[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SOUTH CAROLINA]

# The Reactivity of Diphenylethylene and Related Olefins toward Free Radicals. Evidence for Anomalous Reactions of Radicals from Diphenylethylene

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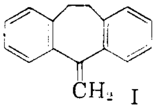
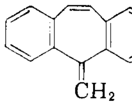
RECEIVED DECEMBER 8, 1958

The reactivity toward methacrylate radicals of diphenylethylene (DPE), methylenedibenzocycloheptadiene (I) and dibenzoheptafulvene (II) has been studied both by measuring the retardation of methacrylate polymerization caused by these olefins and the composition of the "copolymers" formed when methyl methacrylate is polymerized in their presence. Of greatest interest is the fact that the ultraviolet spectra of the methacrylate-DPE and methacrylate-I copolymers show an intense maximum in the 290–310 mμ region which vanishes on short treatment of the copolymer with dilute base. This behavior is strongly suggestive of the presence in the copolymers of 1,4-cyclohexadiene type units of structures VII and X, resulting from anomalous reaction of the olefin free radicals at the *p*-position of one of the aromatic rings. The quantitative variation of the intensity of this maximum with total olefin content suggests VII and X arise at least predominantly from termination reactions of radicals from DPE or I. Comparison of the reactivity data for I and II shows no indication of any enhanced aromaticity for II or the radical derived therefrom.

A recent study[1] has shown that dibenzofulvene (9-methylenefluorene) is extremely reactive toward free radicals, being about 200 times more reactive than styrene toward methyl methacrylate radicals. We were interested in obtaining data on the reactivity of related olefins and therefore undertook a study of the behavior of diphenylethylene, 1-methylene-2,3,6,7-dibenz-2,6-cycloheptadiene (I) and 1-methylene-2,3,6,7-dibenzcycloheptatriene (II). In I as in diphenylethylene the two aromatic rings cannot be simultaneously coplanar with the 1-carbon, but unlike diphenylethylene, I is a crystalline solid which can be more readily purified. Dibenzoheptafulvene (II) was included because studies of several ionic reactions[2,3] and the ultraviolet spectra[3] of certain compounds related to II have yielded somewhat conflicting evidence concerning the possibility of enhanced aromaticity of II or the related carbonium ion III. We hoped our work would provide information on this point for both II and the radical IV.


I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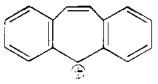
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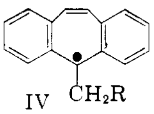
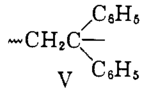
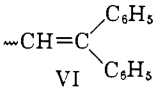
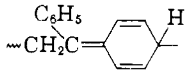
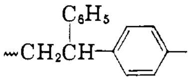

IV

After obtaining the reactivity data using the retardation-of-polymerization method,[1,4] we attempted to check some of our results by determining the composition of "copolymers" produced when methyl methacrylate was polymerized in the presence of diphenylethylene, I or II. In the course of this work we happened to examine the ultraviolet spectra of the diphenylethylene–methacrylate copolymers and found to our surprise that they exhibited a strong maximum at 290 mμ. This maximum is inconsistent with structures such as V or VI which should not have maxima beyond about 265 mμ,[5] but it is consistent with VII. Since VII should be readily isomerized to VIII, additional evidence for VII is the observation that when the copolymer was briefly treated with 0.15 *M* sodium methoxide in methanol–benzene and then reisolated the ultraviolet absorption spectrum was radically changed to one similar to those expected for structures such as V and VIII. Similar behavior was also exhibited by the methyl methacrylate–I copolymers.


$$\sim CH_2\overset{C_6H_5}{\underset{C_6H_5}{C}}{-}$$
V

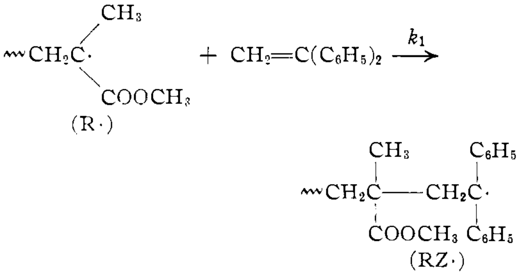

$$\sim CH{=}\overset{C_6H_5}{\underset{C_6H_5}{C}}$$
VI

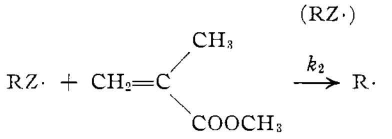

VII


VIII

## Results and Discussion

All three olefins markedly retard the azobisisobutyronitrile (AIBN)-initiated polymerization of methyl methacrylate. It is thus possible to obtain data concerning their reactivity by the retardation-of-polymerization method.[1,4] The kinetically


