

For the ethyl radical, B has a value of 58.5 gauss.⁶ Solution of the equations, $a_{\text{axial-H}} = B\rho \cos^2 \theta_{\text{axial}}$, $a_{\text{equat-H}} = B\rho \cos^2 \theta_{\text{equat}}$, and $\theta_{\text{equat-H}} = \theta_{\text{axial-H}} + 120^\circ$ (tetrahedral α -carbon atom) gives the results listed in Table I.⁶ It is interesting that the value of θ_{axial} for the α -hydrogens of the 4-*t*-butylcyclohexane-1,2-dione radical-anion is the same as found for cyclohexene by n.m.r.⁷

Our results demonstrate the application of e.s.r. to conformational analysis of nonrigid systems and suggest the use of e.s.r. for structural determinations of rigid ketonic systems, such as the steroidal ketones. Work in this area is in progress.

(5) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963). These authors determined $Q\beta$ (CH₃). Since $\cos^2 45^\circ$ (free rotation) is $1/2$, B is twice their value of $Q\beta$ (CH₃).

(6) Two values of $B\rho$ and two values of θ (except when $\cos^2 \theta_{\text{equat-H}} = 0$) are obtained. Unrealistic solutions ($B\rho > 58.5/2$) have not been listed.

(7) G. V. Smith and H. Kriloff, *J. Am. Chem. Soc.*, **85**, 2016 (1963). These authors use a dihedral angle for axial hydrogens equivalent to $90^\circ - \theta_a$.

(8) (a) Alfred P. Sloan Foundation Fellow, 1959-1963; (b) National Institutes of Health Predoctoral Fellow, 1962-1963.

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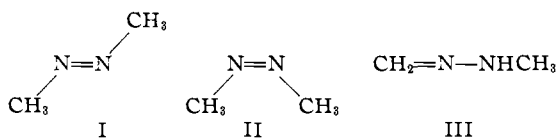
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Photoisomerization of Azomethane

Sir:

Although *cis-trans* isomerization is well-established for aromatic azo compounds,^{1,2} it has not been observed in the aliphatic series. We wish to report experiments in which the photochemical *cis-trans* isomerization of azomethane and the isolation of pure *cis*-azomethane have been achieved.



Azomethane (I), which exists in the *trans* configuration,³⁻⁵ photolyzes readily in the gas phase, yielding nitrogen and two methyl radicals. In agreement with previous work,⁶ the quantum yield (ϕ_{N_2}) for the photolytic decomposition of gaseous azomethane (I) by 365- μ light was found to be 1.0 ± 0.1 . In marked contrast, the quantum yield decreases dramatically when azomethane is irradiated in solution. Thus, for carefully degassed 5×10^{-3} M solutions in isooctane, ethanol, *N,N*-dimethylformamide, and water at 25° , the quantum yields, determined by nitrogen formation,

(1) G. Zimmerman, L. Chow, and U. Paik, *J. Am. Chem. Soc.*, **80**, 3528 (1958); E. Fischer, *ibid.*, **82**, 3249 (1960).

(2) *cis* and *trans* isomers of difluorodiazine (N₂F₂) are known: C. B. Colburn, F. A. Johnson, A. Kennedy, K. McCallum, L. C. Metzger, and C. O. Parker, *ibid.*, **81**, 6397 (1959); J. H. Noggle, J. D. Baldeschwieler, and C. B. Colburn, *J. Chem. Phys.*, **37**, 182 (1962).

(3) W. West and R. B. Killingsworth, *ibid.*, **6**, 1 (1938).

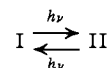
(4) G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Company, Inc., Princeton, N. J., 1945, p. 357.

(5) I. D. Brown and J. D. Dunitz, *Acta Cryst.*, **13**, 28 (1960).

