New Addition Reactions. IV. The Addition of Schiff Bases to Diketene

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For the cyclic addition of unsaturated components to diketene, two possible paths may be considered.

The type 1 reaction including the reaction of diketene with ketones(1), carbodiimides(2) and enamines(3), and the formation of dimeric dehydroacetic acid(4) are already known, but examples of the type 2 addition have not been reported. We wish to report the formation of type II adduct by the reaction of diketene with some Schiff bases.

Treatment of diketene with *N*-benzylidene-*t*-butylamine in chloroform gave a cyclic adduct, 1-*t*-butyl-6-phenyl-2, 4-piperidinedione (III), in an excellent yield. The structural assignment was made on the basis of its elementary analysis, infrared spectrum, dinitrophenylhydrazone formation, and a positive ferric chloride test. No evidence for the formation of a type I adduct was observed. Similar reactions with *N*-methylene-*t*-butylamine and *N*-methylenecyclohexylamine also gave the corresponding piperidinediones, but the yields were very low. In the spectra (Nujol) of all adducts obtained, two sharp bands at 1700~1725 cm^{-1} (keto CO) and 1633~1650 cm^{-1} (lactam CO) regions, along with two other bands (conjugated C=C, 1550 cm^{-1} and OH,

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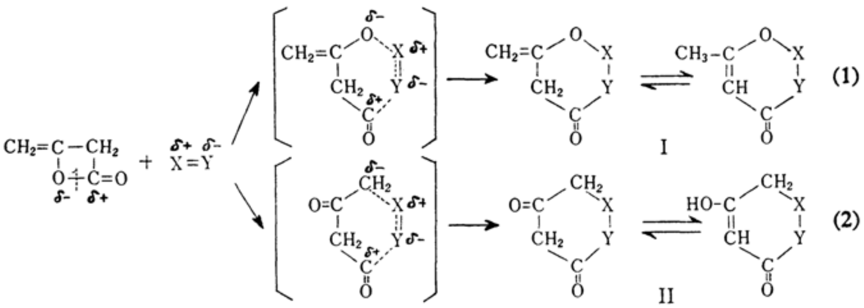
1) M. F. Carroll and A. R. Bader, *J. Am. Chem. Soc.*, **75**, 5400 (1953).

2) R. N. Lacey and W. R. Ward, *J. Chem. Soc.*, **1958**, **2134**.

3) B. B. Millward, *J. Chem., Soc.*. **1960**, 26; S. Hünig, E. Benzing and K. Hübner, *Chem. Ber.*, **94**, 486 (1961).

4) A. B. Boese, Jr., *Ind. Eng. Chem.*, **32**, 21 (1940); T. Isozima, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zassi*), **57**, 773 (1954).



3290~3300 cm⁻¹) assigned to the enolic structure of II, were observed.

In cases where *N*-benzylideneaniline and *N*-benzylidenecyclohexylamine were used as Schiff bases, the desired adduct could not be isolated from the resinous reaction mixtures. On the other hand, when diketene was treated with *N*-isopropylidenecyclohexylamine, the formation of a polymer of diketene was observed. Its melting point and infrared spectrum were essentially in accord with those of a polyester obtained by the aluminum isopropoxide-[5] or potassium *t*-butoxide-[6]catalyzed polymerizations of diketene.

The failure of the desired cyclization appears to depend largely on the nature of the Schiff base used, especially its degree of dimerization or trimerization[7], its basicity and its bulkiness; but a detailed explanation is not possible at the present time.

Experimental[8]

1-*t*-Butyl-6-phenyl-2, 4-piperidinedione (III).—A mixture of 30 g. (0.19 mol.) of *N*-benzylidene-*t*-butylamine (prepared by the procedure of Emmons[9]) and 17 g. (0.19 mol.) of diketene in 100 ml. of chloroform was refluxed for 5 hr. After removal of the solvent, there was obtained 37 g. (80%) of crude 1-*t*-butyl-6-phenyl-2, 4-piperidinedione. Recrystallization from benzene gave the pure product which melted at 108~109°C. This adduct gave a dark-red color with ethanolic ferric chloride on standing for several hours.

Found: C, 73.68; H, 7.85; N, 5.53. Calcd. for $C_{15}H_{19}NO_2$: C, 73.34; H, 7.81; N, 5.71%.

The 2, 4-dinitrophenylhydrazone after recrystallization from ethanol melted at 230°C with decomposition.

Found: C, 59.23; H, 5.61; N, 16.24. Calcd. for $C_{21}H_{24}N_5O_5$: C, 59.14; H, 5.67; N, 16.42%.

1-*t*-Butyl-2, 4-piperidinedione.—To a stirred solution of 6 g. (0.07 mol.) of freshly distilled *N*-methylene *t*-butylamine[9] in 100 ml. of ether was added slowly 6.7 g. (0.08 mol.) of diketene at room temperature. After completion of the addition, the mixture was heated at 30°C for 3 hr. The resultant precipitate was collected, and weighed 1 g. (8%). An analytical sample was obtained by recrystallization from benzene, m. p. 159~160°C.

Found: C, 63.87; H, 9.23; N, 8.52. Calcd. for $C_9H_{15}NO_2$: C, 63.88; H, 8.94; N, 8.28%.

1-Cyclohexyl-2, 4-piperidinedione.—A mixture of 11 g. (0.10 mol.) of *N*-methylenecyclohexylamine[10] and 300 ml. of ether was stirred and cooled to −15°C, 25 g. (0.30 mol.) of diketene was added dropwise to this solution at such a rate so as to maintain that temperature. After the addition of diketene, the stirring was continued at the same temperature for 1 hr. and at 0°C for 5 hr. The tar-like product that separated was extracted with petroleum ether. Removal of the solvent by distillation gave 0.5 g. (3%) of the crude adduct. After one recrystallization from toluene, the adduct melted at 182~186°C. The analysis was somewhat unsatisfactory, but the infrared spectrum was quite similar to that of III.

Found: C, 66.75; H, 9.04; N, 7.14. Calcd. for $C_{11}H_{17}NO_2$: C, 67.66; H, 8.78; N, 7.17%.

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[5] J. Furukawa et al., ibid., **65**, 254 (1962).
[6] Our data, unpublished.
[7] Cf. M. M. Sprung, *Chem. Revs.*, **26**, 311 (1940).
[8] All temperatures are uncorrected.
[9] W. D. Emmons *J. Am. Chem. Soc.*, **79**, 5748 (1957).
[10] J. Graymove, *J. Chem. Soc.*, **1947**, 1118.