to furnish a suitable environment in which the essential action may take place."

In considering the rearrangement of triphenylmethyl hydroxylamine and its relation to the Hofmann, Lossen and Curtius rearrangements, Stieglitz states, "In the formation of water, containing the stable negative hydroxyl, the oxime hydroxyl deprives the nitrogen atom of two electrons. . . ."   In 1916, referring to the same types of rearrangements, he said, "In recent years the initial force leading to the rearrangements has been sharply defined, on the basis of the electron theory of valence, as residing in the instability of the charges on the radicals held by nitrogen . . . and to the great tendency of these radicals to go over into their stable forms . . . by absorption of electrons from neighboring atoms. . . ."[6]

The conception of bivalent carbon as an intermediate in rearrangements has been used by many including Nef, Tiffeneau, Lucas and, most recently, Hellerman,[7] who combines the bivalent carbon assumption with a transfer

[4] See pp. 3279, 3448.

[5] Jones, *Am. Chem. J.*, **50**, 441 (1913); Stieglitz and Leech, THIS JOURNAL, **36**, 272 (1914); Stieglitz and Stagner, *ibid.*, **38**, 2047 (1916); *Cf. Am. Chem. J.*, **18**, 751 (1896); **29**, 49 (1903); *Proc. Natl. Acad. Sci.*, **1**, 207 (1915).

[6] After this paper was presented at New Haven, a colleague of Dr. Stieglitz informed the author that similar conceptions had been applied to C—C rearrangements by Dr. Stieglitz in his advanced classes for several years. Since the meeting Dr. Stieglitz has kindly made available unpublished theses by R. B. Cooper, 1930, and G. W. Ayer, 1931, in which oxonium salts of pinacol are prepared and a mechanism for the rearrangement is proposed which is entirely analogous to that of the present paper. See also the Dohme Lecture by Dr. Stieglitz at Johns Hopkins University, February 19, 1932.

[7] Hellerman, THIS JOURNAL, **50**, 1718 (1928).

of electrons. The bivalent carbon mechanism could not be applied to tertiary alcohols or related compounds. P. A. Krueger of this Laboratory has called attention to the fact that the assumption of bivalent carbon will not account for the facts even with a secondary alcohol like pinacolyl alcohol which gives tetramethylethylene and *unsym.*-methylisopropylethylene on dehydration, whereas the assumption of bivalent carbon would indicate tetramethylethylene and *tert.*-butylethylene as the products to be expected.

In recent years Meerwein and his co-workers have added materially to our knowledge of rearrangements and have shown that conditions which favor ionization also favor rearrangement in many cases. In certain cases they have proved that it is the positive ion which undergoes rearrangement rather than the molecule.[8] The present study is an extension of this work but is not limited to cases in which ordinary ionization is possible.[9]

The English school of organic chemists, including Robinson, Ingold, Shoppee and their students, has long emphasized the dependence of various types of rearrangements on electron transfer within the molecule.[10]

The present study involves, then, a fusion and a simplification as well as a more general application of much that has gone before. Most organic molecules which give poor yields of "metathetical" products, or of products obtained by elimination of an inorganic molecule, or which give rearranged products, contain a portion which can be indicated electronically in one of the following ways

$$(1) \quad :\ddot{A}:\ddot{B}:\ddot{X}: \qquad (2) \quad \ddot{A}::\ddot{B}:\ddot{D}:\ddot{X}:$$

in which X is usually oxygen or halogen or other strongly electronegative atom and A, B and D are atoms like carbon and nitrogen which are neither strongly electronegative nor strongly electropositive. In the original compound, each atom has a completed octet of electrons and the linking is due to the shared electrons. These compounds are usually very stable and relatively inactive. They remain so only while all the octets are complete. System (1) is involved in such "two atom" rearrangements, as the pinacolic, the retropinacolic, the Hofmann, the Beckmann and many others, some of which have been named and some of which stand merely as isolated abnormalities of organic chemistry. System (2) is found in many types of allylic or triad rearrangements.

When a molecule containing System (1) is brought into a reaction which results in the *removal of X*[11] from its attachment to atom B, then, *regardless*

8 *Cf.* Lipp, *Ber.*, **65**, 242 (1932).

