

REACTIONS OF PHENYL ISOCYANATE WITH VINYL ETHERS

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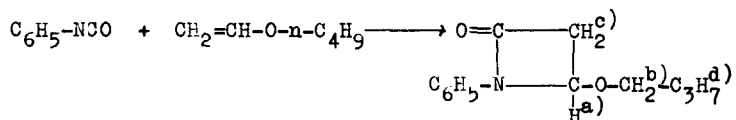
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It has been reported that β -lactam can be synthesized from aryl isocyanate with diazomethane¹⁾ or enamines²⁾.

It has been also recently found that the reactions of chlorosulfonyl isocyanate with olefin affords α -lactam³⁾.

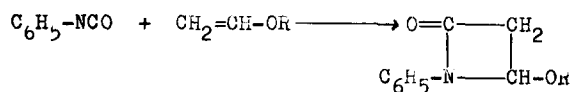
In the present paper, the reactions of phenyl isocyanate with vinyl ethers are described. When equimolar amounts of *n*-butyl vinyl ether and phenyl isocyanate were heated at 150° (bath temperature) for 20 hr., a large amount of liquid, boiling at 120-125° under 1 mmHg, was obtained.

The elemental analysis and the molecular weight measurement show that the product is a 1:1 adduct of the starting materials. Further, its infrared spectrum has an intense peak at 1760 cm^{-1} attributable to carbonyl group of α -lactam. The result of n.m.r. spectrum also supports the α -lactam structure; it shows absorptions at τ a) 4.65 (triplet, 1 proton), b) 6.52 (triplet, 2 protons), c) 7.05 (doublet, 2 protons), d) 8.55-9.10 (multiplet, 7 protons) and five aromatic protons at low field.



Similarly, β -lactams were isolated by the reactions of phenyl isocyanate with ethyl, β -chloroethyl, iso-butyl, 2-ethylhexyl and dodecyl vinyl ethers under similar condition. These results are listed in Table I.

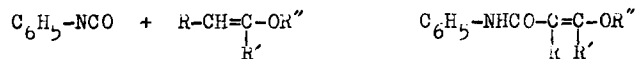
Table 1



R	Reaction Time (hr.)	Yield (%)	B.p. (°C/mmHg)	Analysis		
				Found	(Calcd.)	
				C	H	N
n-C ₄ H ₉	10	44	120-3/1	71.04 (71.20)	7.74 7.82	6.39 6.39)
iso-C ₄ H ₉	20	62	120/0.07	71.29 (71.20)	8.07 7.82	6.48 6.39)
C ₄ H ₉ -CHCH ₂ C ₂ H ₅	24	51	158/0.09	73.89 (74.14)	9.46 9.15	5.20 5.09)
C ₁₂ H ₂₅	13	7	*			
C ₂ H ₅	10	3	119/5			
Cl-CH ₂ CH ₂	13	4	*			

* undistillable (Reaction Temperature; 150°)

On the other hand, when substituted vinyl ethers such as 1-cyclohexenyl ethyl ether, isopropenyl ethyl ether or α -ethoxy styrene were used in the above experiment, the corresponding β -lactams could not be obtained, but β -alkoxy α, β -unsaturated carboxylic anilides were produced.



Reference

- 1) J. C. Sheehan and P. Izzo, J. Am. Chem. Soc., 70, 1985 (1948); J. C. Sheehan and P. Izzo, *ibid.*, 71, 4079 (1949)
- 2) M. Perelman and S. A. Mizesak, J. Am. Chem. Soc., 84, 4988 (1962)
- 3) R. Graf, *Ann.*, 661, 111 (1963)