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

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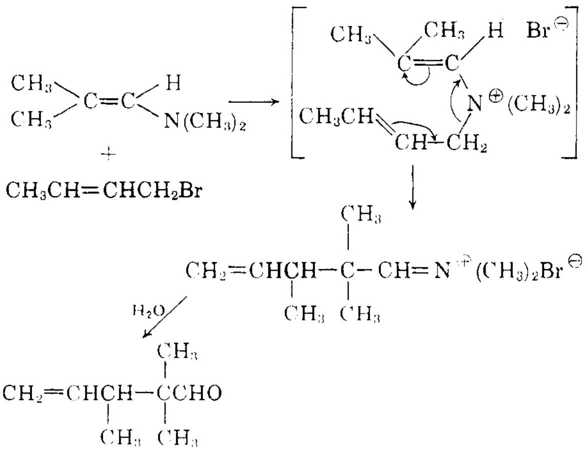
The carbon alkylation of a number of enamines containing no β-hydrogens by means of allylic and benzyl halides was recently reported by Opitz and Mildenberger.[1] We had made numerous attempts to obtain carbon alkylation of isobutenylamines, that is, enamines derived from isobutyraldehyde, by various 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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[6] F. B. Dains, R. Q. Brewster, and C. P. Olander, *Org. Syntheses*, **Coll. Vol. I**, 447 (1941).

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

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

conditions used, gave 2,2-dimethyl-4-pentenal when treated with methyl tosylate followed by hydrolysis.

When *N*,*N*-dimethylisobutenylamine was treated with benzyl bromide in acetonitrile,[1] an exothermic reaction occurred. Hydrolysis of the reaction mixture as soon as the exothermic reaction was over and after six and one-half and twenty-four hours of refluxing gave, respectively, 0, 26, and 37% yields of α,α-dimethylhydrocinnamaldehyde. These results also suggested the probability of initial nitrogen-alkylation followed by N-to-C migration of the benzyl group. This was shown to be feasible by treatment of *N*-isobutenyl-*N*-methylbenzylamine in acetonitrile with methyl iodide. Hydrolysis of the reaction mixture after thirteen hours of refluxing gave α,α-dimethylhydrocinnamaldehyde in 47% yield.[3]

EXPERIMENTAL[4]

The enamines used were prepared as follows:

N,N-Dimethylisobutenylamine. A chilled mixture of isobutyraldehyde (288 g., 4 moles), potassium carbonate (150 g.), and xylene (500 ml.) was charged to an autoclave. Dimethylamine (200 g., 4.4 moles) was added and the autoclave was then sealed and rocked for 4 hr. at 100°. The bomb was cooled, the product discharged, and the liquid decanted. Distillation through an efficient column gave 122 g. of forerun, b.p. 53–87°, and 216 g. (55%) of *N*,*N*-dimethylisobutenylamine, b.p. 87–88°, n_D^{20} 1.4221. Gas chromatographic analysis indicated the product to be about 97.5% pure.

Anal. Calcd. for $C_6H_{13}N$: C, 72.7; H, 13.2. Found: C, 73.0; H, 13.7.

Similar runs in which less potassium carbonate or less xylene was used gave poor results, as did allowing the crude reaction mixture to stand several hours before decantation and distillation. *N*-Allyl-*N*-methylisobutenylamine, b.p. 130–131° at atm. press., n_D^{20} 1.4434, was prepared according to the method of Benzing.[5]

Anal. Calcd. for $C_8H_{15}N$: C, 76.7; H, 12.1. Found: C, 77.0; H, 11.9.

N-Isobutenyl-*N*-methylbenzylamine, b.p. 50–54° at *ca.* 1 mm, n_D^{20} 1.5123, was prepared according to Benzing.[5]

Anal. Calcd. for $C_{12}H_{17}N$; C, 82.2; H, 9.8. Found: C, 82.3; H, 10.0.

Technical grade crotyl bromide (Aldrich Chemical Co.) was used without purification. Gas chromatographic analysis indicated that two major components were present in a ratio of 85:15. Winstein and Young[6] found the equilibrium mixture to contain 87% 1-bromo-2-butene and 13% 1-bromo-2-methylpropene.