9 See p. 3441.

10 See "Annual Reports of the Chemical Society" since 1923.

11 This point in the present hypothesis called forth much criticism from the referees. In some reactions the first step appears to be an actual ionization (Meerwein) but, more often, it involves the formation of an addition compound such as an oxonium salt which is then decomposed to form the final products. The entire process behaves more

of the mechanism of the process, X keeps a complete octet of electrons and leaves B with only a sextet of electrons, an "open sextet" (Prévost). Thus at some instant System (1) becomes

$$: \ddot{A} : \ddot{B} \ + \ : \ddot{X} :$$
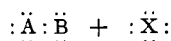
Three different changes may take place.

1. The positive organic fragment,[12] depending on the chemical nature and environment of A and B, may have a life long enough to allow it to combine with a negative ion Y in the reaction mixture.

$$: \ddot{A} : \ddot{B} \ + \ : \ddot{Y} : \ \longrightarrow \ : \ddot{A} : \ddot{B} : \ddot{Y} :$$
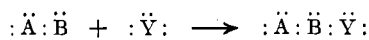
In such a case, the reaction is "normal," no rearrangement takes place, and the process resembles the simple metathetical reactions of inorganic chemistry. It is not usual for an organic reaction to follow this course entirely.

2. If the atom A has a hydrogen attached to it, the fragment can be stabilized by the loss of a proton.

$$\overset{H}{: \ddot{A} : \ddot{B}} \ \longrightarrow \ H^+ \ + \ : \ddot{A} : : \ddot{B} :$$
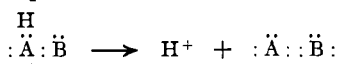
The product is an olefin or other unsaturated molecule.[13] This process is very common in organic reactions and has led many to believe that the olefin is an intermediate product in such reactions instead of merely a by-product.[13a]

3. The nature and environment of A and B may be such that B has the greater attraction for electrons or that A can more readily dispense with a pair of its electrons. In either case a change in the fragment will leave A with an open sextet.

like an activation than an ordinary ionization. It might be assumed that a single molecule suffers the separation of the ion X with a complete octet, leaving the rest of the molecule deficient in electrons. This residue then undergoes a change which liberates energy and "activates" another molecule. One of the simplest sources of energy in such a system would be the loss of a proton and the formation of an olefinic linkage. This may account for the common formation of olefins in reactions which might be expected to be simple metatheses (see p. 344).

    [12] This positive organic "ion" differs from ordinary positive ions which contain completed electron shells. It resembles the "Cl^+ ion" which is indicated by certain reactions of hypochlorous acid. The analogy is significant.

$$: \ddot{C} \ \big| : \ddot{O} : H \qquad : \ddot{Cl} \ \big| : \ddot{O} : H$$

The positive organic ion also resembles a "stripped atom" (Millikan) more than it does an ordinary ion. The extraordinary instability of such an "ion" accounts for many of the peculiarities of organic reactions.

    [13] Just as a proton in the 2 position to the positive carbon can be eliminated with the formation of an olefinic linkage, so a proton in the 5 or 6 position might be eliminated with the formation of a 5- or 6-membered ring. This is what happens in the formation of indene derivatives by a rearrangement which has been published since this paper was presented [Ottilie Blum-Bergmann, *Ber.*, **65**, 109 (1932)].

    [13a] See pp. 3442, 3448.

$$:\ddot{A}:\ddot{B} \longrightarrow \ddot{A}:\ddot{B}:$$

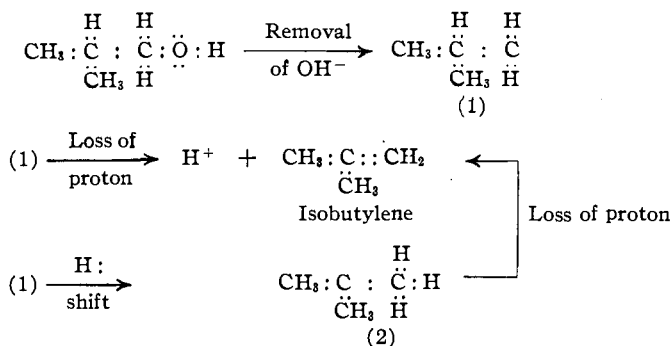*The shift of the electron pair includes the atom or group which it holds.*

