was no apparent change in viscosity of the solution. After standing at room temperature for 18 hr., however, the entire mixture had solidified. Methanol (100 ml.) was added, and the white solid (1.9 g.) was isolated by filtration on a Büchner funnel. This solid was completely dissolved in 40 ml. of benzene, and was reprecipitated by filtration into 400 ml. of methanol. There was obtained 1.7 g. (85%) of a white, powdery solid, m.p. 275–290°; $[\eta]_{\text{inherent}} = 0.26$. Residual unsaturation: 5–10%.

(4) *Free radical initiation:cumene hydroperoxide.* The monomer (1.0 ml.) containing approximately 40 mg. of cumene hydroperoxide was sealed off under nitrogen in a small test tube, and was kept in boiling water for 5 days. The polymer obtained was an opaque, nonflowing plastic, which was, however, soft, not brittle, and could easily be scratched. The softening point of this plastic material, taken on a hot stage, was 85°. It was completely soluble in benzene; precipitation into methanol gave 0.56 g. (56%) of a white powder, m.p. 240–270°; $[\eta]_{\text{inherent}} = 0.128$. Residual unsaturation: approximately 3%.

(5) *Thermal polymerization.* The monomer (1.0 ml.) was sealed under nitrogen in a small test tube, and was kept in *o*-dichlorobenzene, heated to its reflux temperature, for 5 days. The polymer obtained was a clear, nonflowing plastic, which, however, was soft and could easily be scratched. Its softening point, taken on a hot stage, was 90°. This plastic solid was completely dissolved in benzene, and was precipitated into methanol to give 0.54 g. (54%) of a white powdery solid, m.p. 260–290°; $[\eta]_{\text{inherent}} = 0.154$. Residual unsaturation: approximately 3%.

(6) *Ziegler-type polymerization.* The catalyst was prepared in a dry box in an atmosphere of nitrogen by adding titanium tetrachloride (0.12 g.; 0.00063 mole) to a solution of aluminum triisobutyl (0.1 g.; 0.0005 mole) in dry *n*-heptane (2.05 g.). The monomer (5.0 g.) was added, and the mixture was allowed to stand under nitrogen in a stoppered bottle at room temperature for 72 hr. After precipitation into methanol, there was obtained 2.79 g. (56%) of a white powdery solid, m.p. 185–200°, $[\eta]_{\text{inherent}} = 0.041$. Residual unsaturation: 5–10%.

Polymers of 2,7-diphenyloctadiene-1,7. (1) *Cationic initiation:boron trifluoride.* The procedure used was the same as that described above for the boron trifluoride–initiated polymerization of 2,6-diphenylheptadiene-1,6. From 1.0 g. of monomer there was obtained 0.06 g. (6%) of solid polymer after two precipitations from benzene into methanol. Polymer m.p. 115–150°; no residual unsaturation (no infrared absorption at 900 or 1625 cm.$^{-1}$); $[\eta]_{\text{inherent}} = 0.021$.

Anal. Calcd. for $(C_{20}H_{22})_x$: C, 91.55; H, 8.45. Found: C, 91.10; H, 8.51.

(2) *Cationic initiation titanium tetrachloride.* Under conditions like those described above for the titanium tetrachloride–initiated polymerization of 2,6-diphenylheptadiene-1,6, this monomer (1.5 g.) was allowed to react with the catalyst (0.12 g.; 0.07 ml.) in 5.5 ml. of purified *n*-heptane for 40 hr. at room temperature. At the end of this time, the reaction was quenched by the addition of 10 ml. of methanol. There was obtained an oily, viscous liquid, insoluble in the solvent. The solvent was carefully decanted, the oil was dissolved completely in benzene, and precipitated into methanol to give 0.70 g. (47%) of a tan-colored powder, m.p. 87–128°; $[\eta]_{\text{inherent}} = 0.039$. Residual unsaturation: approximately 2–5%.

(3) *Ziegler-type polymerization.* The catalyst was prepared as described above. From 2.0 g. of monomer there was obtained 1.5 g. of a white, powdery solid, m.p. 95–157°; $[\eta]_{\text{inherent}} = 0.040$. This polymer possessed no residual unsaturation.

