Further reaction time (up to twenty-four hours) did not produce significant changes. Under similar conditions, N-acetylcysteine and thioglycolate also inactivated gliotoxin, whereas 10 mg. per cc. of S-methylcysteine had no effect.

The antibacterial activity of reduced gliotoxin could be regenerated immediately by titration with iodine solution or slowly by exposure to oxygen.

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Catalytic Conversion of Aldols over Chromia Catalysts

BY J. R. COLEY AND V. I. KOMAREWSKY

Recently it has been shown[1] that branched aldehydes having an *alpha*-substituted carbon atom do not undergo the complex dehydrogenation-condensation reactions when subjected to catalytic conversion over a chromia catalyst at 400° to give either ketones and olefins or unsaturated aldehydes. This was unexpected since the catalytic condensation had been assumed to be similar to a conventional liquid phase aldol condensation.

It has therefore been of interest to examine the behavior of several aldols when subjected to these conditions.

Procedure.—The aldols were prepared by the procedure of Batalin and Slavina.[2] They were vaporized and passed over a chromia catalyst at 400° in a vertical furnace at a space velocity of 0.1 as previously described.[3] The products were distilled in a 36-inch super-cal Heli Grid Podbielniak Column.

Results.—The results obtained are given in the following table.

Aldol	Ketone	B. p., °C.	Yield, %
$CH_3CH(OH)C(CH_3)_2CHO$	$CH_3COCH(CH_3)_2$	95	12.0[a]
$(CH_3)_2CHCHOHC(CH_3)_2CHO$	$[(CH_3)_2CH]_2CO$	124	6.5[b]
$(C_2H_5)CH_2CHOHCH(C_2H_5)CHO$	$(C_3H_7)_2CO$	144	61.0[c]
$(C_4H_9)CH_2CHOHCH(C_4H_9)CHO$	$(C_6H_{13})_2CO$	[e]	82.8[d]

[a] 2,4-Dinitrophenylhydrazone, m. p. 116–117°. [b] 2,4-Dinitrophenylhydrazone, m. p. 85–86°. [c] Semicarbazone, m. p. 134–135°. [d] Dihexylcarbinol, m. p. 40.0–40.5°. [e] M. p. 32.0–32.5°.

These results indicate that the step blocking the conversion of *alpha*-substituted aldehydes is not the primary condensation step but the secondary decarbonylation and dehydrogenation step. The major product obtained from the catalytic conversion of the aldols of *alpha*-substituted aldehydes was the original aldehyde. This is the product normally expected from thermal decomposition of aldols.

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[1] V. I. Komarewsky and L. G. Smith, THIS JOURNAL, **66**, 1116 (1944).

[2] V. S. Batalin and S. E. Slavina, *J. Gen. Chem. U. S. S. R.*, **7**, 202 (1937).

[3] V. I. Komarewsky and J. R. Coley, THIS JOURNAL, **63**, 700, 3269 (1941); V. I. Komarewsky and T. H. Kritchevsky, *ibid.*, **65**, 547 (1943).

The α-Naphthyl Isocyanate Derivative of *n*-Butylaniline[1]

BY DAVID CRAIG

Kharasch, Richlin and Mayo[2] have described the reaction of butyraldehyde with aniline to produce *n*-butylaniline among other products. They reported that α-naphthyl isocyanate[3] reacted with this *n*-butylaniline as well as with a known sample to form N-*n*-butyl-N-phenyl-N′-α-naphthylurea.

We have found that equivalent weights of the *n*-butylaniline and α-naphthyl isocyanate do react to form almost the theoretical yield of the expected urea which, however, instead of melting at 277° as stated by Kharasch, *et al.*, actually melts at 97–98°. A mixed melting point of this derivative with that prepared from *n*-butylaniline isolated from the reaction of butyraldehyde with aniline showed no depression. Hexane was a satisfactory solvent for recrystallization.

Anal. Calcd. for $C_{21}H_{22}N_2O$: C, 79.20; H, 6.98; N, 8.79. Found: C, 79.18, 79.23; H, 7.01, 6.95; N, 8.67, 8.78.

The single analysis reported by Kharasch and others was 9.03 for nitrogen. This value which is in excellent agreement with 8.97, the nitrogen content of N,N′-di-α-naphthylurea, and the very high melting point of 277° reported by them suggest that under their conditions of reaction, water may have been present or a disproportionation of the expected urea may have occurred. In either case N,N′-di-α-naphthylurea would be expected as a product. The formation of this urea is sometimes troublesome when conducting reactions of α-naphthyl isocyanate with amines in the presence of tertiary amines.[2] Thus *n*-butylaniline (2.0 g.) and 3-ethyl-2-propylquinoline (0.5 g.) reacted with the isocyanate (1.7 g.) at room temperature to form small amounts of N,N′-di-α-naphthylurea, N-*n*-butyl-N-phenyl-N′-α-naphthylurea and presumably N,N′-di-*n*-butyl-N,N′-diphenylurea reported by Wahl.[4] In a subsequent experiment 0.8 g. of N-*n*-butyl-N-phenyl-N′-α-naphthylurea was heated for two hours at 100° with 0.4 g. of 3-ethyl-2-propylquinoline. By extraction with hexane 0.1 g. of N,N′-di-α-naphthylurea was obtained. Fortunately N,N′-di-α-naphthylurea is easily isolated due to its extreme insolubility in hexane and other solvents. It melts when pure at 296°. The investigation described here suggests that one feature of the effect of tertiary amines on the reaction of α-naphthyl isocyanate with other amines is the formation of N,N′-di-α-naphthylurea.

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[1] Editor's footnote.—A copy of this Note was sent on its receipt to Dr. M. S. Kharasch for his information. In reply Dr. Kharasch promptly submitted the following statement for publication: "The writer has been aware for a few years that through an error on his part (and not of his co-workers) the melting point of the derivative of *n*-butylaniline with α-naphthyl isocyanate (isolated in the reaction of *n*-butyraldehyde and aniline) had been incorrectly reported [Kharasch, Richlin and Mayo, THIS JOURNAL, **62**, 497 (1940)]. Due to pressure of other work this oversight had not been corrected. The melting point of the derivative as obtained by us was 87–89°. By some unexplainable lapse of intelligence, the melting point of the N,N′-di-α-naphthylurea prepared in the course of that work was confused in the writing of the text with that of N-*n*-butyl-N-phenyl-N′,α-naphthylurea. The writer is grateful to Dr. Craig for making the appropriate correction, but he wishes to point out that none of the results or conclusions of that article are thereby invalidated." M. S. KHARASCH.

[2] Kharasch, Richlin and Mayo, THIS JOURNAL, **62**, 497 (1940).

[3] French and Wirtel, *ibid.*, **48**, 1736 (1926).

[4] Wahl, *Bull. Soc. Chim.*, [5] **1**, 246 (1934)