(6) E. W. R. Steacie, "Atomic and Free Radical Reactions," Vol. I, Reinhold Publishing Corp., New York, N. Y., 1954, p. 376.

were, respectively, 0.17 ± 0.01 , 0.07 ± 0.01 , 0.05 ± 0.01 , and 0.01 ± 0.01 . In addition, fluorescence was not detected in any of these solutions.

However, chemical transformation does attend irradiation of azomethane in degassed solution and can be observed by ultraviolet absorption and by proton magnetic resonance spectroscopy. A solution of azomethane (I, 10^{-2} to 10^{-1} M) in degassed D₂O shows a single sharp resonance lying at $\delta +0.984$ p.p.m.,⁷ and is indefinitely stable in the dark at room temperature. Upon irradiation of the solution at room temperature, a new sharp singlet (II) appears 0.10 p.p.m. to high field from the resonance of I. By following the ratio of the height of the new resonance (II) to that of I as a function of irradiation time, it can be demonstrated that a photochemical equilibrium



is established. Experiments using D₂O as solvent reveal no proton-deuteron exchange with the solvent while coming to and remaining at photochemical equilibrium. This, together with the simplicity of the spectrum of II, demands magnetic equivalence of all the protons of II.

A degassed aqueous solution of I has an absorption maximum at 343 $m\mu$ (ϵ 25); irradiation with 365- $m\mu$ light results in a shift of the apparent maximum to longer wave lengths with a concomitant increase in the optical density maximum (ΔD_{max}). Plots of ΔD_{max} vs. time of irradiation confirm the attainment of photochemical equilibrium, the band undergoing a 70% increase in ΔD_{max} with the establishment of the new maximum at 350 $m\mu$.

From the photochemical steady-state areas of the proton resonance peaks, $K_{D_2O} = [II]/[I] = 0.09 \pm 0.01$, for 365- $m\mu$ light. Under basic conditions II reacts (*vide infra*) at least 100 times faster than I, so that it can be removed selectively from solution. This permits an independent spectrophotometric determination of K , which, over a tenfold concentration range (5×10^{-3} to 5×10^{-2} M) has a value of 0.10 ± 0.01 , in agreement with the proton resonance method.

Additionally, optical density measurements show that methanol, ethanol, and ethyl ether permit attainment of equilibrium with little photolytic decomposition. In methanol, the equilibrium is insensitive to temperature over the range -40 to $+30^\circ$. Indeed, II is even formed on irradiation of an ether glass of I at -196° . The production of II also can be observed in carbon tetrachloride, toluene, and isooctane, although photochemical equilibrium cannot be reached because of concomitant decomposition.

If a solid thin film of pure I is irradiated at -196° , II is formed. Unisomerized I together with the very small amounts of ethane and nitrogen formed by photolytic decomposition may be removed by vacuum distillation at -78° . Further fractionation at *ca.* -50° provides II as a colorless liquid of m.p. -53 to -49° .

II, dissolved in D₂O, shows the expected single sharp proton resonance at 1.08 p.p.m. to high field from HDO. Irradiation of this solution gives back I; there is no dark reversion of II to I. The absorption spectrum of an aqueous solution of II has a maximum at 353 $m\mu$ (ϵ 240).⁸ The value, $K^{365 m\mu} = 0.09$, calculated from the

(7) Chemical shifts are expressed in p.p.m. displacement (negative to low field, positive to high field) from the solvent HDO resonance. (A dilute solution of azomethane in CCl₄ shows its resonance at 3.67 ± 0.02 p.p.m. to low field from internal tetramethylsilane.)

(8) The molar extinction coefficient and λ_{max} accord with values obtained from the literature for cyclic aliphatic azo compounds constrained to a *cis* configuration: S. G. Cohen, R. Zand, and C. Steel, *J. Am. Chem. Soc.*, **83**, 2895 (1961); S. G. Cohen and R. Zand, *ibid.*, **84**, 586 (1962); C. G. Overberger, J. P. Anselme, and J. R. Hall, *ibid.*, **85**, 2752 (1963).

extinction coefficients for pure I and II agrees with the prior determinations. The mass spectrum of II is qualitatively similar to that of I; in particular, the parent peak of each is at m/e 58.⁹ Confirmation of the mass spectral value of the molecular weight of II was obtained by a micro Regnault vapor density determination.

