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MECHANISM OF THE REACTION OF MONO-OLEFINS WITH DIENOPHILES. II. A POSSIBLE FREE-RADICAL MECHANISM

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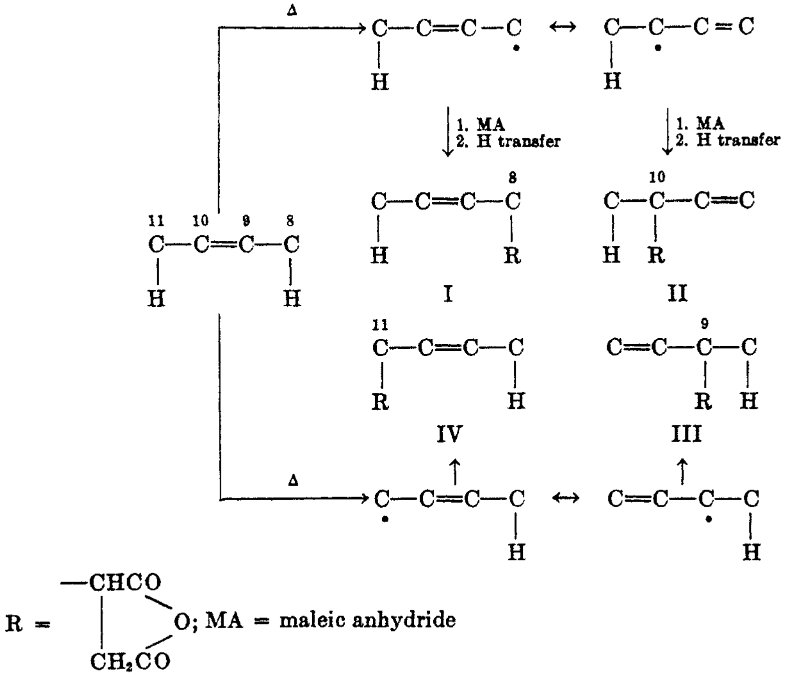
The thermal condensation of olefins with dienophiles can be explained by an ionic mechanism (1), which requires that the dienophile become attached to one of the carbons of the olefinic double bond (2). One exception is inconsistent with the ionic mechanism unless one assumes improbable double-boned shifts before reaction; Bickford and co-workers (3) noted that methyl oleate reacted with maleic anhydride at 220° to form not only the products II and III predicted by the ionic mechanism, but also I and IV. Although they did not present a complete structure proof for I and IV, their oxidation experiments constitute strong evidence for the assigned structures. They suggested a free-radical mechanism, by analogy to that accepted for autoxidation of methyl oleate, in which a hydrogen atom is lost from either α-carbon 8 or 11, followed by addition of the mesomeric radical in either extreme form to maleic anhydride. The reaction then continues by conventional chain propagation steps. Their mechanism accounts for the formation of I and IV, in which the maleic anhydride becomes attached to an α-carbon of the original molecule.[1]



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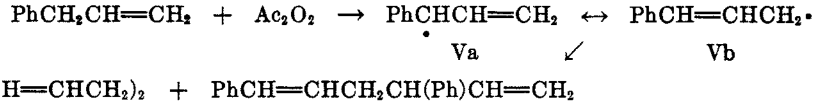
[1] Alder, Pascher, and Schmitz (4) suggested a similar mechanism for the "substituting addition" reaction of allylbenzene and maleic anhydride, following Farmer, Koch, and Sutton (5).

A symmetrically substituted olefin such as methyl oleate would lack the polar character found in the terminal olefins which have been studied in most of the previous work. In order to learn whether Bickford's mechanism could operate with a terminal olefin, we decomposed acetyl peroxide in a mixture of allylbenzene[2] and maleic anhydride. Maleic anhydride can react by a chain process with free radicals to form 1:1 adducts.[3] Allylbenzene alone reacts with acetyl peroxide to form a mesomeric radical which has been isolated in the form of dimers (8, 13).



$$\mathrm{PhCH_2CH{=}CH_2} + \mathrm{Ac_2O_2} \rightarrow \underset{\text{Va}}{\mathrm{Ph\overset{}{\underset{\bullet}{C}}HCH{=}CH_2}} \leftrightarrow \underset{\text{Vb}}{\mathrm{PhCH{=}CHCH_2\cdot}}$$

$$\swarrow$$

$$\mathrm{(PhCH{=}CHCH_2)_2} + \mathrm{PhCH{=}CHCH_2CH(Ph)CH{=}CH_2}$$

Koch (13) argued that the latter result ruled out the radical mechanism originally advanced by Alder for the thermal reaction of allylbenzene with maleic anhydride (4). Cinnamylsuccinic anhydride (related to structure Vb) is the only product isolated (4, 9), whereas it should have been accompanied by α-phenylallylsuccinic anhydride (derived from Va). This argument does not invalidate the free-radical mechanism, however, since in a thermal reaction where the concentration of radicals is low, the reaction may take quite a different course than when the radicals are generated in high concentration by the action of peroxides. Also, a mesomeric radical V might well react differently with another free radical (dimerization) than with a "normal" molecule of maleic anhydride. Further, Vb is a lower-energy form than Va, since the double bond of Vb is conjugated with the ring.

