

a monoester carboxylic acid (VI), m.p. 235–237°. Conversion of the carboxy group of VI to a hydroxy group was achieved by treatment of the acid chloride⁸ of VI with dimethylcadmium,⁹ followed by the Baeyer-Villiger reaction on the resulting methyl ketone (VII)¹⁰ (n.m.r. spectra: OMe (3) 6.29 τ , CO-CH₃ (3) 7.84, NCO-CH₃ (3) 7.93, C-CH₃ (3) 9.15) and finally mild alkaline hydrolysis of the acetate (VIII),¹⁰ ($\lambda_{\text{max}}^{\text{CH}_1}$ 5.81, 6.18, 8.05 μ). The resulting hydroxy compound (IX) melted at 205–206°. Oxidation of IX with chromic acid gave the corresponding ketone (X), m.p. 172–176°, which was carbomethoxylated with dimethyl carbonate and sodium methoxide¹¹ to provide a β -keto ester (XI) (amorphous, $\lambda_{\text{max}}^{\text{CH}_1}$ 5.82, 6.03, 6.20 μ ; $\lambda_{\text{max}}^{\text{EtOH}}$, 253 μ (ϵ 9800)). Reduction of XI with sodium borohydride and treatment of the resulting epimeric alcohols with tosyl chloride provided an unsaturated ester, m.p. 175–180°. This unsaturated ester was hydrogenated and the resulting mixture was treated with sodium methoxide. Chromatography of the saturated compounds separated a dimethyl ester (XII), m.p. 197–199°, and the alkaline hydrolysis of XII gave a monomethyl ester carboxylic acid (XIII), m.p. 248–250°. The identity of XII and XIII with those obtained from atisine^{6,12} was confirmed by means of mixture melting point and infrared spectra, respectively. Conversion of XIII to atisine has recently been reported.¹³ Thus, the first conversion of Garrya alkaloids, veatchine and garryine, to atisine has been achieved. Since garryine has been synthesized,¹ we have now completed in a formal sense the synthesis of atisine also.^{14–16}

Acknowledgment.—The author is grateful to Mr. N. T. Castellucci for his technical assistance throughout this work.

(7) The direct alkaline hydrolysis of the dimethyl ester of IV at room temperature gave a *cis* ester carboxylic acid, m.p. 184–186°. See ref. 6.

(8) The amide group was found to react with oxalyl chloride slowly. Therefore, addition of this reagent was carefully controlled.

(9) D. A. Shirley, "Organic Reaction," Vol. VIII, R. Adams, Ed., John Wiley and Sons, Inc., New York, N. Y., 1954, Chapter 2.

(10) We have experienced difficulties in crystallizing intermediates of this series. The homogeneity of these compounds was confirmed by the identical infrared spectra of every fraction, resulting from two kinds of chromatography (silicic acid and alumina). In addition, thin layer chromatography gave only one spot in every case.

(11) Part II of this series, ref. 8.

(12) The author wishes to thank Professor Pelletier for providing him with an authentic sample.

(13) S. W. Pelletier and P. C. Parthasarathy, *Tetrahedron Letters*, No. 4, 205 (1963).

(14) An elegant synthesis of atisine has recently been reported: W. Nagata, T. Sugawara, M. Narisada, T. Wakabayashi, and Y. Hayase, *J. Am. Chem. Soc.*, **85**, 2342 (1963).

(15) All new crystalline compounds gave satisfactory elementary analyses.

(16) This investigation was supported by a grant (GM 10369) from the National Institutes of Health, Public Health Service.

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Photoisomerization of Diazirine

Sir:

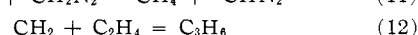
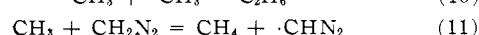
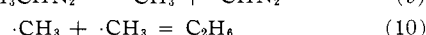
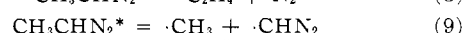
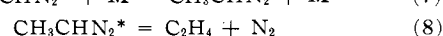
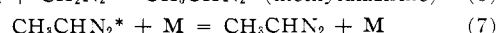
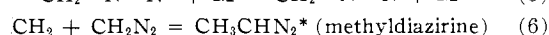
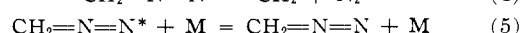
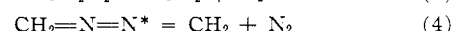
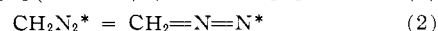
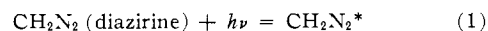
We wish to report the results of preliminary experiments on the photolysis of mixtures of diazirine (cyclic diazomethane), 5–30 mm., and nitrogen, 0–600 mm. The emission from a 200-w., high-pressure Hg lamp (PEK), passing through a Bausch and Lomb monochromator (Catalog No. 33-86-01) set at 3200 Å. (entrance slit, 1.8 mm.; exit slit, 1.0 mm.) and a Corning, CS 7-54, filter, is focused at the center of 10-cm. quartz photolysis cells. We follow the reaction by intermittent ultraviolet analysis of the reaction mixture and by gas chromatographic analysis of the final reaction mixture using a flame ionization detector.