$$\underset{(R\cdot)}{\sim CH_2\overset{CH_3}{\underset{COOCH_3}{C\cdot}}} + CH_2{=}C(C_6H_5)_2 \xrightarrow{k_1} \underset{(RZ\cdot)}{\sim CH_2\overset{CH_3}{\underset{COOCH_3}{C}}{-}CH_2\overset{C_6H_5}{\underset{C_6H_5}{C\cdot}}} \qquad (1)$$


$$RZ\cdot + CH_2{=}\overset{CH_3}{\underset{COOCH_3}{C}} \xrightarrow{k_2} R\cdot \qquad (2)$$

$$RZ\cdot + R\cdot \xrightarrow{k_3} \text{non-radical products} \qquad (3)$$

$$2RZ\cdot \xrightarrow{k_4} \text{non-radical products} \qquad (4)$$

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[1] J. L. Kice, THIS JOURNAL, **80**, 348 (1958).

[2] G. Berti, *J. Org. Chem.*, **22**, 230 (1957).

[3] (a) E. D. Bergmann, *et al.*, *Bull. soc. chim. France*, **18**, 684 (1951); (b) E. D. Bergmann and D. Ginsburg, *Chemistry & Industry*, 45 (1954).

[4] J. L. Kice, THIS JOURNAL, **76**, 6274 (1954).

[5] For the spectra of various model compounds closely related to V and VI see R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1951; see also the spectra of styrene–methacrylate copolymers, Melville, *et al.*, *Trans. Faraday Soc.*, **50**, 279 (1954).

significant reactions involving the olefin (illustrated for diphenylethylene) are presumably 1–4, and from retardation studies it is possible to obtain values for $k_1$, the reactivity of the olefin toward methacrylate radicals, and $k_2/k_3$. The results of the individual kinetic runs are given in Table II, the $k_1$ and $k_2/k_3$ values in Table I.

TABLE I

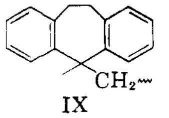
RATE CONSTANTS FOR REACTION OF OLEFINS WITH METHACRYLATE RADICALS AT 50°

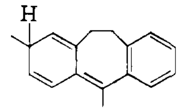
| Compound | $k_1 \times 10^{-2}$, $M^{-1}$ sec.$^{-1b}$ | $(k_2/k_3) \times 10^{10}$ |
|---|---|---|
| Diphenylethylene | 7.2 | 2 |
| I | 3.9 | 9 |
| II | 1.5 | 40 |
| Dibenzofulvene[1] | 2500 | 4 |
| Styrene[a] | 12 | $10^4$ |

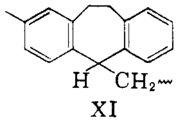
[a] Estimated from data for 60° given by C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, pp. 123, 146. [b] $k_1$ values calcd. from data in Table II using $k_p = 560$ and $k_t = 1.6 \times 10^7$ for methyl methacrylate.

We had hoped the composition of the "copolymers" formed when methyl methacrylate was polymerized in the presence of the various olefins would provide a check on the accuracy of the $k_1$ values in Table I. Unfortunately the marked retarding effect of the olefins makes it impossible to obtain polymers of respectable average molecular weight which also contain an appreciable weight percentage of olefin.[6] As a result none of the copolymers prepared contained over a few per cent hydrocarbon. Consequently the reactivity ratios (see Experimental) obtained from these copolymerization experiments must be regarded as only very approximate and cannot be considered accurate to better than ±40%.[7] Keeping this in mind, one may note that the reactivity ratios indicate the relative reactivity of diphenylethylene, I and II to be in the ratio 3.9:2.8:1 (as compared with 4.8:2.6:1 calculated from the $k_1$ values of Table I). In view of the uncertainty in the copolymerization data the two sets of results appear to be in reasonable agreement. As indicated earlier the most significant results of the copolymerization experiments are the unusual ultraviolet absorption spectra of the copolymers. Before further consideration of the reactivity data in Table I we should like to consider the spectral data.

