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Cyclopolymerization. II. Electron Spin Resonance Studies of the Free-Radical Reactions of Some Diolefins

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Cyclopolymerization. II.
Electron Spin Resonance Studies of the Free-Radical Reactions of Some Diolefins

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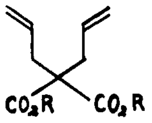
ABSTRACT

ESR spectra have been recorded for a number of radicals generated in a flow cell by interaction of diallylmalonic acid, diallyl ether, diallylamine, and related compounds with amino, hydroxyl, and phenyl radicals in aqueous solution. The results indicate that the radicals initially formed by homolytic addition at one of the double bonds in the diolefins rapidly undergo cyclization to afford product radicals containing five-membered rings.

INTRODUCTION

Electron spin resonance (ESR) spectroscopy has been shown previously to provide a convenient method for the study of intramolecular free-radical reactions. Recent examples include investigations of the cyclization of hex-5-enyl, allylcarbinyl, and allyloxyphenyl radicals [1, 2]; the formation of cyclic alkoxynitroxides from 2-o-nitrophenylalkyl radicals [3]; and the rearrangement of neophyl and β-acyloxyalkyl radicals [1, 4]. In view of the current widespread interest in the structure and mechanism of formation of cyclopolymers [5], it was decided to apply similar ESR methods to the study of the reactions of free radicals with suitable 1,6-diolefin monomers.

The present work is concerned with an exploratory survey of the species formed when diallylmalonic acid (1, R = H), its diethyl ester (1, R = Et), its dianion and the related ether (2) and amine (3) react with three representative free radicals, viz., amino, hydroxyl, and phenyl, generated in a flow system [6, 7] by redox reactions. A later communication [8] will describe the results of a more detailed study of similar reactions of a series of diallylamines.



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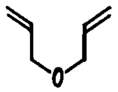

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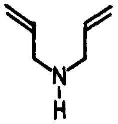

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RESULTS AND DISCUSSION

Hydroxyl and amino radicals were generated by interaction in a flow cell of titanous chloride with hydrogen peroxide and hydroxylamine, respectively [7, 9]. Phenyl radicals were produced by reduction of benzenediazonium ion with titanous ion at high pH (Eq. I), and with $\cdot CH_2OH$ radical, formed by hydrogen-atom abstraction (Eq. II) at low pH [10].

$$PhN_2^+ + Ti^{3+} \longrightarrow Ph\cdot + N_2 + Ti^{4+} \qquad (I)$$

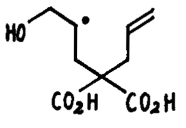
$$HO\cdot + CH_3OH \longrightarrow H_2O + \cdot CH_2OH \qquad (II)$$

$$PhN_2 + \cdot CH_2OH \longrightarrow Ph\cdot + N_2 + CH_2O + H^+ \qquad (III)$$

When hydroxyl radicals were generated in the flow cell in the presence of diallylmalonic acid (1, R = H), the spectrum recorded (Fig. 1) comprised a doublet (1:1) of triplets (1:2:1). This multiplicity requires that the radical formed has a structure in which

FIG. 1. ESR spectrum of the radical formed from diallylmalonic acid and hydroxyl radicals.

the unpaired electron interacts with three protons, two of which are equivalent. Of the various species (4- 8) which could theoretically be formed initially, only two (5, 8) fulfill this requirement. The expected products of addition (4), hydrogen-atom abstraction (6), and addition followed by six-membered ring formation (7) would each give signals of maximum multiplicity $\geqslant$ 10.



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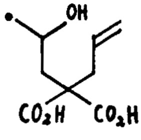

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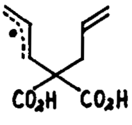

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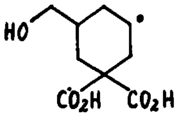
The formation of one (5) of the two structures compatable with the spectral evidence involves addition to the double bond of (1, R = H) in the opposite sense to that normally observed for mono-olefins [7, 11-13], and we therefore conclude that the species present is the



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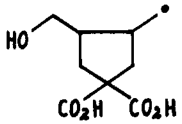