The close structural kinship of II to I is evidenced by their base-catalyzed isomerization to the same product, formaldehyde methylhydrazone (III).¹⁰ This substance is identified directly in the aqueous reaction solution by its proton resonance spectrum, comprising an AB quartet ($\delta_A - 1.88$ p.p.m., $\delta_B - 1.52$ p.p.m., $J_{AB} = 10.6 \pm 0.3$ c.p.s.) arising from the methylene group and a singlet ($\delta + 2.12$ p.p.m.) arising from the methyl group.¹¹

Thus II is bound by the requirements that it is isomeric with I, has all protons identical, shows near-ultraviolet absorption, is formed in photochemical equilibrium with I, and suffers, with I, base-catalyzed isomerization to the same product (III). We conclude that II is *cis*-azomethane.

(9) We are indebted to Dr. G. O. Dudek (Harvard University) for aid in obtaining the mass spectra.

(10) This reaction, together with the stability of II, argues strongly against 1,1-dimethyldiazine $(CH_3)_2N^+=N^-$ as a structure for II. Further evidence is the lack of a significant peak at m/e 44.

(11) These data agree with those for formaldehyde N,N-dimethylhydrazone, $J_{AB} = 10.3 \pm 0.2$ c.p.s.; private communication from Dr. Shapiro, from work by B. L. Shapiro, G. J. Karabatsos, and S. L. Manatt. *J. Am. Chem. Soc.*, **85**, 4041 (1963).

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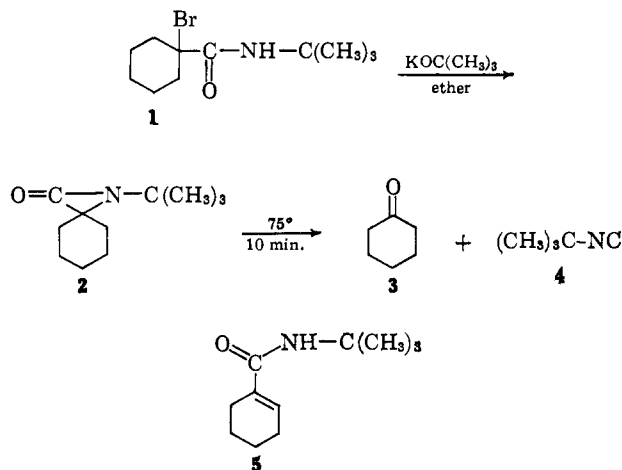
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RECEIVED DECEMBER 16, 1963

The Formation of an Isocyanide and a Ketone from an α -Haloamide

Sir:

We have found that the reaction of 1-bromo-1-N-*t*-butylcarboxamidocyclohexane (1) with potassium *t*-butoxide and subsequent warming produces cyclohexanone (3) and *t*-butyl isocyanide (4) as the major products, together with a small amount of 1-cyclohexene-1-N-*t*-butylcarboxamide (5).¹ This reaction ap-



(1) Recently, we noted the formation of small amounts of acetone and *t*-butyl isocyanide in the isomerization of 1-*t*-butyl-3,3-dimethylaziridinone to *N*-*t*-butylmethacrylamide [J. C. Sheehan and I. Lengyel, *J. Am. Chem. Soc.*, in press.

parently first produces a relatively stable α -lactam, 1-*t*-butyl-3,3-pentamethyleneaziridinone (2), which decomposes on warming (75°). We are unaware of any close analogy to this reaction.

