

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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(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

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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).

methylhexahydro-*s*-triazine and sulfur gave carbon disulfide and 1,3-dimethylthiourea. 1,3-Di-*n*-dodecylthiourea was obtained from the reaction of sulfur and 1,3,5-tri-*n*-dodecylhexahydro-*s*-triazine.

EXPERIMENTAL

t-Octyl isothiocyanate. To 48 g. (1.5 moles) of sulfur heated to 165° was added dropwise during 45 min. a mixture of 25.8 g. (0.2 mole) of *t*-octylazomethine and 25.8 g. (0.2 mole) of *t*-octylamine while the temperature was maintained at 145–155° and the mixture was constantly stirred. A solid material which collected in the condenser was periodically pushed back into the flask. The mixture was then heated to 163° during another 5 min., cooled, diluted with heptane, chilled, and filtered free of 35 g. (1.1 moles) of sulfur. The filtrate was distilled at reduced pressure and then redistilled to give 21 g. (61%) of *t*-octyl isothiocyanate,^{9,10} b.p. 44–46°/0.5 mm.

Anal. Calcd. for C₉H₁₇NS: C, 63.10; H, 10.01; N, 8.18; S, 18.71. Found: C, 63.20; H, 9.84; N, 8.21; S, 18.48.

A mixture of 17.1 g. (0.1 mole) of *t*-octyl isothiocyanate prepared in this manner, 13 g. (0.1 mole) of *t*-octylamine, and 50 ml. of hexane was refluxed for 8 hr., allowed to stand prepared in this manner, 13 g. (0.1 mole) of *t*-octylamine, and 50 ml. of hexane was refluxed for 8 hr., allowed to stand overnight, chilled, and filtered free of 15 g. (50%) of 1,3-di-*t*-octylthiourea⁹ which melted at 109–111° after recrystallization from hexane.

Anal. Calcd. for C₁₇H₃₂N₂S: C, 67.93; H, 12.08; N, 9.32; S, 10.67. Found: C, 68.12; H, 12.16; N, 9.21; S, 10.92.

Primene 81-*R* isothiocyanate. To 48 g. (1.5 moles) of stirred sulfur at 180–190° was added dropwise during 15 min. a mixture of 22 g. (0.1 mole) of Primene 81-*R*-azomethine and 21 g. (0.1 mole) of Primene 81-*R* while there was a steady evolution of gas. The mixture was then stirred another 5 min. while the temperature was raised to 200°, cooled rapidly, diluted with heptane, and filtered free of 41 g. (1.3 moles) of sulfur. The filtrate was fractionated and the material distilling at 80–95°/0.35 mm. (17 g.) was redistilled to give 14 g. (56%) of Primene 81-*R* isothiocyanate, b.p. 80–90°/0.35 mm.

Anal. Calcd. for C_{12–15}H_{22–29}NS: C, 67.54–70.52; H, 10.86–11.44; N, 5.49–6.57; S, 12.55–15.03. Found: C, 69.35; H, 10.97; N, 6.23; S, 13.39.

1,3-Dimethylthiourea. To 48 g. (1.5 moles) of sulfur heated to 150° was added dropwise with stirring 20 g. (0.16 mole) of 1,3,5-trimethylhexahydro-*s*-triazine during 0.5 hr. while the temperature dropped to 110° and there was vigorous refluxing and gas evolution. The mixture was cooled and then distilled to give 12 g. (0.16 mole) of carbon disulfide, b.p. 40–50°, which was identified by preparation of a potassium xanthate from ethyl alcohol, m.p. 225–226°. Shupe¹¹ reported 225–226° for the melting point of the potassium xanthate of ethyl alcohol. The residue in the distillation flask was heated to 175° but no more material distilled. It was then cooled and extracted with toluene, water, and alcohol. The combined extracts were distilled free of solvents at reduced pressure and then diluted with ethyl alcohol. A precipitate of 19 g. (0.6 mole) of sulfur was filtered off and the filtrate was distilled to give 18 g. of distillate, b.p. 120–160°/0.5 mm. This was dissolved in 100 ml. of ethyl alcohol, filtered free of an additional small quantity of sulfur, and redistilled to give 10 g. (0.1 mole) of 1,3-dimethylthiourea,¹²

b.p. 155°/0.9 mm.–140°/0.4 mm., which solidified. A sample for analysis was recrystallized from a toluene-isopropyl alcohol mixture and melted at 50–52°.

Anal. Calcd. for C₃H₈N₂S: C, 34.59; H, 7.74; N, 26.90; S, 30.77. Found: C, 34.83; H, 7.84; N, 26.54; S, 30.76.

1,3-Di-*n*-dodecylthiourea. To a stirred refluxing mixture of 20 g. (0.63 mole) of sulfur and 100 ml. of pyridine was added dropwise during 0.5 hr. 59.1 g. (0.1 mole) of 1,3,5-tri-*n*-dodecylhexahydro-*s*-triazine. The mixture was refluxed for another 0.5 hr. and then cooled. The solid reaction product was recrystallized twice from ethyl alcohol to give 30 g. (0.07 mole) of 1,3-di-*n*-dodecylthiourea,¹³ m.p. 76–78°.

Anal. Calcd. for C₂₆H₅₂N₂S: C, 72.74; H, 12.70; N, 6.79; S, 7.77. Found: C, 72.81; H, 12.70; N, 6.62; S, 7.66.

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(13) H. Z. Lecher and T. H. Chao, U. S. Patent 2,607,803, Aug. 19, 1952; *Chem. Abstr.*, 47, 4904 (1953).

Products Obtained from Acetone, 1-Dimethylamino-3-pentanone and Diethyl Acetonedicarboxylate in the Mannich Reaction

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It has been shown by Mannich and Salzmann¹ that acetone, formalin and aqueous dimethylamine react at room temperature to form 1-dimethylamino-3-butanone (I) and 1-dimethylamino-2-(dimethylaminomethyl)-3-butanone (II). The structure of II has been definitely established.^{1,2}

We found that acetone, paraformaldehyde, and dimethylamine hydrochloride reacted in acetic acid at 95° to form a dihydrochloride which melted at 191–192° after one recrystallization and at 202–203° after two further recrystallizations. This product must have been either the dihydrochloride of II or III. A di(hydrogen oxalate) (m.p. 160–161°) and a dpicrate (m.p. 155–156°) were also prepared. From the comparisons of the melting points of these salts with the melting points mentioned below, it was concluded that the dihydrochloride which we obtained was III.

Cardwell² had allowed 1,5-dichloro-3-pentanone to react with dimethylamine and obtained 1,5-bis(dimethylamino)-3-pentanone in the form of the dihydrochloride (III) (m.p. 191–192°); he also prepared the di(hydrogen oxalate) (m.p. 155–156°).

Since the dihydrochloride of II was unknown, it was prepared and found to melt at 150–151°.

(1) C. Mannich and O. Salzmann, *Ber.*, 72, 506 (1939).
(2) H. M. E. Cardwell, *J. Chem. Soc.*, 1056 (1950).

(9) N. Bortnick, L. S. Luskin, M. D. Hurwitz, and A. W. Rytina, *J. Am. Chem. Soc.*, 78, 4358 (1956).

(10) L. S. Luskin, G. E. Gantert, and W. E. Craig, *J. Am. Chem. Soc.*, 78, 4965 (1956).

(11) I. S. Shupe, *J. Assoc. Offic. Agr. Chemists*, 25, 495 (1942).

(12) Beilstein, IV, 70.