Polymers of 2,5-diphenylhexadiene-1,5. (1) *Cationic initiation:boron trifluoride.* The procedure used was the same as that described above for the boron trifluoride–initiated polymerization of 2,6-diphenylheptadiene-1,6. From 0.4 g. of monomer there was obtained 0.33 g. (83%) of a white powdery solid, m.p. 185–210°; $[\eta]_{\text{inherent}} = 0.083$, after three precipitations from benzene into methanol. Residual unsaturation: 5–10%.

Anal. Calcd. for $(C_{18}H_{18})_x$: C, 92.26; H, 7.74. Found: C, 91.35; H, 7.41.

(2) *Free radical initiation:cumene hydroperoxide.* The monomer (0.50 g.) containing approximately 25 mg. of cumene hydroperoxide was sealed off under nitrogen in a small test tube and was kept in boiling water for 5 days. The tube was then opened, and the contents were poured into 100 ml. of methanol. The white, insoluble solid was isolated and reprecipitated from benzene into methanol to give a very small amount (11 mg.) of white, powdery solid, m.p. 150–170°. The amount isolated was not sufficient for a viscosity measurement. Residual unsaturation: <5%.

(3) *Ziegler-type polymerization.* The catalyst was again prepared by using aluminum triisobutyl and titanium tetrachloride in a mole ratio of 0.8. From 0.5 g. of monomer there was obtained 0.29 g. (58%) of a white, powdery solid, m.p. 157–177°; $[\eta]_{\text{inherent}} = 0.072$. Residual unsaturation: 3–5%.

URBANA, ILL.

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

The Reaction of Free Radicals with Non-benzenoid Aromatic Hydrocarbons. II. 6-Alkylfulvenes and Benzofulvenes

JOHN L. KICE[1] AND FATEMEH TAYMOORIAN

Received March 23, 1960

Kinetic studies of the reactivity of a series of 6,6-dialkylfulvenes and benzofulvenes toward free radicals have provided fairly definite evidence that these substances like their phenyl substituted counterparts undergo radical attack at one of the ring positions and not at the external 6-position. The experimental evidence seems to favor the 2-position as the site of radical attack.

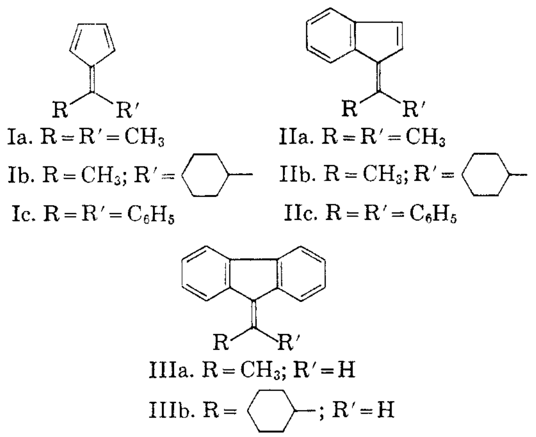
The reactivity of various phenyl substituted fulvenes and benzofulvenes toward free radicals and the site of radical attack on these molecules were the subjects of a previous paper.[2] That study

---

(1) To whom inquiries should be sent: Department of Chemistry, Oregon State College, Corvallis, Ore.

(2) J. L. Kice and F. M. Parham, *J. Am. Chem. Soc.*, **80**, 3792 (1958).

provided convincing evidence that 6,6-diphenylfulvene (Ic) and 6,6-diphenylbenzofulvene (IIc) are attacked by radicals at the ring positions and not at the external 6-position. For several reasons we felt that this result did not ensure that 6,6-dialkylfulvenes and benzofulvenes would also react in similar fashion, and we therefore thought it desirable to carry out experiments which would elucidate the site of radical attack on such alkyl substituted fulvenes and benzofulvenes.

