

## The Photo Reaction between Azoester and Olefins

### 2. 1,2-Dideuteriocyclohexene

GÖRAN AHLGREN, BJÖRN ÅKERMARK, and  
KJELL-IVAR DAHLQUIST

*Department of Organic Chemistry, and Research Group for NMR, Department of Physical Chemistry, Royal Institute of Technology, Stockholm 70, Sweden*

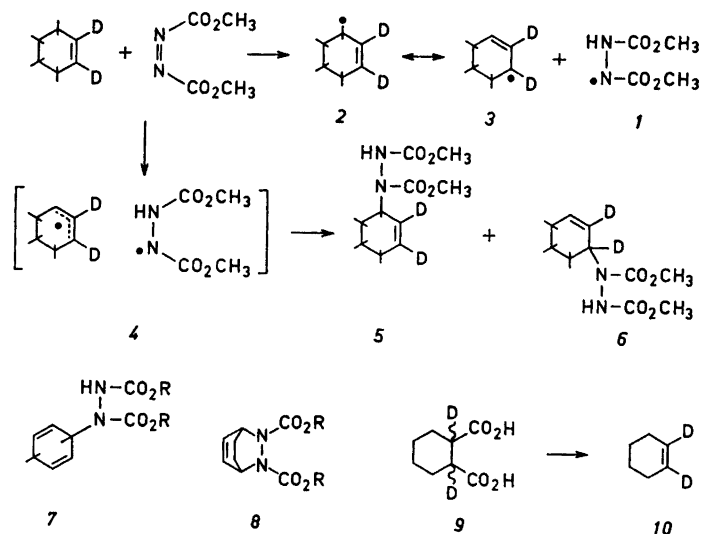
Both the photochemical and the thermal reaction between dimethyl azodicarboxylate and 1,2-dideuteriocyclohexene gave a product consisting of equal parts of the two isomeric dimethyl(dideuterio-3-cyclohexenyl)hydrazodicarboxylates (5) and (6). This result indicates that both reactions proceed *via* a similar intermediate, possibly triplet azoester.

In a previous paper the photochemical addition of azoester to olefins has been described. None of the desired diazetidines were obtained.<sup>1</sup> Instead the products were practically the same as in the thermal addition to olefins (*cf.* Ref. 2). Since this formally violates the Woodward-Hoffmann rules,<sup>3</sup> the reaction between azoester and olefins was further investigated.

Azoester and 1,2-dideuteriocyclohexene were photochemically reacted. A good yield of a product was obtained, which contained equal amounts (within the experimental error,  $\pm 5\%$ ) of (5) and (6). This result indicates that azoester abstracts a hydrogen atom from cyclohexene to give a hydrazoester radical (1) and a cyclohexenyl radical (2). The cyclohexenyl radical (2) is equilibrated with its mesomeric form (3) prior to combination with the hydrazoester radical. The photoaddition between azoester and cyclohexene is therefore not concerted and can not be expected to obey the Woodward-Hoffmann rules (*cf.* Refs. 2, 4).

Unexpectedly, also the thermal addition of azoester and 1,2-dideuteriocyclohexene gave equal amounts of the two products (5) and (6). An explanation for this result would be that the thermal and the photochemical reaction proceed *via* a similar intermediate, presumably the excited triplet azoester. This assumption is supported by MO-calculations which indicate that azoester has an extremely lowlying triplet level,<sup>5</sup> possibly so low that it may be reached by excitation with moderate thermal energy.

No appreciable amount of cyclohexene dimers were formed neither in the thermal nor in the photochemical reaction between azoester and cyclohexene,



indicating that the reaction has considerable cage character.<sup>1</sup> Possibly even a diradical complex (4) is formed, which collapses to the products (5) and (6). 1-Hexene behaves differently to cyclohexene in that azoester is added thermally and photochemically in an *en* reaction with complete migration of the double bond<sup>1</sup> (*cf.* Ref. 2). In the case of 1-hexene hydrogen abstraction and formation of a radical pair is unlikely, since the product from the less stable hexenyl radical is formed exclusively. It nevertheless seems improbable that the mechanisms for the addition of azoester to cyclic and to open olefins are entirely different. Poutsma and Hinman<sup>6</sup> have shown that in the reaction of trichloromethyl radicals and olefins, the ratio between addition to the olefinic double bond and abstraction of an allylic hydrogen from the olefin is considerably greater for 1-octene (101) than for cyclohexene (1.85). Triplet azoester might be expected to behave similarly to the trichloromethyl radical. A reasonable assumption therefore seems to be that in the reaction between azoester and cyclohexene hydrogen abstraction takes place in the rate determining step but in the case of 1-hexene the addition of azoester to the double bond is rate determining.

