

## THERMAL AND PHOTOCHEMICAL ADDITIONS OF AZO ESTERS TO UNSATURATED SYSTEMS—II

### ADDITIONS TO OLEFINS AND DIENES<sup>1</sup>

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**Abstract**—Thermal and photochemical additions of diethyl azodicarboxylate to cycloheptene and cyclooctene gave 3-(diethylbicyarbamyl)-1-cycloheptene and 3-(diethylbicyarbamyl)-1-cyclooctene, respectively. A free-radical mechanism has been suggested for these additions. 1-Methylcyclohexene, on treatment with diethyl azodicarboxylate both under thermal and photochemical conditions, gave a mixture of products consisting of 2-(diethylbicyarbamyl)-1-methylenecyclohexane and 3-(diethylbicyarbamyl)-1-methylcyclohexane. The reaction of *trans*-1,2-dicarbethoxycyclohexa-3,5-diene gave a poor yield of the Diels–Alder adduct under thermal conditions; the same product was obtained in much better yields under photochemical conditions. The reaction of cyclohexa-1,4-diene with diethyl azodicarboxylate under irradiation conditions gave 3-(diethylbicyarbamyl)-cyclohexa-1,4-diene and diethyl hydrazodicarboxylate. Cycloocta-1,5-diene reacts with diethyl azodicarboxylate, both under thermal and photochemical conditions to give 3-(diethylbicyarbamyl)-cycloocta-1,5-diene, a radical substitution product. An attempted reaction of anthracene with diethyl azodicarboxylate, under irradiation conditions, gave none of the expected addition product, but only a photodimer of anthracene.

Thermal addition of diethyl azodicarboxylate to cyclic olefins has been reported to give rise to simple 1:1-addition products and a free-radical mechanism has been suggested by Huisgen and Pohl to account for the effect of radical initiators and inhibitors on these additions.<sup>3</sup> Cyclohexene, for example, reacts with diethyl azodicarboxylate to give 3-(diethylbicyarbamyl)-1-cyclohexene as the product. Quite recently, Ahlgren *et al.* have studied the reaction of 1,2-dideuteriocyclohexene with dimethyl azodicarboxylate and have shown that the product mixture contains both 3-(dimethylbicyarbamyl)-1,2-dideuterio-1-cyclohexene and 3-(dimethylbicyarbamyl)-2,3-dideuterio-1-cyclohexene, formed in approximately equal amounts.<sup>4</sup> These workers have suggested that the reaction proceeds both by a free-radical process and also by an addition-substitution pathway. In the case of cyclic dienes, the reaction with diethyl azodicarboxylate can give rise to products arising either through an addition-substitution mechanism or through a Diels–Alder type of addition. Thus, for example, cyclohexa-1,3-diene reacts with diethyl azodicarboxylate predominantly by an addition-substitution mechanism giving rise to 3-(diethylbicyarbamyl)-1,4-cyclohexadiene. A small amount of the Diels–Alder type of adduct was also isolated from this reaction.<sup>5</sup> The reaction of cyclopentadiene with diethyl azodicarboxylate, on the other hand, gives exclusively, the Diels–Alder addition product.<sup>6</sup>

During the present investigation, we have examined the reaction of a few cyclic olefins and dienes with diethyl azodicarboxylate, with a view to studying the mode of additions in these cases. Thus, the treatment of cycloheptene (I) with diethyl azodicarboxylate (II) gave a 55% yield of a product, identified as 3-(diethylbicyarbamyl)-1-cycloheptene (III). Similarly, the reaction of cyclooctene (IV) with diethyl azodi-

carboxylate gave a 50% yield of 3-(diethylbicybamyl)-1-cyclooctene (V) (Scheme 1). With a view to finding out whether these additions are influenced by the presence of free-radical initiators and inhibitors, we have carried out these reactions in the presence of a free-radical initiator such as benzoyl peroxide and also in the presence of an inhibitor such as hydroquinone. In each case, a mixture of the olefin and diethyl azodicarboxylate was taken in the ratio of 5:1 along with 5% of the modifier over the azo ester concentration. The times taken for the completion of these reactions are indicated in Table 1.

TABLE 1. EFFECT OF RADICAL MODIFIERS ON THE REACTION OF OLEFINS AND DIETHYL AZODICARBOXYLATE

Olefin	Time required for completion of the reaction		
	No Modifier	in the presence of	
		Benzoyl peroxide	Hydroquinone
Cycloheptene	16 h	1 h	20 h
Cyclooctene	16 h	6.5 h	20 h

From these results it is clear that the addition reaction proceeds faster in the presence of a free-radical initiator and it is retarded by an inhibitor. It is apparent that the addition reactions of diethyl azodicarboxylate to both cycloheptene and cyclooctene proceed by a free-radical pathway and not by an addition-abstraction mode.

When the reaction of a substituted cyclohexene such as 1-methylcyclohexene (VI) with diethyl azodicarboxylate was tried, a mixture of 1:1-adducts (VIII, IX and X) was obtained in a 66% yield. In addition, a small amount (5%) of diethyl hydrazodicarboxylate (VII) was isolated from this reaction (Scheme 2).