The quantum yield for the initial disappearance of diazirine (spectrophotometric determination), based on ferrioxalate actinometry, is 2.0 ± 0.5 . A chain reaction which results in the formation of polymer on the walls is probably responsible for the scatter in quantum yield data.

The most significant feature of the spectrophotometric analysis is the identification of diazomethane as a product of photolysis. Diazomethane has a broad, very weak absorption with a maximum at 4100 Å. and a molar decadic extinction coefficient of 3.¹ At shorter wave lengths there are three much stronger absorption maxima (with extinction coefficients, based on the above value of 3 at 4100 Å.) at 2295 (3000), 2175 (10,000), and 2135 (7600) Å. The amount of diazomethane produced in the photolyses is estimated on the basis of this short wave-length absorption; the quantum yield for its formation is about one-tenth that for diazirine disappearance. The concentration of diazomethane builds up initially as a run proceeds, but then it levels off and finally begins to decline as the reactant diazirine is depleted. Scattered light, present in substantial amount in the exit beam from the monochromator, probably causes photolysis of the diazomethane and is responsible for the leveling off and decline of diazomethane concentration with increasing time of photolysis.

Frey and Stevens² have reported the photolysis of diazirine, presumably at higher pressures than reported here, and find ethylene and nitrogen as the major products of the reaction. Methane, ethylene, ethane, and propylene are the major products of the reaction we detect by the chromatographic analyses. At a constant initial pressure of diazirine, the ratio of ethane to ethylene in the products increases with decreasing pressure of added nitrogen. The effect of changing the initial pressure of diazirine is complicated because the photolysis light then penetrates the cell to different extents and the effective reactor volume differs; the product ratios are sensitive to the resulting diffusion effects.

We suggest the following mechanism, which is consistent with the results.



The designation of any product as "activated" does not imply anything concerning the type of activation; electronic or vibrational or both. Reactions 6–12 are written to be analogous to those observed in other systems in which methylene is produced.³ The radicals produced in reactions 9 and 11 probably go on to cause polymerizations. There is no spectrophotometric or chromatographic evidence for the methyldiazirine postulated in reaction 7. Its absorption spectrum must be similar to that of diazirine, but shifted

(1) R. K. Brinton and D. H. Volman, *J. Chem. Phys.*, **19**, 1394 (1951).

(2) H. M. Frey and I. D. R. Stevens, *Proc. Chem. Soc.*, **79** (1962).

(3) J. A. Bell and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **84**, 3417 (1962).

somewhat toward the red.⁴ At low concentrations it would not be detected and it is probably photolyzed under the conditions of our experiments (and those of Frey and Stevens²) to yield ethylene.

This work was undertaken in part to discover whether photoisomerization (reaction 2) did occur and whether we could study wave length and pressure effects on the reaction. Thus far we have observed very little effect of added nitrogen on the yield of diazomethane. The lack of an effect may be due to concomitant destruction of diazomethane by the stray light from the monochromator. Thus far, then, we are unable to make any statement regarding the relative importance of reactions 3 and 4 in producing methylene. One may make arguments for either reaction 3 or 4, or a combination of the two, being primarily responsible for the average properties of methylene formed in the photolysis.² Frey and Stevens did not take the photoisomerization and consequent diazomethane photolysis into account in determining the average properties of the methylene from diazirine,² so the results of their experiments probably should be reassessed.

It is also possible that diazo compounds are intermediates in the pyrolysis of diazirines. Frey and Stevens⁵ point out this possibility and the close correspondence of the activation energy for dimethyldiazirine decomposition, 33 kcal./mole, with the activation energy for diazomethane decomposition, 35 kcal./mole.⁶ In the light of our results it seems that the intermediacy of diazo compounds in the chemistry of the diazirines must be considered.

We are improving our experimental set-up to allow irradiation with more nearly monochromatic light and will report more detailed pressure and wave-length dependencies for this system in the near future.

Acknowledgments.—We are grateful to Dr. William Graham for the gift of a sample of diazirine. We thank the National Science Foundation and the Research Corporation for grants and M. J. A. also thanks the NSF-URPP for support.

(4) H. M. Frey and I. D. R. Stevens, *J. Chem. Soc.*, 3514 (1963).

(5) H. M. Frey and I. D. R. Stevens, *ibid.*, 3865 (1962).

(6) D. W. Setser and B. S. Rabinovitch, *Can. J. Chem.*, **40**, 1425 (1962).

