

THE FULVENES

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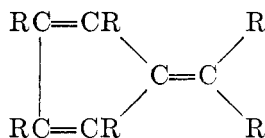
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I. INTRODUCTION AND NOMENCLATURE

The fulvenes are characterized by the "cross-conjugated" structure



in which the R's may be hydrogen, alkyl, aryl, or other groups. Fulvene itself is the unsubstituted compound, C₆H₆.

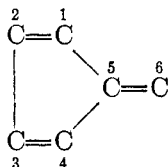
The fulvenes are of exceptional interest for a number of reasons. Fulvene is an isomer of benzene but is very different in color and reactivity. The fulvenes were first prepared and named (Latin, *fulvus*, meaning yellow) in 1900 by Thiele (67), and though their properties were found to be remarkable in a number of ways, only a few of the simple fulvenes were reported in the succeeding fifty-two years. The research that has been done on the fulvenes has usually been inci-

dental to other objectives, and some of it has been quite casual, so that the properties and reactions of the fulvenes have not been completely characterized, except with respect to the Diels-Alder reaction. The data that do appear in the literature are often in disagreement. The fulvenes have an important place in the theory of color, being among the first colored hydrocarbons known. They also pose a special problem in quantum-mechanical calculations, since for the fulvenes the valence bond and molecular orbital methods give quite different results. The great potential of these compounds in the field of polymerization has been virtually neglected.

This review, the first to be prepared on the fulvenes, was written in the hope of calling attention to the fertile field open for research.

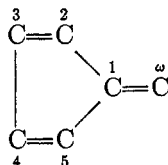
This paper deals only with the simple fulvenes, which may be considered derivatives of cyclopentadiene. It excludes the benzofulvenes and the dibenzofulvenes, which are analogous compounds derived from indene and fluorene, respectively; other systems in which a ring is fused to the fulvene ring, such as dibiphenyleneethylene, pentalene, and the azulenes; the heptafulvenes, which have a seven-membered ring in place of the five-membered ring; the "open" fulvenes, in which there is no bond between the No. 2 and No. 3 carbon atoms; and the fulvalenes. The literature has been covered to June, 1952.

According to latest usage, and to *Chemical Abstracts*, the fulvene system is numbered as shown:



The fulvenes are named simply by naming and numbering substituents to this structure, in the usual fashion. The practice has been not to number substituents on the No. 6 carbon atom unless there are substituents on the ring. For example, the compound 6,6-dimethylfulvene is usually called simply dimethylfulvene.

Some care must be exercised in reading the literature, because the above ring-numbering system is not always used. Articles appearing in German usually use the Beilstein numbering, which is as follows:



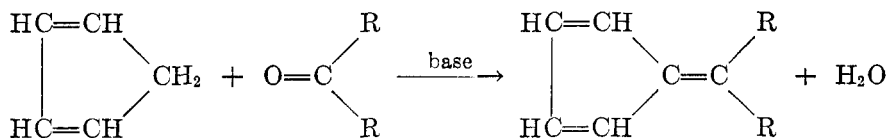
Others have found it convenient to name fulvenes as derivatives of cyclopentadiene; e.g., to refer to dimethylfulvene as isopropylidencyclopentadiene.

In this review the *Chemical Abstracts* nomenclature has been used.

II. SYNTHESSES OF FULVENES

A. By condensation of cyclopentadiene with carbonyl compounds

The fulvenes are most simply prepared by condensing monomeric cyclopentadiene with a ketone or aromatic aldehyde in the presence of a small amount of a base (67, 68, 71).



The reaction takes place rapidly and is evidenced by the appearance of the yellow-to-red color of the fulvene. The lower-molecular-weight fulvenes which are oils are usually separated by steam distillation, followed by extraction with ether and final vacuum distillation. The solid fulvenes may usually be extracted with ligroin or petroleum ether and recrystallized.

The effect of concentration and kinds of condensing agents for the preparation of dimethylfulvene has been studied (22). As little as 5 g. of sodium in 100 ml. of ethyl alcohol, or 100 ml. of 10 per cent potassium hydroxide, for a 5-mole run gave yields of 30–60 per cent, which are the same as the yields obtained when a much larger amount of alkali is used. Sodium hydroxide in alcohol also proved effective. Best results were obtained with 100 ml. of 20 per cent potassium hydroxide in ethyl alcohol for a 5-mole run. When equivalent amounts of cyclopentadiene and acetone and an equal volume of 28 per cent aqueous ammonia were employed, the yields ranged from 25 to 38 per cent. The use of alcoholic ammonia raised the yields to 50–72 per cent, but also resulted in the presence of some amine impurities.