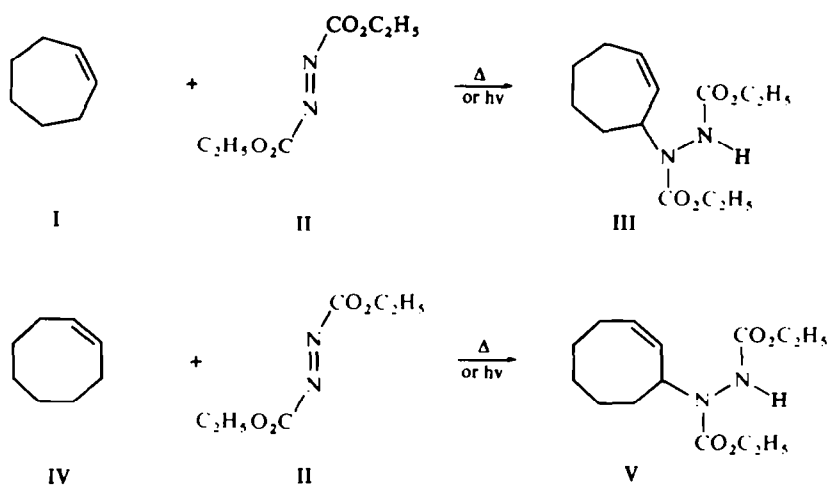
The infrared spectrum of the isomeric mixture of adducts (VIII, IX and X) shows a weak absorption band around  $3436\text{ cm}^{-1}$ , characteristic of the N—H stretching vibrations. The presence of two strong absorption bands at  $1761$  and  $1721\text{ cm}^{-1}$ , respectively, is attributed to the ester carbonyl groups, whereas the absorption bands at  $1660$  and  $730\text{ cm}^{-1}$  are due to the C=C vibrations of the cyclohexene rings present in adducts IX and X. The absorption bands present at  $1645$ ,  $1410$  and  $880\text{ cm}^{-1}$  are assigned to the exocyclic C=CH<sub>2</sub> group present in the isomer VIII.

The NMR spectrum of the mixture of adducts (VIII, IX and X) (Fig 1) shows a triplet centered around  $8.75\tau$  due to the ester methyl protons and a quartet around  $5.82\tau$  due to the ester methylene protons. The cyclic methylene protons appear as a multiplet centered around  $8.6\tau$  and the allylic methylene protons appear as a multiplet around  $7.7\tau$ . The allylic methyl protons appear as a broad singlet around  $8.1\tau$ , whereas the allylic C—H proton shows a multiplet around  $5.4\tau$ . The exocyclic methylene protons (present in VIII) appear as a multiplet around  $5.2\tau$  and the vinylic protons of the cyclohexene ring appear as multiplets around  $4.7$  and  $4.3\tau$  respectively.

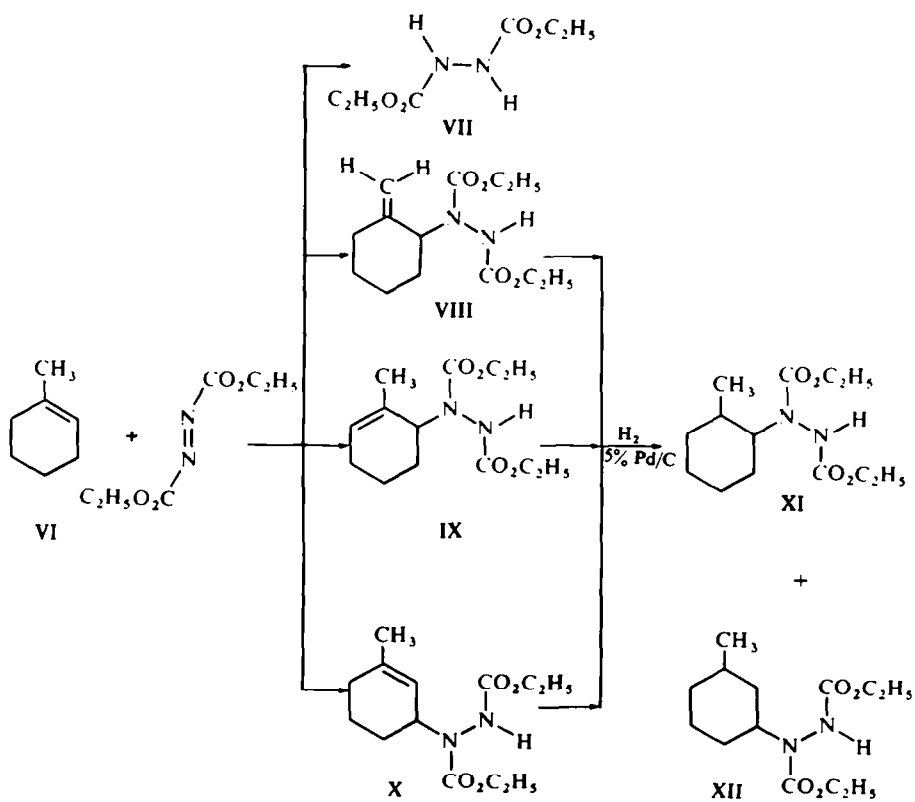
VPC analysis showed that the isomeric mixture of adducts contain approximately 24% of VIII, 42% of IX and 34% of X. Hydrogenation of this mixture of adducts gave a mixture of 1-(diethylbicybamyl)-2-methylcyclohexane (XI) and 1-(diethylbicybamyl)-methylcyclohexane (XII) in a ratio of 65:35, as identified by VPC analysis.