**Evidence for Anomalous Reactions of Radicals from Diphenylethylene and I.**—Examination of the ultraviolet absorption spectra in chloroform of the methyl methacrylate–diphenylethylene copolymers revealed, instead of the expected maximum in the 260–270 mμ region,[5] a much more intense peak at 290 mμ (Fig. 1, curves A and B). A similar phenomenon was observed with copolymers from I, except that in this case $\lambda_{max}$ was at even longer wave lengths (curves C and D, Fig. 1).[8] With both copolymers, if the copolymer was refluxed for a short while in a 0.15 $M$ solution of sodium methoxide in methanol–benzene and then reisolated the ultraviolet absorption was radically changed (curves A′ and C′, Fig. 1). These latter spectra in both cases resemble those which would be expected for structures such as V and VIII or IX and XI.


IX


X


XI

Comparison of curve A for the original diphenylethylene copolymer with the spectra of such model compounds as 1-benzylidene-2-cyclopentene[9] and 1-benzhydrylidene-2-cyclopentene[10] shows the extreme similarity in the spectra and strongly suggests that at least some of the diphenylethylene units in the copolymer have structure VII. Presumably the long wave length maximum in the methacrylate–I copolymers is due to structures such as X. Although these results do not afford unequivocal proof of the presence of VII and X, such structures seem to offer the simplest interpretation of the spectral data consistent with all our data.

The variation in the intensity of the long wave length absorption with total olefin content is also informative. The olefin concentration in the two solutions used to prepare the two diphenylethylene copolymers in Fig. 1 was in the ratio of 2.7:1. The total olefin content of the two copolymers is in the ratio of 2.4:1, in reasonable agreement with expectations in view of the inaccuracies of the C,H analyses. However, the concentrations of the units responsible for the 290 mμ maximum are in the ratio of only 1.75:1. Similarly the total I content of the two methacrylate-I copolymers differs by a factor of 1.8 while the $E$'s differ by only a factor of 1.4. Therefore, while increasing the olefin concentration in the monomer feed results in approximately the expected increase in total olefin content of the copolymer, the concentration of the units responsible for the long wave length maximum does not increase as rapidly. This sort of behavior would be expected if the "special" units arise exclusively (or predominantly) from termination reactions involving the radicals from diphenylethylene or I: First, since both olefins act as effective retarders of methacrylate polymerization, an appreciable fraction of the diphenylethylene or I radicals produced disappear

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(6) If the average molecular weight is too low a sizeable fraction of the polymer, particularly the lower molecular weight material, will be lost in the isolation procedure. In a copolymerization of this type where the added olefin causes marked retardation in the rate of polymerization most chains which contain greater than the average ratio of added olefin to methyl methacrylate will also be of lower than average molecular weight. As a result any attempt to increase the percentage of olefin in the copolymer will not improve the accuracy of the derived reactivity ratio if at the same time it results in too low an $\bar{M}_n$ for the copolymer, since there will be a concomitant loss of low molecular weight olefin-rich polymer in the isolation procedure.

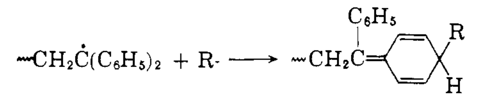
(7) The olefin content of the copolymers was determined from duplicate C,H analyses on each polymer. The difference between the %C in the copolymers and that in pure polymethyl methacrylate was only 0.3–1.0%. Considering the usual uncertainty in a C,H analysis there is obviously considerable uncertainty in the olefin content of the copolymers even with duplicate analyses. This is particularly true for II copolymer #1 and DPE copolymer #1 which contain the smallest amounts of olefin.

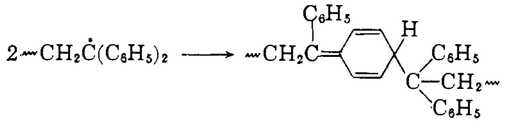
(8) This disparity in $\lambda_{max}$ in the two cases would seem to rule out all possible explanations involving the initiator, impurities in the monomer, impurities in diphenylethylene, etc.