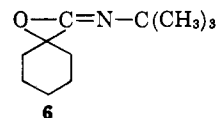
1-Bromo-1-N-*t*-butylcarboxamidocyclohexane (1), m.p. 82–83°, was prepared from 1-bromocyclohexanecarbonyl chloride² and *t*-butylamine in 92% yield. *Anal.* Found: C, 50.33; H, 7.61; N, 5.31; Br, 30.73. A mixture of potassium *t*-butoxide (1.12 g., 10 mmoles) in a solution of 2.62 g. (10 mmoles) of 1 in 100 ml. of absolute ether was stirred for 1 hr. at –15°, the suspension was cleared by centrifugation, and the supernatant solution was concentrated at 0° (reduced pressure, finally at 1 mm.). The residual colorless liquid, which crystallized promptly in an ice bath, showed the strong band in the infrared (CCl₄) at 1835 cm.⁻¹ characteristic of an α -lactam and a weak one at 1675 cm.⁻¹. On the basis of the infrared spectrum it was estimated that α -lactam 2 constituted about 80% of the product.

Without further purification this product was warmed at 75° for 10 min.; at the end of this period the α -lactam-type band in the infrared at 1835 cm.⁻¹ had disappeared completely. The volatile components were removed at 25° (2 mm.) and trapped in a receiver cooled with Dry Ice–acetone. V.p.c. revealed only two components, which were separated by fractional distillation. The first fraction (0.52 g., 63%), b.p. 89–91°, infrared 2135 cm.⁻¹, was identified as *t*-butyl isocyanide by direct comparison with an authentic sample.³

The second fraction, b.p. 155°, infrared 1715 cm.⁻¹, gave a 2,4-dinitrophenylhydrazone (1.84 g., 66%), m.p. 161–162°. A mixture melting point with an authentic sample of cyclohexanone-2,4-dinitrophenylhydrazone was undepressed.

The crystalline residue after the removal of the volatile portion showed two major components on thin layer chromatography (Silica Gel G with 96% benzene–4% ethyl acetate or 95% benzene–5% ether). These were separated by column chromatography (silicic acid with benzene–ether eluent). The first fraction eluted (0.45 g., 17%), m.p. 81–82°, was unchanged starting material (1). The second fraction (0.20 g., 11%), m.p. 113–114°, was identified as 1-cyclohexene-1-N-*t*-butylcarboxamide (5). *Anal.* Found: C, 72.85; H, 10.77; N, 7.95. The infrared spectrum (CCl₄) showed 3420 (NH), 2930 (aliphatic CH), 1670 (amide carbonyl), 1640 (C=C bond), and 1505 (amide 2) cm.⁻¹; $\lambda_{\text{max}}^{\text{EtOH}}$ 211 m μ (log ϵ 4.06). A mixture melting point with an authentic sample, prepared from 1-cyclohexenecarbonyl chloride^{4,5} and *t*-butylamine, was undepressed. The present experiments do not permit a decision as to whether product 5 arose from α -lactam 2 or from 1 by direct dehydrobromination. However, the observation that 1-*t*-butyl-3,3-dimethylaziridinone isomerized to *N*-*t*-butylmethacrylamide¹ on warming supports the first alternative.

Recent evidence⁶ indicates that in the normal state α -lactams have the true lactam structure (as represented by formula 2). However it seems likely that the



(2) J. von Braun, *Ber.*, **67B**, 218 (1934).

(3) *t*-Butyl isocyanide, which can easily be recognized by its repulsive, bitter odor, was synthesized for comparison by the method of I. Ugi and R. Meyr [*Ber.*, **93**, 239 (1960)].

(4) J. Kenner and R. L. Wain, *ibid.*, **72**, 456 (1939).

(5) G. Baddeley, H. T. Taylor, and W. Pickles, *J. Chem. Soc.*, 124 (1953).

(6) H. E. Baumgarten, *et al.*, *J. Am. Chem. Soc.*, **85**, 3303 (1963).