With a view to gaining some information concerning the mode of addition of diethyl azodicarboxylate to 1-methylcyclohexene, this reaction was investigated in

SCHEME 1



SCHEME 2



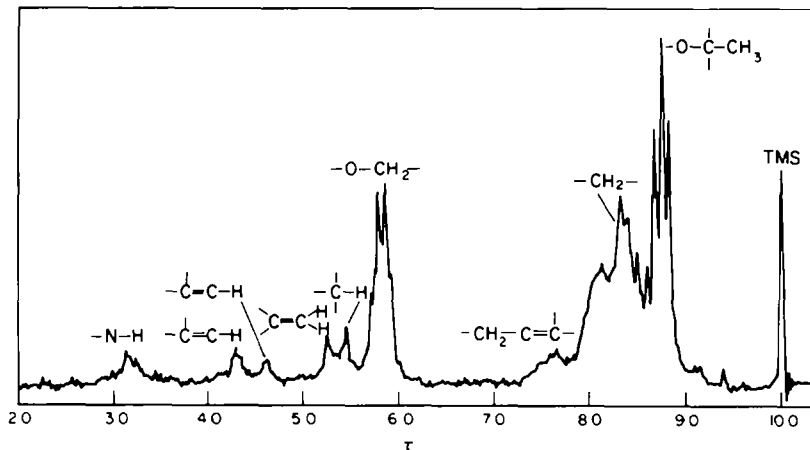


FIG 1. NMR spectrum (100 Mhz) of the mixture of adducts, VIII, IX and X, obtained from the reaction of 1-methylcyclohexene and diethyl azodicarboxylate

the presence of varying concentrations of a free-radical initiator such as benzoyl peroxide. Table 2 shows the changes in product composition with changes in the concentration of the modifier. In each case, 0.05 mole of 1-methylcyclohexene and 0.025 mole of diethyl azodicarboxylate were taken.

TABLE 2. EFFECT OF BENZOYL PEROXIDE ON THE REACTION OF 1-METHYLCYCLOHEXENE WITH DIETHYL AZODICARBOXYLATE

Amount of benzoyl peroxide	Products (composition %)		
	VIII	IX	X
Nil	24	42	34
15 mg	17	35	48
30 mg	10	34	56

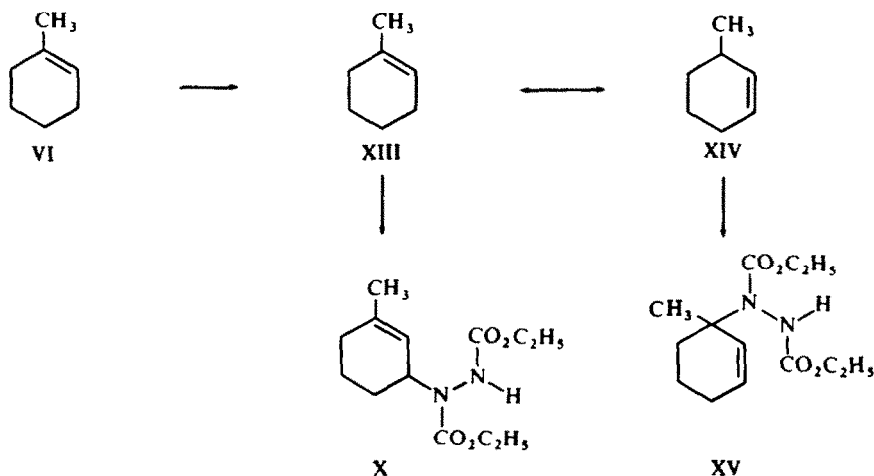
From Table 2 it is apparent that the relative amounts of the adduct VIII in the product mixture decreases with the increase in the concentration of the radical-initiator and this observation is in agreement with an addition-substitution mechanism for the formation of the adduct VIII. The yield of the adduct X, on the other hand, is found to increase with an increase in the concentration of benzoyl peroxide, a fact which suggests that this adduct is formed through a free-radical process. In this connection it might be mentioned that the allylic radical XIII, formed by the hydrogen abstraction from methylcyclohexene can have another resonance structure XIV (Scheme 3). Further addition of the 1,2-dicarbethoxyhydryl radical to XIII and XIV would lead to products X and XV, respectively (Scheme 3). However, it is to be expected that on the basis of steric considerations, the coupling of the radical species

XIV with 1,2-dicarbethoxyhydrazil radical would be less favourable as compared to the coupling reaction of XIII. The importance of such steric considerations in the radical coupling reactions of 4-vinylcyclohexene has been observed earlier by different group of workers.<sup>7, 8</sup>

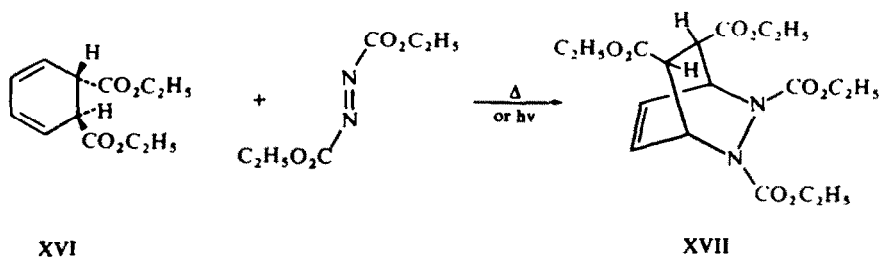
The adduct IX, obtained from the reaction of 1-methylcyclohexene with diethyl azodicarboxylate, may be formed both through an addition-substitution process and also by a free-radical reaction. The decrease in the relative yields of IX with the increase in the concentration of benzoyl peroxide is consistent with this assumption, as free-radical initiators will increase the yield of the product, arising through the free-radical pathway.

It has been reported earlier that cyclic dienes react with diethyl azodicarboxylate giving rise to products, depending on the nature of the diene employed. In this investigation we have examined the reaction of few dienes with a view to studying the nature of the products formed in these reactions. Thus, for example, the reaction of *trans*-1,2-dicarbethoxycyclohexa-3,5-diene (XVI) with diethyl azodicarboxylate gave only a 12% yield of the Diels-Alder adduct XVII (Scheme 4). In addition, an unidentifiable polymeric material was also formed in this reaction.