The preparation of basic fulvenes is readily accomplished by condensing aminoketones with cyclopentadiene, using 3 per cent sodium ethoxide (59).

There are a number of limitations to the usefulness of this general reaction. Aliphatic aldehydes condense with cyclopentadiene, but the products resinify too quickly to be isolated (18, 35, 67, 68). The reaction between cyclopentadiene and formaldehyde leads quickly to a yellow oil, which in a matter of minutes turns orange, then dark red, and finally black. The preparation of methylfulvene, ethylfulvene, and methyl(dimethylvinyl)fulvene has been reported (28, 58), but these compounds were not isolated, since oxygen was immediately added for the purpose of studying the oxygen addition products.

Side reactions include the formation of a fulvene dimer (1) in some cases, and the condensation of a second or third molecule of aldehyde with the fulvene formed (see the section on reactions).

Difficulty is frequently encountered in purifying the fulvene prepared, since the fulvenes in general resinify quite easily and tend to absorb oxygen from the air.

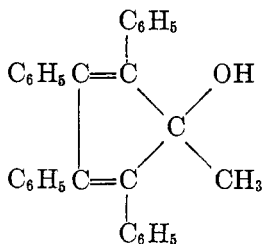
The tri- and tetraphenylcyclopentadienes condense in alkaline solution with aliphatic aldehydes, but do not condense with ketones (26).

The use of a polycarbonyl compound leads to a molecule having more than one fulvene grouping. For example, diacetylbenzene may be condensed with cyclopentadiene to yield a symmetrical difulvene (69).

B. By use of the Grignard reagent

Cyclopentadiene readily reacts with Grignard reagents, RMgX , to yield the corresponding hydrocarbon and a cyclopentadienylmagnesium halide. The new Grignard reagent may be treated in the cold with a ketone to yield a mixture of the fulvene and the corresponding fulvanol, which can be dehydrated to the fulvene (17, 19, 20, 32). This method of preparation gives products which are somewhat easier to purify than does Thiele's method, but the yields are considerably lower. In this method again, aliphatic aldehydes yield no pure product or only resins.

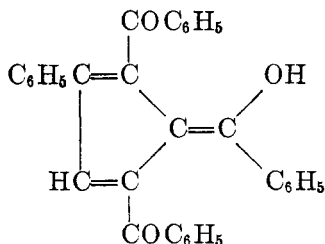
A similar method may be used for the preparation of highly arylated fulvenes (26, 42). Tetracyclone (2,3,4,5-tetraphenylcyclopentadienone) reacts with a Grignard reagent to form an alcohol of the type shown



which can be dehydrated to form the corresponding fulvene. Dehydrating agents which have been used include dry hydrogen chloride in glacial acetic acid, phosphorus pentoxide in absolute benzene, molten potassium bisulfate, and concentrated sulfuric acid in glacial acetic acid. Pyrolysis of the alcohol also yields the fulvene as one of the products (5).

C. Other reactions yielding fulvenes

(1) 1,2-Diaroylethylenes may be condensed in the presence of sodium ethoxide to form 1,4-diaroyl-2,6-diaryl-6-hydroxyfulvenes in moderate to low yield; also formed are benzoic acids and tar. The 1,2-diaroylethanes undergo the same reaction, but less well (31). For example, *trans*-1,2-dibenzoylethylene in dry benzene developed an immediate red color on the addition of sodium ethoxide. After standing 9 hr., a 31 per cent yield of 1,4-dibenzoyl-6-hydroxy-2,6-diphenylfulvene was obtained. These fulvenes are stable to alkali, are decomposed by acids, and are resistant to attack by atmospheric oxygen and by bromine.



1,4-Dibenzoyl-6-hydroxy-2,6-diphenylfulvene

(2) Triphenylcyclopentadiene and tetraphenylcyclopentadiene can be condensed with molten dichlorodiphenylmethane to yield 1,3,4,6,6-pentaphenylfulvene and 1,2,3,4,6,6-hexaphenylfulvene, respectively (26).

