## Photochemical Reaction of Diethyl Azodicarboxylate with Ethers and Alcohols

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ALTHOUGH the reaction of diethyl azodicarboxylate (I) with amines has been known since the work of Diels,<sup>1</sup> the use of ethers as solvents for these and other reactions of (I) indicates their apparent unreactivity. We find, however, that irradiation of (I) in solution in dioxan gives a 1:1 adduct, the structure of which (II) follows from analysis agreeing with  $C_{10}H_{18}O_6N_2$ , infrared ( $\nu_{max}$  1705 and 3300 cm.<sup>-1</sup>) and p.m.r. spectra [ $\tau 2.6$  (intensity 1), NH; 4.6 (1), OCHN; 5.8 (4), O·CH<sub>2</sub>Me; 6.3 (6), dioxan CH<sub>2</sub>'s; 8.7 (6), CH<sub>2</sub>·CH<sub>3</sub>].

The reaction is general for substitution at the  $\alpha$ -position of ethers. A similar 1:1 adduct (III) is formed, for example, by irradiation of (I) in di-n-butyl ether. The excited azo-ester (I) attacks the various kinds of OC-H bonds rather unspecifically, although the rate does increase in the order OCH<sub>3</sub> < OCH<sub>2</sub> < OCH (after statistical correction). Thus unsymmetrical ethers give products from attack on either  $\alpha$ -carbon atom (see entries 3, 4, and 5 in the Table, which shows typical results).

An apparently analogous reaction takes place with alcohols to give ketones, perhaps through unstable intermediates such as (XI) [cf. adduct (VI)]. The much slower rate of the reaction with alcohols than with ethers seems to be due to inhibition by the ketone produced, for addition of



| Substrate                            |   | Wattage of<br>med. pressure<br>lamp  | Time<br>(hr.)   | Temp.<br>(°c)  | Yield (%) and product <sup>a</sup>                     |
|--------------------------------------|---|--|---|--|--|
| Dioxan                               |   | 125  | 6   | 15   | 50 II  |
| Di-n-butyl ether                     |   | 125  | 3   | 15   | · 60 111   |
| 1,2-Dimethoxyethane                  | • •   | 125  | 4.5   | 15   | 47 IV, 29 V  |
| Cyclohexyl methyl ether              |   | 125  | 10  | 15   | (20 VI, 16 VII) <sup>b</sup>                           |
| Methyl n-propyl etherc               |   | 125  | 42  | 15   | 40 VIII, 23 IX   |
| Di-n-butyl ether $(+0.3 \text{ mo})$ | le-   |  |   |  |  |
| % cyclohexanone)                     |   | 125  | 27  | 15   | 60 III   |
| Methylenedioxybenzene                |   | 125  | 3   | Reflux   | 45 X   |
| Ethanol                              |   | 125  | <b>5</b>  | 15   | Acetaldehyde (yield not measured)                      |
| Cyclohexanol                         |   | 500  | 12  | Reflux   | 59 Cyclohexanone                                       |
| Cyclohexanol                         |   | 500  | 47  | 15   | 54 Cyclohexanone                                       |
| 4-t-Butylcyclohexanol                |   | 500  | 12  | Reflux   | 50 4-t-Butylcyclohexanone                              |
| 4-t-Butylcyclohexanol                |   | 500  | 47  | 15   | 46 4-t-Butylcyclohexanone                              |
| Cyclohexanol                         |   | $\mathbf{Dark}$  | 52  | 140  | 18 Cyclohexanone                                       |
|                                      | Substrate<br>Dioxan<br>Di-n-butyl ether<br>1,2-Dimethoxyethane<br>Cyclohexyl methyl ether<br>Methyl n-propyl ether <sup>e</sup><br>Di-n-butyl ether (+0·3 mo<br>% cyclohexanone)<br>Methylenedioxybenzene<br>Ethanol<br>Cyclohexanol<br>Cyclohexanol<br>4-t-Butylcyclohexanol<br>Cyclohexanol | Substrate<br>Dioxan<br>Di-n-butyl ether<br>1,2-Dimethoxyethane<br>Cyclohexyl methyl ether<br>Methyl n-propyl ether <sup>c</sup><br>Di-n-butyl ether (+0·3 mole-<br>% cyclohexanone)<br>Methylenedioxybenzene<br>Ethanol<br>Cyclohexanol<br>Cyclohexanol<br>4-t-Butylcyclohexanol<br>Cyclohexanol | $\begin{array}{cccc} & Wattage of \\ med. pressure \\ lamp \\ \hline \\ Dioxan \dots & & 125 \\ Di-n-butyl ether & & 125 \\ 1,2-Dimethoxyethane & & 125 \\ Cyclohexyl methyl ether & 125 \\ \hline \\ Di-n-butyl ether (+0.3 mole- \\ % cyclohexanone) \dots & 125 \\ \hline \\ Methylenedioxybenzene & & 125 \\ \hline \\ Hendol. & & & 125 \\ Cyclohexanol \dots & & 125 \\ \hline \\ Cyclohexanol \dots & & 125 \\ \hline \\ Cyclohexanol \dots & & 500 \\ Cyclohexanol \dots & 500 \\ 4-t-Butylcyclohexanol \dots & 500 \\ Cyclohexanol \dots & & 500 \\ Cyclohexanol \dots & & 500 \\ \hline \\ \end{array}$ | $\begin{array}{c c c c c c c c c c c c c c c c c c c $ | $\begin{array}{c c c c c c c c c c c c c c c c c c c $ |

| Products | from | ultraviolet | irrad | iation | with | diethyl | azodicarl | boxylate |
|----------|------|-------------|-------|--------|------|---------|-----------|----------|
|----------|------|-------------|-------|--------|------|---------|-----------|----------|

<sup>a</sup> All new compounds had satisfactory analyses (C, H, N), i.r., and p.m.r. spectra.

<sup>b</sup> Not separated pure; ratio of (VI): (VII) estimated from separated 2,4-dinitrophenylhydrazones.

<sup>c</sup> May have contained traces of carbonyl compound.

<sup>1</sup> O. Diels and E. Fischer, Ber., 1914, 47, 2043.

traces of ketone to an ether slows down its reaction markedly (cf. Nos. 2 and 6). The same reaction of alcohol and azo-ester to give ketone and hydrazo-ester proceeds in the dark, although very much more slowly (No. 13).

Since the ether adducts are very sensitive to

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hydrolysis with hot water to give diethyl hydrazodicarboxylate, the expected alcohol and carbonyl compound, the reaction offers a method of cleaving ethers under neutral conditions.

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