

acid, it is not one of the intermediates in acetolysis or formolysis.

Acknowledgment.—I am indebted to Professor S. Winstein for invaluable discussions and suggestions.

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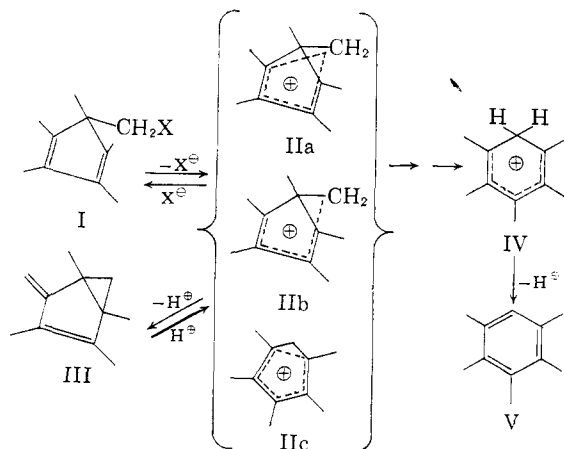
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RECEIVED JULY 11, 1960

CYCLOPENTADIENYLMETHYL DERIVATIVES AS HOMOALLYLIC SYSTEMS^{1,2}

Sir:

Pentamethylcyclopentadienylmethanol (I-OH), very recently prepared by de Vries,³ appeared to be of considerable interest as a homoallylic⁴ system with a conjugated diene group uniquely disposed toward the developing cationic center in ionization of derivatives such as the toluenesulfonate I-OTs. Carbonium ions from ionization of I-OTs were of interest as possibly unique non-classical species and as an example of a possible type of intermediate in isomerization and cracking of aromatic hydrocarbons.⁵ Examination of the behavior of penta-



methylcyclopentadienylmethyl *p*-toluenesulfonate (I-OTs) in solvolysis does indeed show that uniquely stabilized non-classical carbonium ion intermediates are involved.

As is clear from the observed rate constant, acetolysis of I-OTs is anchimerically accelerated. For I-OTs, m.p. 63.0–63.5° (dec.) (correct C, H analysis), derived from I-OH, which was in turn prepared by the method of de Vries,³ the observed acetolysis rate constant at 25° is $1.83 \pm 0.04 \times 10^{-3} \text{ sec}^{-1}$. This is larger than the value for neopentyl toluenesulfonate⁶ by a factor of *ca.*

10^8 . Allowing a power of ten per olefinic group for inductive retardation of anchimerically unassisted ionization,^{4b} we see that ionization of I-OTs must be anchimerically accelerated by a factor of at least 10^{10} .

From acetolysis of 0.04–0.08 *M* I-OTs at room temperature under nitrogen in acetic acid containing 0.11 *M* sodium acetate, there is isolated after 1.2 hours (11 half-lives of I-OTs) an 80% yield of a mixture of a hydrocarbon and the acetate of the parent alcohol, I-OAc. The hydrocarbon is the main component, vapor phase chromatographic analysis giving an 18:1 hydrocarbon:acetate ratio. From infrared and ultraviolet spectra, the hydrocarbon is the interesting compound III prepared by de Vries⁷ by decomposition of the bromobenzenesulfonate I-OBs in pyridine. A specimen of III which we prepared from I-OTs by this method displayed identical vapor phase chromatographic behavior as that of the hydrocarbon fraction from acetolysis of I-OTs. Hydrocarbon III is also very predominantly the product from solvolysis of I-OTs in 70% aqueous acetone, 0.16 *N* in sodium carbonate. No pentamethylbenzene (V) was detectable in these solvolysis products.

When the acetolysis of I-OTs in acetic acid containing sodium acetate was allowed to proceed for 20 hours, the acetate I-OAc was now the main component of the hydrocarbon–acetate product mixture, the acetate:hydrocarbon ratio being 5.5. However, no pentamethylbenzene was observed. When acetolysis of 0.04 *M* I-OTs was carried out at room temperature for 1.2 hours in the absence of sodium acetate, the product was now mainly acetate I-OAc, together with some pentamethylbenzene (*ca.* 9%). A similar mixture of acetate I-OAc and pentamethylbenzene is obtained from hydrocarbon III after 1.2 hours in acetic acid containing 0.05 *M* toluenesulfonic acid. No pentamethylbenzene was produced from acetate I-OAc under the same conditions, however. On addition of alcohol I-OH to ethanesulfonic acid or heating I-OTs above its melting point, large amounts of pentamethylbenzene are formed.

