

Anal. Calcd. for $C_8H_8N_2O_4S$: C, 21.42; H, 4.79; N, 16.67. Found: C, 21.20; H, 4.95; N, 16.38.

R_f value in lutidine:pyridine:water (3:3:4) was 0.51; ninhydrin gave a yellow spot which turned purple on standing.

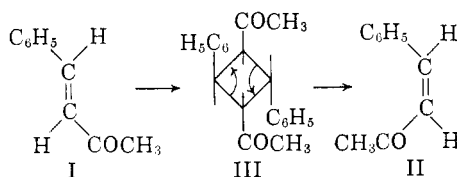
CLAYTON FOUNDATION BIOCHEMICAL INSTITUTE
AND THE DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY OF TEXAS
AUSTIN, TEX.

Photochemical Isomerization of *trans*-Benzalacetone

HERBERT O. HOUSE

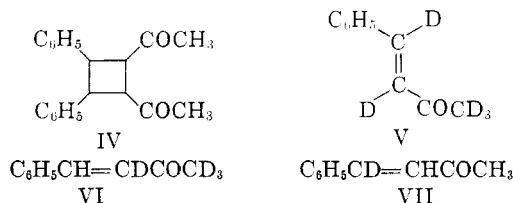
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Investigations of the photochemical isomerization of solutions of *cis*- and *trans*-ethylene derivatives¹⁻³ to have indicated that isomerization occurs *via* an excited singlet or triplet state which collapses to form both isomers. However, the observations that certain photodimers may be formed by irradiation of substituted ethylenes in the solid state but not in solution^{4,5} raised the question as to whether certain head-to-tail photodimers might be intermediates in the photochemical isomerization of substituted ethylenes. For example, a possible course for the isomerization of *trans*-benzalacetone (I) to the *cis* isomer (II) is represented in the accompanying equation.



The irradiation of an ether solution of *trans*-benzalacetone (I) with the light from a low-pressure mercury arc resulted in partial conversion of the *trans* isomer I to both the *cis* isomer (II)⁶⁻⁸ and to a high-boiling liquid which absorbs in the infrared at 1715 cm^{-1} as would be expected of the various stereoisomers of the photodimer III and as well as the corresponding cyclobutane derivatives in which the benzalacetone moieties have dimerized in a head-to-head fashion such as IV.⁹ The nature of this

high-boiling product, presumably a mixture of isomers, is still under investigation. In order to explore the possibility that the photochemical



isomerization of the *trans*-ketone I to the *cis*-ketone (II) involves an intermediate such as III, an equimolar mixture of the *trans*-ketone (I) and the pentadeutero-*trans*-ketone (V) was irradiated as previously described. The *cis*- and *trans*-ketones obtained from this irradiation mixture were examined in a mass spectrometer to determine if the partially deuterated ketones (VI and VII) were present as would be required if the photochemical isomerization involved an intermediate such as III. The results of this analysis indicated that less than 3% of the ketones VI and VII could have been formed and, consequently, that any head-to-tail photodimer such as III formed in the irradiation was not reconverted to monomer in the reaction mixture.

EXPERIMENTAL¹⁰

trans-Benzalacetone- d_5 (V). Benzaldehyde- d_1 , b.p. 85° (40 mm.), n_D^{20} 1.5377 (lit.¹¹ b.p. 178 – 179°), was prepared as previously described.¹¹ The mass spectrum of the product indicated that more than 98% of the material was benzaldehyde- d_1 . Acetone- d_6 was prepared by a series of eight equilibrations of a 0.5 mol. sample of acetone with 2 mol. samples of deuterium oxide containing 0.02 mol. of potassium carbonate. The mass spectrum of the product indicated the presence of 76.03 mol.-% acetone- d_6 , 21.03 mol.-% acetone- d_5 , 2.63 mol.-% acetone- d_4 and 0.25 mol.-% acetone- d_3 .