Reaction of N,N-dimethylisobutenylamine with crotyl bromide. Crotyl bromide (100 g., 0.74 mole) was added all at once to *N*,*N*-dimethylisobutenylamine (75 g., 0.76 mole) in 250 ml. of acetonitrile. The temperature rose to 79° over a 5-min. period and the mixture refluxed gently for about 10 min.

The reaction mixture was allowed to cool slowly to room temperature and then stirred for a total of 5 hr. Water (250 ml.) was added and the mixture was allowed to stand overnight. The oil layer was dissolved in ether, washed with water, and distilled to give, after removal of ether and a small amount of acetonitrile, 46 g. (49%) of 2,2,3-trimethyl-4-pentenal, b.p. 145–146°, n_D^{20} 1.4307. A similar experiment in which the reaction mixture was refluxed for 6.5 hr. after the initial exothermic reaction gave 2,2,3-trimethyl-4-pentenal in 67% yield.

Anal. Calcd. for $C_8H_{14}O$: C, 76.1; H, 11.2. Found: C, 75.8; H, 11.1.

The product had an infrared spectrum identical with that of a sample (b.p. 145.5–146°, n_D^{20} 1.4313) prepared from crotyl alcohol and isobutyraldehyde.[7]

The 2,4-dinitrophenylhydrazone from the crotyl bromide-enamine product melted at 129–130°.

Anal. Calcd. for $C_{14}H_{18}N_4O_4$: C, 54.9; H, 5.9. Found: C, 55.0; H, 5.9.

The corresponding derivative from the crotyl alcohol–isobutyraldehyde product melted at 130–131°. The mixture of the two derivatives melted at 129–131°, which indicates the possible presence of a small amount of 2,2-dimethyl-4-hexenal in the crotyl bromide–enamine product. The assigned structures were fully confirmed by NMR and infrared spectra, although the NMR spectrum of the crotyl bromide–enamine product indicated <5% of an impurity.

Reaction of N-allyl-N-methylisobutenylamine with methyl tosylate. Methyl tosylate (112 g., 0.6 mole) was added to a solution of *N*-allyl-*N*-methylisobutenylamine (85 g., 0.58 mole) in 250 ml. of acetonitrile. There was no evidence of reaction. The mixture was refluxed for 3 hr., then hydrolyzed with 500 ml. of water. Treatment as described in the preceding example gave 30 g. (46%) of 2,2-dimethyl-4-pentenal, b.p. 124–125°, n_D^{20} 1.4195 (reported[7] b.p. 124–125°, n_D^{20} 1.4200).

Reaction of N-isobutenyl-N-methylbenzylamine with methyl iodide. Methyl iodide (14.1 g., 0.1 mole) was added to *N*-isobutenyl-*N*-methylbenzylamine (17.5 g., 0.1 mole) in 30 ml. of acetonitrile. There was a very slight evolution of heat. After 1.5 hr. the mixture was refluxed for 13 hr. Hydrolysis and subsequent treatment as in the preceding examples gave 7.6 g. (47%) of α,α-dimethylhydrocinnamaldehyde, b.p. 57–58° at 1 mm. (reported b.p. 98–101° at 10 mm.[1]), n_D^{20} 1.5097. The infrared spectrum of the product was identical with that obtained from *N*,*N*-dimethylisobutenylamine and benzyl bromide, as described by Opitz.[1] Its structure was fully confirmed by its NMR spectrum.

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[3] We do not wish to imply that the mechanisms proposed in this paper are general, as Dr. Opitz has informed us of several cases in which no rearrangement occurred in the reaction of crotyl bromide with other enamines.

[4] Boiling points and melting points are uncorrected. The latter were determined using a Fisher-Johns melting-point apparatus.

[5] E. Benzing, *Angew. Chem.*, **71**, 521 (1959).

[6] S. Winstein and W. G. Young, *J. Am. Chem. Soc.*, **58**, 104 (1936).

[7] K. C. Brannock, *J. Am. Chem. Soc.*, **81**, 3379 (1959).

Synthesis of 17-Desoxyrauwolscine (17-Desoxy-α-yohimbine)

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In the course of the total synthesis of 17-desmethoxydeserpidine (I) carried out in these laboratories[1] it became necessary to correlate one of the

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[1] F. L. Weisenborn, *J. Am. Chem. Soc.*, **79**, 4818 (1957).