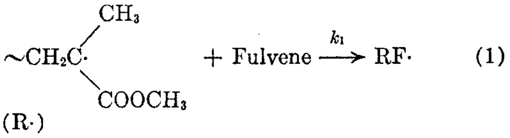


Regrettably, the most direct approach, the examination of the products produced when a radical source is decomposed in benzene solutions of dimethylfulvene or dimethylbenzofulvene, has in our hands proved unsatisfactory. The products of the reaction of 2-cyano-2-propyl radicals with either compound were intractable gums and viscous oils.[3] Although the physical properties and chemical behavior of these materials afford some qualitatively useful information, we felt that kinetic studies of the reactivity of certain alkyl fulvenes and benzofulvenes would provide more conclusive results.

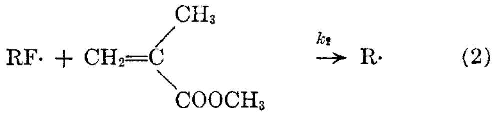
In the dibenzofulvenes (III), where radical attack certainly occurs at the external 6-position, replacement of the methyl group in 6-methyldibenzofulvene (IIIa) with a cyclohexyl group (IIIb) leads to a 2000 fold decrease in the reactivity of the double bond toward methyl methacrylate radicals.[4] This is undoubtedly due to increased steric hindrance to radical attack at the 6-position.[4,5] Similarly, one would expect, if radical attack on 6,6-dimethylfulvene (Ia) took place at the 6-position, that replacement of one of the methyl groups by a cyclohexyl, as in 6-methyl-6-cyclohexylfulvene (Ib), would lead to a drastic decrease in reactivity toward methacrylate radicals. On the other hand, if radical attack occurs at one of the ring positions, the steric consequences of the replacement of methyl by cyclohexyl will be much less and the reactivity of Ib should not differ greatly from that of dimethylfulvene. Similar arguments apply to the benzofulvenes IIa and IIb.

RESULTS AND DISCUSSION

Ia and IIa were prepared by published procedures,[6,7] and the new compounds Ib and IIb were synthesized by analogous methods. The reactivity of the four compounds toward methyl methacrylate radicals (Equation 1) was determined by the retardation-of-polymerization method.[4] The results are shown in Table I as values of k_1, together with values for the ratio k_2/k_3, which can also be obtained from the kinetic data.



$$\underset{(R\cdot)}{\sim CH_2\overset{CH_3}{\underset{COOCH_3}{C}}\cdot} + \text{Fulvene} \xrightarrow{k_1} RF\cdot \qquad (1)$$



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

$$RF\cdot + R\cdot \xrightarrow{k_3} \text{stable products} \qquad (3)$$

$$2RF\cdot \xrightarrow{k_4} \text{stable products} \qquad (4)$$

The results show that substitution of a cyclohexyl for a methyl causes no marked decrease in reactivity either with the fulvenes or the benzofulvenes. This would therefore seem to be convincing evidence that the site of radical attack on 6,6-dialkylfulvenes and benzofulvenes is at the ring positions and not at the external 6-position.[8]

---

[3] We have not studied other radical sources since we learned that Dr. W. B. Smith of Ohio University plans work in this area.

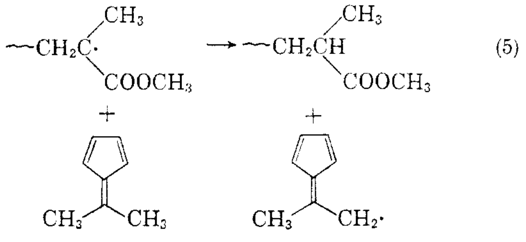
[4] J. L. Kice, *J. Am. Chem. Soc.*, **80**, 348 (1958).

[5] M. Szwarc and F. Leavitt, *J. Am. Chem. Soc.*, **78**, 3590 (1956).

[6] J. Thiele and K. Merck, *Ann.*, **415**, 257 (1918).

[7] J. Thiele, *Ber.*, **33**, 666 (1900).

