

Photochemical Reaction of Diethyl Azodicarboxylate with Ethers and Alcohols

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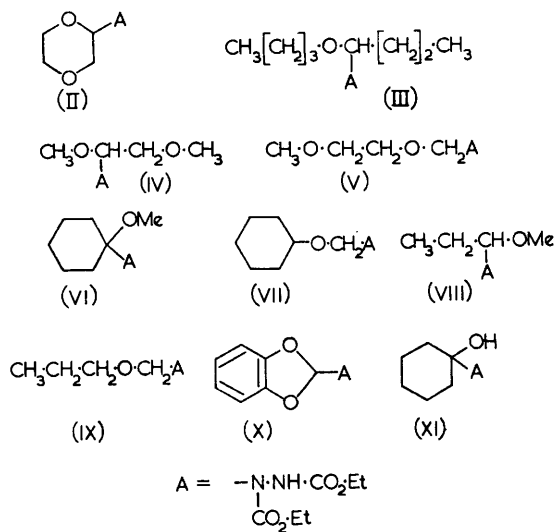
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ALTHOUGH the reaction of diethyl azodicarboxylate (I) with amines has been known since the work of Diels,¹ the use of ethers as solvents for these and other reactions of (I) indicates their apparent unreactivity. We find, however, that irradiation 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 (ν_{\max} 1705 and 3300 cm^{-1}) and p.m.r. spectra [τ 2.6 (intensity 1), NH; 4.6 (1), OCHN; 5.8 (4), O-CH₂Me; 6.3 (6), dioxan CH₂'s; 8.7 (6), CH₂-CH₃].

The reaction is general for substitution at the α -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 unselectively, although the rate does increase in the order OCH₃ < OCH₂ < OCH (after statistical correction). Thus unsymmetrical ethers give products from attack on either α -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



Products from ultraviolet irradiation with diethyl azodicarboxylate

No.	Substrate	Wattage of med. pressure lamp	Time (hr.)	Temp. (°c)	Yield (%) and product ^a
1	Dioxan	125	6	15	50 II
2	Di-n-butyl ether	125	3	15	60 III
3	1,2-Dimethoxyethane	125	4.5	15	47 IV, 29 V
4	Cyclohexyl methyl ether	125	10	15	(20 VI, 16 VII) ^b
5	Methyl n-propyl ether ^c	125	42	15	40 VIII, 23 IX
6	Di-n-butyl ether (+0.3 mole-% cyclohexanone)	125	27	15	60 III
7	Methylenedioxybenzene	125	3	Reflux	45 X
8	Ethanol	125	5	15	Acetaldehyde (yield not measured)
9	Cyclohexanol	500	12	Reflux	59 Cyclohexanone
10	Cyclohexanol	500	47	15	54 Cyclohexanone
11	4-t-Butylcyclohexanol	500	12	Reflux	50 4-t-Butylcyclohexanone
12	4-t-Butylcyclohexanol	500	47	15	46 4-t-Butylcyclohexanone
13	Cyclohexanol	Dark	52	140	18 Cyclohexanone

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

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

^c May have contained traces of carbonyl compound.

¹ 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

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

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