

THE CHEMISTRY OF ISOCYANIC ACID AND ITS DERIVATIVES. II ⁽¹⁾
PREPARATION OF 2-OXO-3-PHENYL-1,3-OXAZETIDINE

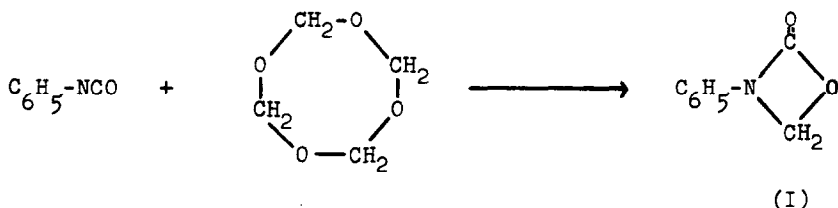
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In the past, many 1,2-oxazetidine derivatives have been reported (2), but no 1,3-oxazetidine has been reported yet.

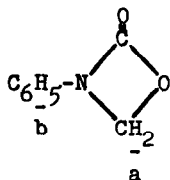
The author obtained 2-oxo-3-phenyl-1,3-oxazetidine (I) by the reaction of phenyl isocyanate with tetraoxane. This is the first example of a four membered ring compound having oxygen and nitrogen at the 1 and 3 positions.



Phenyl isocyanate 5.95 g and tetraoxane 6.00 g were dissolved in 40 ml. of dichloromethane at 0°C. To this solution, 0.5 ml. of boronfluoride etherate was added. It soon became cloudy and finally small white particles precipitated out. These particles increased as time went on. After 24 hours, the product was filtered and washed with dichloromethane. The product 5.6 g was confirmed as polyoxymethylene by elemental and infrared analysis. The solvent and phenyl isocyanate 5.5 g were evaporated from the filtrate. The remaining residue was sublimed. 2-Oxo-3-phenyl-1,3-oxazetidine (I) 0.37 g was obtained as a sublimate at 50-60°C (bath temp.) /

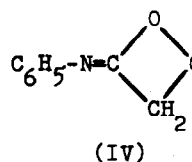
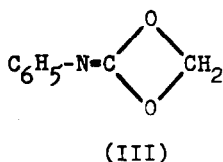
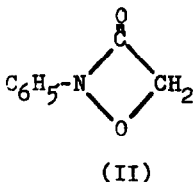
0.005 mmHg. M.p. 127°C. Anal. Calcd. for $C_8H_7NO_2$: C, 64.40; H, 4.73; N, 9.39; Mol.wt. 149.14. Found: C, 64.19; H, 4.66; N, 9.39; Mol. wt. 149.8 (v.p.o. in $CHCl_3$).

N.m.r. ($CDCl_3$) showed a sharp singlet at τ 4.73 (2H) and a wide multiplet at τ 2.5-3.1 (5H) corresponding to a and b hydrogens respectively.



Characteristic infrared peaks were 3400 M, 3045 W, 2920 W, 2000 W, 1942 W, 1911 W, 1860 W, 1818 VS, 1606 M, 1510 M, 1464 W, 1430 M, 1413 M, 1183 W, 1162 M, 1104 S, 1049 S, 1028 M, 904 M, 770 M, 749 M, 725 W and 700 W cm^{-1} (KBr pellet). A very strong peak at 1818 cm^{-1} indicates the presence of strongly strained carbonyl.

Mass spectrum (70 eV) also supported the proposed structure (I), and omitted the other possible structures (II), (III) and (IV), by giving fragment ions at 149 (relative abundance 0.1, parent⁺), 119 (0.88, $C_6H_5-NCO^+$), 105 (9.7, $C_6H_5-N=CH_2^+$), 104 (7.7, $C_6H_5-N=CH^+$), 91 (0.55, $C_6H_5-N^+$), 77 (100, $C_6H_5^+$), 44 (77.5, CO_2^+) and 28 (3.4, CO^+ , NCH_2^+).



Acknowledgement

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References

- (1) Part I. S. Ozaki and T. Kato, International Symposium on Macromolecular Chemistry, Tokyo-Kyoto, Preprints, II-64 (1966).
- (2) C.F. Giffin and R.N. Haszeldine, Proc. Chem. Soc., 1959, 369.