collected by suction filtration, washed with 100 ml. of ice-water, a small amount of ethanol, then ether, and dried at 100°. The second crop amounted to 22 g. The filtrate was diluted with 400 ml. of water and concentrated to a volume of 100 ml. Cooling, filtering, and washing as before gave a third crop, 20 g. The total yield of maleic hydrazide melting over 300° was 144 g. (83%).

(b) **From 1,2-Dimaleic Acid Hydrazine.**—In a 125-ml. erlenmeyer flask was placed a solution of 11.4 g. (0.05 mole) of 1,2-dimaleic acid hydrazine in 75 ml. of water and it was boiled for 30 minutes. The solution was then cooled to 5° and filtered, affording 5.2 g. (93%) of maleic hydrazide, m.p. 300° dec.

The filtrate was evaporated *in vacuo* at 28° affording 6.14 g. of maleic acid, m.p. 127–130°. Assuming that the 0.4 g. of maleic hydrazide which is unaccounted for is contained in the maleic acid residue, the recovery of maleic acid amounted to 100%.

(c) **From Monohydrazonium Maleate.**—In a 100-ml. round-bottom flask was placed a solution of 23.2 g. (0.2 mole) of maleic acid in 25 ml. of water, and 5.0 g. (0.1 mole) of hydrazine hydrate was slowly added with cooling to keep the temperature below 40°. The mixture was then evaporated to dryness *in vacuo* at 25°, and a total of 100 g. of polyphosphoric acid was added to the salt cake. A vigorous exothermic reaction occurred immediately and the slurry yielded a clear colorless solution in two minutes. The solution was heated at 102° for 12 hours, then it was decomposed by pouring it into 300 ml. of ice-water. After stirring to promote crystallization, the slurry was filtered and dried, affording 11.3 g. (100%) of maleic hydrazide, m.p. 300° dec.

(d) **From Hydrazine Hydrate and Maleic Acid.**—In a 125-ml. erlenmeyer flask were placed 5.0 g. (0.1 mole) of hydrazine hydrate and 30 ml. of water. A total of 23.2 g. (0.2 mole) of maleic acid was added in one portion and the mixture was warmed to hasten solution. The resulting solution was boiled until a slurry formed, then it was cooled and filtered, washed with water and dried, affording 7.5 g. of maleic hydrazide. Evaporation of the filtrate to a slurry and filtering gave an additional 4.7 g. of material which after trituration with ether and recrystallization from water yielded 1.3 g. of maleic hydrazide and 1.0 g. of maleic acid. The filtrate was then evaporated to dryness and recrystallized from ether affording 8.8 g. of maleic acid, m.p. 128–130°. The total yield of maleic hydrazide was 8.8 g. (80%) and the total recovery of maleic acid was 9.8 g. (76%).

Acknowledgment.—We are indebted to the Office of Naval Research and to the Purdue Research Foundation for the financial support of this work.

LAFAYETTE, IND.

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

The Reaction of Free Radicals with Non-benzenoid Aromatic Hydrocarbons. I. 6-Phenylfulvenes and Benzofulvenes

BY JOHN L. KICE AND FRED M. PARHAM

RECEIVED JANUARY 23, 1958

The reaction of free radicals with 6-phenylfulvenes and benzofulvenes has been investigated both by reactivity studies using the kinetic method previously employed for the dibenzofulvenes, and by a product study of the reaction of diphenylfulvene with 2-cyano-2-propyl radicals. The results demonstrate that in all cases radical attack occurs at one of the fulvene ring positions and indicate that for the phenylfulvenes such attack occurs at least predominantly at the 2-position while for diphenylbenzofulvene attack apparently occurs at the 3-position. The behavior of the radicals resulting in the two cases differs considerably, that from diphenylfulvene being quite unreactive toward any further reaction other than termination while that from diphenylbenzofulvene shows behavior intermediate between a styryl and a fluorenyl radical. No evidence was found for any substituted fulvenes as radical–fulvene reaction products, a finding consistent with the presumed low degree of aromaticity of the fulvenes.

In recent years there has been considerably increased interest in the chemistry of the non-benzenoid aromatic hydrocarbons.[1] However, to the best of our knowledge there have been no studies of the reactions of these compounds with free radicals. In view of the extensive data on radical reactivity available for benzenoid hydrocarbons[2] and for simple olefins and dienes,[3] similar studies on the non-benzenoid aromatics would seem to be of some interest.

In the present paper we wish to report our initial efforts in this area. These have been concerned with the reaction of free radicals with 6-phenyl-substituted fulvenes and benzofulvenes, especially 6,6-diphenylfulvene (I).