(8)

five-membered cyclic radical (8). The values of the hyperfine splitting constants and of g (see Table 1) are consistent with this structure. Further support for the formation of five-membered cyclic radicals from diallylmalonic acid (1, R = H) was afforded by a study of its reaction with amino radicals in the flow cell. The spectrum recorded (Fig. 2) comprised a quartet (1:3:3:1), which is thought to arise from the radical (11, X = $C(CO_2H)_2$, Z = NH_2) formed by the

TABLE 1. ESR Spectra of Cyclic Radicals (11) Derived from Diolefins (9)[a]

X	Z	a(α-H)	a(β-H)	g
$C(CO_2H)_2$	OH	22.0(t)	24.5(d)	2.0025
$C(CO_2H)_2$	NH_3^+	22.3(q)[b]		2.0026
$C(CO_2^-)_2$	OH	22.3(q)[b]		2.0026
$C(CO_2^-)_2$	Ph	21.9(t)	23.7(d)	2.0026
$C(CO_2Et)_2$	OH	22.2(t)	24.5(d)	2.0025
$C(CO_2Et)_2$	NH_3^+	22.2(q)[b]		2.0025
O	OH	22.0(t)	20.0(d)	2.0025
O	NH_3^+	22.1(t)	18.6(d)	2.0026
O	Ph	22.4(t)	19.9(d)	2.0025
NH_2^+	Ph	22.3(t)	24.2(d)	2.0025
NH	OH	22.4(t)	23.7(d)	2.0025
NH	Ph	22.3(t)	24.4(d)	2.0025
NMe	OH	~23(q)[b]		2.0025
NPr	OH	22.6(q)[b]		2.0025

[a] Hyperfine splitting factor in gauss; (d) 1:1 doublet; (t) 1:2:1 triplet; (q) 1:3:3:1 quartet.

[b] a(α-H) ≃ a(β-H).

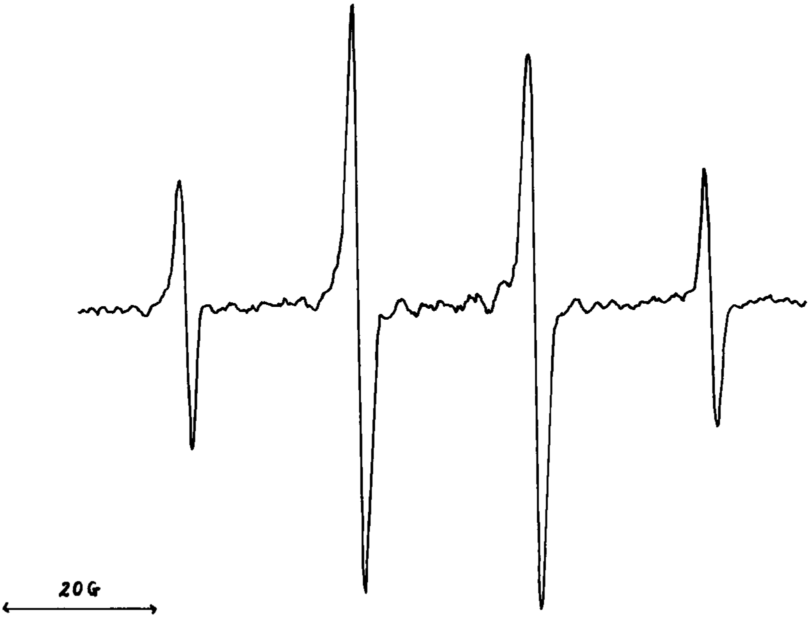
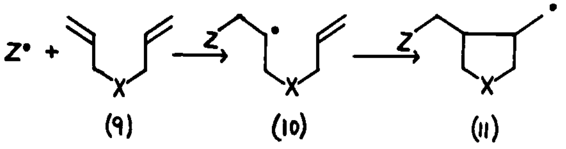


FIG. 2. ESR spectrum of the radical formed from diallylmalonic acid and amino radicals.