The new fragment can then recombine with the ion X or with a new negative ion Y from the reaction mixture. The result is an "abnormal" or rearranged product, the series of changes being

$$:\ddot{A}:\ddot{B}:\ddot{X}: \longrightarrow :\ddot{A}:\ddot{B} \longrightarrow \ddot{A}:\ddot{B}: \longrightarrow :\ddot{Y}:\ddot{A}:\ddot{B}:$$
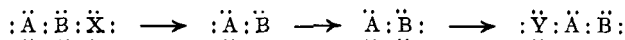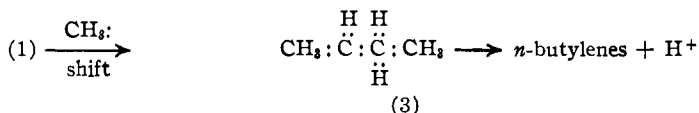
If atom B in the rearranged positive fragment has a hydrogen attached to it, the system may lose a proton. Depending on the other groups attached to A and B, the resulting unsaturated compound may or may not be identical with that obtained by the loss of a proton from the original fragment. It is important to note that the shift of electrons within the positive fragment and the stabilization by loss of a proton are *monomolecular* processes which may effectively compete with the *bimolecular* union of the original or the rearranged fragment with an ion from the reaction mixture. Thus the formation of considerable amounts of abnormal products is to be expected.

A study of these fundamental changes shows that processes in which a strongly electronegative atom or group is *removed* from an organic molecule during a reaction may readily give products other than those of simple metathetical or elimination reactions. Such a conclusion agrees with the facts. This simple mechanism fits all types of rearrangements which involve the transfer of an atom or group from one atom to an adjacent one. Its application is shown by the following examples.

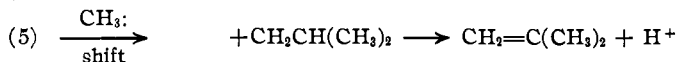The dehydration of isobutyl alcohol gives *normal* butylenes as well as the expected isobutylene.[14]

$$\begin{array}{ccc} \text{H} & \text{H} & \\ CH_3:\ddot{C} : \ddot{C}:\ddot{O}:H & \xrightarrow[\text{of OH}^-]{\text{Removal}} & \begin{array}{cc} \text{H} & \text{H} \\ CH_3:\ddot{C} : \ddot{C} \\ \ddot{C}H_3 & \ddot{H} \end{array} \\ \ddot{C}H_3 & \ddot{H} & (1) \end{array}$$

$$(1) \xrightarrow[\text{proton}]{\text{Loss of}} H^+ + \begin{array}{c} CH_3:C::CH_2 \\ \ddot{C}H_3 \end{array} \longleftarrow$$

Isobutylene

$$(1) \xrightarrow[\text{shift}]{\text{H}:} \begin{array}{c} \text{H} \\ CH_3:C : \ddot{C}:H \\ \ddot{C}H_3 \quad \ddot{H} \end{array}$$
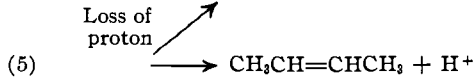
Loss of proton

(2)

[14] Nevole, *Bull. soc. chim.*, [2] **24**, 122 (1875); Le Bel and Greene, *ibid.*, [2] **29**, 306 (1878); *Am. Chem. J.*, **2**, 23 (1880); Konowalow, *Ber.*, **13**, 2395 (1880); *Bull. soc. chim.*, [2] **34**, 333 (1880); Faworski and Debout, *J. prakt. Chem.*, [2] **42**, 153 (1890); Wislicenus and Schmidt, *Ann.*, **313**, 210 (1900); Nef, *ibid.*, **318**, 211 (1901); Ipatiew, *Ber.*, **35**, 1061 (1902); **36**, 1997, 2011 (1903); Senderens, *Bull. soc. chim.*, [4] **1**, 693 (1907); *Ann. chim. phys.*, [8] **25**, 497 (1912); similar results have been obtained in this Laboratory by J. C. Mitchell using a phosphoric acid catalyst at 250°.