Initial qualitative indications that diphenylfulvene is quite reactive toward free radicals were provided by the observations that decomposition of excess azobisisobutyronitrile in degassed benzene solutions of the fulvene led to a disappearance of the fulvene color and that addition of small amounts of the fulvene caused a pronounced retardation of the rate of polymerization of methyl methacrylate.

Reaction of 2-Cyano-2-propyl Radicals with Diphenylfulvene.—To study the reaction of 2-cyano-2-propyl radicals with diphenylfulvene, azobisisobutyronitrile (initial concentration 2.6×10^{-2} *M*) was decomposed in a degassed benzene solution of diphenylfulvene (5.1×10^{-2} *M*) at 78° for 10–12 hours.[4] Two crystalline substances, A, m.p. 258-260°, and B, m.p. 235-236°, were isolated along with intractable gummy non-crystalline residues. Elementary analyses and molecular weight measurements showed compounds A and B to be isomeric substances of the empirical formula, R–F–F–R,

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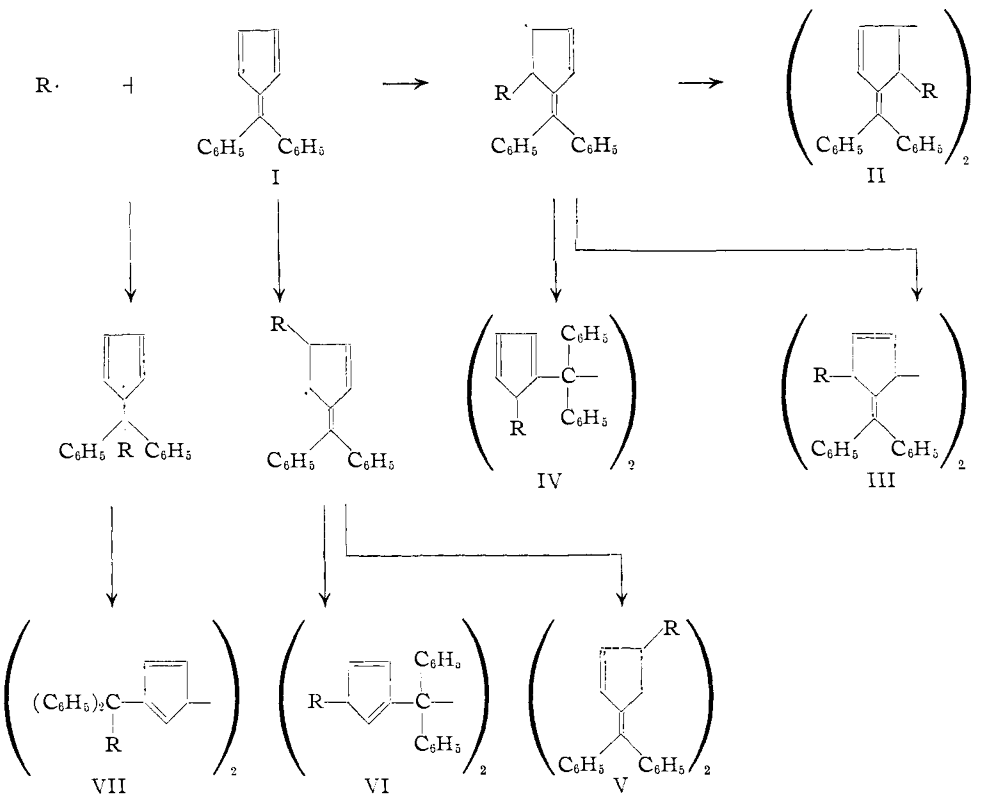
[1] W. Baker and J. F. W. McOmie, "Progress in Organic Chemistry," Vol. 3, Academic Press, Inc., New York, N. Y., 1955, pp. 44–80.

[2] (a) M. Levy and M. Szwarc, THIS JOURNAL, **77**, 1949 (1955); (b) E. C. Kooyman and E. Farenhorst, *Nature*, **169**, 153 (1952); *Trans. Faraday Soc.*, **49**, 58 (1953); (c) J. R. Dunn and W. A. Waters, *J. Chem. Soc.*, 580 (1954); (d) J. Smid and M. Szwarc, THIS JOURNAL, **78**, 3322 (1956).

[3] (a) F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950); (b) F. Leavitt, M. Levy, M. Szwarc and V. Stannett, THIS JOURNAL, **78**, 5493 (1955); (c) M. Szwarc and A. Rajbenbach, *ibid.*, **79**, 6343 (1957); (d) R. P. Buckley and M. Szwarc, *ibid.*, **78**, 5696 (1956); (e) R. P. Buckley, F. Leavitt and M. Szwarc, *ibid.*, **78**, 5557 (1956).

