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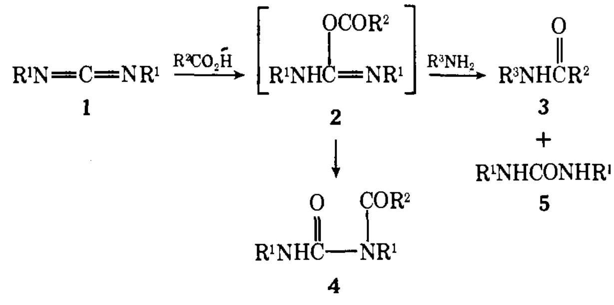
Isolation and Reactivity of a Model for the Carbodiimide–Carboxylic Acid Adduct. *O*-Benzoyl-*N*,*N*-dimethyl-*N*′-(*N*-methyl-2,4-dinitroanilino)isourea

Sir:

We wish to report the crystal structure and reactivity of an analogue of the adduct **2** which is the proposed intermediate in carbodiimide mediated condensations. The isourea undergoes acid-catalyzed inter- and intramolecular acyl transfer in the pH range 3–6 but the complex pH dependency favors the intermolecular reaction (which is necessary for condensation) in more acidic solution.

Carbodiimides, such as dicyclohexylcarbodiimide (DCC, **1**, R^1 = cyclohexyl), have received wide use as reagents to promote condensations, particularly in peptide (**3**) synthesis. However, the exact nature of the intermediates responsible for these reactions remains obscure, although it has been suggested that *O*-acylisoureas (**2**), formed on reaction of the carbodiimide with the carboxylic acid component, might be involved in this reaction[1] and in the related condensations with Woodward's reagent.[2] The failure to isolate or detect **2** was attributed to the occurrence of a rapid[3] O → N acyl transfer to give **4**, which is the product isolated in the absence of added nucleophile; indeed the undesirable formation of **4** can be the major problem in the use of **1** in peptide synthesis.[4]



Reaction of dichloromethylene dimethylammonium chloride[5] with *N*-methyl-*N*-(2,4-dinitrophenyl)hydrazine in chlorobenzene gave the formamidine chloride **6** (88%, mp 102 °C) which on treatment with silver benzoate in chloroform gave the *O*-benzoylisourea **8** (90%, mp 125.5 °C), uncontaminated by isomeric **9** and urea **11**.

Crystals of **8** are monoclinic, space group $P2_1/c$ with four molecules in a cell of dimensions $a = 15.732$ (3) Å, $b = 16.246$ (5) Å, $c = 7.628$ (1) Å, $\beta = 108.94$ (1)°. The structure was solved by direct methods and refined by full-matrix least-squares calculations to an R value of 0.0438 for 1281 independent observed reflections measured with a Hilger and Watts four-circle computer-controlled diffractometer.[10] In the structure (Figure 1) the benzoyl group is clearly trans to the position of the lone pair on the imine nitrogen atom. The C=N bond length is 1.286 (6) Å; other distances are in accord with expected values. (See paragraph at end of paper regarding supplementary material.)

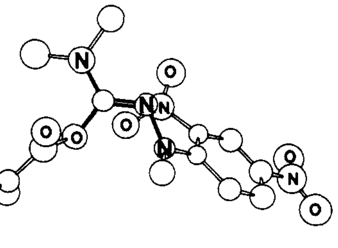


Figure 1. (*Z*)-*O*-Benzoyl-*N*,*N*-dimethyl-*N*′-(*N*-methyl,2,4-dinitroanilino)-isourea (**8**), viewed normal to the plane of the imine moiety.

