

tritium exchange tending toward statistical distribution.

In any event, the possibility of using the *nonradiochemical* n.m.r. properties of tritium in chemical studies has been demonstrated. Tritium is very cheap, about \$2 per curie, and is carrier-free. The synthesis of organic compounds having high levels of tritiation, especially at specific sites, is thus feasible. As a result of the exceedingly short-range, low-energy β radiation of tritium, no special shielding is necessary, the walls of the tube being more than adequate. However, *it is of utmost importance* that good ventilation and other precautions against inhalation in case of breakage or spills be provided. One-tenth of a milliliter of a 1% tritiated organic compound would normally provide in excess of one curie of radiation, a most severe hazard.⁶ A further danger lies in self-radiation damage leading to breakage from pressure build-up, since a 10-curie sample could produce over 1 ml. of H₂ per day.⁷ By comparison, the evolution of helium-3 is negligible, being only *ca.* 10⁻³ ml. per day. It is evident that the radioactivity of tritium represents a nuisance rather than a formidable experimental difficulty.

Acknowledgment.—We thank G. Filipovich for advice on locating the tritium signal, and L. E. LaMar for much help with the radiochemical and safety aspects of the work.

(6) The maximal allowable tritium concentration in air for continuous exposure is given as 2×10^{-7} curie per cubic meter: "Protection Against Radiation," Appendix B, p. 20-11 of the U. S. Atomic Energy Commission Rules and Regulations, Government Printing Office, Washington, D. C., July 25, 1963.

(7) J. A. Stone and P. J. Dyne, *Radiation Research*, **3**, 353 (1962).

(8) (a) Central Research Laboratories; (b) Nuclear Products Department.

CONTRIBUTION NO. 286
CENTRAL RESEARCH LABORATORIES AND
NUCLEAR PRODUCTS DEPARTMENT
MINNESOTA MINING AND MANUFACTURING CO.
ST. PAUL, MINNESOTA 55119

G. V. D. TIERS^{8a}
C. A. BROWN^{8b}
R. A. JACKSON^{8b}
T. N. LAHR^{8b}

RECEIVED DECEMBER 6, 1963

Mass Spectral Studies. II. Molecular Rearrangement Under Electron Impact¹

Sir:

In a few short years mass spectrometry has developed into a powerful tool for structure elucidation.^{2,3} Studies have also been made on fragmentation processes of organic compounds and proton transfers.⁴ We wish to report here on molecular rearrangements under electron impact involving the migration of aryl and alkyl groups. Fragmentation involving such migration accounts for only a very small part of the total ionization current and is, therefore, insignificant compared to the normal modes of fragmentation. Nevertheless, a study of these rearrangements is of considerable significance for a fuller understanding of the mechanism of fragmentation.

In the course of our studies⁵ on aromatic amides, we have discovered a rearrangement involving aryl migra-

(1) Part I: J. Holubek, O. Štrouf, J. Trojáněk, A. K. Bose, and E. R. Malinowski, *Tetrahedron Letters*, **14**, 897 (1963).

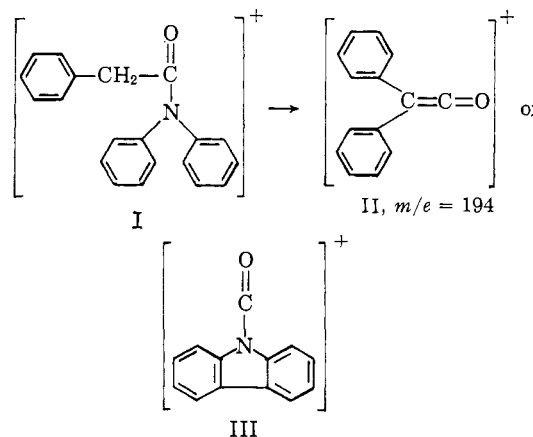
(2) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(3) H. Budzikiewicz, C. Djerassi, and D. W. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964.

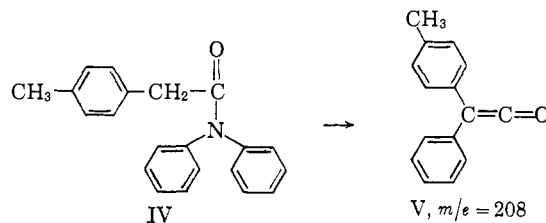
(4) For example, F. W. McLafferty, "Mass Spectrometry of Organic Ions," Academic Press, New York, N. Y., 1963.

(5) K. G. Das, P. T. Funke, and A. K. Bose, *J. Am. Chem. Soc.*, in press.

