washed with water, and dried. The crude product was dissolved in Skellysolve B or dimethoxyethane or a mixture of these two solvents and chromatographed on silicic acid on which a small amount of gummy material was strongly adsorbed. The derivative was then recrystallized from alcohol or alcohol–water mixtures. The crude products could be recrystallized to give substantially constant melting points over a range of two degrees. However, for good analysis it was necessary to remove a small amount of impurity by chromatography.

Acknowledgment.—We are indebted to the National Science Foundation for financial aid in the pursuance of this work.

Reaction of 1-Naphthyl Isocyanate with 3-Hydroxymethyl-3-methoxymethyl-2-butanone. A Reinvestigation

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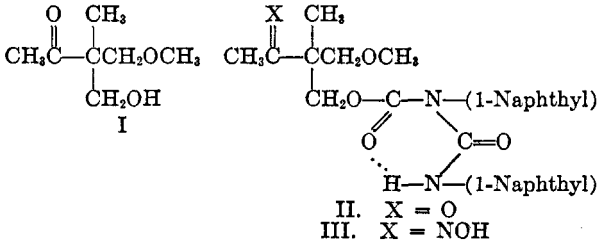
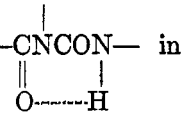
Received December 12, 1961

Upon reaction of 1-naphthyl isocyanate with 3-hydroxymethyl-3-methoxymethyl-2-butanone (I) in the presence of pyridine, Tieman and Gold[2] obtained a compound (no experimental details or yield given), m.p. 162–163°, the analysis of which indicated the empirical formula $C_{29}H_{28}N_2O_5$.[3] They suggested reaction of the second equivalent of isocyanate with the hydroxyl group formed by enolization of the acetyl group, although they noted that the acetate of I did not form a urethane with the isocyanate. The present report identifies by spectral and chemical data the reaction product obtained by Tieman and Gold as (2-methoxymethyl-2-methyl-3-oxo)butyl 2,4-bis(1-naphthyl)allophanate (II).

Several unsuccessful attempts were made to prepare II using the usual methods for the preparation of urethanes. The method of Kogon[4] for the preparation of allophanates was successfully used to prepare II in good yield. The melting point of II was dependent on the rate of heating; melting was accompanied by decomposition and resolidification took place upon further heating. Pyrolysis of II at 170° (below 1 mm.) yielded 1-naphthyl isocyanate. No other product of the pyrolysis (which might include the 1-naphthylurethane of I) was isolated.



Single attempts to reduce the keto group of II with either sodium borohydride or lithium tri-*tert*-butoxyaluminohydride and attempted reaction of II with 2,4-dinitrophenylhydrazine or semicarbazide failed to give isolable products. Sodium hypoiodite did not yield a positive iodoform test with II, although a reaction did occur. In contrast, a color test for methyl or methylene ketones[5] was positive for II and reaction between II and hydroxylamine yielded the oxime III.

Substituted allophanates are distinguishable from urethanes in that the latter, but not the former, possess an absorption band in the region of 6750 cm.$^{-1}$, attributable to the first overtone of the NH stretching vibration at 3500 cm.$^{-1}$.[6] In substituted allophanates the band at 6750 cm.$^{-1}$ is replaced by one at 4831–4877 cm.$^{-1}$ which is characteristic of the hydrogen-bonded grouping  in these compounds.[6] The near infrared spectrum of II in benzene shows a strong band at 4819 cm.$^{-1}$ but absorption in the 6667–7042-cm.$^{-1}$ region is lacking.

The infrared spectrum of II obtained at high resolution possesses twin absorptions at 1725 and 1734 cm.$^{-1}$, which may be assigned to the two allophanate C=O groups.[4] A third band at 1701 cm.$^{-1}$ is probably due to the keto C=O absorption.[7] In the oxime III the characteristic allophanate C=O bands are well resolved peaks at 1727 and 1733 cm.$^{-1}$. A band at 1690 cm.$^{-1}$ may be assigned to the C=N vibration of the oxime.[8]

All the above evidence is in good agreement with the structures postulated for II and III.