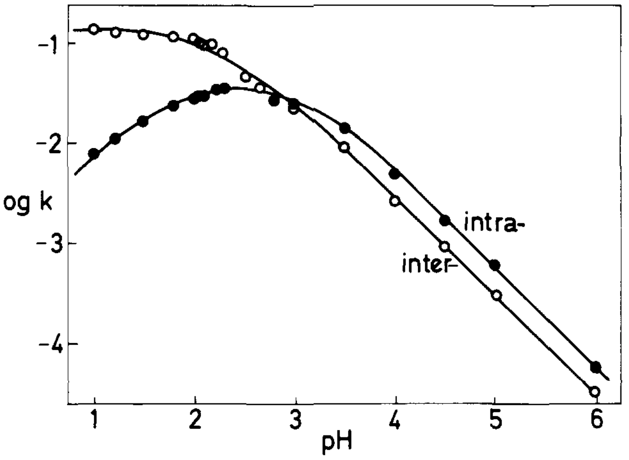
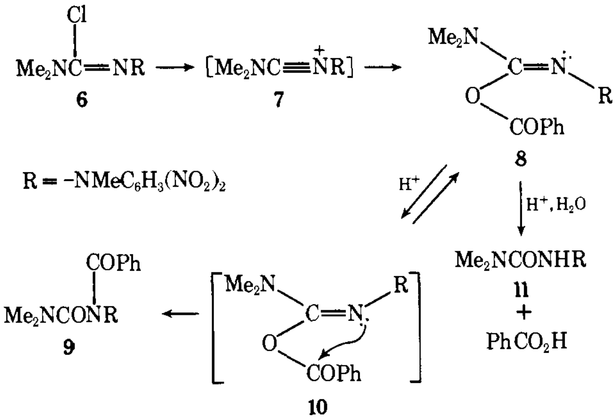


Figure 2. Observed rate constants for the intermolecular conversion of **8** to **11** (open circles) and intramolecular conversion to **9** (closed circles) at 25 °C in 4:1 water–dioxane. The points are experimental and the curves theoretical; for **8** → **11**, $k_{\mathrm{obsd}} = k_1 a_{\mathrm{H}}/(a_{\mathrm{H}} + K_{\mathrm{a}})$, $k_1 = 1.50 \times 10^{-1}\ \mathrm{s}^{-1}$, $K_{\mathrm{a}} = 4.4 \times 10^{-3}$; for **8** → **9**, $k_{\mathrm{obsd}} = k_2 a_{\mathrm{H}} K_{\mathrm{a1}}/(a_{\mathrm{H}}^2 + a_{\mathrm{H}} K_{\mathrm{a1}} + K_{\mathrm{a1}} K_2)$ (see ref 9) with $k_2 = 3 \times 10^{-2}\ \mathrm{s}^{-1}$, $K_2 = 5.2 \times 10^{-4}$.



The stereospecific formation of the *Z* isomer **8** by this route is consistent with the intermediacy of the ion **7** in the reaction sequence; we have recently shown[6] that nucleophiles react with simple nitrilium ions ($-\mathrm{C{\equiv}N^+}-$) to yield only the Z isomer (i.e., that in which the adjacent lone pair and nucleophile are mutually trans). Consistent with this, solvolysis of **6** at pH 6 in dioxane–water in the presence of sodium benzoate also gives **8**.

In contrast to isoureas **2**, **8** could be recrystallized and stored (in the absence of acid or base and protected from light) for extended periods. When dissolved in water–dioxane (4:1) at 25 °C, **8** underwent competing acid catalyzed intermolecular transfer of the acyl group to water to give benzoic acid and **11**, and intramolecular transfer (to give **9**). The pH-rate profiles for both processes (based on the overall rate constants at each pH and the analytically determined relative amounts of **9** and **11** on completion of a kinetic run) are shown in Figure 2. It is seen that at pH >3, N-acylation occurs preferentially (67% at pH 5 and 6) but that intermolecular transfer is then progressively favored as the pH is reduced.

These observations can be rationalized as follows. Rearrangement of **8** to **9** cannot take place unless preceded by nitrogen inversion or rotation about the C=N bond (and the nature of the R group used in **8** is the key element in slowing inversion),[7] giving **10**. Acid catalysis (protonation on imine nitrogen) reduces the C=N double bond character in **8**, facilitating isomerization to **10** and ultimately to **9**. Concomitantly intermolecular transfer of the acyl group to water is facilitated, since protonation of **8** gives a neutral urea as leaving group; intermolecular hydrolysis follows a simple titration curve (Figure 2) with an apparent $\mathrm{p}K_a = 2.35$.[8]

The reduction in the rate of conversion of **8** to **9** at pH <2 occurs since the free bases **8** and **10** are now present largely as their conjugate acids;[9] the N-protonated form of **10** does not undergo O → N acyl transfer to **9**.