[4] A preliminary experiment in which diphenylfulvene was heated alone in benzene at 80° for 10 hours showed that less than 1% of the fulvene had decomposed, thereby ruling out the possibility of the reaction products being contaminated to any extent by fulvene decomposition products.



where R is a 2-cyano-2-propyl group and F is a diphenylfulvene residue. In each run under the above conditions from 29-33% of the original diphenylfulvene was recovered unreacted. Compounds A and B accounted for 24 to 26 mole % of the original fulvene (or for 36–37% of the fulvene which reacts). The ultraviolet absorption spectrum of the gummy non-crystalline residues is very similar (except for somewhat diminished intensity) to that of compound B (Table III). If the diphenylfulvene residues present in this fraction are assumed to have the same molar extinction coefficient at 290 mμ as those present in compound B, it may be calculated that the gummy residues contain about 40% of the original fulvene groups. It would thus appear that between unreacted fulvene, A and B, and the residues we have accounted for almost all of the original fulvene molecules.

Structure of the Reaction Products.—The infrared spectra of A and B were found to be extremely similar. Both showed a well-defined –CN absorption band at 4.45μ and essentially identical absorption throughout the 2–7.5μ region. These facts and the rather slight differences in the remainder of the spectrum suggested that A and B must be closely related structural isomers. The spectrum of the combined residues was also examined and found to be quite similar to those of A and B. Tetramethylsuccinonitrile shows a strong absorption band at 8.75μ. The presence of a weak band at this wave length in the residues and its absence in A and B suggests the presence of some tetramethylsuccinonitrile in the residues.

Of much greater aid in elucidation of structure were the ultraviolet absorption spectra of the various products. These are shown in Table III. It is evident that the absorption spectra of A, B, and the combined residues are all very similar, suggesting that the same chromophore is present both in A and B and in the radical–fulvene reaction products of the residues. Second, the reasonable similarity in the intensity of the absorption for A and B and the residues indicates that essentially all of the radical–fulvene reaction products in the residues possess the chromophore. Third, the position (285–290 mμ) and the intensity (ε 12,000) of the longest wave length absorption maximum severely restrict the choice of chromophores and considerably limit the structural possibilities for such products as A and B, as can be seen from the following discussion.

Attack of a 2-cyano-2-propyl radical on diphenylfulvene could conceivably occur at either of three different positions to produce the three different radicals shown in the outline above.

Coupling of a radical so produced with another of its own kind will lead to products of empirical formula RFFR, *i.e.*, A and B. Assuming that the coupling of the radicals occurs symmetrically, the various structural possibilities for A and B are shown as II–VII. Of these IV, VI and VII are substituted cyclopentadienes and would be expected to have no high intensity absorption maximum beyond about 250 mμ.[5] The same applies to III. Here the isolated double bond should exert no influence, and the spectrum should be similar to that of benzhydrylidenecyclopentane for which we found λ_{max} 250 mμ, log ε 4.16. On the other hand, II and V would be expected to have their maxima at longer wave lengths. In particular Braude and

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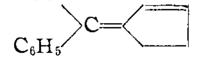
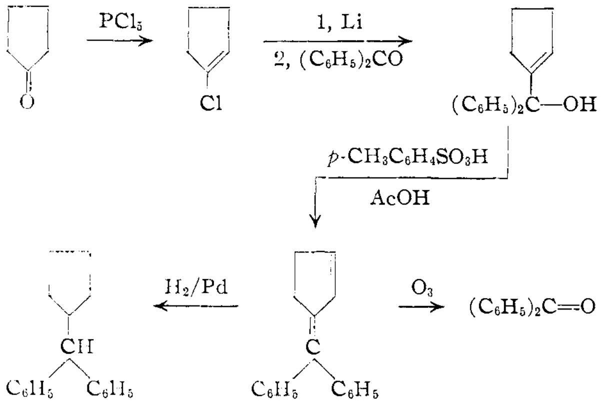
[5] J. S. Powell and K. C. Edson, *Anal. Chem.*, **20**, 510 (1948).

Forbes[6] recently synthesized 1-benzylidene-2-cyclopentene and found its longest wave length maximum to be at 288 mμ with ε 20,000, a result which strongly suggests that the chromophore is present in A and B and that these substances have either structure II or V.



