

A NOVEL REACTION OF CYCLIC KETENE ACETALS
 WITH PHENYL ISOCYANATE THROUGH ZWITTERION

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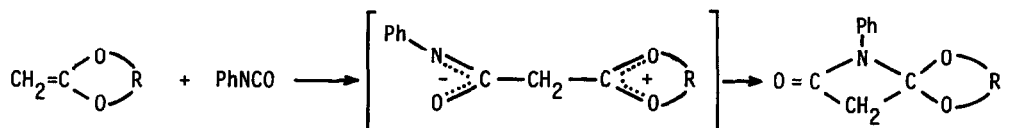
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Summary; A novel reaction of cyclic ketene acetals with phenyl isocyanate through zwitterion was found to yield the corresponding spiro compounds in good yields.

It is known that β -carbon atom of carbon-carbon double bond of ketene acetals has a strong anionoid character because of the electron donating property of the conjugated two oxygen atoms. Most of ketene acetals are subjected to reaction with protic substrates,^{1,2} and easily undergo cationic polymerization.^{3,4} It is anticipated that this unique character of the β -carbon atom is applicable to develop a new polymerization process. We have reported previously the copolymerization of cyclic ketene acetals with carbon disulfide through a macrozwitterion.⁵ Herein we wish to report a novel reaction of cyclic ketene acetals and phenyl isocyanate (PhNCO).

The equimolar reaction was carried out at room temperature without a solvent. Upon the mixing of 4-methyl-2-methylene-1,3-dioxolane (1) and PhNCO, a vigorous exothermic reaction took place immediately to obtain polymer, the infrared (IR) spectrum of which was the same as that of homopolymer of 1 by means of cationic initiators.⁴ On the other hand, 2-methylene-1,3-dioxepane (2) reacted with PhNCO gradually to give a one-to-one adduct (4) almost quantitatively. The IR spectrum of 4 showed a strong carbonyl band at 1770 cm^{-1} , which is the characteristic absorption of four-membered lactam. Therefore, the product 4 was determined to be a spiro compound, 8-phenyl-1,6-dioxo-8-azaspiro[6.3]decan-9-one⁶ by ¹H NMR and elemental analysis. When a solvent



1; R = -CH(CH₃)CH₂-

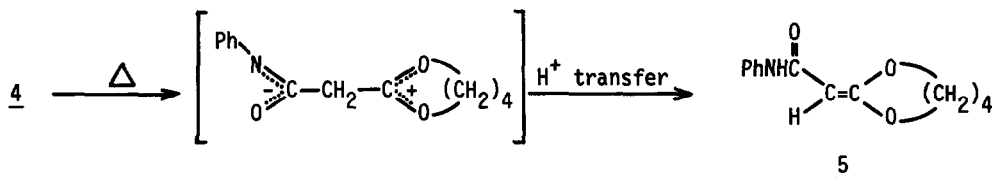
2; R = -(CH₂)₄-

3; R = -CH(CH₃)CH₂-

4; R = -(CH₂)₄-

or a cooling bath to prevent the exothermic reaction was employed, the reaction of 1 and PhNCO proceeded mildly to afford 2-methyl-6-phenyl-1,4-dioxo-6-azaspiro[4.3]octan-7-one(3)⁷ in a good yield.

Further, 3 and 4 were heated at 80°C in bulk. Although a polymer with the complicated structure was obtained from 3, 2-(phenylcarbamoylmethylidene)-1,3-dioxepane(5)⁸ was afforded by the isomerization of 4 in a good yield.



References and Notes

- 1) S. M. McElvain and M. J. Corry, *J. Am. Chem. Soc.*, **76**, 3781(1948).
- 2) H. Fukuda, M. Hirota, and T. Endo, *Tetrahedron Lett.*, **27**, 1587(1986).
- 3) I. Cho and M. S. Gong, *J. Polym. Sci., Polym. Lett. Ed.*, **20**, 361(1982).
- 4) H. Fukuda, M. Hirota, and Y. Nakashima, *J. Polym. Sci., Polym. Lett. Ed.*, **21**, 171(1983).
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- 6) A mixture of 2(1.14 g, 10 mmol) and PhNCO(1.19 g, 10 mmol) was allowed to stand at room temperature for 3 days. The mixture was rubbed with a spatula to give a crystal of 4 (2.33 g, 100%). The crystal was purified by recrystallization from ether; 2.02 g(87 %), mp 74.5-76.0°C. IR(KBr disk), 1770 cm⁻¹(C=O). ¹H NMR(CDCl₃) 7.10-7.70(m, 5H), 3.90-4.20(m, 2H), 3.06-3.90(m, 2H), 3.16(s, 2H), 1.75(m, 4H). Anal. Calcd for C₁₃H₁₅O₃N: C, 66.93%; H, 6.49%; N, 6.01%. Found: C, 67.07%; H, 6.48%; N, 5.80%.
- 7) A solution of 1(1.00 g, 10 mmol) in 10 ml of THF was added slowly to a THF solution(10 mol) of PhNCO(1.19 g, 10 mmol). The mixture was allowed to stand at room temperature for 4 hrs. Then the solvent was removed completely at room temperature under reduced pressure. The residue was recrystallized from ether-n-hexane; 1.68 g(77 %), mp.63.0-64.5°C. IR(KBr disk), 1765 cm⁻¹ (C=O). ¹H NMR(CDCl₃), 7.0-7.6(m, 5H), 4.1-4.2(m, 2H), 3.5-3.8(m, 1H), 3.3(d, 2H), 3.2-3.5(double d, 3H). Anal. Calcd for C₁₂H₁₃O₃N: C, 65.73%; H, 5.99%; N, 6.39%. Found: C, 65.69%; H, 6.02%; N, 6.31%.
- 8) 4(0.2 g, 8.6 mmol) was sealed in a glass ampule and heated at 80°C for 4 days. After the ampule was opened, the reaction product was recrystallized from acetone-ethanol to afford 0.14g(70 %) of 5. mp 159.5-161°C. IR(KBr disk), 1670(C=C), 1625 cm⁻¹(C=O). ¹H NMR(CDCl₃), 8.50(br. s, 1H), 6.90-7.60(m, 5H), 4.72(s, 1H), 4.28(m, 2H), 4.05(m, 2H), 1.90(m, 4H). Anal. Calcd for C₁₃H₁₅O₃N: C, 66.93%; H, 6.49%; N, 6.01%. Found: C, 67.14%; H, 6.48%; N, 6.06%.