

REACTIONS OF LONE PAIR ELECTRON DONORS WITH UNSATURATED ELECTROPHILES.

II. ADDITION OF ETHERS AND SULFIDES TO DIMETHYL AZODICARBOXYLATE¹

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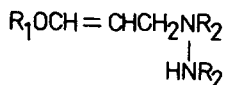
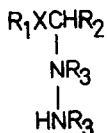
Dibenzyl ether and dialkyl ethers add photochemically to azodicarboxylate (ADC) to give the α -substituted ethers, $R_1NHN R_1CR_2OR_3$.^{2,3,4} Furthermore, tetrahydrofuran (THF) adds to ADC by initiation with dibenzoyl peroxide,⁴ and dibenzyl ether has recently been shown to add by heating alone.⁵ These additions are believed to be of free radical nature.^{2,4} The corresponding sulfide addition may take place thermally, photochemically, and by initiation with dibenzoyl peroxide.^{6,7}

In the present study, it was found that dialkyl ethers add thermally to ADC to give excellent to quantitative yields of the α -substituted ethers (1). Generally, a solution of ADC in excess ether⁸ was heated in the dark in a sealed pyrex tube at 65-120° until the orange color of the ADC was discharged (2-5 hr). A work-up procedure consisting of evaporation of excess ether was sufficient. The reaction was performed on diethyl ether, oxetane, THF, 2-methyl THF, tetrahydropyran and oxepane. The structures were determined by the spectral properties (ir, nmr, and mass spectrometry). The products fulfilled usual criteria for purity (vpc, tlc), and all new compounds showed satisfactory elementary analyses. The THF-adduct was compared with an authentic sample.⁴ In addition to the THF-adduct, the tetrahydropyran adduct is crystalline (m.p. 133-135°), while the other adducts are colorless oils. The addition to 2-methyl THF gives the two products resulting from reaction at either 2-position in a 50:50 ratio.⁹

The presence of a free radical scavenger such as *p*-dinitrobenzene¹⁰ in

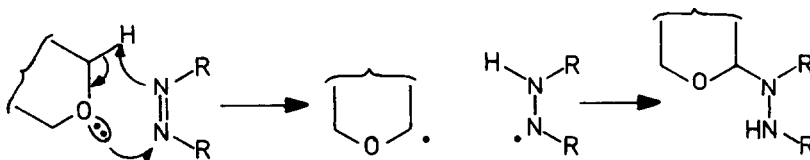
the reaction mixture causes considerable retardation in the additions of oxetane and THF, while the additions of diethyl ether, tetrahydropyran, and oxepane are largely unaffected. The final product yields in the inhibited additions to oxetane and THF are approximately the same as in the more rapid uninhibited additions.

The additions to a series of mixed alkyl-, allyl-, aryl- and benzyl-ethers to ADC were also investigated. The structures were determined as mentioned above. Generally, ADC was heated (100-120°) with a slight excess of ether until the orange color of ADC was discharged (3-10 hr). The work-up procedure consisted of chromatography on silica gel. Dibenzyl ether gives the adduct 2 in 70 % yield (m.p. 125-126°). Benzyl ethyl ether reacts exclusively in the benzylic position to give the adduct 3 in 75 % yield (m.p. 74-76°). Allyl phenyl ether reacts in the vinylic position to give the adduct 4 in 35 % yield (colorless oil). Allyl ethyl ether reacts both in the allylic and the vinylic position to give the adducts 5 and 6 in 40 % and 30 % yield, respectively (colorless oils). Anisol and diphenyl ether do not react with ADC. The additions to a few sulfides were also studied. Thiolane adds to ADC in an extremely rapid and clean reaction (100°, $t_{\frac{1}{2}} = 2$ min) to give the adduct 7 in 90-100 % yield (oil). Dibenzyl sulfide gives the adduct 8 in 75 % yield (m.p. 132-134°). Diallyl sulfide gives the adduct 9 in 40 % yield (oil). Diphenyl sulfide does not react with ADC.



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|----|--------------------------|-----------------|------------------|----|----------------|------------------|
| 1. | R_1 ; R_2 = alkyl | $X = O$ | $R_3 = CO_2CH_3$ | 4. | $R_1 = Ph$ | $R_2 = CO_2CH_3$ |
| 2. | $R_1 = CH_2Ph$ | $R_2 = Ph$ | " " | 6. | $R_1 = C_2H_5$ | |
| 3. | $R_1 = C_2H_5$ | " | " " | | | |
| 5. | " | $R_2 = CH=CH_2$ | " | | | |
| 7. | R_1 ; $R_2 = (CH_2)_3$ | $X = S$ | | | | |
| 8. | $R_1 = CH_2Ph$ | $R_2 = Ph$ | " " | | | |
| 9. | $R_1 = CH_2CH=CH_2$ | $R_2 = CH=CH_2$ | " | | | |

The additions of ethers to ADC seem to be of a radical nature. This is indicated by the inhibiting effect of *p*-dinitrobenzene on the additions of THF and oxetane and the specific addition to the benzylic position of alkyl benzyl ethers. Furthermore, the result of the addition of allyl ethyl ether indicates an allyl radical intermediate. However, it should be pointed out that the same result would be obtained by simultaneous ene addition and reaction at the ether α -position.¹¹ The donating ability of the ether is clearly important, since aryl ethers which are weaker donors than alkyl ethers¹² do not react. Allyl phenyl ether reacts in an ene addition at the vinylic position only. The ether addition may involve cage coupling of a radical pair formed in a possibly concerted electron transfer-proton transfer process as shown below. A similar process has been suggested to explain radical formation in a related system.¹³ Oxetane and THF are particularly prone to undergo free radical chain reactions,¹³ and diffusion of an initially caged radical pair may initiate such a process in these cases.



The sulfide addition to ADC was originally suggested to involve attack on the electrophilic azo grouping by the sulfur atom, possibly in concert with migration of hydrogen from the methylene to the second nitrogen atom.⁶ An ylide intermediate formed in this fashion is favored in a recent study.⁷ Ylides of the sulfides investigated in the present study undergo characteristic rearrangements and eliminations.¹⁴ However, migration of the hydrazyl moiety from the sulfur to the ylide α -carbon may be the most favorable mode of migration in those systems. Furthermore, the fact that the reaction is promoted by irradiation and radical initiators⁷ demonstrates the radical nature of the addition. A caged coupling of a sulfide-hydrazyl radical pair is a conceivable mechanism. The radical pair may be formed by homolysis of the sulfur-nitrogen bond of an ylide intermediate, or in a direct manner as suggested here for the ether addition.

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8. All ethers were assured to be dry and peroxide-free. For details of purification procedures, see ref. 13.
9. The ratio was evaluated from the integrals of the two different methyl groups in the nmr spectrum of the product mixture.
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11. The addition of allyl ethyl ether is considerably faster than that of allyl phenyl ether. This indicates that an ene addition is not important in the former case, since the ene additions in these two systems should be expected to be approximately of the same rate. ADC is known to react *via* allyl radicals in other systems: G. Ahlgren, B. Åkermark, and K.I. Dahlquist, *Acta Chem. Scand.* 22 1129 (1968).
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