Experimental[9]

3-Hydroxymethyl-3-methoxymethyl-2-butanone (I) was prepared according to the procedure of Tieman and Gold.[2]

(2-Methoxymethyl-2-methyl-3-oxo)butyl 2,4-bis(1-naphthyl)allophanate (II) was prepared essentially according to the procedure of Kogon.[4] A mixture of 8.7 g. (0.06 mole) of the alcohol I and 60.8 g. (0.36 mole) of 1-naphthyl isocyanate (protected by a calcium chloride tube) was heated in an oil bath at 130° for 24 hr. Distillation of the reaction mix-

(1) One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture. Mention of trade names and firms does not imply their endorsement by the Department of Agriculture over similar products or firms not mentioned.

(2) C. H. Tieman and M. H. Gold, *J. Org. Chem.*, **23**, 1856 (1958).

(3) Tieman and Gold erroneously reported the formula $C_{29}H_{26}N_2O_5$; their actual analysis is correct for $C_{29}H_{28}N_2O_5$.

(4) I. C. Kogon, *J. Am. Chem. Soc.*, **78**, 4911 (1956).

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(6) I. C. Kogon, *J. Am. Chem. Soc.*, **79**, 2253 (1957).

(7) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, Inc., New York, 1958, p. 132.

(8) Ref. 7, p. 268.

(9) Melting points and boiling points are uncorrected. Infrared spectra were obtained from potassium bromide disks with the Perkin-Elmer spectrophotometers, Models 21 and 221. Near infrared spectra were obtained in benzene solution with the Cary Model 14 spectrophotometer.

ture at 0.05 mm. afforded 79% of the excess isocyanate, b.p. 71–72°. To the residue was added 50 ml. of carbon tetrachloride and the insoluble solid, m.p. 284°, 3.7 g., was filtered from the mixture. To the filtrate was added 100 ml. of petroleum ether (b.p. 30–60°) and after chilling, the crude product II, 14.0 g., was obtained. The filtrate was reduced in volume and 4.4 g. (total crude yield 63%) of solid, m.p. 150–160°, was obtained. Recrystallization of the two crops of crystals from acetone allowed the isolation of II, m.p. 160–161° (lit.,[2] m.p. 162–163°). The total weight of the acetone-insoluble solid (probably *N,N'*-bis(1-naphthyl)urea or the isocyanate dimer) was 6.0 g. An analytical sample of II was recrystallized from aqueous acetone and yielded small, colorless needles, m.p. 159–160°.

Anal. Calcd. for $C_{29}H_{28}N_2O_5$: C, 71.88; H, 5.82; N, 5.78; OCH_3, 6.40. Found: C, 72.54; H, 5.88; N, 5.94; OCH_3, 6.02.

The product II gave a positive test for a methyl ketone using the alkaline sodium nitroprusside reagent.[5] The infrared spectrum of II had bands at 3322 and 3413 cm.$^{-1}$ (free and bonded NH, respectively[10]) and at 1701, 1725, and 1734 cm.$^{-1}$. The near infrared spectrum of a solution of II in benzene showed a strong band at 4826 cm.$^{-1}$ but no band in the range 6667–7042 cm.$^{-1}$. A 2-g. sample of II was heated at 170° below 1 mm. pressure and a small amount of liquid was distilled from the melt by heating to 195° at 0.1 mm. Reaction of this liquid with ethanol gave ethyl 1-naphthylurethane, identified by melting point and mixture melting point with an authentic sample.