[8] The possibility that the observed retardation occurs through chain transfer of one of the alkyl group hydrogens to the methacrylate radical (Equation 5) seems very unlikely for the following reasons: (i) The rate of such a reaction as Equation 5 should probably be about the same for dimethylfulvene, dimethylbenzofulvene, and dimethyldibenzofulvene. For the latter compound previous kinetic studies[3] have shown that the rate of Equation 5 cannot be more than 1/100th the reactivity of Ia or IIa and may actually be much less. (ii) Szwarc[9] has shown that with methyl radicals the rate of hydrogen-atom transfer from dimethyldibenzofulvene is much lower than the rate of addition to the external double bond, a fact which also indicates a rather low reactivity for these hydrogens in homolytic transfer reactions.



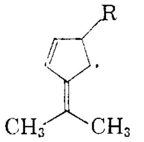
[9] F. Carnock and M. Szwarc, *J. Am. Chem. Soc.*, **81**, 4138 (1959).

TABLE I

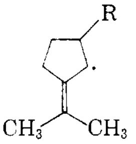
RATE CONSTANTS FOR REACTION OF METHACRYLATE RADICALS WITH ALKYLFULVENES

Compound	$k_1 \times 10^{-2}$ (L./mol.$^{-1}$/Sec.$^{-1}$)	$(k_2/k_3) \times 10^{10}$
Ia	1.8	50
Ib	0.85	17
IIa	0.23	9
IIb	0.65	2

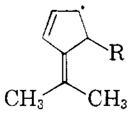
Although the k_1 values clearly indicate that radical attack on the dialkylfulvenes and benzofulvenes occurs at the ring positions, they do not tell us whether the reaction responsible for the observed retardation involves attack on the 2- or the 3-position. We are inclined, however, to believe it is the 2-position for the following reasons: The (k_2/k_3) values for all four of the compounds are much smaller than that observed in the same system for the styryl radical[1] $[(k_2/k_3) \times 10^{10} = 10^4]$. As we doubt that the internal double bond of radical IV would provide much stabilization, we would expect that IV, if formed, would behave in a fashion similar to V and would show a (k_2/k_3) of the same order of magnitude as the styryl radical. On the other hand, VI, resulting from attack at the 2-position, should have considerable additional stabilization and a considerably smaller k_2/k_3 value, reflecting its lower reactivity. The results in Table I are thus in much better accord with attack at the 2-position for all four of the fulvenes and benzofulvenes studied, although before attaching too much significance to this conclusion, one should recall that one recent experience[10] has shown k_2/k_3 is not always a reliable measure of the resonance stabilization of a radical.



IV

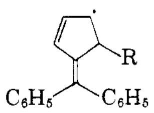


V

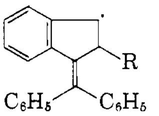


VI

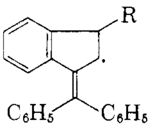
It is of interest to compare the behavior of the 6,6-dialkylfulvenes and benzofulvenes with their phenyl substituted counterparts.[2] In both cases going from the fulvene to the benzofulvene produces no large change in reactivity (k_1). However, going from 6,6-diphenylfulvene to diphenylbenzofulvene causes a 400 fold increase in k_2/k_3 while with the alkyl substituted compounds the k_2/k_3 values of the benzofulvenes are actually somewhat smaller than those of the fulvenes. In the phenyl substituted series the large increase in k_2/k_3 on going from fulvene to benzofulvene was attributed to a change from the 2- to the 3-position as the site of radical attack leading to retardation. One must consequently inquire why such a change is not also observed in the alkyl substituted case. We believe the reason is as follows. For maximum stabilization of the radicals VII and VIII (which would result from attack at the 2-position of the diphenyl compounds) it is necessary that at least one of the phenyl groups be able to be approximately coplanar with the 5-membered ring. This is possible for VII (from diphenylfulvene), but it is not possible for VIII, where the bulky R-group on one side and the aromatic ring on the other prevent either 6-phenyl group from even approaching coplanarity. Consequently radical VIII is not stabilized to the same extent as VII. As a result, VIII and the radical resulting from attack at the 3-position (IX), where one phenyl can still achieve approximate coplanarity, become of comparable stability. As the 3-position probably offers somewhat less steric hindrance to radical attack, it is the reaction at this site which predominates for diphenylbenzofulvene. On the other hand, in the alkyl fulvenes the radicals resulting from attack at the 2-position are approximately equally stabilized for both fulvenes and benzofulvenes, with the result that the k_2/k_3 values do not differ very greatly, and the site of radical attack responsible for retardation remains the same.