(3) When hexachloropropene is treated with aluminum containing small amounts of copper, silicon, zinc, iron, manganese, and magnesium, with or without the presence of aluminum chloride, in diethyl ether at its boiling point, one of the products is hexachlorofulvene. Hexachlorofulvene reacts with aniline to split out hydrogen chloride, yielding a product in which two chlorine atoms have been replaced by phenylamino groups (52).

The hexachlorofulvene was separated by adsorption on activated carbon in a chromatograph column, using diethyl ether as the eluting agent (52).

(4) Toluene circulated over ammonium chromomolybdate catalyst at 475°C. yielded some dimethylfulvene as a secondary product. The concentration of the fulvene was proportional to the concentration of the aromatic compounds formed (34).

Butadiene on pyrolysis at 838°C. gave a mixture of sixteen products, including some dimethylfulvene (43).

When ethylene was passed over compacted carbon at 700°C., a fulvene or fulvene derivative was one of the many products formed (64).

(5) The formation of phenylfulvene from cyclopentadiene by condensation with benzaldehyde can be used to determine quantitatively the amount of cyclopentadiene monomer and dimer in hydrocarbon mixtures. The fulvene is estimated spectrophotometrically (70). The method has been extended to allow analysis of cyclopentadiene and methylcyclopentadiene monomers and dimers in hydrocarbon mixtures. The methylcyclopentadiene reacts more slowly than does cyclopentadiene with acetone and with benzaldehyde. By adding acetone and allowing the mixture to react for 15 min., and in another vessel adding benzaldehyde and allowing this mixture to react for 20 min., at 32°C., the amounts of cyclopentadiene and methylcyclopentadiene can be calculated from the optical densities of the fulvene solutions formed, using a wave length of 4250 Å. The specific extinction coefficient for each solution is calculated, and the concentrations of the fulvenes formed can be calculated by the usual method. Both time and temperature must be carefully controlled (27, 45).

III. REACTIONS OF FULVENES

A. *The Diels-Alder reaction (see table 1)*

The fulvenes may act as the diene or as the dienophile in the Diels-Alder reaction.

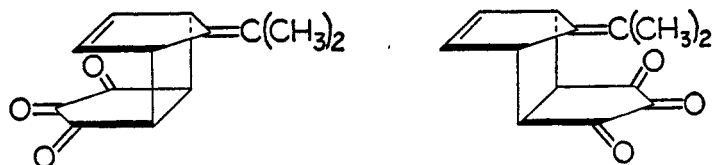
Maleic anhydride adds easily to dimethylfulvene at room temperature, and with brief refluxing adds to diphenylfulvene and styrylfulvene (25). The addition is at the 1,4-positions of the fulvene.

The diene synthesis usually results in only one of the possible stereoisomers, the *cis*-isomer. The situation is different with regard to the fulvenes (3). When

TABLE 1
Melting points of Diels-Alder adducts of some fulvenes

FULVENE	ADDENDUM	MELTING POINT °C.	REFERENCES	
Dimethylfulvene.....	Maleic anhydride	137	(2, 25, 41)	
		112 (endo)	(2)	
Pentamethylenefulvene..	Maleic anhydride	93-93.5 (exo)	(77a)	
		96 (exo)	(2)	
		132 (endo)	(41, 77a)	
		About 148 (endo)	(2)	
Styrylfulvene.....	Maleic anhydride	137-138	(25)	
Diphenylfulvene.....	Maleic anhydride	168	(25, 41)	
		147-148 (exo)	(1)	
		174 (endo)	(1)	
		Dimethyl maleate	147	(1)
		Fumaryl chloride	115-116	(1)
		Dimethyl acetylenedicarboxylate	139	(1)
		Acrylic acid	170 (endo)	(1)
		Acrylonitrile	137 (endo)	(1)
		Methyl vinyl ketone	88	(1)
		Phenyl vinyl ketone	115-117	(1)
		Fumaronitrile	142-142.5	(14)
		Maleonitrile	172-173	(14)
		Acetylenedicarbonitrile	168-169	(14)
		Butadiene (2 moles)	156-158	(1)

the addition was carried out in benzene at 50-60°C., dimethylfulvene and pentamethylenefulvene yielded about 40 per cent of the endo-isomer and 60 per cent of the exo-isomer. Diphenylfulvene yielded only the exo-isomer.



