Experimental. Methyldiimine and acetylenedicarboxylic acid. Potassium hydroxide (1.2 g), potassium hydrogen acetylenedicarboxylate (1.5 g), methylhydrazinehydrosulfate (1.4 g) and a trace of copper(II) acetate were dissolved in water (20 ml) and hydrogen peroxide (30 %, 1.2 ml) added over a period of 20 min. Nitrogen (180 ml) was evolved. The solution was evaporated to dryness, acidified with hydrochloric acid and extracted with ethyl acetate. The solvent was removed to give a residue which contained mainly acetylenedicarboxylic acid. After methylation with diazomethane dimethyl methylmaleate (7 parts), methylmaleic anhydride (7 parts), and dimethyl methylfumarate (3 parts) were detected by means of GLC. The total yield was less than 1 %.

Azo(2-propane) and dimethyl maleate. A solution of azo(2-propane) (2.0 g) and dimethyl maleate (4.0 g) in methanol (50 ml) was irradiated for 25 h with pyrex filtered UV light (Hanau; 75 W). The solvent was removed and the product distilled to give an air sensitive oil (1.8 g) which contained nitrogen. The oil was chromatographed on alumina to give a small ester fraction (0.05 g) which contained mainly dimethyl diisopropylsuccinate in an *erythro:threo* ratio of 3:1. The main product appeared to decompose on the column. Practically identical products were obtained when dimethyl fumarate was used in place of dimethyl maleate.

Photoreaction of azophenylmethane and dimethyl maleate. Azophenylmethane [5] (0.2 g) in dimethyl maleate (2 ml) was irradiated for 24 h at 350 nm in a Rayonet reactor. Dibenzyl, stilbene, and polymeric material was formed but no dimethyl dibenzylsuccinate (GLC).

Thermal reaction of azophenylmethane and dimethyl maleate. A solution of azobenzyl (0.5 g) in dimethyl maleate (2 ml) was held at 150° for 6 h. Only about 5 ml of nitrogen was formed. Dibenzyl, stilbene, and a trace of dimethyl dibenzylsuccinate were formed (GLC) but the main product was 2-benzyl-6-hydroxy-3(2*H*)pyridazinone (*1*) (0.18 g), m.p. 205–207°, lit.[6] 206°. NMR, IR, and masspectral data are in accordance with the proposed structure. (Found: C 64.8; H 5.0; N 13.0. Calc. for $C_{11}H_{10}N_2O_2$: C 65.0; H 4.9; N 13.9).

Thermal reaction of azo-(1-phenylethane) and dimethyl maleate gave a similar product as azophenylmethane probably 2(1-phenylethyl)-6-hydroxy-3(2*H*)pyridazinone, m.p. 180–182°. (Found: C 66.6; H 5.6; N 13.0. Calc. for $C_{12}H_{12}N_2O_2$: C 66.8; H 5.6; N 13.0).

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The Photo Reaction between Azoester and Olefins

1. Cyclohexene, 1-Hexene, and Styrene

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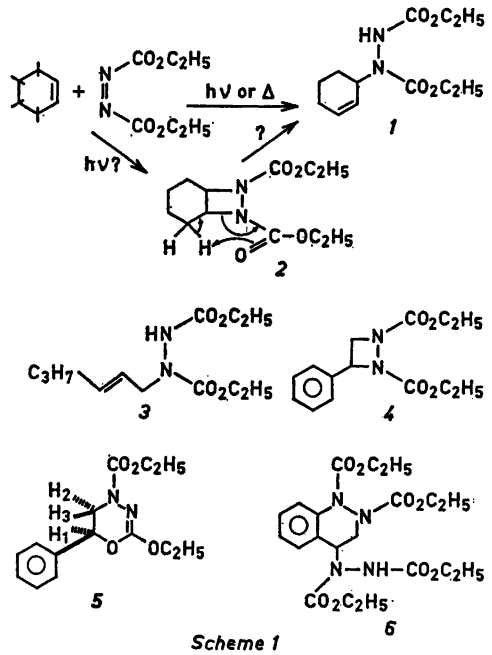
In an attempt to photochemically dialkylate methyl maleate with azo(2-propane) only a trace of methyl 1,2-di-(2-propyl) succinate was obtained.[1] No other defined product could be isolated, but it seemed possible that part of the product was a diazetidine formed by addition of the azocompound and maleate. With the hope to obtain a more stable diazetidine, diethyl azodicarboxylate was photochemically reacted with cyclohexene and 1-hexene. No diazetidins could be isolated from these reactions. Instead, the major products were the alkylated hydrazoesters (*1*) and (*3*), respectively. To rule out the possibility that diazetidins (*e.g. 2*) were first formed which then rearranged to the hydrazoesters

(*e.g.*, *1*, Scheme 1), diethyl azodicarboxylate and styrene were photochemically reacted. The expected diazetidine (*4*) from this reaction cannot rearrange according to Scheme 1. Small amounts of a compound, which from analytical and spectroscopic data presumably is (*5*), were isolated and possibly a trace of the diazetidine (*4*).

(*7*), has insufficient energy to yield a strained ring.