(2-Methoxymethyl-2-methyl-3-oximino)butyl 2,4-bis(1-naphthyl)allophanate (III) was prepared by refluxing for 2 hr. a solution of II, hydroxylamine hydrochloride, and pyridine in absolute ethanol. The oxime (80% yield), after three recrystallizations from aqueous ethanol, had m.p. 168–169°.

Anal. Calcd. for $C_{29}H_{29}N_3O_5$: C, 69.72; H, 5.85; N, 8.41. Found: C, 69.76; H, 5.78; N, 8.34.

The infrared spectrum of III showed a broad band at about 3268 cm.$^{-1}$ (free and bonded NH and OH[10]) and three well resolved bands at 1690, 1727, and 1733 cm.$^{-1}$.

Acknowledgment.—The authors wish to thank Sylvia H. Miles, Gordon J. Boudreaux, and Elizabeth R. McCall for the spectral data, and Lawrence E. Brown, Alva F. Cucullu, and Marian C. Willis for the analyses.

(10) Ref. 7, p. 5.

Mannich Bases and Aromatic Amines in Amine Exchange Reactions

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Received December 18, 1961

It was of interest to determine if Schiff bases could be obtained by reaction of hydrochlorides of Mannich bases with primary arylamines in the presence of a condensation agent.

After a mixture of β-dimethylamino- (I) or β-piperidinopropiophenone hydrochloride (II), aniline, zinc chloride-aniline complex,[1] and ethanol had been refluxed, the reaction product isolated in each instance proved to be β-phenylaminopropiophenone. It was evident, therefore, that amine exchange reactions, instead of Schiff base formation, had taken place; these reactions are similar to those which have been reported[2–6] for Mannich bases or their salts and aliphatic amines.

When I or II was allowed to react with other aromatic amines such as *p*-chloroaniline, *p*-toluidine, *p*-anisidine, or *p*-phenetidine, the products, β-arylaminopropiophenones, obtained from interaction of either I or II with a specific amine were identical.

In order to establish identity, the β-arylaminopropiophenones were synthesized from β-chloropropiophenone and the required arylamine. β-*p*-Toluidinopropiophenone was also obtained when I was heated under reduced pressure and the phenyl vinyl ketone formed was allowed to react with *p*-toluidine.

In an attempt to obtain a Schiff base of the desired type in a different manner, a mixture of equimolar amounts of acetophenoneanisil, dimethylamine hydrochloride, paraformaldehyde, and ethanol was heated for two hours on a water bath; only oily intractable material was obtained.

Experimental

β-Arylaminopropiophenones (Table I).—A. A mixture of the hydrochloride of the Mannich base (I or II) (0.02 mole) the required amine (0.02 mole), and 25 ml. of absolute ethanol was refluxed for 6 hr. After 12 hr. at room temperature, the precipitate was recrystallized from absolute ethanol.

B. A mixture of β-chloropropiophenone[7] (0.0065 mole), the required amine (0.015 mole), and water was heated for 30 min. at 100°, cooled, and the precipitate was recrystallized from ethanol.

The melting points and mixed melting points of corresponding products prepared by methods A and B were identical.

The products are insoluble in water, slightly soluble in benzene and ether, and soluble in chloroform.

The hydrochlorides, which are insoluble in water, were prepared by mixing a solution of β-arylaminopropiophenone in dry acetone with dry acetone made acid to congo red by passing in dry hydrogen chloride, and recrystallizing the precipitate from alcohol.

β-Anilinopropiophenone hydrochloride and β-*p*-phenetidinopropiophenone hydrochloride separated only on trituration after addition of ether. The former was recrystallized from alcohol–acetone mixture. The hydrochloride of β-*p*-toluidinopropiophenone was recrystallized from alcohol–ether mixture.

β-*p*-Toluidinopropiophenone.—Compound I (4.0 g.) was heated in an oil bath at 160–170° under 18 mm. pressure. The phenyl vinyl ketone which distilled (1.8 g.), b.p. 114–116°/18 mm., was dissolved in chloroform and refluxed with

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