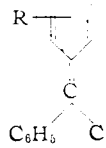
To provide further confirmation of this point we undertook the synthesis of 1-benzhydrylidene-2-cyclopentene (VIII) by the reaction sequence establishing the structure of VIII by quantitative hydrogenation to the known benzhydrylcyclopentane and ozonization to benzophenone. The ultraviolet absorption spectrum of VIII is shown in Table III. Not only does the maximum occur at the same wave length, but the position of the minimum and the general shape of the curves are strikingly similar; and these facts, coupled with the isolation of benzophenone from the permanganate oxidation of A, seem to demonstrate rather convincingly that A and B have either structure II or V and are therefore stereoisomers of either 4,4′-benzhydrylidene-5,5′-(α-cyanoisopropyl)-[1,1′-bi-2-cyclopentenyl] or 5,5′- benzhydrylidene-2,2′-(α-cyanoisopropyl)-[1,1′-bi-3-cyclopentenyl].



VIII

This clearly rules out radical attack at the 6-position and demonstrates that radical attack on diphenylfulvene occurs at one of the ring positions. Unfortunately there appears to be no simple way to determine from further product studies whether A and B have structure V, and radical attack therefore occurs at the 3-position, or whether alternatively A and B have structure II and radical attack occurs at the 2-position. Consideration of the reactivity data for the various compounds studied does, however, strongly indicate that the reaction of diphenylfulvene which leads to the pronounced retardation of methyl methacrylate polymerization occurs by radical attack on the 2-position; although as we shall see later this fact does not permit the unambiguous formulation of A and B as stereoisomers of structure II.

All of the radical–fulvene reaction products were colorless and this fact, coupled with the absence in all fractions of any absorption maximum at wave lengths beyond 300 mμ, indicates that substituted fulvenes IX are not important reaction products. The absence of such products is not surprising in view of the presumed low degree of aromaticity of the fulvenes.



IX

Kinetic Studies of Reactivity toward Free Radicals.—As mentioned earlier addition of small amounts of diphenylfulvene caused a pronounced retardation in the rate of polymerization of methyl methacrylate. In previous papers[7] we have shown how quantitative measurements of the degree of retardation as a function of initiator and retarder concentration can provide useful information concerning the reactivity of a substance toward free radicals. The results of the individual runs for the various compounds studied in the present work are given in Table I.

TABLE I

RESULTS OF INDIVIDUAL KINETIC RUNS AT 50° IN METHYL METHACRYLATE

Compound	(AIBN) × 10^3, moles/liter	(Fulvene) × 10^3, moles/liter	$\phi \times 10^{2a}$
6,6-Diphenylfulvene	5.11	1.67	27.0
	5.07	2.95	16.4
	5.20	6.34	8.03
	11.4	3.05	22.2
	2.36	3.04	11.4
6-Methyl-6-phenylfulvene	5.87	2.95	35.9
	5.60	4.62	26.2
	5.08	11.7	12.8
	13.4	4.36	33.4
	3.02	5.00	21.9
6,6-Diphenylbenzofulvene	5.01	5.71	40.8
	4.94	11.6	26.8
	5.40	23.4	16.7
	10.5	5.36	42.9
	1.78	5.59	39.2
1-Benzhydrylidene-2-cyclopentene (VIII)	5.30	10.1	38.8
	2.72	9.95	37.8
	11.4	10.2	39.3
	5.01	5.25	52.5
	5.43	19.7	26.0

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

Of the four reactions of kinetic importance involving the fulvene (illustrated for diphenylfulvene) it is possible by suitable treatment of the kinetic data[7a] to obtain values for k_1, the reactivity of the fulvene, and k_2/k_3. Values of k_1 and k_2/k_3 so obtained for the compounds studied are shown in Table II.

The first point to note is that while diphenylfulvene and diphenylbenzofulvene are both quite

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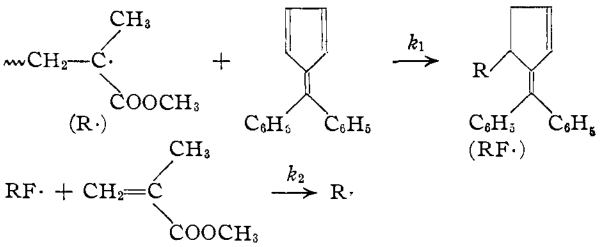
[6] E. A. Braude and W. F. Forbes, *J. Chem. Soc.*, 1755 (1951).

[7] (a) J. L. Kice, THIS JOURNAL, **76**, 6274 (1954); (b) **80**, 348 (1958).