The preliminary hydrogen dissociation would be energetically the most difficult step in Bickford's mechanism, and hence rate-controlling. The rate of such a free-radical dissociation should be independent of maleic anhydride concentration. A kinetic study was accordingly undertaken.

RESULTS AND DISCUSSION

Several mole ratios of allylbenzene and maleic anhydride (4.5:1, 1.1:1, and 1:3) were heated in the presence of catalytic amounts of acetyl peroxide at 80–95°. The products varied from colorless to yellowish polymers to black, sticky tars. Other than some unreacted starting materials, no pure compounds could be isolated. Since cinnamylsuccinic anhydride, the product of the thermal condensation, can readily be separated from accompanying polymers by distillation (9), we are confident that no more than traces could have been present. Maleic anhydride does not readily homopolymerize, and in copolymerizations it shows a pronounced alternating tendency. In the runs with excess maleic anhydride,

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[2] Allylbenzene was selected since other olefins, especially of the isobutylene type, form polymers with maleic anhydride in the presence of peroxides (6, 7). The radical from allylbenzene (V) is a less reactive radical than other free radicals (resonance stabilization) and hence would be more likely to react by addition than by hydrogen abstraction (8). Furthermore, the results could be compared with those from the thermal reaction (4, 9).

[3] For example, alkylbenzenes react through their α-hydrogens with maleic anhydride under the influence of heat (10), light, or benzoyl peroxide (11) to form benzylsuccinic acids. Fluorene and acenaphthene appear to react with particular ease (12).

conditions should have been particularly favorable for production of the 1:1 adduct.

We also confirmed Alder's statement (14) that cinnamylsuccinic anhydride is not formed when propenylbenzene is heated with maleic anhydride.

The rate of the thermal reaction of allylbenzene with maleic anhydride was studied at three temperatures. The data are best represented by a second-order expression: $-\frac{d[MA]}{dt} = k_2[MA][olefin]$ (MA is maleic anhydride). The second-order rate constants drift slightly because of analytical difficulties, but the data cannot be represented by first order or three-halves order equations nor by various chain processes.

The conclusion is inescapable that the reaction of allylbenzene with maleic anhydride cannot be a radical chain process involving an initial dissociation of an α-hydrogen to a radical V, since when V is generated in the presence of maleic anhydride, no 1:1 adduct is formed. The polymer formed as a byproduct in the thermal reaction may result from such a radical, however.

The kinetic experiments bear out this statement and show further that the transition state of the thermal reaction contains a molecule each of olefin and maleic anhydride. Mechanisms involving a rate-determining homolytic (or heterolytic) separation of the π-electrons of either double bond are likewise excluded. It is hoped that more accurate rate data will permit a more detailed representation of the transition state either as a dipolar ion or as a cyclic hydrogen-bonded form (15) since the entropies of activation of the two processes should be quite different.

The preceding conclusions apply to terminal olefins but cannot be extended to unpolarized symmetrical compounds in view of Bickford's results. An attempt was made to detect a hydrogen-abstraction mechanism with the 1,3-diarylpropenes $C_6H_5CH{=}CHCH_2C_6H_4Cl$-*p* and $C_6H_5CH_2CH{=}CHC_6H_4Cl$-*p* (16), but unfortunately, no 1:1 adducts could be isolated when either compound was heated with maleic anhydride.

Of possible significance is the fact that the thermal reaction of allylbenzene with maleic anhydride gives almost identical results both in the presence and absence of free-radical inhibitors such as hydroquinone and diphenylamine. Although on the surface, this result would appear to exclude any free-radical mechanism, such an interpretation is probably not justified, since these compounds would doubtless be acylated by maleic anhydride at the high temperatures and long times required.

EXPERIMENTAL

Reactions with acetyl peroxide. Maleic anhydride was distilled before use; allylbenzene, prepared by the coupling of phenylmagnesium bromide with allyl bromide, was fractionated and the portion boiling at 155–156° was employed.