Skell and Etter<sup>7</sup> have shown that in the reaction between ethoxycarbonyl methylene and cyclohexene insertion and addition to the double bond take place to approximately equal extent. Another explanation for the results from the addition of azoester and olefins is therefore that competing allylic insertion and *en*-addition of azoester take place at equal rates. Since practically identical results are obtained in the photochemical and the thermal reaction also this interpretation would require a similar intermediate in both cases.

It is interesting to note that mixtures of azoester and olefins show charge transfer band in the UV. The position of the charge transfer band is roughly correlated with the electron density of the olefinic double bond (Table 1).

Table 1. Charge transfer absorption of azoester and some olefins.

Olefin	Wavelength (nm)
1-Hexene	245
Cyclohexene	290
1-Methylcyclohexene	290
Styrene	310

Table 2. Charge transfer absorption of azoester in different solvent mixtures.

Solvent	Wavelength (nm)
Cyclohexene	290
Cyclohexene-cyclohexane 1:1	287
Cyclohexene-cyclohexane 1:4	276
Cyclohexene-cyclohexane 1:9	267
Cyclohexene-1,2-dimethoxymethane 1:9	270

The nature of the absorption band is obscure, since its wavelength is drastically changed on dilution with saturated solvents. (Table 2.) The influence of the charge transfer absorption on the photo reactions of azoester with olefins is also uncertain since essentially the same products are obtained as in the thermal reactions. In the case of cyclic dienes this is not true. The thermal addition of azoester and 1,3-cyclohexadiene gives about 85 % of (7) and 15 % of (8)<sup>8</sup> whereas in the photochemical addition only (8) is formed.<sup>9</sup> This is not readily explained in terms of a common intermediate in the thermal and photochemical reactions. One explanation would be that the photochemical reaction is modified by charge transfer absorption.

1,2-Dideuteriocyclohexene (10) was prepared by lead tetraacetate oxidation of 1,2-dideuteriocyclohexane-1,2-dicarboxylic acid (9). The acid (9) was obtained by deuteration of cyclohexane-1,2-dicarboxylic anhydride with deuteriosulfuric or deuteriohydrochloric acid.

Catalytic deuteration of cyclohexene-1,2-dicarboxylic acid and its diethyl-ester gave the saturated compound containing deuterium randomly distributed around the ring.

Metallation of cyclohexene, followed by addition of deuterium oxide also failed to give the desired product (*cf.* Ref. 10).

## EXPERIMENTAL

IR spectra were recorded with a Perkin Elmer 421, NMR-spectra with a Varian A60 spectrophotometer. The chemical shifts were determined in  $\text{CDCl}_3$  and are expressed as  $\delta$ -units relative to TMS as internal standard.

*1,2-Dideuteriocyclohexane-1,2-dicarboxylic acid* (9). a) A mixture of cyclohexane-1,2-dicarboxylic anhydride (8.3 g) and dideuteriosulfuric acid (25 ml, obtained by equilibrating excess sulfurtrioxide and deuterium oxide) was kept at 110–120° for 2 h. The mixture was poured onto ice and extracted with ethyl acetate. Evaporation of the solvent gave quantitative yield of 1,2-dideuteriocyclohexane-1,2-dicarboxylic acid (90 % deuterium), m.p. 222–224° (lit.<sup>11</sup> m.p. for *trans*-cyclohexane-1,2-dicarboxylic acid 219–220°). No deuteration occurred in dilute sulfuric acid at 180°.

b) A mixture of cyclohexane-1,2-dicarboxylic anhydride (26 g) and deuteriohydrochloric acid (from 5.9 g thionyl chloride and 13 ml deuterium oxide) was heated at 180–185° for 20 h in a sealed tube. 1,2-Dideuteriocyclohexane-1,2-dicarboxylic acid (9) (17.7 g, 63 % deuterium) was isolated in the usual manner.

