

124. The Photochemical Methylenecyclopropane Rearrangement of *Feist's* Ester

by Jacques Kagan

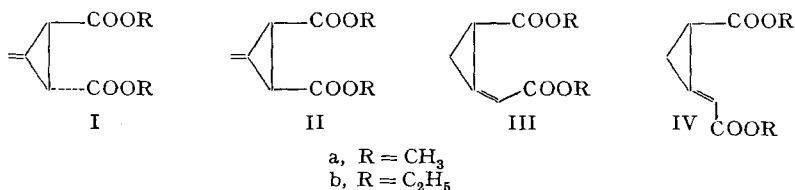
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Summary. In contrast to the thermal rearrangement, the photochemically induced methylenecyclopropane rearrangement of diethyl *trans*-methylenecyclopropane-2,3-dicarboxylate (I) and of ethyl ethoxycarbonylcyclopropylideneacetate (*syn* or *anti*) produced diethyl *cis*-methylenecyclopropane-2,3-dicarboxylate. A true photoequilibrium was not observed.

The methylenecyclopropane rearrangement is of current interest [1]–[4], but its only photochemical study to date did not allow for a determination of the stereochemical fate of vicinal substituents [2]. I now report on this, using *Feist's* ester as a model.

In their beautiful study, *Doering & Roth* [1] showed that *Feist's* ester (Ia) thermally rearranged to IIIa and IVa at 164°, and that the *cis* isomer IIa was not involved significantly in the conversion. These authors did not study the reverse reaction; and I found that IIIb and IVb were thermally equilibrated with Ib but not with IIb.



In striking contrast, *each isomer could be converted into the other three photochemically*. Thus, irradiation of a 1% (*w/v*) solution of Ib in acetonitrile at 253.7 nm under nitrogen in a *Rayonet* apparatus for up to 40 h yielded a mixture in which the proportion of isomers was 92.3% Ib, 0.4% IIb, 3.6% IIIb and 3.6% IVb. The irradiation of IIb under the same conditions yielded 7.2% Ib, 78.1% IIb, 7.5% IIIb and 7.5% IVb. Irradiation of either IIIb or IVb resulted in the very rapid formation of an equimolar mixture of these two. Further irradiation of this mixture for 40 h gave 29% Ib, 5% IIb, 33% IIIb and 33% IVb. These analyses were performed gas-chromatographically, taking into account only the peaks corresponding to the four isomers under consideration. The nature of the other reaction products will be described later.

The data of *Doering & Roth* showed that the rates of thermal interconversion starting from Ia or IIa were different, that non-concerted racemization and decomposition processes occurred, and that a thermal equilibrium was not established [1]. In this work an equilibrium was not obtained photochemically either, and the situation is comparable to another photochemical *cis-trans* isomerization reaction of a 1,2-disubstituted cyclopropane [4]. The product ratio did not vary significantly with increased time of photolysis, but a slow and steady decomposition took place. On the

other hand, this product ratio was solvent dependent, and in benzene, for example, the *cis* isomer (IIb) predominated (0.8%) over IIIb and IVb (0.15% each) formed by irradiation of Ib.

Extensive solvent participation was observed during photolysis in chloroform or ethyl acetate. The isomeric methylenecyclopropanes could not be isolated in these solvents, but many higher molecular weight products were obtained.

Two mechanistic pathways must operate. A well-known *cis-trans* isomerization for the unsaturated esters IIIb and IVb, and the formation of a trimethylenemethane with very low quantum efficiency from any one of the four isomers explain the photochemical results. Return of the diradical to ground state traps enough energy to produce the *cis* isomer which is not attainable by the thermal route. It is worth noting that the 1:1 ratio of IIIb to IVb observed in the photolysis of Ib and IIb does not necessarily reflect the product ratio as closure of the diradical took place, since facile *cis-trans* photochemical isomerization of these products was observed. Furthermore, the rates of interconversion and decomposition of the four isomers must be comparable, so that further changes in proportions occurring during prolonged irradiations are not appreciable at these low concentration levels. Finally, the above results suggest that racemization will take place in the photochemical formation of IIIb and IVb from optically active Ib.

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Experimental Part

The sample of IIb was prepared by esterification of the corresponding acid [5], and IIIb and IVb were isolated by preparative gas chromatography following thermal isomerization of Ib at 170°. The irradiations were performed in a *Rayonet* apparatus, equipped with low pressure mercury lamps. The solutions were placed in a quartz vessel, and were flushed with nitrogen for 30 min. prior to irradiation. A slight positive pressure of nitrogen was maintained over the solution during photolysis. A small amount of the solution to be irradiated was placed in a flask wrapped with aluminium foil and placed alongside the photolysis vessel during each photolysis. No thermal isomerization was detected.

The product analyses were performed with a *Perkin-Elmer* 270 gas chromatograph-mass spectrometer and with a *Hewlett-Packard* F & M 402 gas chromatograph with on-column injection at 145°, using 15% EGSS-X on Chromosorb W. The injection of pure samples showed that no appreciable isomerization occurred during the analyses, and that the detector responses were comparable for all four isomers.

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