$$(1) \xrightarrow[\text{shift}]{CH_3:} \qquad CH_3 : \overset{H}{\underset{\ddot{H}}{\ddot{C}}} : \overset{H}{\ddot{C}} : CH_3 \longrightarrow n\text{-butylenes} + H^+$$

$$(3)$$

In a similar way isobutyl iodide reacts with lead oxide to give both isobutylene and butene-2.[15]

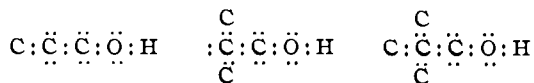If instead of dehydrating isobutyl alcohol, it is treated with hydrobromic acid, the product is not pure isobutyl bromide but contains tertiary butyl bromide (Michael). Under the conditions, only fragments (1) and (2) are formed in effective amounts. In other words, only hydrogen rearranges. At higher temperatures and with dehydrating catalysts fragment (3) is formed in large amounts by the shift of a methyl.

The dehydration of *normal* butyl alcohol gives isobutylene and all three normal butylenes instead of only the expected butene-1.[16] The probable steps in this process follow. For the sake of simplicity the atom in an open sextet is indicated by a + without any assumption as to its ionic properties.

$$CH_3CH_2CH_2CH_2OH \longrightarrow CH_3CH_2CH_2CH_2+ \xrightarrow[\text{shift}]{H:} CH_3CH_2C^+HCH_3$$

$$(4) \qquad\qquad\qquad (5)$$

$$(4) \xrightarrow[\substack{\text{Loss of} \\ \text{proton}}]{} CH_3CH_2CH{=}CH_2 + H^+$$

$$(5) \longrightarrow CH_3CH{=}CHCH_3 + H^+$$

$$(5) \xrightarrow[\text{shift}]{CH_3:} +CH_2CH(CH_3)_2 \longrightarrow CH_2{=}C(CH_3)_2 + H^+$$
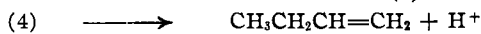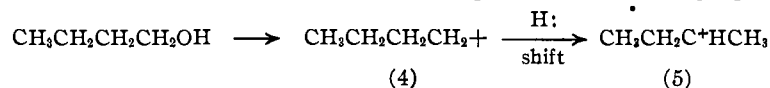
Exactly similar changes take place during the dehydration of secondary butylcarbinol to give mainly trimethylethylene and small amounts of pentene-2 and *unsym.*-methylethylethylene.[17]

The tendency to rearrangement increases with the number of carbon atoms attached to "A" in the two atom system.

$$C : \ddot{C} : \ddot{C} : \ddot{O} : H \qquad \overset{C}{\underset{\ddot{C}}{:\ddot{C}}} : \ddot{C} : \ddot{O} : H \qquad C : \overset{C}{\underset{\ddot{C}}{\ddot{C}}} : \ddot{C} : \ddot{O} : H$$

Thus compounds containing the last of these systems, the "neopentyl alcohol" system, give mainly rearrangement products in any reaction in which the hydroxyl is removed. They give esters of organic acids without rearrangement but all attempts to replace the hydroxyl by halogen lead to rearranged products.[18] Thus neopentyl alcohol itself (tertiary butylcar-

[15] Eltekow, *Ber.*, **13**, 2404 (1880).

[16] Senderens, *Bull. soc. chim.*, [4] **1**, 692 (1907). Lucas was unable to obtain any isobutylene from butanol-1 or -2 (private communication).

[17] Wischnegradsky, *Ann.*, **190**, 350 (1877); Étard, *Compt. rend.*, **86**, 488 (1878); Kondakow, *Ber.*, **25**, Ref. 570 (1892); Tissier, *Ann. chim. phys.*, [6] **29**, 326 (1893).