A solution of 33 g. (0.34 mole) of maleic anhydride in 30 g. (0.25 mole) of allylbenzene was maintained at 85–90° while a solution of 0.01 mole of acetyl peroxide in 0.04 mole of allylbenzene was added dropwise. The contents of the flask was a colorless, semi-transparent polymer at room temperature. The mixture was distilled at 0.3 mm. until the pot temperature reached 322°, but no cinnamylsuccinic anhydride [b.p. 197°/0.25 mm. (9)] distilled.

In a second run, to 35 g. (0.30 mole) of allylbenzene at 85–90° were added simultaneously dropwise a solution of 10 g. (0.085 mole) of acetyl peroxide in 0.30 mole of allylbenzene and a solution of 20 g. (0.20 mole) of maleic anhydride in 0.30 mole of allylbenzene. After cooling, a resinous, yellowish, opaque mass was obtained. After the excess allylbenzene was removed by heating at 15 mm., 20 g. of the residue was distilled, giving 1.3 g. of a dark-brown liquid, b.p. 160–221°/0.5 mm. This material was boiled with sodium carbonate solution to hydrolyze any anhydrides, extracted with ether, acidified with sulfuric acid, and again ether-extracted. The latter ether extract, which should have contained any cinnamylsuccinic acid, was evaporated but only a trace of dark oily residue was obtained. Hydrolysis of a sample of the original residue gave a solid acid of indefinite melting point. This acid was somewhat unsaturated, as shown by absorption of 0.0016 mole of hydrogen over palladium on barium sulfate by a 2 g. sample. However, permanganate oxidation of a sample under mild conditions gave no detectable trace of benzoic acid.

In a third run, 18 g. (0.16 mole) of acetyl peroxide in 47 g. (0.40 mole) of allylbenzene was added dropwise to 118 g. (1.2 moles) of maleic anhydride at 80–90°. No cinnamylsuccinic anhydride could be isolated from the black, sticky mass.

Reaction of propenylbenzene with maleic anhydride. When 11.8 g. (0.1 mole) of propenylbenzene and 9.8 g. (0.1 mole) of maleic anhydride in 10 ml. of *o*-dichlorobenzene and a little hydroquinone were refluxed for 21 hours, the mixture was orange-brown. After the solvent was removed at 15 mm., the residue was distilled. An orange semi-solid material (2.6 g.) was collected at a bath temperature of 200–280°, and the residue was very dark and viscous. The distillate was recrystallized from benzene, yielding 0.62 g., m.p. 126–128°. The analytical sample was recrystallized twice more, m.p. 127.0–127.7°.

Anal. Calc'd for $C_{12}H_8O_2$: C, 78.25; H, 4.38.
Found: C, 78.21, 77.95; H, 4.50, 4.44.

The compound did not react with bromine or permanganate. Attempts to determine neutral equivalents gave erratic results. Since it clearly was not the known cinnamylsuccinic anhydride or an isomer, it was not further investigated.

Rate study. Equimolar amounts of maleic anhydride and allylbenzene dissolved in *o*-dichlorobenzene were placed in a large test tube surmounted by an air condenser with a drying tube. The tube was suspended in the vapors of a suitable boiling solvent for thermostating. Aliquots were taken at various times and shaken with water. Separate experiments had shown that maleic anhydride was hydrolyzed rapidly and extracted into the water layer, while cinnamylsuccinic anhydride was unaffected. Titration of the separated water layer with standard alkali gave a measure of unreacted maleic anhydride at a given time. Point-to-point calculation using the equation $k_2 = \frac{1}{t}\frac{x}{a(a-x)}$ gave reasonably constant values of k provided the first point was neglected. The error in the first point may reflect the time required to attain thermal equilibrium. The plot of $\frac{1}{a-x}$ against time was a satisfactory straight line.

From these data and the Arrhenius equation, the energy of activation is 20 kcal./mole and the pre-exponential frequency factor is 10^7 liters/mole/hour, approximately.

TABLE I

RATE OF REACTION OF ALLYLBENZENE WITH MALEIC ANHYDRIDE

T, °C.	k_2, liters/mole/hour
127	2.41×10^{-4}
139	5.07×10^{-4}
153	1.07×10^{-3}

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SUMMARY

The reaction of terminal olefins with maleic anhydride does not involve preliminary separation of the hydrogen atom *alpha* to the olefinic double bond. The conclusion is based upon the fact that allylbenzene and maleic anhydride do not form a 1:1 adduct when heated in the presence of acetyl peroxide, and also that the thermal reaction to form cinnamylsuccinic anhydride is first-order in olefin and in maleic anhydride. With symmetrical, unpolarized olefins like methyl oleate, a free-radical mechanism may be operative.

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