Fluxional Isomerism of a Malonate Anion – An Instance of Intramolecular Homoconjugate Addition

By S. DANISHEFSKY,* J. DYNAK, and M. YAMAMOTO

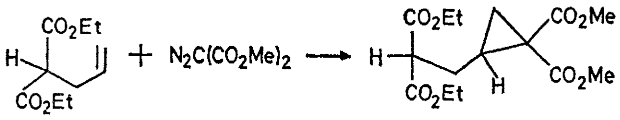
(*Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania* 15213)

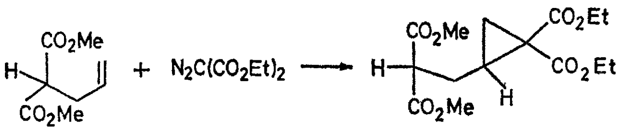
Summary The rapid interconversion of two cyclopropanes bearing two alkoxycarbonyl groups at the 1-position and a ββ-dialkoxycarbonylethyl group at the 2-position, *via* their anions, has been observed.

WE have investigated modifications of the Michael reaction.[1] We report here the first example of intramolecular 1,5-(homoconjugate) addition in the context of cyclopropane tetraesters (I) and (II).

Copper-catalysed cycloproponation of diethyl allylmalonate (III) by dimethyl diazomalonate (IV) affords (I). Similarly, cycloproponation of (V) by (VI) gives (II). In each case, the products were obtained in homogeneous form by distillation followed by chromatography on silica gel.

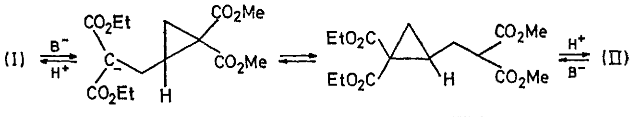
N.m.r. spectroscopy allows for a clear differentiation of the individual compounds. For (I) (CCl_4,Me_4Si, 60 MHz) the two methoxy-resonances give rise to signals at δ 226·3 and 223·5. Though the ethoxycarbonyl groups are chemically equivalent, their methylene resonances are seen as two quartets centred at δ 252·8 and 251·5 and their methyl resonances as two triplets centred at δ 77·5 and 76·5. The malonyl proton gives rise to a triplet centred at δ 202·3. The same pattern is seen in the n.m.r. spectrum of (II). The chemically equivalent methoxy-groups give rise to two singlets, δ 225·5 and 224·2. The non-equivalent ethoxy-groups are seen as two quartets, δ 254·0 and 250·5 and two triplets, δ 79·3 and 77·3. The resonance of the malonyl proton is displaced to δ 205·8. The remainder of the spectrum is superimposable with the corresponding regions of (I). The n.m.r. spectrum of a 1 : 1 mixture of (I) and (II) allows for discernment of the individual components with an integration accuracy of ±5%. Of particular analytical value is the methoxy-region wherein four distinct lines are seen, the outer ones belong to (I) and the inner ones to (II). The ethoxy (methylene and methyl) and malonyl regions allow for a supporting estimation of the relative amounts of the isomers.

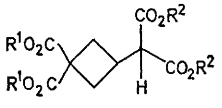

(III) (IV) (I)


(V) (VI) (II)

Treatment of either (I) or (II) with 1 equiv. of dimsylsodium in Me_2SO at room temperature for 15 min followed by quenching affords a 1 : 1 mixture of the two compounds as shown by the resultant n.m.r. spectra. We were unable to detect the presence of (VII), which might have been produced from the alternative mode of homoconjugate attack under these, or more forcing conditions.

While the intramolecular nature of the reaction has not been rigorously established, it seems most likely that the equilibration of (I) and (II) occurs *via* the respective enolates (Ie) and (IIe) which interconvert *via* homoconjugate addition. The sequence is a counterpart of intramolecular conjugate addition.[2]


(Ie) (IIe)


(VII)

The potential importance of the reaction lies in its application to the construction of other ring systems. Such applications would also involve substrates in which the possibility of alkylation by either the methine or methylene carbon exists. Both permutations have now been observed in high yield and will soon be reported.

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[1] (a) J. E. Dolfini, K. Menich, P. Corliss, R. Cavanaugh, S. Danishefsky, and S. Chakrabartty, *Tetrahedron Letters*, 1965, 4421; (b) S. Danishefsky, G. Rovnyak, and R. Cavanaugh, *Chem. Comm.*, 1969, 636.

[2] R. B. Woodward, F. J. Brutschy, and H. Baer, *J. Amer. Chem. Soc.*, 1948, **70**, 4216.