[18] Beilstein, 4th ed., Vol. I, p. 152, Spl. Vol. I, p. 54; Edgar, Calingaert and Marker, THIS JOURNAL, **51**, 1487 (1929).

binol) gives tertiary amyl halides and olefins formed from the rearranged fragment. The alcohol of this type which has been most studied is pinacolyl alcohol (methyl-tertiary-butylcarbinol) which gives none of the expected tertiary butylethylene on dehydration but only the rearranged products, tetramethylethylene and *unsym.*-methylisopropylethylene. Attempts to convert pinacolyl alcohol to the corresponding halide also give only rearranged products.[19]

An even more surprising failure to give a "normal" dehydration is shown by isopropyl-tertiary-butylcarbinol[20] which gives none of the expected product, 2,2,4-trimethylpentene-3.[21] In this case, the loss of a tertiary hydrogen to give an olefin is more difficult than the shift of a methyl group and its electron pair from the neopentyl system. A case in which the hydroxyl of the neopentyl alcohol system is tertiary and has no alpha hydrogens is presented by diphenyl-tertiary-butylcarbinol.[22] This substance is dehydrated with extraordinary ease to give 2,2-diphenyl-3-methylbutene-3 with the shift of a methyl group. On the other hand, a purely aliphatic neopentyl alcohol with a tertiary hydroxyl, methylethyltertiarybutylcarbinol[23] gives the "normal" dehydration product, and a lesser amount of the rearranged product.

The rearrangement of borneol to camphene and the many similar rearrangements in the terpene and other series studied so brilliantly by Meerwein follow this same course.[24] In each case the open sextet left after removal of the hydroxyl or halogen is completed by the transfer of an electron pair from an adjacent carbon with the corresponding shift of a carbon–carbon linkage.

The pinacolone rearrangement and rearrangements of other types of glycols, iodohydrins and related compounds follow a similar course. The more reactive hydroxyl or halogen atom is removed in the course of the reaction, leaving an open sextet which is completed by a rearrangement. An interesting variant of this reaction is the conversion of isobutylene dibromide and trimethylethylene dibromide into isobutyraldehyde and methyl isopropyl ketone by merely heating with water.[25] In each case the

---

[19] These results with neopentyl alcohol and pinacolyl alcohol have been entirely confirmed in this Laboratory, see p. 3431.

[20] Unpublished results of A. L. Houk of this Laboratory.

[21] This substance has been separated from "di-isobutylene" and its properties determined for identification purposes; Whitmore and Wrenn, THIS JOURNAL, **53**, 3136 (1931), and unpublished results of C. O. Tongberg. J. D. Pickens and J. M. Church of this Laboratory.

[22] Ramart-Lucas, *Compt. rend.*, **179**, 634 (1924); Marvel and Bateman, THIS JOURNAL, **49**, 2914 (1927).

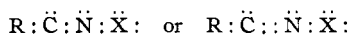[23] Unpublished results of K. C. Laughlin of this Laboratory.

[24] Meerwein, *Ber.*, **53**, 1815 (1920); **55**, 2500, 2533 (1922); *Ann.*, **453**, 16 (1927).

[25] Unpublished results by H. S. Rothrock and W. L. Evers of this Laboratory; *cf.* Eltekow, *J. Russ. Phys.-Chem. Soc.*, **10**, 215 (1878); Froebe and Hochstetter, *Monatsh.*, **23**, 1075 (1902).

tertiary bromine is removed with its octet and a hydrogen with its electron pair shifts.

The conversion of aliphatic amines to alcohols by treatment with nitrous acid is unusually subject to side reactions.[26]   Thus isobutylamine gives mainly tertiary butyl alcohol and isobutylene.[27]   In this case the intermediate product loses a hydroxyl or other ion with a complete octet and a nitrogen molecule with its ten electrons, thus leaving a carbon with an open sextet which makes possible the usual rearrangement.[28]   Interesting cases of this rearrangement are the conversion of cyclopropylamine into allyl alcohol by nitrous acid[29] and the Demjanow rearrangement[30] which has recently been shown by Fuson[31] to take place with aliphatic as well as with alicyclic amines.

