

Mechanism of the Cycloaddition of Electrophilic Olefins to Enamines

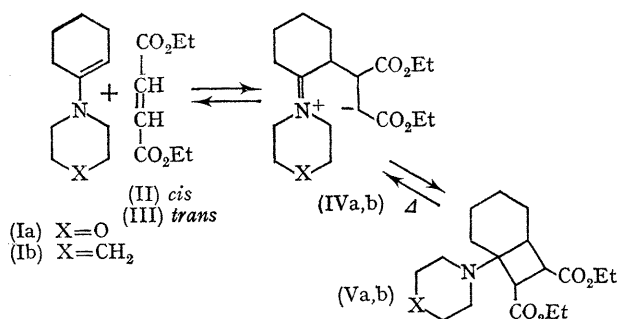
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CYCLOADDITION of electrophilic olefins to the enamine double bond leads to cyclobutane derivatives.¹ Such adducts could arise either from the corresponding dipolar intermediate *via* a two-step process or by direct cycloaddition *via* a synchronous attack.[†] We have therefore re-examined the reaction of cyclohexanone enamines with diethyl maleate and fumarate.^{1b}

Both *cis*- (II) and *trans*-olefins (III) reacted with 1-morpholinocyclohexene (Ia) giving the same cyclobutane derivative (Va) (77%), as shown by t.l.c. analysis and by comparison of the perchlorates and of the products of hydride reduction. G.l.c. analysis revealed that (Va) dissociated on heating to give the starting enamine (Ia) and fumarate (III). Under the same conditions, maleate did not isomerize. Moreover, when reaction of (Ia) was performed with a large excess of diethyl maleate, the unchanged olefin was recovered as the more stable *trans*-isomer. Similarly, 1-piperidinocyclohexene (Ib) gave the same product (Vb) with (II) and (III). These findings are con-

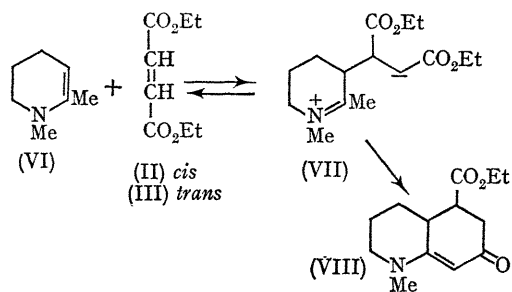
sistent with a two-step mechanism with reversible formation of a dipolar intermediate (IV) as shown below.



Complete absence of secondary amine[‡] in the enamine was ensured by using preparative g.l.c. and collecting the enamine separately in a bottle containing a large excess of maleate.

[†] A concerted mechanism has been reported for the cycloaddition of aryl azides to 1-pyrrolidinocyclohexene; R. Huisgen, G. Szeimies, and L. Möbius, *Chem. Ber.*, 1967, **100**, 2494.

After 2 hr., g.l.c. analysis of the reaction mixture revealed only the presence of enamine and fumarate; no trace of



maleate was detected, which indicated that the isomerization had still occurred.

The possibility of isomerization through reversible *N*-alkylation² of the enamine could be ruled out, since *N*-cyclohexylpiperidine, as well as other tertiary amines,³ did not convert maleate into fumarate.

The reaction of 1,2-dimethyl-3,4,5,6-tetrahydropyridine (VI) with excess of diethyl maleate occurred with irreversible slow formation of compound (VIII), but a partial isomerization of maleate into fumarate was still observed. This confirms the reversibility of the *C*-alkylation.

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† Secondary amines readily cause isomerization of maleate into fumarate; G. R. Clemo and S. B. Graham, *J. Chem. Soc.*, 1930, 213.

¹ (a) K. C. Brannock, A. Bell, R. D. Burpitt, and C. A. Kelly, *J. Org. Chem.*, 1964, **29**, 801; (b) K. C. Brannock, R. D. Burpitt, V. W. Goodlett and J. G. Thweatt, *ibid.*, p. 813; (c) I. Fleming and J. Harley-Mason, *J. Chem. Soc.*, 1964, 2165; I. Fleming and M. H. Karger, *J. Chem. Soc. (C)*, 1967, 226.

² G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrel, *J. Amer. Chem. Soc.*, 1963, **85**, 207.

³ E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, 1962, p. 344.