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 hydro- gen. However, certain ene reactions involving azodicarboxylates show a radical behavior. In an earlier paper in this series, the addition of diethyl azodicarboxylate to cyclohexene was shown to take place via radical intermediates. An additional example of such behavior is presented here.

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\begin{align*}
\text{C} & \quad \text{N} \\
\text{R} = \text{CO}_2\text{C}_2\text{H}_5 & \quad \text{R} \quad \text{N} \\
\text{H} & \quad \text{H} \\
\text{R} & \quad \text{R} \\
1 & \quad 2
\end{align*}
\]

The 2:1 adduct 2 between azodicarboxylate and styrene is formed via an ene reaction of the initial Diels-Alder 1:1 adduct 1. 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 intermediary 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, 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run in ether solution at 25.0 ± 0.5°C. The reaction flask was equipped with a rubber septum through which samples were withdrawn with a syringe at suitable intervals.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.

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* Attempts to isolate the intermediate 1 have been unsuccessful.


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