The rearrangements of Hofmann, Lossen, Curtius and Beckmann all involve the system

$$R:\overset{..}{\underset{..}{C}}:\overset{..}{\underset{..}{N}}:\overset{..}{\underset{..}{X}}: \quad \text{or} \quad R:\overset{..}{\underset{..}{C}}::\overset{..}{\underset{.}{N}}:\overset{..}{\underset{..}{X}}:$$

If X is removed with its octet in the course of the reaction, a rearrangement of R: takes place in the usual way.[32]

$$R:\overset{..}{\underset{..}{C}}:\overset{..}{\underset{..}{N}} \longrightarrow \overset{..}{\underset{..}{C}}:\overset{..}{\underset{.}{N}}:R \qquad R:\overset{..}{\underset{..}{C}}::\overset{..}{\underset{.}{N}} \longrightarrow \overset{..}{\underset{..}{C}}::\overset{..}{\underset{.}{N}}:R$$

The resulting product, depending on the groups involved and the conditions of the reaction, is an isocyanate, an amine, or a substituted amine. In certain types of compounds, X is sometimes removed with only a sextet of electrons (as positive halogen by hydrolysis) and the remaining fragment has a complete octet and consequently cannot rearrange.   J. G. Aston of this Laboratory was the first to recognize that the shifting group in the Hofmann and related rearrangements cannot rearrange internally during its transfer from carbon to nitrogen because it has its full complement of electrons during this transfer.   This prediction has been strikingly confirmed in the case of the amide of *tert.*-butylacetic acid.[33]

Although rearrangement of compounds containing carbonyl groups and no group corresponding to the X in the systems discussed so far might be expected to follow a very different course, such may not be the case. The only difference is that an atom with an open sextet may be formed by

[26] Hellerman, THIS JOURNAL, **50**, 1718 (1928); Hellerman and Garner, "Aliphatic Diazo Compounds.   II," Buffalo Meeting, American Chemical Society, September 3, 1931.

[27] Linnemann. *Ann.*, **162**, 24 (1872); Henry. *Compt. rend.*. **145**, 899 (1907).

[28] See p. 3141.

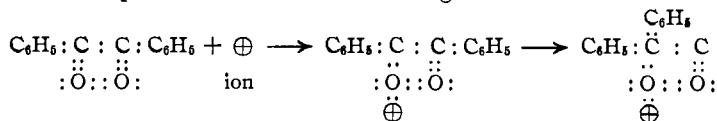[29] Kishner. *J. Russ. Phys.-Chem. Soc.*, **37**, 317 (1905).

[30] Demjanow, *Ber.*, **40**, 4397 (1907).

[31] Private communication.

[32] In the Curtius rearrangement of acid azides, triarylmethyl azides and benzyl azide, X is a pair of nitrogen atoms with ten electrons.
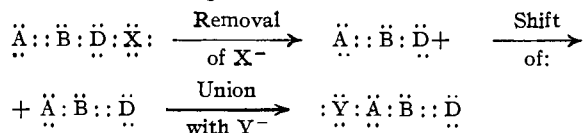
[33] See p. 3436.

the *addition* of a positive ion instead of by the *removal* of a negative ion. Thus the first step in the benzilic acid rearrangement becomes

$$C_6H_5 : C : C : C_6H_5 + \oplus \longrightarrow C_6H_5 : C : C : C_6H_5 \longrightarrow C_6H_5 : \overset{C_6H_5}{\underset{}{C}} : C$$
$$\overset{..}{\underset{..}{:O::O:}} \qquad ion \qquad \overset{..}{\underset{..}{:O::O:}} \qquad \overset{..}{\underset{..}{:O::O:}}$$
$$\oplus \qquad\qquad \oplus$$

The carbon with the open sextet then attracts the electron pair and phenyl group from the adjacent carbon. Addition of an hydroxyl ion to the rearranged fragment converts it to benzilic acid. A similar result is obtained in the conversion of trisubstituted acetaldehydes to ketones by concentrated sulfuric acid.[34] The initial addition product of the aldehyde with a proton undergoes rearrangement because of an open sextet and then loses a proton to give the enolic form of the ketone.