(9) E. A. Braude and W. F. Forbes, *J. Chem. Soc.*, 1755 (1951).

(10) J. L. Kice and F. M. Parham, THIS JOURNAL, **80**, 3792 (1958).

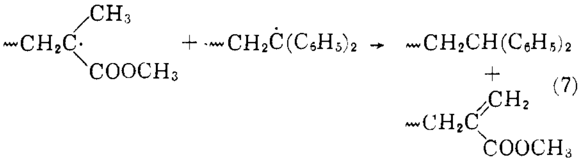
through termination reactions. Second, by reference to the kinetics of these degradative copolymerizations, it can be shown that if the termination processes involving the I or diphenylethylene radicals follow the course shown in eq. 5 and 6 the fraction of the total olefin present as VII or X will *decrease quite markedly with increasing olefin concentration*, and of course, the concentration of


(5)


(6)

VII or X in the copolymer will not increase as rapidly as the total olefin content. A more quantitative examination of the present results, as outlined in footnote 11, certainly seems to suggest that the majority of VII or X arises from termination reactions involving the olefin radicals. (The uncertainties in the total olefin content of the copolymers inherent in the C,H analyses and our ignorance of the exact molar extinction coefficients for VII and X render any more exacting examination of the data of questionable value.)

That VII or X should arise predominantly from termination reactions is also the most plausible theoretical interpretation of the experimental results. Only steric hindrance would seem likely to cause diphenylethylene radicals to undergo reaction at the $p$-position of an aromatic ring rather than at the 1-carbon. While there almost certainly is some steric hindrance to the addition of a diphenylethylene radical to the methacrylate double bond,[11] we doubt that this could be important enough to cause the anomalous behavior observed. On the other hand, there is far more serious hindrance to any normal combinative termination reaction involving the present polymer radicals. Furthermore, *an important additional factor which should enhance the likelihood of reactions such as 5 and 6 is the fact that termination is a highly exothermic process of very low activation energy.* For such a reaction Hammond's Principle[12] predicts *the transition state will closely resemble the reactants.* As a result the loss of aromaticity attending the formation of VII and X should have no significant effect on the energy of the transition states for reactions 5 and 6, and such reactions might easily occur to the exclusion of such disproportionative termination processes as 7, which might otherwise seem more likely to predominate.



$$\sim CH_2\overset{CH_3}{\underset{COOCH_3}{C}}\cdot + \sim CH_2\dot{C}(C_6H_5)_2 \rightarrow \sim CH_2CH(C_6H_5)_2 + \sim CH_2\overset{CH_2}{\underset{COOCH_3}{C}} \qquad (7)$$

