

A NOVEL ROUTE TO 2-CARBAMOYL CYCLOALKANONES BY THE ADDITION REACTION OF
SILYL ENOL ETHERS TO ISOCYANATES

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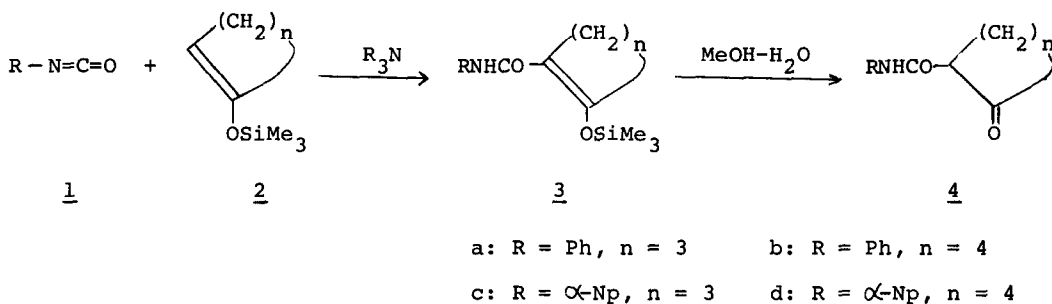
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(Received in Japan 4 August 1973; received in UK for publication 17 September 1973)

Silyl enol ethers are currently much interested in respect to the reaction of enolate anion, and many reports have been made on the formation and spectra of these compounds.¹ Little has been known, however, about the reactivity on the β -carbon of these compounds except trimethylsilylacetals.² We have found that silyl enol ethers behave as a nucleophilic reagent like enamines in sharp contrast with ordinary vinyl ethers which are known to lack reactivity toward aliphatic, aromatic and benzoyl isocyanates.³ Now, we wish to report an enamine-like addition of silyl enol ethers to isocyanates which furnishes a novel route to 2-carbamoylcycloalkanones.



1- Trimethylsilyloxycyclopentene (2, $n = 3$)⁴ or 1-trimethylsilyloxycyclohexene (2, $n = 4$)⁴ was found to react with phenyl isocyanate or α -naphthyl isocyanate in the presence of a catalytic amount of a tertiary amine⁵ such as pyridine or

triethylamine at 130-160° for 10-20 hr to give a 2-(N-arylcarbamoyl)cycloalkan-1-one 4 after treatment with MeOH-H₂O. The structure of the intermediate 2-(N-arylcarbamoyl-1-trimethylsilyloxy)cycloalkene 3 was confirmed by IR and NMR spectra, e.g., 3a (R = Ph, n = 3): NMR(CDCl₃) δ 0.40 (s, 9H) (Me), 1.64 (m, 2H) (CH₂), 2.37 (m, 4H) (CH₂), 6.64-7.50 (m, 5H) (Ph) and 8.96 (s, 1H) (NH); IR(KBr disk) 3360 (ν NH), 1650 (ν C=O), 1625 (ν C=C) and 1530 cm⁻¹ (Amide II). Thus, the silyl enol ether 2 can be used in place of the corresponding enamines⁶ such as morpholinocyclohexene in high yield, as shown in the Table.

Table 2-(N-Arylcarbamoyl)cycloalkanones 4 Obtained by the Reaction of Silyl Enol Ethers with Isocyanates⁸

	R	n	Conditions	Yield(%)	Mp(°C)
<u>4a</u>	C ₆ H ₅	3	130°, 12 hr	94	102-104 (lit., ⁶ 102-104)
<u>4b</u>	C ₆ H ₅	4	160°, 24 hr	72	105-107 (lit., ⁶ 106-108)
<u>4c</u>	α -C ₁₀ H ₇	3	130°, 12 hr	97	101-103 (lit., ⁷ 102.5-103.5)
<u>4d</u>	α -C ₁₀ H ₇	4	160°, 24 hr	83	168-170

REFERENCES AND FOOT NOTES

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3. Ordinary vinyl ethers are reactive toward sulfonyl isocyanates. But, the predominant pathway for the reaction is reported to be [2 + 2] cycloaddition. c.f., F. Effenberger and R. Gleiter, *Chem. Ber.*, **97**, 1576 (1964); F. Effenberger and G. Kiefer, *Angew. Chem.*, **79**, 936 (1967).
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5. The reaction of 1-trimethylsilyloxycyclopentene with α -naphthyl isocyanate is found to proceed smoothly at 130° without tertiary amine. In other cases, however, heating at higher temperature for a prolonged period of time must be required when tertiary amine is not used.
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8. The NMR and IR spectra and elemental analyses of these compounds were consistent with the assigned structures.