(7a) For the method of plotting the data see ref. 7. In the present study the best plots were obtained in the various cases as follows: Diphenylfulvene, c = any value less than 5×10^{-2}; methylphenylfulvene, c = any value less than 10^{-1}; diphenylbenzofulvene, c = 2×10^{-1}; benzhydrylidenecyclopentene, c = 2×10^{-1}.

reactive and of comparable reactivity toward methyl methacrylate radicals, diphenyldibenzofulvene is less than 10^{-4} as reactive. This demonstration that the incorporation of all four fulvene ring positions into aromatic rings leads to a dramatic decrease in reactivity is in itself strongly indicative that free radical attack on the 6-phenylfulvenes and benzofulvenes occurs at one of the ring positions, and is thus in complete accord with the results of the product studies.



$$RF\cdot + R\cdot \xrightarrow{k_3} \text{stable products}$$

$$2RF\cdot \xrightarrow{k_4} \text{stable products}$$

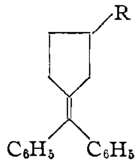
TABLE II

REACTIVITY TOWARD METHYL METHACRYLATE RADICALS AT 50°

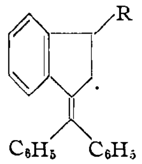
Compound	$k_1 \times 10^{-2}$, liter/mole sec.	$(k_2/k_3) \times 10^{10}$
6,6-Diphenylfulvene	6.3	0.2
6-Methyl-6-phenylfulvene	3.6	2.5
6,6-Diphenylbenzofulvene	8.5	70
6,6-Diphenyldibenzofulvene[a]	<0.0004	..
1-Benzhydrylidene-2-cyclopentene	6.7	90
Styrene[b]	12	10^4
Butadiene[b]	21	

[a] J. L. Kice, THIS JOURNAL, 80, 348 (1958). [b] Estimated from data for 60° given by C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 123, 146.

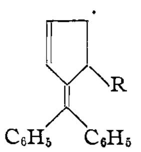
Second, it is evident that diphenylbenzofulvene and benzhydrylidenecyclopentene (VIII) have very similar values of k_1 and k_2/k_3. This means that not only are the compounds of similar reactivity but also that the RF· radicals resulting in the two cases show like behavior as regards addition to the methacrylate double bond or termination. In the case of the cyclopentene, radical attack presumably occurs at the 3-position to give radical X, and the similar behavior of the radicals formed in the two cases strongly suggests that diphenylbenzofulvene is also attacked in such fashion as to produce radical XI, which we would expect to show behavior closely akin to X. While it might have been thought that the benzofulvene should react with methacrylate radicals somewhat less rapidly than VIII because of the presumed greater loss of resonance energy on addition of a radical to the 3-position of the former compound, the actual additional resonance energy of the molecule due to the complete diphenylbenzofulvene system may be quite small, in which case the observed results are perfectly consistent with attack on the 3-position. It is our view that although the present results cannot conclusively rule out the possibility of radical attack on diphenylbenzofulvene at the 2-position, the similarity of both the k_1 and k_2/k_3 values is much more consistent with attack at the 3-position. It might be noted that the k_2/k_3 values for radicals X and XI indicate them to occupy a position intermediate between the styryl radical and the fluorenyl radicals previously studied.[7b]



X



XI



XII

Radical attack at the 3-position of diphenylfulvene should produce a radical whose behavior would be expected to be closely comparable to that of X, while attack at the 2-position should lead to a radical (XII) with greater possibilities for resonance stabilization and presumably quite different behavior. The vastly different k_2/k_3 values for the radicals from diphenylfulvene and VIII thus seem to point to attack at the 2-position. Furthermore since we believe the magnitude of k_2/k_3 should be an approximate measure of the stability of the radical[7b] (the smaller the value of k_2/k_3 the more stable the radical) and since radical XII should be more resonance stabilized than X, the considerably smaller k_2/k_3 value observed for diphenylfulvene is entirely in accord with expectations based on attack of methyl methacrylate radicals on the 2-position.

Although these results suggest that the reaction of diphenylfulvene responsible for the retardation involves the attack of methacrylate radicals at the 2-position, one is immediately tempted to inquire why the value of k_1 observed for this reaction is not much larger than the value of this quantity observed for benzhydrylidenecyclopentene, in view of the considerably greater stability of radical XII. Two factors could account for the low reactivity of diphenylfulvene: (1) the resonance energy of the fulvene system and (2) steric hindrance to radical attack at the 2-position. If the fulvene system itself does indeed make a respectable contribution to the over-all resonance energy of the molecule[8] it is easy to see that any enhancement of reactivity caused by the increased stability of the radical XII might be substantially counterbalanced by the greater loss in resonance energy attending radical addition in the case of the fulvene. On the other hand, one could also attribute the low reactivity of diphenylfulvene to steric hindrance to radical attack on the 2-position, since examination of models and previous results[3b,7b] indicating the importance of steric factors in radical addition reactions strongly suggest that there might be important steric hindrance to radical attack on the 2-position of diphenylfulvene.