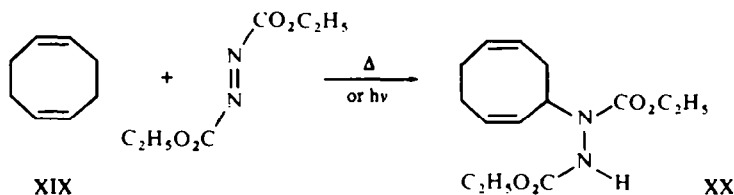
SCHEME 3



SCHEME 4



SCHEME 5



The reaction of cycloocta-1,5-diene (XIX) with diethyl azodicarboxylate, under thermal conditions, gave a 39% yield of 3-(diethylbicarbamyl)-cycloocta-1,5-diene (XX) (Scheme 5). The nature of the adduct XX reveals that this addition proceeds by a free-radical process.

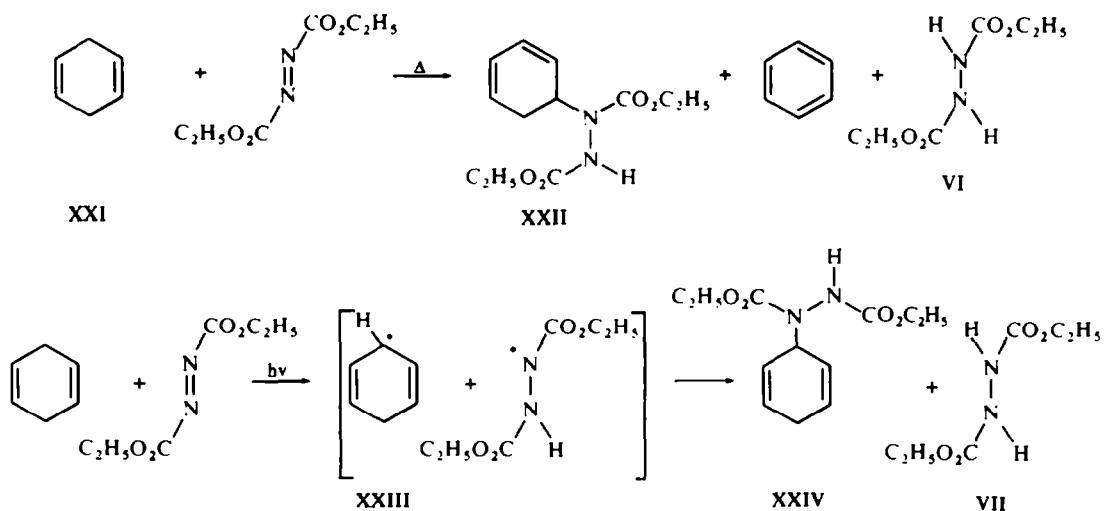
The photochemical addition of a cyclic olefin such as 1,2-dideuteriocyclohexene to dimethyl azodicarboxylate has been recently reported to give rise to a mixture of isomeric 1:1-adducts, identical to those formed under thermal conditions.<sup>4</sup> During the present investigation we have studied the photo-addition of diethyl azodicarboxylate to a few cyclic olefins. Thus, the reaction of cycloheptene with diethyl azodicarboxylate under conditions of irradiation, in the absence of any solvent gave a 66% yield of 3-(diethylbicarbamyl)-1-cycloheptene (III), identical to the product obtained under thermal conditions. Similarly, the reaction of cyclooctene with diethyl azodicarboxylate gave a 60% yield of 3-(diethylbicarbamyl)-1-cyclooctene (V) (Scheme 1). The reaction of a substituted olefin such as 1-methylcyclohexene with diethyl azodicarboxylate gave an overall yield of 70% of the product mixture consisting of 1:1-isomeric adducts, similar to those formed under thermal conditions (Scheme 2).

The photo-addition of azo-esters to some cyclic dienes have been studied in recent years. Thus, for example, the reaction of cyclohexa-1,3-diene with diethyl azodicarboxylate under irradiation conditions has been reported to give a 87% yield of the Diels-Alder adduct,<sup>9</sup> a product formed only in minor amounts under thermal conditions. On the other hand, the reaction of cyclohexa-1,4-diene with duroquinone under irradiation conditions gave chiefly benzene and duroquinol.<sup>10</sup>

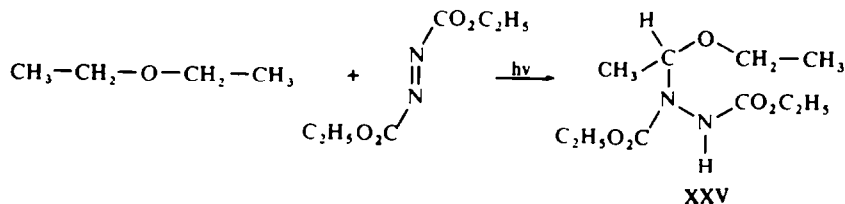
Franzus had investigated the addition of diethyl azodicarboxylate to cyclohexa-1,4-diene (XXI) and had shown that the adduct XXII is formed by an addition-substitution process (Scheme 6). In addition, products, such as benzene and diethyl hydrazodicarboxylate (VII), were also isolated from this reaction. The steric hindrance offered by the 1,4-axial hydrogens of cyclohexa-1,4-diene to the approach of the azo ester is probably responsible for the appreciable dehydrogenation. It might, however, be pointed out that recent spectroscopic evidence favours a nearly planar conformation for cyclohexa-1,4-diene in which the hindrance offered by the 1,4-axial hydrogen atoms will not be appreciable.<sup>11, 12</sup>