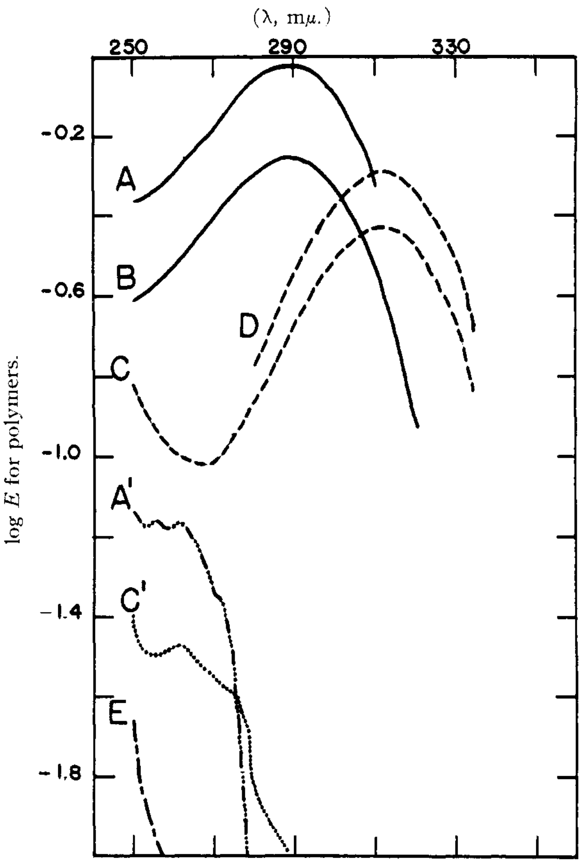


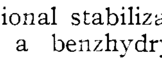
Fig. 1.—All spectra in $CHCl_3$; $E$ = optical density/g. polymer per liter of solution: curve A, diphenylethylene-(DPE)-methyl methacrylate(MMA) copolymer 2, monomer feed (MMA)/(DPE) = 36; curve $A'$, same copolymer after treatment with dilute base; curve B, DPE-MMA copolymer **1**, monomer feed (MMA)/(DPE) = 97; curve C, MMA-I copolymer 1, monomer feed (MMA)/(I) = 40; curve C′, same copolymer after treatment with base; curve D, MMA-I copolymer 2, monomer feed (MMA)/(I) = 20; curve E, pure MMA polymer.

**Discussion of the Reactivity Data of Table I.**—Clearly comparison of the results for I and II does not indicate any exceptional behavior for II or radical IV. The reactivity of II is somewhat less than I, and IV is somewhat more prone than the radical from I to add to monomer rather than undergo cross-termination. Our results do not seem to indicate any particular enhanced stabilization for IV, for were this the case $k_2/k_3$ for IV should presumably be much smaller than the value of the same quantity for the radical from I.[1] This is in interesting contrast to Berti's[2] conclusions regarding the carbonium ion III. From com-

[11] Assuming the termination reactions involving the olefin radicals to occur as in eq. 5 and 6, one can estimate from the results of the kinetic studies the fraction, $\delta$, of the total olefin units in each copolymer which would be expected to have either structure VII or X. For diphenylethylene copolymer 2 (the one with the higher total diphenylethylene content) $\delta = 0.23$, while $\delta = 0.30$ for diphenylethylene copolymer 1. For the methacrylate-I copolymers $\delta = 0.12$ for 1 and $\delta = 0.093$ for 2. For either olefin multiplication of the ratio of the $\delta$'s by the previously given ratio of total olefin content gives a predicted ratio for the concentration of VII or X in the copolymers. It is interesting to note that in both cases the calculated value of this ratio is quite close to the observed ratio of the extinction coefficients, being 1.9 for the diphenylethylene copolymers (found 1.8) and 1.4 for the I copolymers (found 1.4).

[12] G. S. Hammond, THIS JOURNAL, **77**, 348 (1955).

parison of the $pK_{R^+}$[13a] of III with those of tropylium,[13b] benzotropylium,[13c] benzhydryl[13a] and fluorenyl[13a] carbonium ions he concluded there was substantial additional stabilization of III beyond that found for a benzhydryl carbonium ion. On the other hand, Bergmann, *et al.*,[3a] concluded from examination of the ultraviolet and infrared spectra of XII, II, several benzylidene dibenzocycloheptatrienes, and their dibenzocycloheptadiene analogs that they could find no evidence indicating any particular aromaticity for II, and they believe that II is correctly represented by a nonplanar structure.



XII

In comparing the results in Table I for I and diphenylethylene with those for dibenzofulvene the most striking feature is the fact that although dibenzofulvene is about 300–600 times more reactive toward methacrylate radicals than diphenylethylene or I the RZ· radicals from the three olefins do not differ greatly as regards their relative propensities to add to monomer or cross-terminate ($k_2/k_3$).

In the past $k_2/k_3$ has often seemed an excellent measure of the stability of the RZ· radical,[1] being larger the less stable the radical. At first glance, therefore, the present results seem to rule out Szwarc's hypothesis[14] attributing the high reactivity of the dibenzofulvenes to the stability of the fluorenyl radical. However, as there would seem sound theoretical basis for expecting the fluorenyl radical to be at least somewhat more stable than the diphenylmethyl radical, we feel it is rather more likely that other factors are important in the present instance, factors which cause both $k_1$ and $k_2/k_3$ for diphenylethylene and I to be considerably smaller than would otherwise be the case. These factors, which are envisaged to be primarily steric in origin, are outlined in footnote 15.

**Acknowledgments.**—The authors gratefully acknowledge the financial support of National Science Foundation Grant #NSF-G4205.

