observation. The most significant result for hot atom chemistry is the formation of *both* labeled molecules as products, indicative of a complex reaction mechanism involving the combination of two species to form the labeled product.

The differences in the organic yields for gas and liquid phase experiments with alkyl halides have been discussed in terms of the effect of the solvent "cage" in holding two reactive species in the near vicinity of one another until combination can occur, and in terms of the presence of a "brush heap" of radicals formed by the excited recoil atom.[3-6] The present experiments show that a racemization process is occurring in this system, but that it has not been completed prior to the combination reaction in the liquid phase at 25°. We interpret the observation of competitive racemization and combination reactions as strong support for the importance of "cage" effects in keeping the reacting species in close proximity.

The experiments carried out at lower temperatures show that both temperature and phase effects can be observed, leading to increased racemization of the radioactive product, but with no appreciable effect on the *sum* of the yield of the two diastereomers. The results in the liquid phase are consistent with a slightly higher activation energy for combination (probably for diffusion together) than for racemization. The chloro-*sec*-butyl radicals presumably involved here are similar to those which exhibit "bridged-radical" behavior in photobromination,[13] and such structures may possibly be involved during the racemization process. Bridged radicals are, however, not required on the basis of the present data alone. The low temperature results demonstrate also that the physicochemical differences between diastereomers also affect the degree of racemization observed for the radioactive products.

Since the nuclear histories of (n,γ) reactions can be quite different, comparison of these results with similar experiments for other (n,γ) halogen radioactivities, as well as with radioactive halogens from particle-emitting nuclear reactions, should be quite helpful in understanding the mechanism(s) involved in eq. 1.

(13) P. S. Skell, D. L. Tuleen, and P. D. Readio, *J. Am. Chem. Soc.*, **85**, 2849 (1963).

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Tritium Nuclear Magnetic Resonance Spectroscopy. I. Observation of High-Resolution Signals from the Methyl and Methylene Groups of Ethylbenzene. The Nonradiochemical Use of Tritium as a Tracer

Sir:

While proton n.m.r. spectroscopy has become commonplace, and deuterium n.m.r. spectra have been studied carefully[1] despite inherently low intensity and inferior resolution, to our knowledge high-resolution tritium n.m.r. spectroscopy is here reported for the first time. Our sample of neat ethylbenzene contained over-all 32.1 curies per ml. by conventional radioassay, which corresponds to about 1 atom % tritium. It was

(1) P. Diehl, and Th. Leppert, *Helv. Chim. Acta*, **47**, 545 (1964).

prepared by catalytic addition at room temperature of a small, measured amount of pure tritium, over palladium on charcoal, to the triple bond of phenylacetylene, followed by a large excess of hydrogen to achieve complete saturation of the side chain. The product was purified by bulb-to-bulb distillation and 0.3 ml. of it was transferred to and sealed in a high-quality n.m.r. sample tube.[2] By proton n.m.r. spectroscopy the chemical purity of the sample was confirmed, but owing to the low isotope content it was not possible to observe proton splitting by the tritium.

For observation of tritium our 40.000 Mc.p.s. Varian n.m.r. spectrometer was operated at *ca.* 8800 gauss. The sample temperature was 24°. The signal was weak but readily located by manual sweep from the proton region, and was self-identifying as it cannot be produced by any other material.[3] High resolution was retained despite the large change in magnetic field, and some further improvement was achieved by means of the field-trimming coils. The spectrum consisted of two first-order multiplets, the higher-field one due to the $-CH_2T$ group being apparently a triplet of triplets. The splittings were analyzed by computer techniques to yield the coupling constants, $J_{TCH} = 13.8 \pm 0.1$ c.p.s. and $J_{TCCH} = 8.11 \pm 006$ c.p.s. As a result of the low signal-to-noise ratio, it was not possible to detect the potentially greater complexity of the X part of an A_2B_2X spectrum.[4] The weaker peak, due to the $-CHT-$ group, was less clearly seen but appeared to be a doublet of quadruplets, as would be expected for X in an A_3BX case. The coupling constants were estimated from the computer analysis as: $J_{TCH} = 15.0 \pm 0.1$ c.p.s. and $J_{TCCH} = 7.9 \pm 0.1$ c.p.s. If due allowance be made for the 6.66% higher magnetic moment of tritium,[3b] one would predict J_{TCCH} to be 8.10 ± 0.01 c.p.s. on the basis of the proton spectrum.[5b] The observed chemical shift between the tritium peaks was 1.355 ± 0.006 p.p.m., in good agreement with (though 1% smaller than) the measured proton shift.[5b] No signal was found for aryl tritium; it is estimated that no more than 5% of the tritium content could have been present in the ring.