In the present investigation, we have examined the reactions of some cyclic dienes with diethyl azodicarboxylate under photolytic conditions. Thus, the photolysis of a mixture of cyclohexa-1,4-diene and diethyl azodicarboxylate in diethyl ether gave a 68% of diethyl hydrazodicarboxylate as the only isolable product. However, when the reaction was carried out in benzene, the products formed were diethyl hydrazodicarboxylate (VII) (34%) and 3-(diethylbicarbamyl)-1,4-cyclohexadiene (XXIV) (Scheme

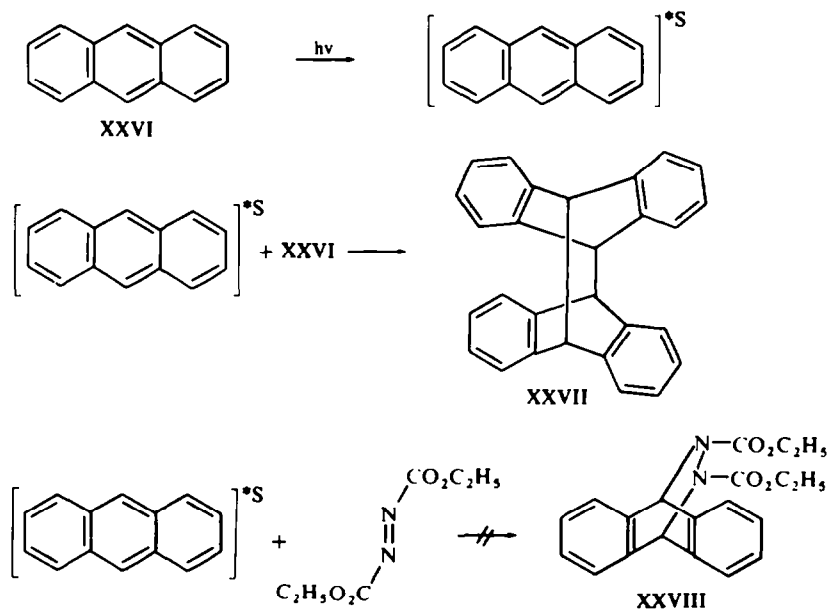
SCHEME 6



SCHEME 7



SCHEME 8



6). The nature of the adduct XXIV indicates that the photo-addition may be proceeding through a free-radical process. However, the involvement of a completely free cyclohexa-1,4-dienyl radical (XXIII) in the reaction is to be ruled out, as this radical would readily isomerize to the more stable conjugated cyclohexa-1,3-dienyl radical. It is therefore probable that the cyclohexa-1,4-dienyl radical and the 1,2-dicarbethoxy-hydrazyl radical exist as a radical pair within a solvent cage and that they recombine rapidly to give rise to the adduct XXIV.

With a view to discovering the reasons for the absence of any addition product in the photo-reaction of cyclohexa-1,4-diene with diethyl azodicarboxylate in ether, we have attempted the photo-reaction of diethyl azodicarboxylate with diethyl ether alone. Irradiation of a mixture of diethyl azodicarboxylate in excess of diethyl ether gave rise to an unstable 1:1-adduct (XXV), which on treatment with water gave acetaldehyde, identified through its 2,4-dinitrophenylhydrazine derivative (Scheme 7). In this connection, mention might be made of the recent report of the reaction of ether, in general, with diethyl azodicarboxylate to give rise to adducts which undergo hydrolysis to the corresponding aldehydes.<sup>13</sup>

The photochemical addition of diethyl azodicarboxylate to 1,2-dicarbethoxy-cyclohexa-3,5-diene was found to give a 43% yield of the Diels–Alder adduct XIX, which was formed only in very poor yields under thermal conditions (Scheme 4).

The photo-reaction of cycloocta-1,5-diene and diethyl azodicarboxylate gave a 60% yield of 3-(dicarbamyl)-cycloocta-1,5-diene XX (Scheme 5).

Photochemical dimerization of anthracene has been investigated by several groups of workers.<sup>14,15</sup> This reaction may be regarded as a special case of the Diels–Alder type of reaction, taking place between the excited singlet state of anthracene and the ground state anthracene molecules. Recently, the photoaddition of anthracene to maleic anhydride has been reported to give rise to a Diels–Alder adduct.<sup>16</sup> Similarly, the Diels–Alder addition of few *cis*-azo compounds to anthracene have been studied.<sup>17</sup> Although some of the azo compounds have been reported to quench the fluorescence of anthracene.<sup>18</sup> Our attempted photo-addition of anthracene to diethyl azodicarboxylate in cyclohexane solution gave only the dimer of anthracene (XXVII) and none of the Diels–Alder addition product XXVII (Scheme 8). We believe that diethyl azodicarboxylate is not a good quencher for the excited singlet state of anthracene. This view, however, cannot be confirmed, without carrying out fluorescence quenching experiments using anthracene and diethyl azodicarboxylate.

## EXPERIMENTAL

All m.ps. and b.ps. are uncorrected. IR spectra were recorded on a Perkin–Elmer Model 137 Infracord spectrometer. UV spectra were determined on a Beckmann-DB spectrophotometer. NMR traces were taken on either Varian HR-100 or A-60 spectrometers, using TMS as internal standard. VPC analyses were carried out using an F & M Model-700 VPC instrument, and on a silicon rubber column (6' ×  $\frac{1}{8}$ "), employing hydrogen as carrier gas. Molecular weights were determined using a Machrolab Vapor Pressure Osmometer or by mass spectrometry.