## Experimental

**Preparation and Purification of Materials.—Diphenylethylene** was prepared by the usual method,[17] b.p. 94–95° (3 mm.). The olefin was subsequently further purified by either of two procedures. The first procedure consisted of careful fractional distillation at reduced pressure under a nitrogen atmosphere. The center cut, b.p. 128° (8 mm.), was retained for use. The second procedure involved fractional low temperature crystallization. The original diphenylethylene was fractionally crystallized six times, about 10% of the material being discarded each time. Diphenylethylene purified by either method gave identical results in the reactivity and copolymerization studies. The purified diphenylethylene was stored at −20° under nitrogen until used.

**1-Methylene-2,3,6,7-dibenz-2,6-cycloheptadiene** (I) was prepared from benzal phthalide[18] by the four-step synthesis of Cope and Fenton.[19] The sublimed olefin was recrystallized from methanol, m.p. 66–67°. It was stored under nitrogen at −20° until used.

**1-Methylene-2,3,6,7-dibenzcycloheptatriene** (II).—2,3,6,7-Dibenz-2,6-cycloheptadien-1-one was prepared from benzal phthalide[18] by the method of Cope and Fenton.[19] The ketone was then converted to dibenzcycloheptatrienone (XII) by Triebs and Klinkhammer's procedure.[20] This ketone was treated with methyl magnesium iodide and the resulting tertiary carbinol dehydrated to the desired olefin by Triebs and Klinkhammer's method.[20] Upon recrystallization from methanol II melted at 119–120°. It was stored in the same fashion as I.

**Methyl methacrylate** was purified as previously described.[4] The purification of **azobisisobutyronitrile** has also been previously mentioned.[4]

**Procedure for Kinetic Runs.**—For diphenylethylene the procedure was that previously described for dibenzofulvene.[1] For the other olefins the procedure followed that used for the substituted dibenzofulvenes.[1] All of the kinetic runs were carried out at 50°. The results of the individual runs with the three compounds are given in Table II.

TABLE II

RESULTS OF INDIVIDUAL KINETIC RUNS AT 50° IN METHYL METHACRYLATE

| Compound | (AIBN) $\times 10^3$, mole/liter | (Olefin) $\times 10^4$, moles/liter | $\phi \times 10^{2a}$ |
|---|---|---|---|
| Diphenylethylene | 3.66 | 13.8 | 6.82 |
| | 3.89 | 18.6 | 5.75 |
| | 3.91 | 6.56 | 10.4 |
| | 3.76 | 2.09 | 22.6 |
| | 7.59 | 5.50 | 13.2 |
| I | 4.36 | 8.44 | 24.0 |
| | 4.80 | 4.22 | 36.2 |
| | 4.97 | 1.94 | 53.2 |
| | 1.64 | 8.75 | 21.7 |
| | 11.1 | 8.31 | 26.9 |
| II | 4.13 | 3.80 | 75.5 |
| | 4.38 | 15.6 | 48.9 |
| | 2.18 | 9.84 | 56.5 |
| | 2.21 | 15.5 | 48.2 |
| | 3.96 | 9.87 | 56.9 |

[a] $\phi = R/R_0$, where $R$ = rate of polymerization in the presence of the olefin and $R_0$ = rate in absence of olefin at the same initiator concentration; $R_0 = 1.36 \times 10^{-4}$ $(\mathrm{AIBN})^{1/2}$.

**Preparation of Copolymers.**—The same general procedure was followed in every case. The desired amounts of azobisisobutyronitrile, methyl methacrylate and olefin were weighed into a glass stoppered flask. A weighed amount of the resulting solution was transferred to a tube which was

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(13) (a) N. C. Deno, J. J. Jaruselski and A. Schriesheim, THIS JOURNAL, **77**, 3047 (1955); (b) W. von E. Doering and L. H. Knox, *ibid.*, **76**, 3203 (1954); (c) H. H. Rehnhard, E. Heilbronner and E. Eschenmoser, *Chemistry & Industry*, 415 (1955).

(14) M. Szwarc and F. Leavitt, *ibid.*, **78**, 3590 (1956).