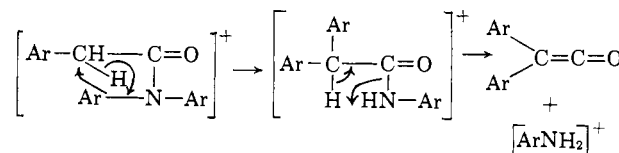
tion from nitrogen to carbon. In the spectrum of N,N-diphenylphenylacetamide (I) the peak at $m/e = 194$ ($\sim 0.2\%$ Σ_{50})⁶ could be assigned the diphenylketene structure (II). A carbazole type of structure (III) formed by the loss of two protons from one of the simple cleavage products can also account for $m/e = 194$.



Definitive evidence on aryl migration was obtained when we observed only a peak at $m/e = 208$ and not at 194 in the spectrum of N,N-diphenyltolylacetamide (IV). A carbazole type of structure cannot be assigned to this fragment (V). This rearrangement was supported by a metastable peak at $m/e = 144$ (calcd. 143.7 for $m/e = 301 \rightarrow 208$).



Indirect evidence was obtained by deuteration studies on these amides. The dideuterated forms of N,N-diphenylphenylacetamide and N,N-ditolylphenylacetamide where the deuterium atoms were in the benzylic position showed very small peaks at $m/e = 194$ and 208, respectively. It is difficult to conceive that the formation of the carbazole type of structure could be prevented by deuterium incorporation on the methylene group. On the other hand, if aryl migration were the normal mode in the nondeuterated compound, the deuterium isotope effect may have made the aryl migration too slow to be significant. We suggest the following mechanism for aryl migration which involves the simultaneous transfer of a phenyl group and a proton. Double transfers of protons have been postulated⁷ by earlier workers.



(6) This per cent value indicates the intensity of a peak relative to the sum of intensities of all peaks from $m/e = 50$ to the molecular ion peak.

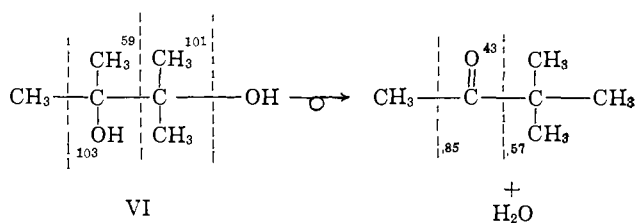
(7) See F. W. McLafferty and M. C. Hamming, *Chem. Ind. (London)*, 1366 (1958), and C. Beard, J. M. Wilson, H. Budzikiewicz, and C. Djerassi, *J. Am. Chem. Soc.*, **86**, 269 (1964).

In the mass spectra of *N,N*-diphenylphenylacetamide and *N,N*-ditolylphenylacetamide, peaks corresponding to $C_6H_5NH_2$, $m/e = 93$, and $CH_3C_6H_4NH_2$, $m/e = 107$, were observed.

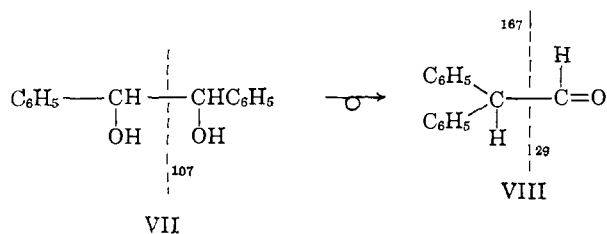
A comparison of the relative intensities of the peak at $m/e = 208$ in the spectra of *N,N*-ditolylphenylacetamide and IV, respectively, showed that as expected from chemical analogy⁸ *p*-tolyl ($\sim 1.0\%$ Σ_{50}) is a better migrating group than phenyl ($\sim 0.2\%$ Σ_{50}). Other examples of migration of aryl and alkyl groups taking place under electron impact have also been observed. We suggest that these rearrangements parallel the Beckmann and pinacol-pinacolone rearrangements known to take place in solution. In the mass spectrometer, however, no solvent is present nor is there a possibility for anything except intramolecular rearrangements.⁹

Thus, the mass spectrum of benzophenone oxime shows a peak corresponding to $m/e = 105$ ($\sim 4.0\%$ Σ_{40}) which can best be explained as the fragment $C_6H_5C=O$ to be expected from the Beckmann rearrangement product phenylacetanilide. The metastable peak at $m/e = 56.5$ supports this rearrangement (calcd. 56.0 for $m/e = 197 \rightarrow 105$). As a matter of fact, a direct comparison has shown that the spectrum of benzophenone oxime contains all the peaks found for phenylacetanilide. Analogous results have been obtained with the oximes of acetophenone and *p*-tolyl methyl ketone.