Rather surprisingly, area measurements, made by planimeter upon well-displayed spectra run at a variety of power levels and swept in both directions, yielded the value 1.96 ± 0.06 for the $(-CH_2T)/(-CHT-)$ ratio. If simple addition of T_2 prevailed, the ratio would be 1.00, while if catalytic randomization of the ethyl group occurred, the value would be 1.50. The ratio would indeed be 2.00 if randomization were complete at the tritiated styrene stage; additional experiments would of course be required to establish that point. By "randomization" is meant intra- and intermolecular

(2) Size E, available from Nuclear Magnetic Resonance Specialties, Inc., New Kensington, Pa. These inexpensive precision tubes, designed for use with the Varian A-60 spectrometer, were chosen for safety reasons, as they have slightly thicker walls than the Varian tubes. To clarify and strengthen them, S. L. Manatt has suggested briefly etching the outer surface with aqueous HF.

(3) Tritium has spin $1/2$, and its n.m.r. resonance frequency is the highest known for any nucleus, namely 45.414 Mc.p.s. at 10,000 gauss: (a) H. L. Anderson and A. Novick, *Phys. Rev.*, **71**, 372 (1947); (b) F. Bloch, A. C. Graves, M. Packard, and R. W. Spence, *ibid.*, **71**, 551 (1947).

(4) R. E. Richards and T. Schaefer, *Proc. Roy. Soc.* (London), **A246**, 429 (1958).

(5) (a) R. E. Glick and A. A. Bothner-By, *J. Chem. Phys.*, **25**, 362 (1956), give 7.37 ± 0.10 c.p.s. (b) Our own measurements, based on an A_3B_2 analysis of the 60 Mc.p.s. spectrum of neat ethylbenzene, are $J_{HCCH} = 7.59 \pm 0.01$ c.p.s. and $\delta = 1.369 \pm 0.002$ p.p.m., at 25°. Our error values are in every case stated as the standard deviation of the averaged value.

tritium exchange tending toward statistical distribution.

In any event, the possibility of using the *nonradio-chemical* 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 H_2 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.

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Mass Spectral Studies. II. Molecular Rearrangement Under Electron Impact[1]

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 studies[5] on aromatic amides, we have discovered a rearrangement involving aryl migra-

(1) Part I: J. Holubek, O. Štrouf, J. Trojánek, 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 $m/e = 194$.
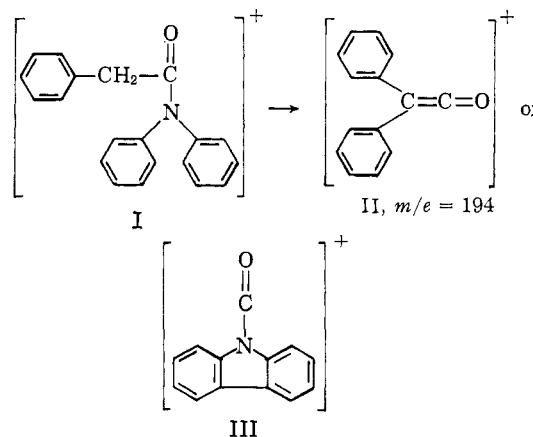
Definitive evidence on aryl migration was obtained when we observed only a peak at $m/e = 208$ and not at 194 in the spectrum of N,N-diphenyltolylacetamide (IV). A carbazole type of structure cannot be assigned to this fragment (V). This rearrangement was supported by a metastable peak at $m/e = 144$ (calcd. 143.7 for $m/e = 301 \rightarrow 208$).
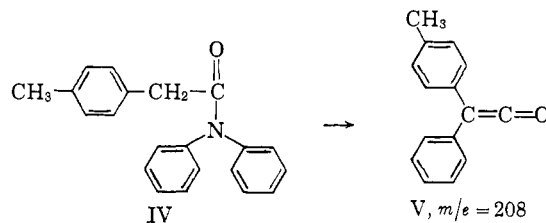
Indirect evidence was obtained by deuteration studies on these amides. The dideuterated forms of N,N-diphenylphenylacetamide and N,N-ditolylphenylacet-amide where the deuterium atoms were in the benzylic position showed very small peaks at $m/e = 194$ and 208, respectively. It is difficult to conceive 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 postulated[7] by earlier workers.
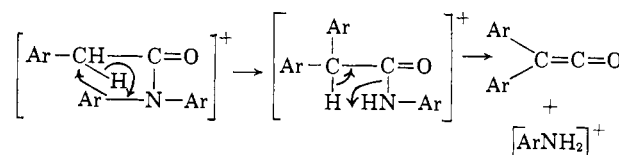
(6) This per cent value indicates the intensity of a peak relative to the sum of intensities of all peaks from $m/e = 50$ to the molecular ion peak.

(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).