TABLE II

ANALYTICAL DISTILLATION OF MIXED ETHERS

| Fraction | B.P. | Composition, ml.[a] | | | | | |
|---|---|---|---|---|---|---|---|
| | | *cis*-Ether | *trans*-Ether | Methanol | Carbonyl Compounds[b] | Other Impurities | Total |
| 1 | 37-45 | 21.4 | 0.8 | 2.0 | 0.2 | 0.1 | 24.5 |
| 2 | 45 | 39.8 | 3.4 | 0.1 | 0.2 | 0.0 | 43.5 |
| 3 | 45-48 | 1.8 | 3.7 | 0.0 | 0.0 | 0.0 | 5.5 |
| 4 | 49 | 0.1 | 16.8 | 0.1 | 0.0 | 0.0 | 17.0 |
| Residue | | 0.0 | 0.8 | 0.0 | 0.5 | 4.7 | 6.0 |

[a] Composition determined by infrared analysis. [b] Calculated as acetone.

The reaction mixture was then neutralized with 0.3 g. of sodium methoxide and distilled with fractionation. The following fractions were collected: I, b.p. 50-89°, 1580 g.; II, b.p. 89°, 1490 g.; residue, 95 g. Analysis of fraction I by vapor phase chromatography showed that it consisted of 50 g. of propionaldehyde (0.9 mole), 1095 g. of acetone (19.0 moles), 170 g. of methanol (5.3 moles), 50 g. of acetone dimethyl ketal (0.5 moles), and 215 g. of propionaldehyde dimethyl acetal (2.1 moles). Analysis of the residue showed that it contained 5 g. of the acetal, and higher boiling materials. Fraction II was propionaldehyde dimethyl acetal (1490 g., 14.4 moles, 73% yield). Total yield of the acetal was 84%.

*Pyrolysis of acetal to methyl propenyl ethers.* The pyrolysis column was a 65-cm. glass tube (28 mm. I.D.) wrapped with a nichrome heating wire and equipped with five equally spaced thermocouple wells. The first 5 cm. was packed with glass wool to serve as a preheater. The remainder of the column was packed with berl saddles which had been washed with a 1% aqueous solution of phosphoric acid and dried. Propionaldehyde dimethyl acetal (420 g., 4.0 moles) was passed through the column at 300-325° at a rate of 65-75 ml./hr. The pyrolyzate was collected in a stirred receiver containing 1.0 g. of sodium methoxide in 50 ml. of methanol. Chromatographic analysis showed 81% conversion to methyl propenyl ethers. The pyrolyzate was combined with an equal volume of toluene and washed three times with a total of 400 ml. of dilute aqueous sodium hydroxide. The toluene layer was separated, dried over potassium carbonate, and distilled. The fraction boiling up to 60° (235 g.) was collected by distillation and found by chromatographic analysis to consist almost entirely of methyl propenyl ethers with a ratio of *cis* to *trans* isomers of approximately 5:2. Yield based on unrecovered acetal was nearly quantitative.

*Separation of cis and trans isomers.* The mixed ethers were distilled on a 1200 × 19 mm. column packed with $^1/_{16}$ in. glass helices with a reflux ratio of 50:1. End fractions containing 80% or more of one isomer were collected, and middle fractions were re-distilled. These 80% fractions were combined and redistilled to give fractions 95% pure or better which were combined and redistilled. When sufficient amounts of each isomer were obtained for characterization, chromatographically better than 99% pure, distillation was discontinued. The physical properties were determined on these products and are summarized in Table I.

A 96.5-ml. batch of the mixed isomers was analytically distilled on a concentric tube column having 145 theoretical plates at total reflux. The column was operated at a reflux ratio of 100:1 during the day and total reflux overnight for approximately 30 days. Results of the distillation are summarized in Table II.

*Anal.* Calcd. for $C_4H_8O$: C, 66.63; H, 11.18. Found for *cis*: C, 66.43; H, 10.99. Found for *trans*: C, 66.68; H, 11.21.