(15) A previous estimate[1] from Szwarc's "methyl affinities"[16] predicted diphenylethylene should be about four times more reactive than styrene toward methacrylate radicals. Since it is now found to be less reactive this seems clear indication that the addition of a methacrylate radical to diphenylethylene or I involves significant steric hindrance. Examination of molecular models suggests the steric strain in reaction 2 is even greater. It can also reasonably be argued that the rate constant of the anomalous termination reaction 5 will not be too much smaller than that expected for $k_3$ in the absence of steric hindrance. Thus it is possible for both $k_1$ and $k_2/k_3$ for I or diphenylethylene to be smaller than would be the case in the absence of these steric considerations. Provided that such steric effects are of much less importance for dibenzofulvene than for I the results in Table I may be explained without abandoning Szwarc's[14] hypothesis. Models of the intermediates involved do indeed suggest there is considerably less hindrance in the dibenzofulvene reactions.

(16) F. Leavitt, M. Levy, M. Szwarc and V. Stannett, *ibid.*, **77**, 5493 (1955).

(17) "Organic Syntheses," Coll. Vol. I, 2nd. ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 226.

(18) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 61.

(19) A. C. Cope and S. W. Fenton, *ibid.*, **73**, 1673 (1951).

(20) W. Triebs and H.-J. Klinkhammer, *Ber.*, **84**, 671 (1951).

then attached to the vacuum line and degassed three times in the usual fashion. After being sealed off under vacuum the tube was heated for the desired length of time at 50°. It was then removed from the bath, opened, and the polymer precipitated by addition of the contents of the tube to over 10 times its volume of stirred hexane. The polymer was dissolved in benzene and reprecipitated twice more. The conversion was below 10% in every case. The olefin content of the copolymers was estimated from C,H analyses of samples which had been dried at 60° *in vacuo* for 48 hr. As a check on the accuracy of the method a sample of pure polymethyl methacrylate was also analyzed. The analytical results[21] are: pure poly-MMA, C, 59.92; H, 8.08. (Calcd. C, 59.98; H, 8.05.) MMA-DPE copolymer 1, monomer feed, (MMA)/(DPE) = 97; polymer analysis, C, 60.17; H, 7.95; polymer composition, (MMA)/(DPE) = 235. MMA-DPE copolymer 2, monomer feed, (MMA)/(DPE) = 36; polymer analysis, C, 60.51; H, 7.86; polymer composition, (MMA)/(DPE) = 98. MMA-I copolymer 1, monomer feed, (MMA)/(I) = 40; polymer analysis, C, 60.43; H, 8.06; polymer composition, (MMA)/(I) = 131. MMA-I copolymer 2, monomer feed, (MMA)/(I) = 20; polymer analysis, C, 60.89; H, 8.35; polymer composition, (MMA)/(I) = 72. MMA-II copolymer, monomer feed, (MMA)/(II) = 21; polymer analysis, C, 60.24; H, 7.80; polymer composition, (MMA)/(II) = 208.

Since the polymerizations are all strongly retarded the use of the usual copolymerization equation to calculate $r_1$ from these data would not be justified. However, in view of the high (MMA)/(olefin) ratios of all experiments, the only reactions of importance in determining the "copolymer" composition should be reaction 1 and the normal propagation reaction, the amount of methacrylate consumed by reaction 2 being negligible compared to that consumed in the normal propagation reaction. As a result $r_1$ was calculated from the equation

$$\frac{d(\text{MMA})}{d(\text{olefin})} = \frac{k_p(\text{MMA})}{k_1(\text{olefin})} = r_1\frac{(\text{MMA})}{(\text{olefin})}$$

The values so obtained were: MMA-DPE, $r_1$ = 2.4, 2.7; MMA-I, $r_1$ = 3.3, 3.6; MMA-II, $r_1$ = 9.9.

**Isomerization of Copolymers.**—A weighed amount (about 0.15 g.) of the copolymer was dissolved in about 15 ml. of dry benzene, and the solution was added to a solution of sodium methoxide in methanol prepared by dissolving 0.1 g. of sodium in 10 ml. of anhydrous methanol. The solution was heated to reflux under nitrogen for 5 hr., cooled, poured into a large quantity of water, and the benzene layer washed several times with water. The benzene layer was then dried over sodium sulfate, filtered, and the polymer precipitated by the slow addition of the benzene solution to a large volume of well stirred hexane. The precipitated polymer was dissolved in benzene and reprecipitated with hexane. After thorough vacuum drying its ultraviolet absorption spectrum was determined in chloroform solution.

COLUMBIA, S. C.

