

Southern Regional Research Laboratory (1)

Tetracyclic Acetal from *N,N'*-Dimethylurea and Glyoxal

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The acid-catalyzed addition of *N,N'*-dimethylurea to glyoxal to form 4,5-dihydroxy-1,3-dimethyl-2-imidazolidinone (I) has been studied by n.m.r. (2). This study showed that at a pH of 2.0 the formation of I was essentially complete within 2 hours after the starting materials were mixed. It was noted, however, that if the reaction was allowed to continue for several hours beyond the point at which the dimethylurea was consumed, at least one other product began to appear in the n.m.r. spectrum of the reaction mixture.

A second product has now been isolated from this solution and identified. This material melts at 237-239° with decomposition and is soluble in chloroform but insoluble in water. It is thus easily distinguished from the water soluble glycouril (II) (m.p. 225-227°) which is formed by the addition of *N,N'*-dimethylurea to glyoxal at elevated temperatures (3).

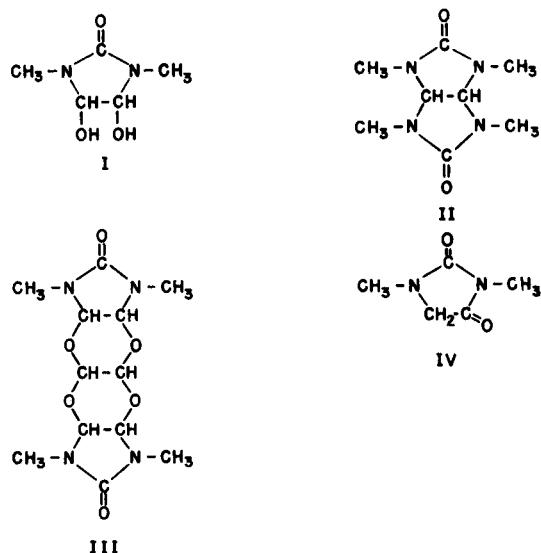
The most probable structure for this unknown product seemed to be the bis-(1,3-dimethyl-2-imidazolidinono)[4,5-b, 4',5'-g]-1,4,5,8-naphthodioxane (III) or the *N,N'*-dimethylhydantoin (IV). The hydantoin could arise from a pinacol-type rearrangement of I; other hydantoin derivatives have been reported in similar reactions (3). But compound IV has not been found previously in acid-catalyzed additions using dimethylurea (2). In this case also, compound IV may be ruled out on the basis of melting point (lit. 44°; observed 237°). The elemental analysis and molecular weight of the unknown product indicate a molecular formula of $C_{12}H_{18}N_4O_6$. Thus III would appear to be the correct structure. The infrared spectrum of the unknown showed strong absorptions attributable to amide carbonyl stretching and ether C-O-C stretching but no absorption indicative of the presence of a hydroxyl function. The n.m.r. spectrum in chloroform solution exhibited only three sharp singlets at 4.50, 5.09, and 7.10 τ with intensities in the ratio of 2:1:6. These are assignable to the $>N-CH-O-$, $-O-CH-O-$, and $>N-CH_3$ moieties of structure III. The appearance of all three signals as singlets indicates that all the ring junctions are *trans* fused.

As further confirmation of the assignment of structure III to this material, crystalline I was found to react with glyoxal to give a product identical to that obtained from the dimethylurea glyoxal reaction. This is in agreement with the known preparation of the parent naphthodioxane from ethylene glycol and glyoxal (4).

EXPERIMENTAL (5)

III From the Addition of Dimethylurea to Glyoxal.

The reaction was carried out at pH 2 as previously described (2)



except that the reaction mixture was allowed to stand at room temperature for 3 days or longer. A crystalline precipitate formed at room temperature and was collected on a filter. Recrystallization from chloroform gave colorless crystals, m.p. 237-239°, dec.

Anal. Calcd. for $C_{12}H_{18}N_4O_6$: C, 45.85; H, 5.77; N, 17.83; O, 30.54; mol. wt., 314. Found: C, 45.27; H, 5.95; N, 17.92; O, 30.86; mol. wt., 322.

Infrared data (in cm^{-1}): 2990 (m), 1740 (s), 1510 (s), 1480 (m), 1408 (m), 1345 (m), 1303 (m), 1245 (m), 1075 (s), 1035 (s), 983 (s), 928 (m), 907 (m), 860 (w), 802 (m), 739 (m), 663 (w).

Acetal Formation (III) From 4,5-Dihydroxy-1,3-dimethyl-2-imidazolidinone (I) and Glyoxal.

To 5.84 g. of I was added 2.90 g. of 40% glyoxal. The solution was adjusted to pH 2 using 6 N hydrochloric acid and left standing at room temperature. Compound III crystallized from the solution after 7 and 19 days to yield 2.0 g. of crude product, m.p. 231-235°, dec. The n.m.r. spectrum of the product was identical to that formed from dimethylurea and glyoxal.

REFERENCES

- (1) One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.
- (2) S. L. Vail, R. H. Barker, and P. G. Mennitt, *J. Org. Chem.*, **30**, 2179 (1965).
- (3) J. Nematollahi and R. Ketcham, *ibid.*, **28**, 2378 (1963) and references therein.
- (4) W. Baker and F. B. Field, *J. Chem. Soc.*, **88** (1932) and references therein.
- (5) Melting points are uncorrected. Glyoxal used was 40% "pure" grade supplied by Dr. F. Jonas Co. N.m.r. spectra were obtained on a Varian A-60A spectrometer calibrated with tetramethylsilane as an internal standard. Infrared spectra were obtained in KBr discs using a Perkin-Elmer model 21 spectrophotometer. Use of a company or product name by the Department does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

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