While it is clear that anchimerically assisted ionization of I-OTs leads to non-classical⁴ homoallylic ions such as II, it is not clear exactly how to represent the electron delocalization, nor how many such discrete species need to be written. This is illustrated with ions IIa, doubly homoallylic, IIb, singly homoallylic, and IIc, monohomocyclopentadienyl.⁸ Even more delocalized structures are conceivable. Kinetic control of products in basic acetic acid or aqueous acetone solvents leads very predominantly to hydrocarbon III by proton loss. However, this hydrocarbon re-adds a proton even in basic acetic acid solvent and the carbonium ion II leads to some acetate I-OAc, so that acetate I-OAc can become the predominant product from more thermodynamic control.

Carbonium ions of the II-variety do not lead to pentamethylbenzene, prior rearrangement to ion IV through an unspecified number of stages pre-

(7) L. de Vries, *ibid.*, **82**, 5242 (1960).

(8) (a) S. Winstein, J. Sonnenberg and L. de Vries, *ibid.*, **81**, 6523 (1959); (b) S. Winstein, *ibid.*, **81**, 6524 (1959).

(1) This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

(2) Research sponsored by the Office of Ordnance Research, U. S. Army.

(3) L. de Vries, *J. Org. Chem.*, in press.

(4) S. Winstein, *et al.*, *THIS JOURNAL*, (a) **70**, 838, 3528 (1948); (b) **72**, 5795 (1950); (c) **76**, 18 (1954); (d) **77**, 4183 (1955); (e) **78**, 592 (1956); (f) **78**, 4347, 4354 (1956); (g) **81**, 4399 (1959); (h) **82**, 2084 (1960).

(5) R. F. Sullivan, C. J. Egan, G. E. Langlois and R. P. Sieg, "A New Reaction that Occurs in the Hydrocracking of Certain Aromatics," Petroleum Division, American Chemical Society, New York, N. Y., Sept. 11–16, 1960.

(6) S. Winstein and H. Marshall, *THIS JOURNAL*, **74**, 1120 (1952).

sumably being required. This rearrangement evidently involves the transition state of highest energy in the series of steps involved in formation of the various products mentioned.

It is a pleasure to acknowledge helpful discussions with Dr. L. de Vries of the California Research Corporation, Richmond, California. Also, we are indebted to Dr. de Vries for information about his work prior to its publication.

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RECEIVED JULY 25, 1960

FROZEN NH AND NH₂ RADICALS FROM THE PHOTODECOMPOSITION OF HYDRAZOIC ACID¹

Sir:

Electronic spectra of NH² and NH₂³ in the gas phase are well known, and recently these fragments, from electrical discharges in NH₃ and N₂H₄, have been trapped and identified in solid rare gases^{4,5} at 4.2° K. The gas phase electronic spectrum of N₃ has been identified tentatively.⁶ There has been much discussion about these three free radicals as possible intermediates in the photodecomposition of hydrazoic acid in a matrix at low temperature.⁷

We wish to report at this time the results of some preliminary experiments concerning the photodecomposition products of HN₃ trapped in krypton and xenon at 4.2° K. *The electronic absorption spectrum clearly and convincingly demonstrates the presence of NH in considerable amounts and the presence of NH₂ as a secondary reaction product.* The presence of N₃ is suggested tentatively. This is exactly the sequence of products indicated by kinetic studies.⁸ A subsidiary mechanism, taking place simultaneously from another part of the potential surface to give H + N₃ directly, cannot be entirely ruled out by these findings since it is at present difficult to estimate the relative concentrations of products in trapped radical experiments. Secondary reactions need not necessarily depend on diffusion of the primary products through the rare gas matrix, because, at the 60:1 mole ratio used, the probability of finding at least one HN₃ molecule as a HN₃ nearest neighbor is 0.18.

Purified Kr or Xe at 1.2 mm. was allowed to leak at the rate of 1.5 ml. (S.T.P.)/min. into the system through a trap containing about 0.1 g. HN₃. The trap was maintained at a temperature of $-108 \pm 2^\circ$, which fixed the mole ratio of rare gas to HN₃ at 60 ± 20 . For photolysis, the full arc of a Xe high pressure lamp was used; this gives some intensity down to about 2000 Å. The photolysis was carried out either (I) during the

(1) Supported in part by the National Science Foundation and the Office of Ordnance Research.

(2) R. N. Dixon, *Can. J. Phys.*, **37**, 1171 (1959).

(3) K. Dressler and D. A. Ramsay, *Phil. Trans. Roy. Soc. (London)*, **A251**, 553 (1959).