VII



VIII



IX

Exponents of the use of free valence as a means of predicting the preferred position for radical attack would expect that with the fulvenes the 6-position should intrinsically be the most reactive.[11] Our finding that dialkylfulvenes undergo radical attack at the ring positions does not, however, constitute evidence contradicting the correctness of predictions based on free valence, as one would expect that steric hindrance from the alkyl 6-substituents would bring about an enormous decrease in the rate of reaction at the 6-position, as witness our previous observation that 6,6-dimethylbenzofulvene is at least 10^6 times less reactive toward methacrylate radicals than dibenzofulvene itself. Under such circumstances the less hindered ring positions might easily become more reactive than the 6-position. We had hoped to be able to investigate this point more fully through study of fulvene itself, but unfortunately despite numerous careful attempts we were unable to to repeat the recent reported preparation of this compound.[12a] Angus and Bryce-Smith[12b] have

---

[10] J. L. Kice and F. Taymoorian, *J. Am. Chem. Soc.*, **81**, 3405 (1959).

[11] E. D. Bergmann, "The Fulvenes," Chap. 3 in *Progress in Organic Chemistry*, V. 3. Academic Press, New York, N. Y., 1955; *cf.* pp. 90–6.

[12] (a) J. Thiec and J. Wiemann, *Bull. soc. chim. Fr.*, [5], **23**, 177 (1956). (b) H. J. F. Angus and D. Bryce-Smith, *J. Chem. Soc.*, 1409 (1960).

also recently reported inability to repeat Thiec and Wiemann's work.

EXPERIMENTAL

Preparation of fulvenes. Dimethylfulvene (Ia). This was prepared by the method described by Thiele.[7] After purification by fractional distillation, the center cut, b.p. 43–44°/10 mm., was degassed on the vacuum line and distilled into a number of small ampoules which were then sealed and stored in the dark at −20°. Ia melts slightly above 0° and when stored as described shows no evidence of dimer or polymer formation even on relatively prolonged storage.

Dimethylbenzofulvene (IIa). The preparative procedure of Thiele and Merck[6] was followed with the additional precaution that the reaction mixture was kept under a nitrogen atmosphere. The reaction mixture was poured into water and the organic layer was taken up in benzene. The benzene layer was washed repeatedly with water, dried over sodium sulfate, and the benzene removed under reduced pressure. The residue was fractionally distilled through a short Vigreux column, and IIa was collected as a yellow oil, b.p. 89–93°/2 mm. Confirmation of the purity of IIa was provided by comparison of its ultraviolet absorption spectrum with that previously reported.[13] Purified IIa was stored under nitrogen at 0° until used.

Methylcyclohexylfulvene (Ib). Methyl cyclohexyl ketone was prepared by the method described by van Woerden.[14] A mixture consisting of 25.2 g. (0.2 mole) of the ketone and 13.2 g. (0.2 mole) of freshly distilled cyclopentadiene was added with stirring to a solution of 5 g. of sodium in 75 ml. of ethanol. The solution was stirred at room temperature for 3 hr. under nitrogen, at the end of which time it was poured into 250 ml. of water. The fulvene which separated was taken up in methylene chloride; the methylene chloride solution was washed with water, dried over sodium sulfate, and the methylene chloride removed under reduced pressure. The crude fulvene was purified by two fractional distillations under reduced pressure through a Vigreux column. There was obtained 8.0 g. (23%) of pure 6-methyl-6-cyclohexylfulvene, b.p. 72–73°/0.5 mm. Ultraviolet absorption spectrum in isooctane λ_{max}, 360 mμ (log ϵ, 2.5).