To a solution of 10.5 g. (0.098 mol.) of benzaldehyde- d_1 , and 10 ml. of deuterium oxide in 17 g. (0.27 mol.) of acetone- d_6 was added, dropwise and with stirring, a solution of sodium deuterioxide prepared from 0.2 g. (0.087 gram-atom) of sodium and 5 ml. of deuterium oxide. The resulting solution was stirred at room temperature for 100 min. and then diluted with a solution prepared from 1.6 g. (0.012 mol.) of phosphorus trichloride and 20 ml. of deuterium oxide. The product, extracted with three portions of benzene, was dried over magnesium sulfate and distilled under reduced pressure. The ketone, collected at 141 – 145° (17 mm.), amounted to 10.35 g. (70%). The gas chromatogram of the product exhibits a peak with essentially the same retention time as *trans*-benzalacetone and no peak corresponding in retention time to *cis*-benzalacetone. The infrared spectrum¹² has a

- (1) G. M. Wyman, *Chem. Revs.*, **55**, 625 (1955).
- (2) C. Reid, *Quart. Revs. (London)*, **12**, 205 (1958).
- (3) For a discussion of the photochemical isomerization of azobenzene, see G. Zimmerman, L. Y. Chow, and U. J. Paik, *J. Am. Chem. Soc.*, **80**, 3528 (1958).
- (4) A. Mustafa, *Chem. Revs.*, **51**, 1 (1952).
- (5) D. B. Miller and H. Shechter, 133rd Meeting of the American Chemical Society, San Francisco, Calif., April 13–18, 1958, Abstracts of Papers, p. 79 N.
- (6) E. Baroni and H. Seifert, *Naturwissenschaften*, **29**, 560 (1941); *Chem. Abstr.*, **37**, 2358 (1943).
- (7) G. van Bree, *Bull. soc. chim. belges*, **57**, 71 (1948).
- (8) R. E. Lutz, C. R. Bauer, and R. H. Jordan, *J. Am. Chem. Soc.*, **72**, 4300 (1950).

(9) A very small amount of a crystalline photodimer, m.p. 142 – 143° , has been obtained from benzalacetone by A. Butenandt, L. Karlson-Poschmann, G. Failer, U. Schiedt, and E. Biekert, *Ann.*, **575**, 123 (1951). This photodimer was assigned the structure IV.

(10) The infrared spectra were determined with a Baird, Model B, or a Perkin-Elmer, Model 21, double beam infrared recording spectrophotometer fitted with a sodium chloride prism. The gas chromatograms were obtained with an 8 mm. \times 215 cm. column packed with silicone oil on 50–80 mesh ground firebrick.

(11) K. Wiberg, *J. Am. Chem. Soc.*, **76**, 5371 (1954).

band at 1660 cm^{-1} with a shoulder at 1680 cm^{-1} (conj. C=O) and lacks bands at 1420 cm^{-1} and 1350 cm^{-1} (COCH_3) and at 975 cm^{-1} (*trans*-CH=CH) which are present in the spectrum of the nondeuterated *trans* ketone. The mass spectrum of the product indicated that a maximum of 11.5% of tetradeuterated species and 5.5% of trideuterated species could have been present in the product. A more reliable criterion for subsequent analysis was the deuterium content about the carbon-carbon double bond; 96% of the product had two deuterium atoms and 4% of the product had one deuterium atom in this portion of the molecule.

Irradiation of *trans*-benzalacetone (I). A solution of 10 g. of *trans*-benzalacetone in 125 ml. of ether was irradiated with a low pressure mercury-vapor arc lamp, samples being removed periodically for analysis by gas chromatography. After 73 hr. 48% of the benzalacetone present was the *cis* isomer. Extrapolation of a plot of composition *vs.* time indicated that at photochemical equilibrium from 50 to 55% of *cis*-benzalacetone would be present. The comparable irradiation for 19 hr. of a solution of the isomeric benzalacetones containing 89% of the *cis* ketone afforded a mixture in which 55% of the benzalacetone present was the *cis* isomer. A series of fractional distillations of the combined mixtures obtained from several irradiations afforded, in addition to the starting *trans*-benzalacetone, *cis*-benzalacetone, b.p. 119–125° (17 mm.), n_D^{27} 1.5600 [lit. b.p. 67–68° (0.2 mm.),¹³ 107° (9.5 mm.),⁷ n_D^{20} 1.5649,¹³ n_D^{15} 1.56623⁷] and a viscous oil, b.p. 173–205° (0.15 mm.), which exhibits absorption in the infrared at 1715 cm^{-1} . The infrared spectra¹² of the *cis*- and *trans*-benzalacetone samples are essentially identical with those published previously.¹³ The gas chromatogram of the *cis*-isomer indicated that no more than 7% of the *trans* isomer was present.