While the reactivity data seem to clearly indicate that radical attack on the 2-position of diphenylfulvene is responsible for the retardation observed, it should be noted that these same results

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[8] J. H. Day (*J. Org. Chem.*, **22**, 214 (1957)) estimates the resonance energy of the fulvene system in diphenylfulvene at ~10 kcal. using a heat of combustion method.

do not unequivocally establish that compounds A and B have structure II. To be sure, if the resonance energy of the fulvene system is appreciable (as Day's[8] result would seem to indicate) one would certainly expect the reactivity of the 3-position of the fulvene to be considerably less than that of benzhydrylidenecyclopentene, and in that event reaction at the 2-position would be the only reaction of any consequence either kinetically or product-wise. On the other hand, if the resonance energy of the fulvene system is negligible, one might well expect the reactivity of the 3-position of the fulvene to be closely comparable to that of VIII. Attack at the 3-position would lead to a relatively reactive radical which is so much less efficient kinetically in retarding the polymerization of methyl methacrylate that unless the 3-position is at least twice as reactive as the 2-position the occurrence of the reaction will not be experimentally evident in the presence of the much more effective 2-position retardation reaction.[9] Thus, although such a reaction need not alter the observed kinetics, it might easily account for an appreciable fraction of the products of any reaction of diphenylfulvene with free radicals. For this reason it is not possible to completely rule out structure V for compounds A and B.

One other set of experiments is of some interest. As is evident from Table II 6-methyl-6-phenylfulvene is comparable in its reactivity parameters to diphenylfulvene, and is therefore also a fairly effective retarder of methyl methacrylate polymerization. As might be expected from that result, the azobisisobutyronitrile-initiated homopolymerization of the fulvene is extremely slow. A degassed sample of pure methylphenylfulvene 0.05 M in AIBN heated at 50° for 24 hours yielded less than 0.4% of methanol-insoluble material (presumably low molecular weight polymer), corresponding to a polymerization rate of less than 0.015%/hour. On the other hand, other samples also 0.05 M in AIBN but heated at 50° in an oxygen atmosphere for 24 hours yielded 18% of methanol-insoluble material shown by analysis to be an approximately 1:1 methylphenylfulvene: O_2 copolymer. This corresponds to a polymerization rate of 0.8%/hour or at least 50 times the rate *in vacuo*. The behavior of the fulvene is thus akin to that of indene, which also polymerizes faster in the presence of oxygen than in its absence, although in that case the rate in oxygen is only seven times the *in vacuo* rate.[10]

Experimental

6,6-Diphenylfulvene.—Eleven grams (0.17 mole) of freshly prepared cyclopentadiene was added slowly to a solution of sodium ethoxide (prepared from 4.0 g. of sodium and 120 ml. of absolute ethanol) containing 28.8 g. (0.16 mole) of benzophenone. After the addition was complete the resulting red solution was heated gently on the steam-bath for 5–10 minutes and then cooled. All operations were carried out under nitrogen. Orange-red crystals separated, and the solution was allowed to stand overnight in the icebox. The crude fulvene was then filtered off and recrystallized from absolute ethanol. This yielded 20.4 g. (56%) of diphenylfulvene, m.p. 82–82.5° (lit.[11] 82°). The material used for kinetic studies was stored in evacuated sealed tubes in the dark at −20° until used. The material used for the product studies was stored under nitrogen under otherwise similar conditions.

6,6-Diphenylbenzofulvene.—The preparative procedure of Thiele and Merch[12] was followed with the additional precaution that the reaction mixture was kept under a nitrogen atmosphere. The crude product was recrystallized once from ethanol to give an orange-yellow powder, m.p. 104–110°. This was further purified by chromatography with hexane on alumina. The orange colored hexane fractions were combined, the hexane removed under reduced pressure, and the residue recrystallized from ethanol. There was thus obtained pure diphenylbenzofulvene, m.p. 114–115°. This was stored under nitrogen at −20° until used.

6-Methyl-6-phenylfulvene.—To a solution of 5 g. of sodium in 75 ml. of absolute ethanol was added slowly a mixture of 24 g. (0.2 mole) of acetophenone and 13.2 g. (0.2 mole) of freshly distilled cyclopentadiene. After stirring for three hours under a nitrogen atmosphere, the deep red mixture was poured into about 250 ml. of water, and the organic layer taken up in methylene chloride. The methylene chloride layer was washed with water until the washings were neutral, dried over sodium sulfate, and the methylene chloride removed under reduced pressure at room temperature. The residue, a ruby-red oil, was fractionally distilled through a short Vigreux column, and the fraction boiling 70–72° (0.3 mm.) retained; yield 15 g. (45%). The material was stored under nitrogen at 0° and before use was distilled in a molecular still.