(4) M. McCarty, Jr., and G. W. Robinson, *THIS JOURNAL*, **81**, 4472 (1959).

(5) G. W. Robinson and M. McCarty, Jr., *J. Chem. Phys.*, **30**, 999 (1959).

(6) B. A. Thrush, *Proc. Roy. Soc. (London)*, **A235**, 143 (1956).

(7) M. Van Thiel and G. C. Pimentel, *J. Chem. Phys.*, **32**, 133 (1960), and earlier references cited in this paper.

(8) See, for example, refs. 6 and 7.

NH from Hydrazoic Acid Photolysis in Kr, 4.2° K.

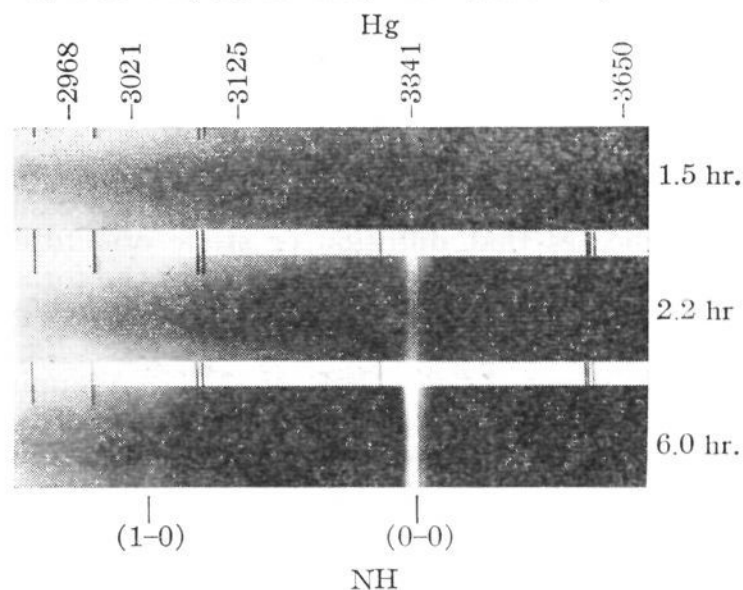


Fig. 1.—NH from the photodecomposition of HN₃ while being deposited in solid Kr at 4.2° K.; photolysis times are on the right.

deposition (photodeposition) as in a previous study of diazomethane,⁹ or (II) after the HN₃ had been deposited for 6 hours in the dark. Spectra were photographed on a Bausch and Lomb medium quartz spectrograph using, as background source, the high pressure Xe continuum for the ultraviolet and a tungsten filament lamp for the visible.

After 4.5 hours of photolysis in experiment I, the NH absorption appeared with approximately the same intensity as after 2 to 3 hours of photolysis in experiment II. The intensity of NH in II was not dependent on the rare gas used.

The R₁₁ (1) lines of the NH (0,0) and (1,0) bands in Kr (see Fig. 1) were found at $\gamma_{\text{vac}} = 29507 \pm 10 \text{ cm.}^{-1}$ and $\gamma_{\text{vac}} = 32460 \pm 15 \text{ cm.}^{-1}$ respectively. The position of the (0,0) band is in excellent agreement with the value $29509 \pm 6 \text{ cm.}^{-1}$ previously reported³ for NH in Kr, showing that the trapping site in each case is substantially the same. The broad, high-frequency component of the "doublet" corresponds to the unresolved P and Q branches. Weaker doublets appear 130 cm.⁻¹ to the blue, 150 cm.⁻¹ and 230 cm.⁻¹ to the red of the main doublet, possibly indicating the presence of multiple trapping sites. The details of the fine structure are the same whether the photolysis is carried out by I or II.

It was estimated that, in II after 3 hours, about 20% of the HN₃ had been converted to trapped NH. This estimate was made by comparing the integrated intensity of NH with that of benzene under identical deposition conditions, and by taking into account the fact that $f = 0.008$ for the NH transition¹⁰ and $f = 0.0014$ for the 2600 Å. system of benzene.¹¹ According to the above estimate the solid contains roughly 0.3% of NH. These concentration estimates, however, are based upon a number of uncertainties and should not be taken too seriously.

(9) M. McCarty, Jr., and G. W. Robinson, *THIS JOURNAL* **82**, 1859 (1960).

(10) R. G. Bennett and F. W. Dalby, *J. Chem. Phys.*, **32**, 1716 (1960).

(11) H. B. Klevens and J. R. Platt, as quoted by J. N. Murrell and J. A. Pople, *Proc. Phys. Soc. (London)*, **69A**, 245 (1956).