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Intramolecular Ligand Exchange in Seven-Coordinate Structures

Sir:

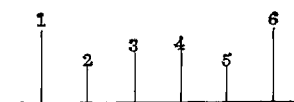
We find that the F^{19} n.m.r. spectrum of highly purified IF_7 consists of a broad, symmetrical two-line pattern with a peak separation of about 4400 c.p.s. at 56.4 Mc. ($\delta = -254$ p.p.m., CF_3COOH).² The peak separation is field independent and thus the two peaks do not represent chemically shifted nuclei. A careful search failed to reveal any other resonance. The spectrum sharpens slightly with temperature increase, and it is not grossly altered in going from liquid IF_7 to solutions of IF_7 . We conclude that there is spectroscopic equivalence of fluorine atoms in IF_7 by the following reasoning.³ The F^{19} n.m.r. spectrum of seven

(1) Iodine heptafluoride was stored in a stainless steel cylinder over sodium fluoride for six months and then carefully fractionated in a quartz vacuum system fitted with Delmar-Urry "O" ring connectors and compression valves in which the "O" rings and bores were made from fluorocarbon elastomers and resins. Our samples of IF_7 did not attack quartz over a long period of time.

(2) Our observation is in agreement with those of (a) L. G. Alexakos, C. D. Cornwell, and S. B. Pierce, *Proc. Chem. Soc.*, 341 (1963); (b) L. W. Reeves, E. J. Wells, N. Bartlett, and S. Beaton, private communication.

(3) H. S. Gutowsky and C. J. Hoffman reported a "multiple" IF_7 F^{19}

spectroscopically equivalent fluorine atoms bound to a single iodine ($I = 5/2$) atom should be a sextet with a symmetrical variation in line width if the rate of quadrupolar relaxation is slow⁴:



Using Anderson's⁵ theory on exchange and motional narrowing in n.m.r. spectral lines together with the transition probabilities predicted by Pople's theory,⁴ it can be shown that, as the rate of quadrupolar relaxation is increased, lines 1 and 6 and 3 and 4 move toward the center of the pattern while 2 and 5 move outward. The relative rates of shift of the pairs of lines are 2025:216:783 for the lines pairs 1,6:3,4:2,5, respectively. As the lines shift, they also broaden considerably. At intermediate rates of quadrupolar relaxation, the composites of lines 1 through 6 will comprise a symmetrical two-line pattern as is observed. A possible representation is sketched in Fig. 1; this is not a unique

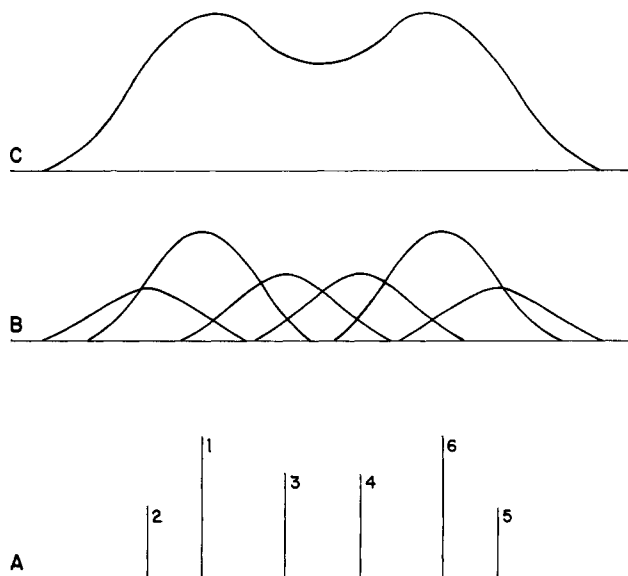


Fig. 1.—Calculated F^{19} n.m.r. spectrum for the case of an intermediate quadrupolar relaxation rate in iodine heptafluoride: A, position of lines; B, estimated line shapes; C, resultant F^{19} spectrum.

solution nor have line shapes been rigorously calculated. Consistent with our interpretation of an intermediate rate of quadrupolar relaxation for liquid IF_7 , the F^{19} spectrum sharpens slightly on temperature increase to $\sim 100^\circ$, broadens significantly for IF_7 solutions at -78° , and as reported by Alexakos, Cornwell, and Pierce^{2a} is a single resonance for gaseous IF_7 . The magnitude of the IF coupling constant is of the order of 1000 c.p.s.

There is spectroscopic (n.m.r.) equivalence of fluorine atoms in ReF_7 ⁶; a single resonance is observed at low field.^{2b} It is presumed that in the rhenium case there is faster quadrupole relaxation than in IF_7 so that any vestige of Re-F coupling is lost. The quadrupole moments of Re^{185} and Re^{187} are about 4.5 times as large as that of I^{127} .

We suggest that the ground states of odd numbered high-coordinate structures commonly have close-lying

spectrum and interpreted this as showing nonequivalent fluorine nuclei [*J. Chem. Phys.*, **19**, 1259 (1951)].

(4) J. A. Pople, *Mol. Phys.*, **1**, 168 (1958).

(5) P. W. Anderson, *J. Phys. Soc. Japan*, **9**, 316 (1954).

(6) H. Selig and E. L. Muetterties, unpublished work. Data were obtained for liquid ReF_7 and for ReF_7 solutions in WF_6 .