2,2′-Azobisisobutyronitrile and methyl methacrylate were purified as previously described.[7]

Benzhydrylidenecyclopentane.—Three and one-half grams of diphenylfulvene, 0.1 g. of 5% Pd/C catalyst, and 100 ml. of absolute ether were cooled for 15–20 minutes in a Dry Ice-bath and then quickly shaken for 15 minutes with hydrogen under a pressure of 20 p.s.i. The resulting colorless solution was filtered, and the ether evaporated to give an oil which deposited crystals on standing at room temperature. Two recrystallizations from ethanol gave 1.1 g. (31%) of benzhydrylidenecyclopentane, m.p. 61–63° (lit.[13] 62.5–63°). The ultraviolet absorption spectrum in isoöctane showed a maximum at 250 mμ (log ε 4.16) and a minimum at 231 mμ (log ε 4.03).

1-(1-Cyclopentenyl)-diphenylcarbinol.—1-Chloro-1-cyclopentene was prepared by the method of Braude and Forbes.[6] The organolithium compound[6] was prepared from 4.3 g. of lithium and 22.7 g. of the halide, and 49.5 g. of benzophenone in 75 ml. of anhydrous ether was added over the course of 1 hr. to the ethereal solution of 1-(1-cyclopentenyl)-lithium. The solution was stirred for about 6 hours at room temperature and hydrolyzed by addition of saturated ammonium chloride solution. The ether layer was separated, washed with water and dried over anhydrous magnesium sulfate and potassium carbonate. The ether was removed under reduced pressure, and the residual oil treated with hexane and allowed to stand overnight in the cold. The crystals which formed were filtered off. The yield of crude carbinol was 13 g. (20%). Two recrystallizations of this material from hexane gave pure 1-(1-cyclopentenyl)-di-

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(9) The complicated kinetic situation wherein the fulvene can react with methacrylate radicals in two different ways to produce two different RF· radicals of unlike behavior does not permit a completely general analysis. However, provided one considers unimportant cross-termination between the two different RF· radicals and is considering sufficiently strongly retarded polymerizations that he can neglect the normal ($2R\cdot \xrightarrow{k_t}$ stable products) termination reaction, it is possible to obtain meaningful solutions for a number of special cases. In particular, if one endows the 3-position of the fulvene with reactivity parameters (k_1, k_2/k_3, etc.) of similar value to those for VIII it can be shown that as long as the k_1 value for the 2-position of the fulvene is not much smaller than that for the 3-position, and as long as the k_2/k_3 value for the RF· radical produced by attack on the 2-position is as small as 5×10^{-11}, one simply could not detect by our method the occurrence of the 3-position reaction, since it would contribute essentially nothing to the observed retardation. While the occurrence of such a reaction could approximately double the rate of consumption of fulvene, one must remember that we are dealing with only a retarded polymerization where the disappearance of fulvene is essentially negligible anyway.

(10) G. A. Russell, THIS JOURNAL, **78**, 1041 (1956).

(11) J. Thiele, *Ber.*, **33**, 672 (1900).

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phenylcarbinol, m.p. 133–135°. *Anal.* Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.23; H, 7.19. The ultraviolet absorption spectrum in isoöctane showed maxima at 253, 259 and 270 mμ. However, the extinction coefficient for even the strongest of these (259 mμ) was only 430.

1-Benzhydrylidene-2-cyclopentene.—Five grams of 1-(1-cyclopentenyl)-diphenylcarbinol was dissolved in 100 ml. of glacial acetic acid containing 0.1 g. of *p*-toluenesulfonic acid monohydrate, and the solution was allowed to stand under nitrogen for 24 hr. at room temperature. The blue-green solution was poured into 300 ml. of ice water, and the organic layer taken up in ether. The ether solution was washed with water, dilute sodium carbonate, then water again, and dried over anhydrous sodium sulfate. The ether was removed under reduced pressure, and the hexane-soluble portion of the residue was chromatographed on alumina using hexane as eluent. The first fractions were evaporated under reduced pressure and the residues recrystallized from methanol, yielding 2.9 g. (63%) of 1-benzhydrylidene-2-cyclopentene, m.p. 51–53°.

A 0.496-g. sample of the diene was ozonized in 50 ml. of ethyl acetate at −30°. The ozonide was decomposed with aqueous hydrogen peroxide, and the work-up of the neutral fraction afforded on treatment with 2,4-dinitrophenylhydrazine 0.486 g. (63%) of benzophenone 2,4-dinitrophenylhydrazone, m.p. 239–240°.