Irradiation of a mixture of *trans*-benzalacetone I and *trans*-Benzalacetone- d_5 (V). A solution of 5.02 g. (0.032 mole) of *trans*-benzalacetone- d_5 and 5.13 g. (0.035 mole) of *trans*-benzalacetone in 125 ml. of ether was irradiated for 20 hr. as previously described. After fractional distillation, the following fractions containing mixtures of the *cis*- and *trans*-benzalacetones were obtained (a) 0.63 g., b.p. 127–131° (18 mm.), 67% *cis* isomer; (b) 2.18 g., b.p. 131–142° (18 mm.), 39% *cis* isomer; (c) 1.85 g., b.p. 142–145° (18 mm.), 7% *cis* isomer. The mass spectra of fractions (a) and (c) indicated that the maximum amount of products VI and VII which could have been formed in the irradiation were 3% and 1%, respectively.

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DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE 39, MASS.

(12) Determined as a solution in carbon tetrachloride.

(13) G. Gamboni, V. Theus, and H. Schinz, *Helv. Chim. Acta*, **38**, 255 (1955).

(14) The mass spectra were determined with a CEC 21-103 C Mass Spectrometer equipped with a heated inlet system operated at 140°.

Action of Sulfur on Primary Amine-Formaldehyde Condensates

RICHARD C. MANSFIELD

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The reaction of formaldehyde with aromatic primary amines, *n*-alkyl primary amines, or *sec*-alkyl

primary amines normally yields the cyclic trimeric azomethines, 1,3,5-trisubstituted hexahydro-*s*-triazines.^{1,2} A unique property of the *t*-alkyl primary amines is their reaction with formaldehyde to give relatively stable monomeric *t*-alkyl azomethines.³

The reaction of these primary amine-formaldehyde condensates with sulfur has not been systematically investigated although Scott and Watt⁴ obtained 1,3-dicyclohexylthiourea from sulfur and cyclohexylazomethine and Kawaoka⁵ obtained phenyl isothiocyanate or 1,3-diphenylthiourea from sulfur and phenylazomethine depending on reaction conditions. Since both cyclohexylazomethine and phenylazomethine apparently exist as trimers and yet have given different types of products when reacted with sulfur, it seemed of interest to determine what type of product would be obtained from the reaction of the relatively stable monomeric *t*-alkylazomethines and sulfur.

Azomethines of four amines, *t*-octylamine,⁶ Primene 81-R,⁷ methylamine, and *n*-dodecylamine were used in this investigation. *t*-Octylazomethine reacted with sulfur under a variety of conditions to give *t*-octyl isothiocyanate. Reaction occurred with a very vigorous exotherm and evolution of hydrogen sulfide to give yields of about 50% of *t*-octyl isothiocyanate when mixtures of *t*-octylazomethine and excess sulfur were heated to reflux. It was necessary to limit the size of reactions of this type to about 0.1 mole of *t*-octylazomethine because of the rather violent nature of the reaction. The reaction proceeded under somewhat better control when *t*-octylazomethine was added dropwise to excess molten sulfur at 155° or to refluxing mixtures of sulfur and pyridine or *t*-octylamine. In experiments of this type it was necessary to clear the condenser repeatedly of an unidentified solid which collected.⁸ Yields of 35–65% were obtained and experiments were limited in size to 0.2 mole of *t*-octylazomethine. The reaction proceeded even more smoothly to give 61% of *t*-octyl isothiocyanate when a mixture of *t*-octylazomethine and *t*-octylamine was added dropwise to excess molten sulfur at 145–165°. No dialkyl thiourea was isolated from these reactions.

The reaction of Primene 81-R-azomethine with sulfur under similar conditions gave the corresponding isothiocyanate while the reaction of 1,3,5-tri-

(1) J. G. Miller and E. C. Wagner, *J. Am. Chem. Soc.*, **54**, 3698 (1932).

(2) L. Kahovec, *Z. physik. Chem.*, **B43**, 364 (1939); *Chem. Abstr.*, **33**, 8118 (1939).

(3) M. D. Hurwitz, U. S. Patent 2,582,128, Jan. 8, 1952; *Chem. Abstr.*, **46**, 8146 (1952).

(4) W. Scott and G. W. Watt, *J. Org. Chem.*, **2**, 148 (1937).

(5) Y. Kawaoka, *J. Soc. Chem. Ind. Japan*, **43**, No. 2, Suppl. binding 53, 151 (1940); *Chem. Abstr.*, **34**, 6131, 6487 (1940).

(6) 1,1,3,3-Tetramethylbutylamine.

(7) Primene 81-R is the proprietary designation of Rohm & Haas Company for a mixture of *t*-alkyl primary amines which is principally *t*-C₁₁H₂₃NH₂ to *t*-C₁₄H₂₉NH₂.

(8) H. D. Porter, *J. Am. Chem. Soc.*, **76**, 127 (1954).