The mass spectrum of pinacol (VI) shows peaks corresponding to $M - 18$, 43 ($\sim 0.8\%$ Σ_{40}), 57 ($\sim 2.5\%$ Σ_{40}), and 85 ($\sim 1.6\%$ Σ_{40}). These observations can be satisfactorily accounted for on the basis of the pinacolone rearrangement under electron impact.¹⁰ Deuteration studies support this.



Rearrangement of hydrobenzoin (VII) to diphenylacetaldehyde (VIII) through a phenyl migration has to



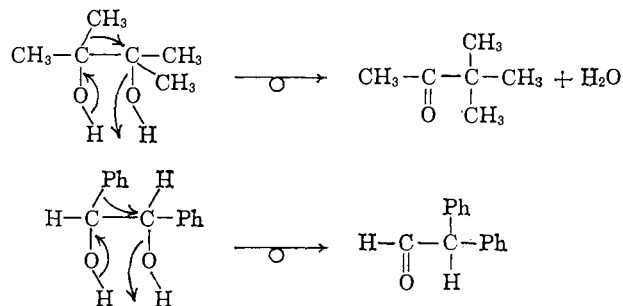
(8) H. Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1938, p. 275; see also G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1960, p. 593.

(9) All the spectra were recorded on a type 21-103C mass spectrometer operating at 70 e.v. using an all-glass inlet system heated to temperatures well below the melting point of samples to minimize thermal breakdown. The compounds used did not contain any of the suggested rearrangement products as contaminants.

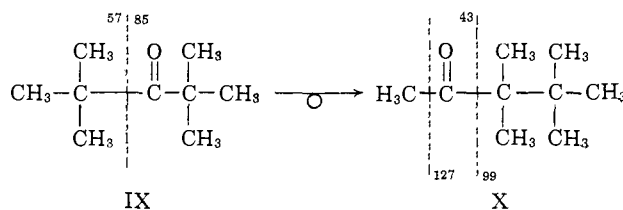
(10) The possibility of thermal rearrangement can be discounted because the pinacol-pinacolone rearrangement takes place thermally only at high temperatures in the presence of alumina; see G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1960, p. 537.

be assumed to account satisfactorily for the mass spectrum of hydrobenzoin.

A six-centered mechanism without invoking a carbonium ion can be written for the pinacol-pinacolone and similar rearrangements.



It has been reported¹¹ that di-*t*-butyl ketone (IX) rearranges in the presence of sulfuric acid to methyl heptyl ketone (X). The mass spectrum of IX does show peaks at $m/e = 99$ ($\sim 0.2\%$ Σ_{40}) and 43 ($\sim 1.2\%$ Σ_{40}) indicating alkyl migration under electron impact.¹²



Studies on isotope-labeled compounds and work on other types of rearrangement is in progress.

Acknowledgment.—This work was supported in part by a grant (MH-03930) from the U. S. Public Health Service. We are grateful to Dr. J. H. Davis and Dr. L. Z. Pollara for their active interest.

(11) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 333.

(12) At this stage it is not possible to exclude other mechanisms to account for some of the peaks in the mass spectra of VI and IX.

DEPARTMENT OF CHEMISTRY AND
CHEMICAL ENGINEERING
STEVENS INSTITUTE OF TECHNOLOGY
HOBOKEN, NEW JERSEY

P. FUNKE
K. G. DAS
AJAY K. BOSE

RECEIVED MARCH 13, 1964

Concerning the Nonphotochemical Biosynthesis of Vitamin D₃ in Fish¹

Sir:

The pioneering work of Bills² on cod and catfish showed that neither irradiation nor diet allowed an adequate explanation for the origin of vitamin D in the fish studied, and measurements by Hulburt^{3a} and by Atkins and Poole^{3b} have indicated that sea water

(1) Supported in part by grants from the American Cancer Society (No. P-292) and the National Institutes of Health (No. CRTY-5001). W. R. N. wishes to acknowledge a stimulating discussion on the origin of the vitamins D which he had in 1958 with Dr. Konrad Bloch. This discussion formed part of the impetus to undertake this investigation. We are also most grateful to Mr. Charles Wheeler of the U. S. Fish and Wildlife Service and Dr. John S. Rankin of the University of Connecticut for supplying live Atlantic bass.

(2) C. E. Bills, *J. Biol. Chem.*, **72**, 751 (1927).

(3) (a) E. O. Hulburt, *J. Opt. Soc. Am.*, **17**, 15 (1928); (b) W. R. C. Atkins and H. H. Poole, *Trans. Roy. Soc. (London)*, **B222**, 129 (1933).