*1,2-Dideuteriocyclohexene* (10). 1,2-Dideuteriocyclohexane-1,2-dicarboxylic acid (10.2 g, 90 % deuterium) was dissolved in pyridine (120 ml), lead tetraacetate (30 g) added and the mixture was kept at 50–60°. The product was continuously removed by a stream of nitrogen and collected in an efficient cool trap. After 20 h a mixture of pyridine and deuteriocyclohexene (12 ml) was obtained from the trap. Distillation on a spinning band column gave 1,2-dideuteriocyclohexene (0.7 g, 90 % deuterium).

*Thermal addition of dimethyl azodicarboxylate and cyclohexene.* A mixture of dimethyl azodicarboxylate (1.43 g) and cyclohexene (0.80 g) was heated in a sealed tube at 100° for 6 h. The product was chromatographed on silica to give dimethyl (3-cyclohexenyl)hydrazodicarboxylate (0.44 g), m.p. 131–132° (from cyclohexane). A small amount of dimethyl hydrazodicarboxylate was also isolated. (Found: C 52.6; H 7.0. Calc. for  $C_{10}H_{16}N_2O_4$ : C 52.6; H 7.1). IR ( $cm^{-1}$ ): 3200 (NH), 1700 (CO). NMR: 1.70, 1.84 (m,  $CH_2$ ), 3.70 ( $OCH_3$ ), 4.76 (s, C=C-CH-N), 5.54 (d, C=CH-N), 5.87 (d, HC=C-N), 7.00 (s, broad, NH).

*Thermal addition of dimethyl azodicarboxylate and 1,2-dideuteriocyclohexene.* This was carried out as above. Within the estimated error in the integration, 5 %, the NMR spectrum of the product proved this to be a mixture of equal amounts of the two isomeric dimethyl-(dideuterio-3-cyclohexenyl)hydrazodicarboxylates (5) and (6).

*Photochemical addition of dimethyl azodicarboxylate and cyclohexene.* A mixture of dimethyl azodicarboxylate (1.40 g) and cyclohexene (0.80 g) was irradiated with pyrex filtered UV light. The product was chromatographed to give dimethyl (3-cyclohexenyl)hydrazodicarboxylate (0.80 g) and a small amount of dimethyl hydrazodicarboxylate.

*Photochemical addition of dimethyl azodicarboxylate and 1,2-dideuteriocyclohexene.* This was done as above. The NMR spectrum of the mixture of dimethyl (deuterio-3-cyclohexenyl)hydrazodicarboxylate obtained was identical with that of the deuterated product from the thermal addition.

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#### REFERENCES

1. Ahlgren, G. and Åkermark, B. *Acta Chem. Scand.* **21** (1967) 2910.
2. Thaler, W. A. and Franzus, B. *J. Org. Chem.* **29** (1964) 2226.
3. Hoffmann, R. and Woodward, R. B. *J. Am. Chem. Soc.* **87** (1965) 2046.
4. Huisgen, R. and Jakob, F. *Ann.* **590** (1954) 37.
5. Alm, T. *Unpublished results.*
6. Poutsma, M. L. and Hinman, R. L. *J. Am. Chem. Soc.* **86** (1964) 3807.
7. Skell, P. S. and Etter, R. M. *Proc. Chem. Soc.* **1961** 443.
8. Franzus, B. *J. Org. Chem.* **28** (1963) 2954.
9. Askani, R. *Chem. Ber.* **98** (1965) 2551.
10. Tori, K., Aono, K., Hata, Y., Muneyuki, R., Tsuji, T. and Tanida, H. *Tetrahedron Letters* **1966** 9; Lochman, L., Pospisil, J. and Lim, D. *Tetrahedron Letters* **1966** 257.
11. Diels, O. and Alder, K. *Ber.* **62** (1929) 554.

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