Hydrogenation of 0.113 g. of 1-benzhydrylidene-2-cyclopentene was carried out in absolute ether at room temperature using Pd/C as catalyst. The hydrogen uptake was 106% of theory for two C=C double bonds. Removal of the catalyst by filtration and evaporation of the ether gave crystalline material of m.p. 35.5–36.5°. A mixed melting point with an authentic sample of benzhydrylcyclopentane[13] (m.p. 36–38°) showed no depression.

Decomposition of Azobisisobutyronitrile in the Presence of Diphenylfulvene.—The reaction was carried out in reagent grade benzene which had been further purified by being refluxed over sodium and then fractionally distilled. The reaction vessel was a Claisen flask which had been modified by sealing off the sidearm and attaching a ₸ 10/30 joint to one neck. Diphenylfulvene (3.58 g.) and azobisisobutyronitrile (1.32 g.) were weighed into the vessel, which was then attached to the vacuum line through the ₸ joint, the open neck sealed off, and the reaction vessel evacuated. The benzene (300 ml.) was degassed twice in the usual manner and distilled into the reaction vessel, which was then sealed off. The vessel was placed in a constant temperature bath at 78° for 10–12 hr., then cooled in Dry Ice–acetone to freeze the contents and opened. Almost all of the benzene was then removed under reduced pressure. Some hexane was added to the residue and the solution was cooled. The white powder which separated was collected on a filter. A second crop of solid was obtained by adding additional hexane to the filtrate and cooling the solution. After the volume of the filtrate was reduced somewhat by evaporation, the filtrate was chromatographed on alumina. The first fractions, eluted with hexane, consisted of unreacted diphenylfulvene (1.03 g.). The eluent was then changed to 1:4 benzene–hexane and then to 1:2 benzene–hexane, followed by 1:1 benzene–hexane and finally pure benzene. Only gummy residues were obtained from these later chromatographic fractions. The weight of the combined residues was 2.26 g.

The solid fractions (1.18 g.) obtained from the reaction mixture before chromatography could be separated by fractional crystallization from acetone into two pure compounds: A, the less soluble in acetone, m.p. 258–260°, and B, m.p. 235–236° (mixed m.p. with A 219–235°). Compound A crystallized in the form of plates while B came out of solution as long acetone-containing needles, from which the acetone was removed by vacuum drying. Calcd. for $C_{44}H_{40}N_2$: C, 88.85; H, 6.76; N, 4.69; mol. wt., 596. Found: Compound A, C, 88.01; H, 6.87; N, 4.60; mol. wt. (Rast), 583, 567. Compound B, C, 88.31; H, 6.81; N, 4.67; mol. wt. (Signer), 630.

Various attempts were made to obtain pure crystalline compounds from the gummy chromatography residues. While solid fractions could be obtained by dissolving the residues in ethanol and precipitation with water, these were not pure and had broad indefinite melting points. Attempts to purify these solids further by fractional crystallization were not successful.

TABLE III

ULTRAVIOLET ABSORPTION SPECTRA IN ISOÖCTANE

Compound	$\lambda_{\max}$, mμ (log ε)[a]	λ_{min}, mμ (log ε)
1-Benzhydrylidene-2-cyclopentene	290 (4.29)	250 (3.85)
Compound A	285 (4.09)	250 (3.97)
Compound B	290 (4.09)	255 (3.87)
"Residues"	290 (3.97)	255 (3.83)

[a] The extinction coefficients for A, B, and the residues are all calculated on the basis of an equivalent weight of 300.

Oxidation of Compound A.—A sample of 0.476 g. of compound A was dissolved in about 200 ml. of purified[14] reagent grade acetone and to the stirred solution 0.35 g. of potassium permanganate was added in small portions. After the mixture was stirred for four hours at room temperature the permanganate color had entirely disappeared. The solution was filtered, the filtrate diluted with water, and the acetone was removed by distillation. The residue was taken up in benzene and the benzene solution was refluxed for one hour with an acidified solution containing 1.2 g. of potassium permanganate. The mixture was cooled, and dilute hydrogen peroxide was added to destroy the MnO_2. The benzene layer was separated, extracted with dilute sodium hydroxide, washed with water, dried over sodium sulfate, and evaporated at reduced pressure. The residue on treatment with 2,4-dinitrophenylhydrazine gave 0.07 g. (12%) of benzophenone 2,4-dinitrophenylhydrazone, m.p. 238–240°.

Procedure for Kinetic Runs.—For methylphenylfulvene the procedure was similar to that employed for dibenzofulvene.[7b] For the other compounds studied in the present work the procedure was identical to that used for the substituted dibenzofulvenes.[7b] All runs were carried out at 50°.

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