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## Preparation and Reactions of 2,4-Tolylene Diisothiocyanate

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The patent literature refers to the formation of polythiourethanes from diisothiocyanates and various difunctional compounds possessing active hydrogen. The objective of this work was to prepare 2,4-tolylene diisothiocyanate and to investigate its reactions with diols, polyols and diamines in a preliminary way. A method similar to that of Connolly and Dyson[5] was chosen for the preparation.

2,4-Tolylene diisothiocyanate[1,2] has been prepared by heating 2,4-tolylene-ω-diphenyldithiourea with concentrated hydrochloric acid and from 2,4-tolylenediamine and thiophosgene.[3]

Lellmann[4] heated 2,4-tolylenediamine with ammonium thiocyanate at 120-130° to obtain this product. In all of these preparations the yields were low.

Phenyl isothiocyanate[5] has been made by treating aniline dissolved in hydrochloric acid with stannous chloride and perchloromethyl mercaptan.

Yields of 2,4-tolylene diisothiocyanate obtained by the method described herein using perchloromethyl mercaptan were low. The product consisted of yellow needles. Much unidentified dark colored

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(1) O. Billeter and A. Steiner, *Ber.*, **18**, 3294 (1885).

(2) R. Lussy, *Ber.*, **8**, 669 (1875).

(3) A. Steiner, *Ber.*, **20**, 230 (1887).

(4) E. Lellman, *Ann.* **221**, 10 (1883).

(5) J. M. Connolly and G Malcom Dyson, Jr., *Chem. Soc.*, 679 (1935).

viscous product insoluble in hydrochloric acid was formed along with the main product which was isolated from the acid solution by steam distillation.

The product was also made in very small yield from 2,4-tolylenediamine, carbon disulfide, and lead nitrate according to the method of Dains *et al.*[6] for phenyl isothiocyanate. A condensation product of 2,4-tolylene diisothiocyanate with castor oil dried satisfactorily on baking. 2,4-Tolylene diisothiocyanate condensed with 1,4-butanediol and with 1,10-decanediol to form thiourea types of structures.

## EXPERIMENTAL

*Preparation of 2,4-tolylene diisothiocyanate from perchloromethyl mercaptan.* Perchloromethyl mercaptan (240 g., 1.3 moles) was added slowly at room temperature to a solution of 36.8 g. (0.3 mole) of 2,4-tolylenediamine dissolved in 2200 ml. of water, 800 ml. of concd. hydrochloric acid, and 498 g. (2.2 moles) of stannous chloride dihydrate while stirring efficiently for 6 hr. On standing overnight a reddish brown gummy mass separated at the bottom of the aqueous solution. When this mixture was steam distilled, the reddish brown product distilled, was filtered with suction, and air dried at room temperature. This crude product was dissolved in 500 ml. of petroleum ether (b.p. 35–55°) and chilled in a refrigerator. Yellow needle crystals (6.6 g.) formed and were filtered off, m.p. 55°; lit.[1] m.p. 56°. A second crop of crystals produced by further evaporation weighed 1.65 g. Yield based on original amine was 15.4%. Another similar experiment gave 21.6%.

*Anal.* Calcd. for $C_9H_6N_2S_2$: N, 13.6. Found: N, 12.16.

*2,4-Tolylene diisothiocyanate from carbon disulfide and lead nitrate.* 2,4-Tolylenediamine (12.2 g., 0.1 mole) dissolved in 100 ml. of methanol was cooled to 10°. To this solution 15.2 g. (0.2 mole) of carbon disulfide was added slowly during 1 hr. A slight temperature rise occurred. The whole mass crystallized, was allowed to stand overnight, was filtered on a Buchner funnel, and the crystals were washed with 100 ml. of ether. The yellow crystals were steam distilled with 3500 ml. of water containing 66.2 g. (0.2 mole) of lead nitrate. When 2500 ml. of water had condensed, yellow crystals appeared on its surface. These were extracted with ether and the ether evaporated giving 1.16 g. of yellow solid, m.p. 54°; lit.[1] m.p. 56°. Yield of 2,4-tolylene diisothiocyanate was 5.83% based on 2,4-tolylenediamine. Lead acetate was unsatisfactory as a replacement for lead nitrate.

