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Short Communications

The Reaction between Diethyl Azodicarboxylate and Styrene in the Presence of a Radical Inhibitor*

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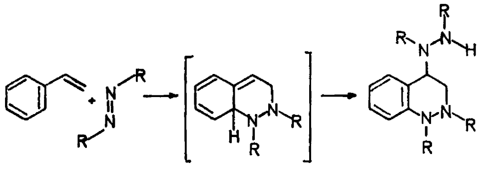
The ene reaction is generally considered to be a six-centred cyclic process, the double bond shift being concerted with transfer of allylic hydrogen.[1] However, certain ene reactions involving azodicarboxylates show a radical behavior.[1,2] In an earlier paper in this series, the addition of diethyl azodicarboxylate to cyclohexene was shown to take place *via* radical intermediates.[3] An additional example of such behavior is presented here.



The 2:1 adduct *2* between azodicarboxylate and styrene is formed *via* an ene reaction of the initial Diels-Alder 1:1 adduct *1*.[4] Qualitative kinetic studies now show that the formation of the adduct *2* is strongly inhibited when a radical inhibitor (*t*-butylresorcinol) is present in the reaction mixture. In fact, an aged mixture of styrene and *t*-butylresorcinol even failed to give the adduct *2* with diethyl azodicarboxylate. A kinetic study of the formation of the adduct *2* showed the reaction to be first order in styrene and first order in azodicarboxylate. The disappearance rate of styrene is unaffected by the presence of *t*-butylresorcinol in the reaction mixture. Thus, the formation of the intermediate *1* is the rate-determining step.* Furthermore, the effect of the radical inhibitor indicates that the subsequent ene reaction takes place to a significant extent *via* a radical chain mechanism. A related process seems to be the self-induced free radical polymerisation of styrene. In that case, radicals are generated in the reaction between styrene and the Diels-Alder type dimer of styrene,[5] a compound very similar to the intermediate *1*.

Experimental. The kinetic experiments were run in ether solution at 25.0 ± 0.5 °C. The reaction flask was equipped with a rubber septum through which samples were withdrawn with a syringe at suitable intervals. Styrene was quantitatively determined by GLC and diethyl azodicarboxylate by UV measurements at 400 nm. GLC was done on a Varian 1200 gas chromatograph equipped with a Varian 480 integrator.

UV Spectra were determined with a Beckman Dk2-spectrophotometer.

1. Hoffman, H. M. R. *Angew. Chem. Int. Ed. Engl. 8* (1969) 556.
2. Fahr, E. and Lind, H. *Angew. Chem. Int. Ed. Engl. 5* (1966) 372.
3. Ahlgren, G., Åkermark, B. and Dahlquist, K. J. *Acta Chem. Scand. 22* (1968) 1129.
4. Diels, O. and Alder, K. *Justus Liebigs Ann. Chem. 450* (1926) 237.
5. Mehnert, P. *Angew. Chem. Int. Ed. Engl. 13* (1974) 781.

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* Cycloaddition Reactions, Part 7. Part 6: Ahlgren, G. and Åkermark, B. *Tetrahedron Lett.* (1974) 987.

* Attempts to isolate the intermediate *1* have been unsuccessful.