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[21] Analyses by Galbraith Labs., Knoxville, Tenn. All analyses are average of duplicate determinations; DPE = diphenylethylene; MMA = methyl methacrylate.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, FACULTY OF SCIENCE, CAIRO UNIVERSITY]

# Photochemical Reactions in Sunlight. Experiments with Benzo(h)quinoline-5,6-quinone, Monoimine and Monoxime Derivatives in Sunlight and in Dark

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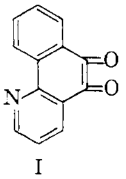
RECEIVED SEPTEMBER 22, 1958

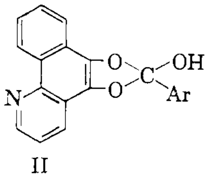
The photochemical addition reaction of aldehydes to heterocyclic nitrogen *o*-quinones, such as benzo(h)quinoline-5,6-quinone (I) has been carried out, yielding the photoproducts listed in Table I. A similar photo-reaction takes place between benzo(h)quinoline-5,6-quinone monoimine and aromatic aldehydes, yielding colorless products believed to have structure such as V, (*cf.* Table II). 2-*p*-Methoxyphenylbenzo(h)quinoline-oxazole (VII, R = $C_6H_4OCH_3$-*p*) has been obtained either by heating the photo-product of the reaction of benzo(h)quinoline-5,6-quinone monoxime and the aldehyde or by allowing IV to react with *p*-methoxybenzaldehyde in the dark, in the presence of piperidine. The photochemical addition of I to olefins such as stilbene, α,α-diphenylethylene, triphenylethylene and benzalphthalide, has been investigated. The photoproducts are listed in Table III. 3-Phenylbenzo(f)quinoxaline-5,6-quinone (XV) and compound I react with ethereal diazomethane solution and with diphenyldiazomethane to give the corresponding methylene ethers (XVIIa, XVIIb and XVIa, XVIb). Whereas, I is stable toward the action of 9-diazofluorene, XV reacts under the given experimental conditions to yield XVIIc. Benzo(h)quinolinoxazole (VII, R = H) is obtained either by the action of ethereal diazomethane on IV and/or VIII or by the action of dimethyl sulfate on VIII.

In continuation of our previous work, the action of aromatic aldehydes on heterocyclic nitrogen *o*-quinones has been extended.[1-3]

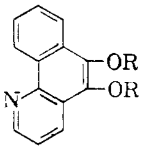
We have allowed the yellow benzo(h)quinoline-5,6-quinone (I) to react with aromatic aldehydes in the absence of oxygen and have found that addition takes place in molecular proportions. The colorless photo-products (*cf.* Table I) are obtained in good yield in most cases and separate during exposure. It is believed that these 2-arylbenzo(h)quinoline-(5,6)-1:3-dioxol-2-ol derivatives have constitutions such as II or the corresponding open form.



I



II



IIIa, R=H
b, R=$COCH_3$

Compound II(Ar=$C_6H_4OCH_3$-*p*) is typical of compounds having such structures. It is colorless, insoluble in cold aqueous sodium hydroxide solution and gives no color with ferric chloride. It yields *p*-methoxybenzoic acid and I on treatment with cold concentrated sulfuric acid. The formation of I may be attributed to the action of sulfuric acid on the intermediate 5,6-dihydroxybenzo-

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[1] A. Mustafa, A. H. E. Harhash, A. K. E. Mansour and S. M. A. E. Omran, THIS JOURNAL, **78**, 4306 (1956).

[2] A. Shönberg, A. Mustafa and S. M. A. D. Zayed, *ibid.*, **75**, 4302 (1953).

[3] It has been shown that the photo-addition of aldehydes to *o*-quinones is a general reaction which may be carried out with *o*-benzoquinone derivatives (A. Schönberg, *et al.*, *J. Chem. Soc.*, 1364 (1951)), α-naphthoquinone derivatives (A. Schönberg, *ibid.*; A. Mustafa, *et al.*, ref. 1, phenanthraquinone (A. Mustafa, *ibid.*, 997 (1947); A. Mustafa, *Nature*, **166**, 108 (1950)), acenaphthenequinone (A. Sircar and S. Sen, *J. Indian Chem. Soc.*, 997 (1947)), and chrysenequinone (A. Mustafa, *J. Chem. Soc.*, 1034 (1951)).