*Anal.* Calcd. for $C_9H_6N_2S_2$: N, 13.6. Found: N, 11.6.

*Reaction of 2,4-tolylene diisothiocyanate with castor oil.* Five grams of castor oil, 3 g. of 2,4-tolylene diisothiocyanate, 8 g. of xylene, and 0.03 g. of sodium hydroxide as a catalyst, 1% based on the diisothiocyanate, were heated together for 5.5 hr. at 144–147°. During this heating the color of the mixture darkened with little change in viscosity. A 0.0015-inch film of the product was cast and cured for 16 hr. at 149° in an oven after which the film was only slightly tacky indicating that condensation had occurred.

*Reaction with 1,4-butanediol.* 1,4-Butanediol (0.45 g., .005 mole) and 1.03 g. (0.005 mole) of 2,4-tolylene diisothiocyanate were warmed together for 2.5 hr. at 66–99°. A brown, brittle resin formed on cooling this mixture. Infrared examination of this resin and comparison with an unchanged mixture indicated that a thiourethan was formed.

*Reaction with 1,10-decanediol.* 1,10-Decanediol (0.87 g., 0.005 mole) and 2.06 g. (0.005 mole) 2,4-tolylene diisothiocyanate were heated together for 6.5 hr. at 82–99° and 0.5 hr. at 140°. A brown resin, viscous at room temperature, was formed. Infrared examination of the resin indicated the presence of a thiourethan band.

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[6] F. B. Dains, R. Q. Brewster, and C. P. Olander, *Org. Syntheses*, **Coll. Vol. I,** 447 (1941).

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# The Chemistry of Isobutenylamines. II. Alkylation with Allylic and Benzyl Halides

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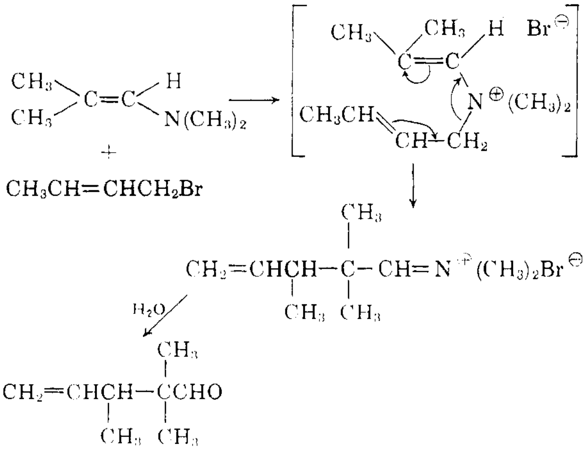
The carbon alkylation of a number of enamines containing no $\beta$-hydrogens by means of allylic and benzyl halides was recently reported by Opitz and Mildenberger.[1] We had made numerous attempts to obtain carbon alkylation of isobutenylamines, that is, enamines derived from isobutyraldehyde, by various saturated alkyl halides and tosylates, but had obtained only nitrogen alkylation. Therefore, it appeared possible that in Opitz's successful carbon alkylations, nitrogen alkylation might indeed have occurred first, followed by rearrangement of the carbon-alkylated product. This possibility was also suggested by Elkik[2] for carbon alkylation with allyl halides.

We therefore treated *N*,*N*-dimethylisobutenylamine in acetonitrile with crotyl bromide according to Opitz's procedure, and obtained, after hydrolysis, 2,2,3-trimethyl-4-pentenal rather than 2,2,-dimethyl-4-hexenal, as had been reported. We believe that the reaction initially involves nitrogen alkylation as follows:



Further evidence for the proposed mechanism was provided by the fact that *N*-allyl-*N*-methylisobutenylamine, which was itself stable under the

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[1] G. Opitz and H. Mildenberger, *Angew. Chem.*, **72,** 169 (1960).

[2] E. Elkik, *Bull. Soc. Chim. France*, 972 (1960).