In view of the considerable sensitivity of fulvenes to oxygen, Ib was converted for analysis to its hexahydro derivative, 1-cyclopentyl-1-cyclohexylethane. Six grams of Ib was hydrogenated over platinum oxide in ethanol at 25° and 15 p.s.i. After 3.5 hr. the catalyst was removed by filtration, the solvent evaporated, and the residue distilled. There was obtained 3.5 g. (56%) of 1-cyclopentyl-1-cyclohexylethane, b.p. 103–104°/7 mm.

Anal. Calcd. for $C_{13}H_{24}$: C, 86.58; H, 13.42. Found: C, 86.12; H, 13.04.

6-Methyl-6-cyclohexylbenzofulvene (IIb). To 4 g. of sodium in 200 ml. of ethanol was added 16.7 g. (0.132 mole) of methyl cyclohexyl ketone and 20 g. (0.17 mole) of freshly distilled indene. The solution was refluxed under nitrogen for 8 hr. It was then poured into water and the organic layer was taken up in methylene chloride. The methylene chloride solution was washed and dried and the solvent removed under reduced pressure. The crude product was chromatographed on alumina using hexane as eluant and 100 g. of alumina for each 10 g. of crude product. The hexane was removed and the residues containing the benzofulvene were heated at 60–65° at 12–14 mm. pressure in order to remove unchanged indene. The residue from this treatment was then distilled in a molecular still (bath temp., 140°; pressure, 0.05 mm.) giving 6.0 g. (20%) of IIb. Ultraviolet absorption spectrum in isooctane: λ_{max}, 322 mμ (log ϵ, 3.79); 309 mμ (log ϵ, 3.86).

Four grams of IIb was hydrogenated over palladium-charcoal in ethanol solution for 4 hr. at room temperature and 15 p.s.i. The catalyst was removed by filtration, and the solvent was evaporated. The residue was distilled under reduced pressure giving 3.0 g. (74%) of 1-(1-cyclohexyl-1-ethyl-)indane, b.p. 143–145°/3 mm.

Anal. Calcd. for $C_{17}H_{24}$: C, 89.41; H, 10.59. Found: C, 89.57; H, 10.81.

Methyl methacrylate and *2,2'-azobisisobutyronitrile* were purified as previously described.[15]

Procedure for kinetic runs. For all of the compounds the procedure was the same as that previously used for dibenzofulvene.[4]

The results of the individual runs are given in Table II. The method of obtaining the k_1 and k_2/k_3 values from these data has been described.[4] In the present work the best plots were obtained in the various cases as follows: Ia and Ib, $c = 0.075$; IIa, $c =$ any value less than 0.1; IIb, $c =$ any value less than 0.01.

TABLE II

RESULTS OF INDIVIDUAL KINETIC RUNS AT 50° IN METHYL METHACRYLATE

Compound	(AIBN) × 10^3 (moles/l.)	(Fulvene) × 10^3 (moles/l.)	$\phi \times 10^{2a}$
Ia	5.41	67.0	23.8
	4.58	39.2	30.6
	9.62	50.1	28.0
	2.72	59.1	25.2
	2.91	37.9	32.1
	12.7	47.3	29.1
	6.17	40.3	31.5
Ib	4.93	42.0	28.5
	2.75	34.4	29.7
	10.4	52.4	26.6
	10.7	47.0	28.8
	3.84	24.3	36.6
	5.69	103	15.8
IIa	5.57	20.9	64.5
	5.34	46.3	44.7
	5.37	81.3	31.8
	2.46	45.6	40.1
	10.7	46.1	49.5
IIb	5.74	38.8	20.2
	6.08	109	8.30
	6.18	49.3	16.8
	10.4	59.6	15.3
	2.82	57.4	13.7

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

Acknowledgment. We gratefully acknowledge the financial support of the National Science Foundation through NSF Grant G-4205.

COLUMBIA, S. C.

---

(13) A. Pullman, *et al.*, *Bull. soc. chim. France*, [5], **18**, 702 (1951).

(14) S. van Woerden, *Rec. trav. chim.*, **45**, 135 (1926).

(15) J. L. Kice, *J. Am. Chem. Soc.*, **76**, 6274 (1954).