

On the Basic Hydrolysis of Disubstituted Isocyanurates (I)

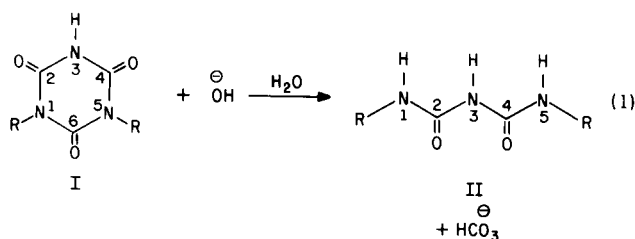
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Sir:

Shortly before the turn of the last century, it was reported that 1,3,5-trialkylisocyanurates undergo alkaline hydrolysis to give the corresponding trialkyl biuret (2,3). Very little information concerning this reaction has since been published.

It is the purpose of this communication to present our preliminary findings on the base catalyzed hydrolysis of disubstituted isocyanurates. We have found that disubstituted isocyanurates (I) undergo alkaline hydrolysis to give exclusively 1,5-disubstituted biurets (II) as shown in eq. 1.




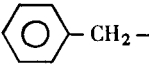
For example, a solution of 21.1 g. (75 mmoles) of diphenyl isocyanurate (I, R = ϕ) in 300 ml. of 1 M sodium hydroxide was heated at 75° for 20 minutes. The insoluble, white, solid product was collected by filtration, washed with water, and dried to constant weight, 17.5 g. (92% yield). The product was identified as a diphenylbiuret from its elemental analysis. The product (4) was shown to be 1,5-diphenylbiuret (II, R = ϕ), rather than the 1,3-isomer on the basis of its nmr spectrum. Thus, the product (in d_6 -DMSO) showed two sharp singlets at δ 8.98 (1H) and 9.64 (2H) which correspond to the N-H groups in the 3-position and 1 (5) positions, respectively.

By way of contrast, an authentic sample of 1,3-diphenylbiuret (in d_6 -DMSO) showed a broad singlet at δ 6.54 (2H) for the NH_2 group and a sharp singlet at δ 11.34 (1) for the N-H group.

As summarized in Table I, the rate at which I undergoes hydrolysis is profoundly dependent on the nature of the R group. It appears that the rate increases as the electronegativity of the hydrocarbon R group increases. This also correlates with the $\text{p}K_a$ of I which was found to decrease as R is made more electronegative.

TABLE I

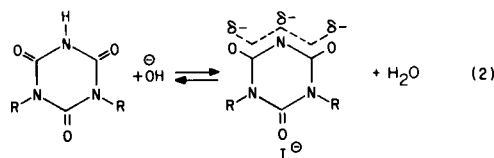
Basic Hydrolysis of Disubstituted Isocyanuric Acids (I) (a)

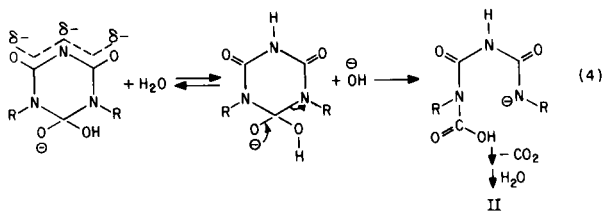
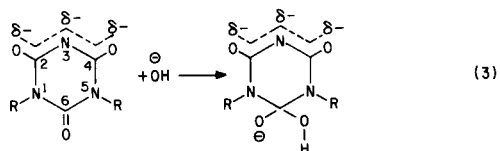
R	$\text{p}K_a$	Temp., °C	Time, Hours	Yield, %
	6.51	75	0.3	96
		75	0.3	4
$\text{CH}_2=\text{CHCH}_2-$	7.21	75	0.3	< 1
$\text{CH}_2=\text{CHCH}_2-$		75	6	50
$n\text{-C}_4\text{H}_9-$	7.82	95	18	0

(a) $[\text{I}^-]_0 = 0.25 \text{ M}$; $[\text{OH}^-] = 0.75 \text{ M}$.

The exclusive formation of the 1,5-biuret (II) to the total exclusion of the 1,3-biuret, a consequence of preferred nucleophilic attack by OH^- at the 6 position, indicates that the conjugate base (Γ^-) of I rather than I is the reacting species (eq. 3). In (Γ^-), the 6 carbonyl is the most electron deficient and presents the minimum electrostatic barrier to attack by OH^- as compared to the 2 and 4 carbonyls which are involved in charge delocalization.

The marked effect of the R group on rate indicates that bond breaking (eq. 4) is probably rate determining. Aryl, and to a lesser extent, allyl groups assist in dispersing the negative charge developing on nitrogen, whereas alkyl groups cannot.





REFERENCES

- (1) Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, California, March, 1968.
- (2) M. Mencki, *Ber.*, **9**, 1011 (1876).
- (3) E. Fischer, *ibid.*, **31**, 3773 (1898).
- (4) The melting point, 220-221° (ethanol), was of no assistance in identifying the product as melting points ranging from 209° to 255° have been reported in the literature.

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