It is not clear, whether the difference in the thermal and the photochemical reaction between azoester and styrene is caused by different thermal and photochemical reactivity of the azoester or by intervention of excited styrene molecules in the photo-



Scheme 1

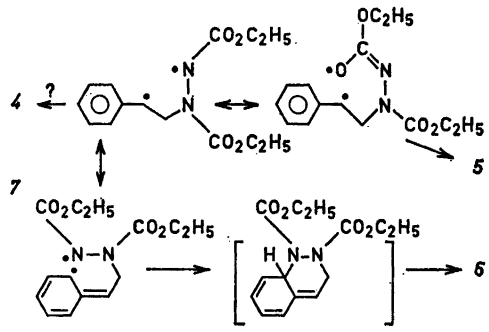
From this result it seems improbable that a diazetidine is initially formed in the photoreaction between azoester and olefins.

The major part of the reaction product between azoester and styrene was polymeric, but the normal thermal addition product was also formed. It is interesting to note that the thermal product actually consists of two compounds, one major that is the reported [2] product (*6*) and one minor which has an IR-spectrum very similar to that of (*6*). The minor compound has not been obtained in pure state.

According to IR-data, ester units are incorporated into the polymeric product. The copolymer of styrene and azoester, the diazetidine (*4*), the 1:1 adduct (*5*) and 1:2 adduct (*6*) could all be formed from the diradical (*7*) (Scheme 2).

The lack of appreciable diazetidine formation may indicate that the diradical, reaction. However, from azoester and cyclohexene and 1-hexene, respectively, essentially the same products are formed in the thermal and photochemical reaction. This is contrary to the result obtained with, *e.g.*, maleic anhydride and olefins [3] and is a formal violation of the Woodward-Hoffman rules for cycloadditions. The reason for this is being further investigated.

Experimental. Photoaddition of cyclohexene and diethyl azodicarboxylate. A solution of diethyl azodicarboxylate (2.00 g) in cyclohexene (60 ml) was irradiated for 16 h with pyrex filtered UV-light (75 W Hanau medium pressure lamp used as light source). Excess solvent was removed and the product chromatographed on silica. Essentially pure diethyl (3-cyclohexenyl)hydrazodicarboxylate (*1*) (1.5 g), m.p. 45—51° was isolated. The structure (*1*) of the photoadduct was proved by comparison



Scheme 2

with an authentic sample, m.p. 46–51°, prepared by thermal addition according to Huisgen and his coworkers [4] (lit.[4] m.p. 55–56°).

NMR (δ-units from tetramethylsilane as inner standard) 1.22 (t, CH_3), 1.8 (m, CH_2), 4.18 (q, O–CH_2–), 4.72 (s, C=C–CH–N), 5.75 (m, H–C=CH), 7.78 (s, broad, NH).

No diazetidine appeared to be formed in the photoaddition. The formation of a trace of cyclohexene dimer was indicated by GLC.

Photoaddition of 1-hexene and diethyl azodicarboxylate. Diethyl (1-hexenyl-2)hydrazodicarboxylate (*3*) was prepared as described above for (*1*). (*3*) was also prepared by heating azoester and 1-hexene (*cf.* Ref. 5). Diethyl (1-hexenyl-2)hydrazodicarboxylate (*3*) prepared photochemically could not be obtained completely pure according to analytical data, but NMR and IR spectra were identical with those of (*3*) from the thermal reaction. (Found: C 53.3; H 8.2. Calc. for $C_{12}H_{22}N_2O_4$: C 55.8; H 8.6) NMR: 0.88 (t, C–CH_3), 1.22 (t, O–C–CH_3), 1.3 (m, CH_2), 2.0 (q, C=C–CH_2–), 3.98 (d, C=C–CH_2–N), 4.10 (q, O–CH_2–), 5.5 (two d, J 14 cps, H–C=C–H), 7.2 (s, broad N–H).

No diazetidine appeared to be formed in the photo addition.

Photoaddition of styrene and diethyl azodicarboxylate. A mixture of diethyl azodicarboxylate (2.00 g) and freshly distilled styrene (60 ml) was irradiated as described above. The temperature was kept at +10° to diminish the rate of thermal addition. After 16 h excess styrene was removed at room temperature to yield a large polymeric residue (14 g). The residue was dissolved in benzene, mixed with silica gel (20 g) and the solvent evaporated. The mixture of silica gel and product was charged on a short silica column (20 g), and eluted with light petroleum-ether 1:1. The material eluted (0.70 g) was crystallized from ether to give a mixture (0.20 g) of (*6*) [2] and another compound which had a similar IR-spectrum as (*6*). The structure of the second compound, which is also formed in the thermal addition of styren and azoester, has not yet been determined.

The solvent was removed from the mother liquor and the residue repeatedly chromatographed on silica to give a small amount (0.10 g) of (*5*). IR (cm^{-1}): 1700 (C=O), 1660 (N=C<). NMR: 1.31 and 1.33 (t, O–C–CH_3), 3.31 (q, H_3, J_{13} 9 cps, J_{23} 13 cps), 4.28 and 4.31 (q, O–CH_2–), 4.43 (q, H_2, J_{12} 3 cps), 5.30 (q, H_1). (Found: C 60.4; H 6.9. Calc. for $C_{14}H_{18}N_2O_4$: C 60.4; H 6.5).

Very small amounts (0.006 g) of another compound were also isolated. It could not be obtained quite pure but the IR data indicated that it might be the desired diazetidine (*4*). IR 1740 (s, broad), 1450, 1380, 1300 (s, broad), 1160, 1030. No N–H absorption.

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