illustrated reaction sequence (9 → 10 → 11). The quartet multiplicity indicates that the values of a(α-H) and a(β-H) are approximately the same. In this case the presence, in detectable concentration, of the simple addition product (10) can be unambiguously precluded since it is known that compounds of this general type show additional triplet multiplicity (1:1:1) due to interaction of the free electron with the β-nitrogen atom [9, 13]. Attempts to obtain a spectrum for the



phenyl-substituted radical (11, X = $C(CO_2H)_2$, Z = Ph) were unsuccessful. When aqueous solutions containing 1) benzenediazonium borofluoride and hydrogen peroxide, and 2) diallylmalonic acid (1, R = H), titanous chloride, and methanol were mixed in the ESR flow cell, the signal detected was very weak. It comprised several overlapping spectra of which only that ascribed to the hydroxyl adduct (8) could be identified. It thus appears that the reaction of hydroxyl radicals with the monomer is sufficiently rapid to compete effectively with the hydrogen-atom transfer reaction (Eq. II).

Interaction of benzenediazonium ion with titanous ion in alkaline solution containing diallylmalonate dianion [9, X = $C(CO_2^-)_2$] gave a somewhat stronger ESR signal. Of the several overlapping spectra detected, the major one, comprising a doublet (1:1) of triplets (1:2:1), is attributed to the five-membered cyclic radical [11, X = $C(CO_2^-)_2$, Z = Ph]. The spectrum of the hydroxyl-substituted cyclic radical [11, X = $C(CO_2^-)_2$, Z = OH] showed the quartet multiplicity expected when a(α-H) = a(β-H). It overlapped a weaker spectrum which was identified as that due to the radical formed from EDTA (used to form a complex with titanous ion in alkaline solution) by hydrogen-atom abstraction [14].

The diester [9, X = $C(CO_2Et)_2$] gave satisfactory spectra for the appropriate cyclic radicals [11, X = $C(CO_2Et)_2$, Z = OH or NH_2] when treated with hydroxyl or amino radicals in acid solution. In the latter case the spectrum of another species was detected, but it could not be identified.

The major species detected when hydroxyl, amino, or phenyl radicals were generated in the presence of diallyl ether (9, X = O) were the appropriately substituted five-membered cyclic radicals (11, X = O, Z = OH, NH_2, or Ph). Spectral parameters are given in Table 1.

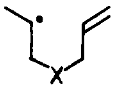
When hydroxyl or amino radicals were generated in the presence of diallylamine (9, X = NH) in acid solution, only the five-membered cyclic radical (9, X = NH_2^+, Z = OH or NH_2) was detected (see following paper) [8].

When phenyl radicals were generated in the presence of diallylamine in acid solution by reduction of benzenediazonium ion with $\cdot CH_2OH$ (Eqs. II and III), a doublet of triplets was recorded. It is attributed to the phenyl adduct (11, X = NH_2^+, Z = Ph) rather than to the product of addition of $\cdot CH_2OH$ (11, X = NH_2^+, Z = CH_2OH), because when the diazonium salt was omitted from the reaction mixture, the signal detected was that of $\cdot CH_2OH$ [7].

Since the ability of protonated diallylamine monomers to readily undergo polymerization is not shared by the related free bases [15], it was deemed advisable to study the ESR spectra of species formed by reaction of diallylamine and some related amines with hydroxyl and phenyl radicals in aqueous alkaline solution. When hydroxyl radicals were generated in the presence of diallylamine (9, X = NH) at pH 8, only the five-membered cyclic radical (11, X = NH, Z = OH) was detected. The signal, which was of lesser intensity than that reoorded for the same reactants at low pH, comprised a quartet (1:3:3:1) but the central lines were broad and asymmetric, and it was possible to deduce separate values for a(α-H) and a(β-H) from the total width of the spectrum. A satisfactory spectrum was also obtained for the phenyl-substituted cyclic radical (11, X = NH, Z = Ph), but the radicals (11, X = NMe or NPr, Z = OH) formed by reaction of hydroxyl radicals with N-methyl- or N-propyldiallylamine gave very weak spectra, interpretation of which was made difficult by the presence of radicals formed from EDTA.