### Starting materials

Cycloheptane, cyclooctene, 1-methylcyclohexene and cyclohexa-1,4-diene were purchased from Aldrich and Co. (USA). Cycloocta-1,5-diene was obtained from Columbia Petrochemicals (U.S.A.). All the olefins were freshly distilled before use.



Diethyl azodicarboxylate, b.p. 70–72° (0.5 mm) was prepared in 85% yield by the oxidation of diethyl hydrazodicarboxylate with chlorine.<sup>19</sup>

*trans*-1,2-Dicarbethoxycyclohexa-3,5-diene (XVI). Cyclohexa-3,5-diene-*trans*-1,2-dicarboxylic acid, m.p. 210° was prepared in a 70% yield by Na/NH<sub>2</sub> reduction of phthalic acid, as previously reported.<sup>20</sup> Esterification of cyclohexa-3,5-diene-*trans*-1,2-dicarboxylic acid, employing EtOH and TsOH gave a 65% yield of *trans*-1,2-dicarbethoxycyclohexa-3,5-diene (XVI), b.p. 124–126° (0.5 mm). (Found: C, 64.00; H, 7.3. Calc for C<sub>12</sub>H<sub>16</sub>O<sub>4</sub>: C, 64.29; H, 7.14%.) IR spectrum (neat)  $\nu_{\max}$ : 1710 cm<sup>-1</sup> (ester C=O) and 1625 cm<sup>-1</sup> (C=C). The uv spectrum of XVI in EtOH showed an absorption maximum at 225 m $\mu$  ( $\epsilon$ , 3,900).

#### *Thermal addition of cycloheptene to diethyl azodicarboxylate*

A mixture of cycloheptene (9.6 g, 0.1 mole) and diethyl azodicarboxylate (8.7 g, 0.05 mole) was heated around 85–90° in a sealed pyrex tube for 40 h. The excess of olefin was removed under vacuum and the residual product was distilled under reduced pressure to give 7.4 g (55%) of 3-(diethylbicycambyl)-1-cycloheptene (III), b.p. 137–138° (0.04 mm) and  $n_D^{25}$  1.4836. (Found: C, 57.38; H, 7.9; 10.76. Calc for C<sub>13</sub>H<sub>22</sub>O<sub>4</sub>N<sub>2</sub>: C, 57.77; H, 8.15; N, 10.4%). IR spectrum (in CCl<sub>4</sub> soln) of III showed prominent absorption bands at 3350 (N–H), 1760 and 1725 (ester, C=O) and 1650 cm<sup>-1</sup> (C=C). NMR spectrum (CCl<sub>4</sub>): 3.1  $\tau$  (1H, NH), 4.4  $\tau$  (2H, vinylic), 5.38  $\tau$  (1H, tertiary proton), 5.95  $\tau$  (4H, ester methylene; quartet,  $J = 7$  cps), 7.88  $\tau$  (2H, allylic methylene), 8.31  $\tau$  (6H, methylene) and 8.74  $\tau$  (6H, ester methyl; triplet,  $J = 7$  cps).

#### *Thermal addition of cyclooctene to diethyl azodicarboxylate*

Cyclooctene (1.7 g, 16 mmole) and diethyl azodicarboxylate (1.4 g, 8 mmole) was heated together for 45 h at 85–90° in a sealed tube, under N<sub>2</sub>. Work-up of the mixture by distillation gave 1.1 g (50%) of 3-(diethylbicycambyl)-1-cyclooctene (V), b.p. 141–142° (0.04 mm) and  $n_D^{25}$  1.4845. (Found: C, 59.02; H, 8.37; N, 10.1; M.W. 286 (Osmometry). Calc for C<sub>14</sub>H<sub>24</sub>O<sub>4</sub>N<sub>2</sub>: C, 59.16; H, 8.45; N, 9.86%; M.W. 284). The infrared spectrum of V in CCl<sub>4</sub> soln was characterized by absorption bands at 3400 (NH), 2930, 2860, 1485, 1370 (CH), 1760, 1725 (ester C=O) and 1650 cm<sup>-1</sup> (C=C). NMR spectrum (CCl<sub>4</sub>): 2.6  $\tau$  (1H, NH), 4.35  $\tau$  (2H, vinylic), 5.00  $\tau$  (1H, tertiary), 5.18  $\tau$  (4H, ester methylene; quartet,  $J = 7$  cps), 7.83  $\tau$  (2H, allylic methylene), 8.4  $\tau$  (8H, methylene) and 8.75  $\tau$  (6H, ester methyl; triplet,  $J = 7$  cps).

#### *Thermal addition of 1-methylcyclohexene to diethyl azodicarboxylate*

A mixture of 4.8 g (0.05 mole) of 1-methylcyclohexene and diethyl azodicarboxylate (4.3 g, 0.025 mole) was heated at 85–90° in a sealed tube for 12 hr. The excess of olefin was removed by distillation and the residual liquid was chromatographed on alumina. Elution with a mixture of benzene and MeOH (50:1) gave a product, which on distillation gave 4.4 g (66%) of a mixture of 2-(diethylbicycambyl)-1-methylene-cyclohexane (VIII), 6-(diethylbicycambyl)-1-methyl-1-cyclohexene (IX) and 3-(diethylbicycambyl)-1-methyl-1-cyclohexene (X), b.p. 116–180° (0.06 mm) and  $n_D^{25}$  1.4785. (Found: C, 57.55; H, 8.02; N, 10.59%. Calc for C<sub>13</sub>H<sub>22</sub>O<sub>4</sub>N<sub>2</sub>: C, 57.77; H, 8.14; N, 10.37%). VPC analysis of the isomeric adduct mixture showed the presence of three peaks due to VIII, IX and X in the area ratio of 24:36:42 and with retention times of 276 secs, 306 secs and 342 secs, respectively (column temp 170°; hydrogen gas flow rate 45 ml/min). Further elution of the alumina column with a mixture of benzene and MeOH (19:1) gave 0.2 g (5%) of diethyl hydrazodicarboxylate (VII), m.p. 132–33° (mixed m.p.).