The rearrangements in triad systems which have been studied so intensively in recent years, especially by the English school of organic chemists, involve similar changes.[35] Thus

$$\overset{..}{\underset{..}{A}} :: \overset{..}{\underset{..}{B}} : \overset{..}{\underset{..}{D}} : \overset{..}{\underset{..}{X}} : \quad \xrightarrow[\text{of } X^-]{\text{Removal}} \quad \overset{..}{\underset{..}{A}} :: \overset{..}{\underset{..}{B}} : \overset{..}{\underset{..}{D}} + \quad \xrightarrow[\text{of:}]{\text{Shift}}$$

$$+ \overset{..}{\underset{..}{A}} : \overset{..}{\underset{..}{B}} :: \overset{..}{\underset{..}{D}} \quad \xrightarrow[\text{with } Y^-]{\text{Union}} \quad : \overset{..}{\underset{..}{Y}} : \overset{..}{\underset{..}{A}} : \overset{..}{\underset{..}{B}} :: \overset{..}{\underset{..}{D}}$$

My sincere thanks are due my colleagues, J. G. Aston, P. A. Krueger and R. V. McGrew, for their help and criticisms in the development of this work. Special recognition is due Dr. McGrew for his help in the direction of the experimental studies on which the accompanying papers are based.[36]

Summary

Many of the "abnormal" reactions of organic chemistry, including most intramolecular rearrangements, are correlated by the following simple assumptions.

1. A non-ionic attachment between an atom like carbon or nitrogen and an electronegative atom or group *is broken during the reaction*.

2. At the instant of removal of the electronegative group, it takes a completed octet of electrons with it.

3. The atom which had shared an electron pair with the electronegative group is thus left with only a sextet of electrons.

4. This deficiency of two electrons may induce a migration of an electron pair from an adjacent atom, thus giving rise to "abnormal" or rearranged products.

[34] Tiffeneau and Orékhoff, *Compt. rend.*, **182**, 67 (1926); Danilov, *Ber.*, **60**, 2390 (1927); Ramart-Lucas and Guerlain, *Bull. soc. chim.*, [4] **49**, 1860 (1931).

[35] For summaries and references see Prévost, *Compt. rend.*, **184**, 1460 (1927); Ingold and Burton, *J. Chem. Soc.*, 904 (1928); Ingold and Shoppee, *ibid.*, 1199 (1929); Ingold, *ibid.*, 2752 (1931).

[36] See pp. 3431–3454.

5. In the case of carbonyl compounds a carbon with an open sextet may be formed by the addition of a positive ion to the oxygen. In this case also the presence of the open sextet induces rearrangement.

6. The application of these simple principles is already proving helpful in experimental studies of "abnormal" reactions of simple aliphatic compounds.

STATE COLLEGE, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF FLORIDA]

ACYL DERIVATIVES OF ORTHO-AMINOPHENOL. I

BY C. B. POLLARD, C. E. SPARKS AND M. L. MOORE

When diacyl derivatives of *o*-aminophenol were prepared by the usual methods, it was found in many cases that the order of introduction of the two different acyl groups has no influence upon the formation of the diacyl, identical products being isolated from the two acylations. The position of the acyl groups can be determined by removing the groups attached to the oxygen by saponification with dilute alkali, and determining from the physical constants of the remaining monoacylated product the group attached to the nitrogen. The identical diacyls mentioned above were found to saponify to yield identical products, as would be expected.

The formation of identical rather than isomeric products on reversing the order of acylation indicated that during acylation a rearrangement must have occurred in one of the two cases. The formation of isomeric diacyls and the production of the same saponification product indicate that a rearrangement must have occurred during saponification. Some evidence has indicated that certain acyl groups have more power than others to bring about this migration, weight and acidity of the groups being considered to have the predominating influence in their obtaining a position in the more basic amino group.

Previous work on this subject by Ransom,[1] Ransom and Nelson,[2] Nelson and Rothrock,[3] and Raiford and Clark[4] is discussed in the literature.

The work of Pollard and Nelson,[5] using phenylacetyl chloride as one of the acylating agents in each diacyl throughout a series of experiments, indicated that relative acidity and weight are not the controlling factors in this type of rearrangement.

[1] Ransom, *Am. Chem. J.*, **23**, 1 (1900).

[2] Ransom and Nelson, THIS JOURNAL, **36**, 390 (1914).

[3] Nelson and Rothrock, *ibid.*, **51**, 2761 (1929).

[4] Raiford and Clark, *ibid.*, **48**, 483 (1926).

[5] Pollard and Nelson, *ibid.*, **53**, 996 (1931). A more extensive bibliography is given in this article.