The results obtained clearly indicate that the species present in the flow cell in highest concentration when 1,6-diolefins of the general type (9) are treated with hydroxyl, amino, or phenyl radicals, are five-membered cyclic radicals (11). Since the stationary concentration of any radical is a function of both its rate of formation.and its rate of destruction, it is difficult to obtain quantitative data from the flow method. Nevertheless, in cases such as those described here, in which the possible radicals are of similar structure and consequently should be destroyed at similar rates, it is reasonable to ascribe the highest rate of formation to that radical detected in greatest concentration. Hence the fact that only five-membered cyclic radicals were detected in these experiments indicates that the processes leading to their formation are very much faster than those giving rise to six-membered cyclic radicals. Also, since the initially formed adducts of the general type (10) were not detected, it is reasonable to conclude that the rates of their conversion into cyclic radicals (11) are considerably greater than their rates of formation.

These conclusions accord with the results of recent kinetic studies [16] in which it was demonstrated that the radicals (12, X = CH_2 or 0) rapidly undergo 1,5-intramolecular addition to afford (13, X = CH_2 or 0). The rate of 1,6-cyclization is very much slower. On simple thermochemical grounds the preference for 1,5-cyclization leading to primary radicals is unexpected since six-membered ring formation affords the thermodynamically more stable secondary radicals.* It is likely that intramolecular radical addition processes are under kinetic control and their outcome is determined by steric and electronic factors which effect the transition state but not the relative stabilities of the final products [17].



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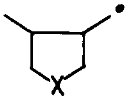

(13)

The data presented in Table 1 show that α- and β-couplings were satisfactorily resolved for most of the cyclic radicals detected. As

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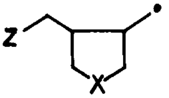
*Other factors, such as steric ring strain and the presence of heteroatoms, could influence the relative stabilities of our five- and six-membered ring radicals.

expected for a series of closely related primary radicals, the values of a(α-H) are approximately the same. The magnitude of a(β-H) is a function of the average dihedral angle formed between the half-filled orbital and the β-C—H bond. The variation in a(β-H) detected in the radicals (11) reflects variations in the relative rotamer populations of their $-CH_2\cdot$ groups, arising presumably from nonbonded interactions. However, apart from the fact that cyclic ether radicals (11, X = O) show lower values of a(β-H) than do others in the series, no clear trend is discernable.

All of the spectra recorded showed relatively large line widths. Possible explanations for this phenomenon include the effect of rapid conformational change between the various puckered forms of the five-membered rings, and the possible presence of cis- and trans-radicals, (14) and (15), expected to have similar, but not identical, spectra. Although the separate geometrical isomers were not detected in this work, related investigations [16] suggest that both should be formed with possibly the cis (14) predominating.



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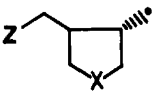

(15)

Finally, the relevance of the present studies to cyclopolymerization deserve comment. On the basis of the ESR and kinetic [16] evidence for the high preference for five-membered ring formation, it seems reasonable to conclude that simple 1,6-diolefins of the general type (9) will afford polymers comprising mainly five-membered cyclic units. (This conclusion is not necessarily valid for monomers which contain substituted double bonds [8, 18].) The failure of such monomers to afford cross-linked polymers except at very high monomer concentration reflects the high rate of intramolecular addition as compared with intermolecular addition of uncyclized radicals. However, the factors responsible for the relative reluctance of unprotonated diallylamines to undergo polymerization have not been identified. Although the ESR studies indicate that they can form five-membered cyclic radicals, there may be competing processes (e.g., formation of allylic radicals) which, although not detected, are sufficiently important to prevent efficient propagation.

EXPERIMENTAL

ESR Spectra

A Varian E9 ESR spectrometer equipped with 100 kHz modulation and an X-band Klystron was used in conjunction with a flow cell [3] which allowed the mixing of the two reactant solutions approximately 0.2 sec before entering the cavity. Splitting constants were measured to within ± 0.1 g and g-values to within ±0.0001. The instrument was calibrated with Fremy's salt.

The methods used for the generation of hydroxyl, amino, and phenyl radicals were similar to those previously described [4, 9, 10]. For reactions conducted in alkaline media, EDTA (8 g/liter) was added to the titanous chloride solution, and the pH was then adjusted by addition of ammonia. Generally the monomer (4 g/liter) was dissolved in the solution containing the titanous ion. However, in the case of the sparingly-soluble substrates diallyl ether and diethyl diallylmalonate, both solutions were saturated by shaking with the monomer.

Materials

Diallylmalonic acid and its diethyl ester were prepared in the usual way [19]. Other materials were commercial samples.

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