#### *Hydrogenation of the mixture of adducts from the reaction of 1-methylcyclohexene and diethyl azodicarboxylate*

The isomeric mixture of adducts VIII, IX and X (1 g) was hydrogenated in 15 ml of abs EtOH, containing 0.1 g of 5% Pd/C at 60 psi for a period of 48 h. Removal of the catalyst and of the solvent gave a product which was distilled under vacuum to give a 95% yield (0.95 g) of a mixture of products consisting of 1-(diethylbicycambyl)-2-methylcyclohexane (XI) and 1-(diethylbicycambyl)-3-methylcyclohexane (VII), b.p. 140–143° (0.05 mm) and  $n_D^{25}$  1.4650. (Found: C, 57.12; H, 8.65; N, 10.40. Calc for C<sub>13</sub>H<sub>24</sub>O<sub>4</sub>N<sub>2</sub>: C, 57.35; H, 8.82; N, 10.29%). IR spectrum (in CCl<sub>4</sub> soln)  $\nu_{\max}$ : 3422 (NH), 2980, 2930, 1470, 1365 (CH) and 1755, 1718 cm<sup>-1</sup> (ester C=O). VPC analysis of the mixture of XI and XII showed the presence of two peaks in the ratio of 65:35 and with retention times of 525 secs and 575 secs, respectively (column temp 175°; hydrogen gas flow rate 45 ml/min).

#### *Thermal addition of trans-1,2-dicarbethoxycyclohexa-3,5-diene to diethyl azodicarboxylate*

A mixture of 2.5 g (0.01 mole) of *trans*-1,2-dicarbethoxycyclohexa-3,5-diene and diethyl azodicarboxylate (1.74 g, 0.01 mole) was heated at 85–90° for 15 h. Distillation of the product mixture gave 0.5 g (12%) of

the adduct XVII, b.p. 268–270° (0.005 mm) and  $n_D^{25}$  1.4815. (Found: C, 54.57; H, 6.71; N, 6.97. Calc for  $C_{18}H_{26}O_8N_2$ : C, 54.28; H, 6.53; N, 7.05%). IR spectrum of XVII (in  $CCl_4$  soln) showed prominent absorptions at 2910, 1450, 1390, 765 (CH) and 1750, 1700  $cm^{-1}$  (Ester C=O). NMR spectrum of XVII in  $CCl_4$  soln showed three overlapping triplets centered around 8.88, 8.76 and 8.64  $\tau$  ( $CH_3$  protons) and multiplets centered around 6.20  $\tau$  (tertiary protons), 4.75 (allylic tertiary protons) 5.88  $\tau$  (ester methylene protons) and 3.4  $\tau$  (vinylic protons).

#### *Thermal addition of cycloocta-1,5-diene to diethyl azodicarboxylate*

A mixture of cycloocta-1,5-diene (5.4 g, 0.05 mole) and diethyl azodicarboxylate (4.3 g, 0.025 mole) was heated at 85–90° for 15 h. The excess of olefin was removed under vacuum and the residual product was distilled under reduced pressure to give a 39% yield (2.7 g) of 3-(diethylbicarbamyl)-cycloocta-1,5-diene (XX), b.p. 162–165° (0.06 mm) and  $n_D^{25}$  1.4931. (Found: C, 59.75; H, 7.9; N, 10.11; M.W. 289 (Osmometry). Calc for  $C_{14}H_{22}O_4N_2$ : C, 59.58; H, 7.8; N, 9.93%; M.W. 282). The IR spectrum of XX (neat) showed prominent absorptions at 3365 (NH), 1765, 1720 (ester C=O) and 1660, 765  $cm^{-1}$  (*cis* HC=CH). NMR spectrum ( $CCl_4$ ): 3.1  $\tau$  (1H, NH), 4.7  $\tau$  (4H, vinylic), 5.04  $\tau$  (1H, tertiary proton), 6.0  $\tau$  (4H, ester methylene; quartet  $J = 7.5$  cps), 7.72  $\tau$  (6H, allylic methylene and 8.77  $\tau$  (6H, ester methyl; triplet,  $J = 7.5$  cps).

#### *Photo-addition of cycloheptene to diethyl azodicarboxylate*

A mixture of cycloheptene (19.2 g, 0.2 mole) and diethyl azodicarboxylate (3.5 g, 0.02 mole) was irradiated in a Rayonet Photochemical Reactor (3500 Å, Hg lamp) for 55 h, at room temp. The excess of olefin was removed under reduced pressure and the residual product was distilled under high vacuum to give a 66% yield (3.6 g) of 3-(diethylbicarbamyl)-1-cycloheptene (III), b.p. 137–139° (0.04 mm) and  $n_D^{25}$  1.4836. The adduct III was found to be identical in all respects to the product obtained from the thermal reaction.