The formation of the *O*-acylisourea by this route has the advantage that **8** is formed stereospecifically as the isomer which does not undergo rapid intramolecular acyl transfer in neutral solution. Moreover the generation of **7** from **6** (and thus the formation of **8**) is pH independent, so that **8** can readily be synthesized in neutral solution. The role of acidic catalysis in the further reactions of **8** has also been demonstrated; the wasteful intramolecular reaction which is acid catalyzed can be suppressed, relative to intermolecular acyl transfer to water, by the use of excess acid.

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Supplementary Material Available: Final fractional coordinates (2 pages). Ordering information is given on any current masthead page.

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(8) A $\mathrm{p}K_a$ of ca. 2.0 was determined for **8** spectrophotometrically by extrapolation of the optical density at 280 nm to 0% reacted (using a stopped-flow spectrophotometer). All rate constants were determined in 1:4 dioxane–water at 25 °C ($\mu = 1.0$) in the absence of added buffer either (a) using a Cary 14 spectrophotometer, when the pH in the cell was controlled by a Radiometer pH-stat assembly or (b) at low pH where a Durrum-Gibson stopped flow spectrophotometer was used.

(9) A similar rate reduction in intramolecular acyl transfer was previously noted (R. F. Pratt and T. C. Bruice, *J. Am. Chem. Soc.*, **94**, 2823 (1972)) for *S*-acylisothioureas, and our rationalization is consistent with the mechanism previously proposed.

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Book Reviews

Physics of Quantum Electronics. Volume 3. Laser Induced Fusion and X-Ray Laser Studies. Edited by STEPHEN F. JACOBS, MARLAN O. SCULLY, MURRAY SARGENT III (University of Arizona), and CYRUS D. CANTRELL III (Los Alamos Scientific Laboratory). Addison-Wesley Publishing Co., Reading, Mass. 1976. xi + 667 pp. $27.50.

The volume contains a compilation of papers concerning laser-induced fusion, high-power lasers, and potential x-ray laser systems, based on lectures presented at the Physics of Quantum Electronics Summer School held at Santa Fe, New Mexico, in summer 1975.

The first section of this volume contains five papers which discuss the then status of laser-induced fusion. The first paper provides a brief overview while the following paper discusses theoretical models concerning various aspects of implosion physics, laser-plasma coupling, energy production, etc., of importance in laser-induced fusion. The remaining papers in this section discuss the experimental work undertaken in various laboratories and include details of both the diagnostic procedures used and the preliminary experimental results obtained. Papers in the second section concern high-power laser systems. The first provides a review of high-energy visible and UV lasers. The following paper discusses the operation and construction of high-power iodine lasers. A third paper contains a detailed theoretical treatment of unstable laser resonators which includes the effects of the laser medium. The final section in this volume comprises four papers which describe research directed toward the development of a coherent source of x-rays. The first paper discusses theoretically the nature of the amplification in a swept-gain x-ray laser. Following papers concern proposed soft x-ray laser systems pumped by photoionization, and the prospects for observing soft x-ray amplification in a laser-generated plasma. The final paper discusses the generation of UV radiation through third harmonic conversion in metal vapors.

The papers contained in this volume are intended to present recent developments in a manner which can be understood by a reader with no previous specialized background. Many of the papers successfully accomplish this goal, although in certain cases the nonspecialist reader will have to undertake a considerable amount of additional reading if he is to achieve a thorough understanding of the material presented. Nonetheless, a significant amount may be learned from an initial reading of any paper, and the many references cited in each article, some as recent as 1975, will be of value to the reader interested in any particular detailed topic. The volume contains a detailed index and provides the interested graduate student or researcher with a good introduction to the problems associated with laser-induced fusion and the generation of coherent x-ray radiation.

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