#### *Photo-addition of cyclooctene to diethyl azodicarboxylate*

A mixture of 22 g (0.2 mole) cyclooctene and 3.5 g (0.02 mole) of diethyl azodicarboxylate was irradiated for 48 h in a Rayonet Photochemical Reactor (3500 Å, Hg lamp). Work-up of the mixture as in the previous case gave a 60% yield (3.3 g) of 3-(diethylbicarbamyl)-1-cyclooctene (V), b.p. 141–142° (0.04 mm) and  $n_D^{25}$  1.4845. The adduct V was shown to be identical in all respects to the product obtained under thermal reaction.

#### *Photo-addition of 1-methylcyclohexene to diethyl azodicarboxylate*

Irradiation of a mixture of 1-methylcyclohexene (9.6 g, 0.1 mole) and diethyl azodicarboxylate (1.74 g, 0.01 mole) for 12 h and work-up of the mixture as in the earlier cases gave a 70% (1.9 g) yield of the mixture of adducts (VIII, IX and X), b.p. 116–118° (0.06 mm) and  $n_D^{25}$  1.4785. VPC analysis revealed that the composition of this mixture was identical to the product mixture obtained from the thermal reaction.

#### *Photo-addition of cyclohexa-1,4-diene to diethyl azodicarboxylate*

(a) *In benzene solution.* A mixture of 6 g (0.075 mole) of cyclohexa-1,4-diene and 8.7 g (0.05 mole) of diethyl azodicarboxylate in 700 ml of dry benzene was irradiated for 15 h, using a medium pressure Hg lamp (450 watts). Removal of the solvent under vacuum gave a product which was chromatographed on alumina. Elution with a mixture of benzene and MeOH (20:1) gave a product which was distilled under vacuum to give a 23% yield (2.8 g) of 2-(diethylbicarbamyl)-cyclohexa-1,4-diene (XXIV), b.p. 123–124° (0.004 mm) and  $n_D^{25}$  1.4908. The identity of XXIV was established by a comparison of its IR spectrum with that of an authentic sample.<sup>21</sup>

Further elution of the alumina column with the same solvent mixture gave a 34% yield (3 g) of diethyl hydrazodicarboxylate (VII), m.p. 132–133° (mixed m.p.).

(b) *In diethyl ether.* Irradiation of a mixture of cyclohexa-1,4-diene (9 g, 0.112 mole) and diethyl azodicarboxylate (8.7 g, 0.05 mole) in diethyl ether (750 ml) for 5 h and work-up of the mixture as in the previous case gave a 68% yield (6.0 g) of diethyl hydrazodicarboxylate, m.p. 132–133° (mixed m.p.). No other product could be isolated from this reaction.

#### *Photo-reaction of diethyl ether and diethyl azodicarboxylate*

A mixture of 1.8 g (0.01 mole) of diethyl azodicarboxylate and diethyl ether (175 ml) was irradiated for 20 h. Removal of the solvent and unchanged diethyl azodicarboxylate (0.8 g) gave a product, which was distilled under vacuum to give 1 g (70%) of the ether adduct XXV, b.p. 105–107° (0.04 mm) and  $n_D^{25}$  1.4365.

IR spectrum of XXV (in  $\text{CCl}_4$ ) showed absorption bands at 3400 (NH) and 1755, 1725  $\text{cm}^{-1}$  (ester  $\text{C}=\text{O}$ ).

Treatment of 0.62 g (2.5 mmole) of the adduct XXV with 5 ml of water gave a product mixture which, when reacted with an ethanolic solution of 2,4-dinitrophenylhydrazine containing a small amount of  $\text{H}_2\text{SO}_4$  yielded 0.30 g (50%) of acetaldehyde 2,4-dinitrophenylhydrazone, m.p. 165–166° (mixed m.p.).

*Photo-addition of trans-1,2-dicarbethoxycyclohexa-3,5-diene to diethyl azodicarboxylate*

A mixture of *trans*-1,2-dicarbethoxycyclohexa-3,5-diene (11.5 g, 0.052 mole) and diethyl azodicarboxylate (8.2 g, 0.49 mole) in 650 ml cyclohexane was irradiated under  $\text{N}_2$  for 80 h. Removal of the solvent and distillation of the residual liquid under vacuum gave a 43% yield (8 g) of the Diels–Alder adduct XVII, b.p. 268–270° (0.005 mm) and  $n_D^{25}$  1.4815. The adduct XVII was found to be identical in all respects to the product obtained from the thermal reaction.

*Photo-addition of cycloocta-1,5-diene to diethyl azodicarboxylate*

A mixture of cycloocta-1,5-diene (4.06 g, 0.037 mole) and diethyl azodicarboxylate (2.1 g, 0.012 mole) was irradiated in a Rayonet Photochemical Reactor (3500 Å, Hg lamp) for 15 h at room temp. The excess of the diene was removed by distillation and the residual product on distillation under vacuum gave a 60% yield (2 g) of 3-(diethylcarbonyl)-cycloocta-1,5-diene (XX), b.p. 161–164° (0.06 mm) and  $n_D^{25}$  1.4931. The adduct XX was shown to be identical in all respects to the product obtained from the thermal reaction.

*Photo-reaction of anthracene with diethyl azodicarboxylate*

A mixture of 1.8 g (0.01 mole) of anthracene and diethyl azodicarboxylate (1.74 g, 0.01 mole) in 750 ml of cyclohexane was irradiated for 12 h at room temp, using a 450 watt medium pressure Hg lamp. The solid that separated out was filtered to give a 95% yield (1.7 g) of dianthracene, m.p. 264–265° (lit<sup>15</sup> m.p. 267–268°). Work-up of the filtrate gave 1.6 g (88%) of unchanged diethyl azodicarboxylate.

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