The endo-adduct

The exo-adduct

Maleic anhydride adducts of dimethylfulvene

Further investigation of the diene reaction with diphenylfulvene (1) showed that the endo-adduct was formed with maleic anhydride when the reaction was carried out in cold benzene or boiling ether, while in boiling xylene the exo-adduct was the principal product. Dimethyl maleate added to form the dimethyl ester of the endo-adduct. Fumaryl chloride in ether formed the *trans*-diacid chloride. Dimethyl acetylenedicarboxylate added to diphenylfulvene to form a solid melting at 139°C. Acrylic acid on standing with diphenylfulvene for 2-3 months formed 40 per cent of the endo-adduct and an oily mixture of isomers which could not be purified. Acrylonitrile and diphenylfulvene, left to stand at room temperature for several months, gave an 80-90 per cent yield of an endo-adduct and small amounts of an oily isomer. This same reaction carried out on a steam bath for 3 days gave a 20-30 per cent yield of the endo-adduct and more of the oily isomer. Methyl vinyl ketone added to give a solid adduct. Vinyl phenyl ketone added to give a solid adduct which decomposed on attempted purification.

When diphenylfulvene was heated with butadiene in dioxane for 18 hr. at 170-180°C., the fulvene acted as the dieneophile, yielding a fluorene derivative as a product.

Alder and Trimborn (4) have further studied the effect of temperature on the stereoisomerism of the diphenylfulvene adduct with dimethyl acetylenedicarboxylate, and its dissociation in solution.

Alder and Ruhmann (2) studied the addition of maleic anhydride to dimethylfulvene and to pentamethylenefulvene. Both endo- and exo-adducts were formed in each case, the relative amounts depending somewhat on conditions, higher temperatures favoring the exo-adduct.

Woodward and Baer (77a) earlier obtained similar results for the addition of maleic anhydride to pentamethylenefulvene. They further found that the endo-adduct slowly dissociates in the cold in ethyl acetate or benzene solution to give the fulvene and maleic anhydride, while the exo-adduct is stable even in boiling benzene.

The pentamethylenefulvene, styrylfulvene, and dimethylfulvene adducts with maleic anhydride are dissociated in solution at all temperatures (41). The adduct with diphenylfulvene dissociates in solution much more slowly. These adducts can not be stabilized by conversion to the corresponding acids, because they dissociate faster than they are hydrolyzed.

The fulvene made from cyclopentadiene and β -ionone reacted with maleic anhydride to give a very dark red solution, but yielded no crystalline compound (40). The same result was obtained when quinone was used in place of maleic anhydride.

Diphenylfulvene readily forms adducts with fumaronitrile, maleonitrile, and acetylenedicarbonitrile (14).

B. Hydrogenation

The hydrogenation of fulvenes has been studied in some detail. They are hydrogenated in the presence of platinum or palladium in ethyl alcohol or acetic acid in the cold and at ordinary pressure; or with nickel on pumice under pres-

sure at 100–120°C. (37). Dimethylfulvene, ethylmethylfulvene, and diethylfulvene gave saturated hydrocarbons in less than 50 per cent yield. There is no sharp difference in the rate of addition at the three double bonds. With diphenylfulvene the first two moles of hydrogen are taken on rapidly, but the third mole very slowly; with platinum or palladium the first mole of hydrogen adds most rapidly. In acetic acid solution there are no steps at all in the addition, the hydrogen merely adding more and more slowly, with the color of the fulvene persisting well past the addition of one mole of hydrogen.

The color of the fulvene persists after the addition of one mole of hydrogen to diphenylfulvene when the solvent is alcohol, diethyl ether, or cyclohexane (38). The product is a complex mixture, with unreacted fulvene as the main product. The third mole of hydrogen adds notably more slowly than the first two. The rate and products vary somewhat with the solvent and with the catalyst. Similar hydrogenation of dimethylfulvene yields comparable results (39). The addition of two moles of hydrogen yields a mixture of products.

Isopropylmethylfulvene is hydrogenated over platinum black in ethyl alcohol or with Raney nickel under 105 atm. pressure (36). There is no sharp break in the hydrogenation rate curve that would indicate consecutive hydrogenation of the three double bonds.

Hydrogenation of dimethylfulvene proceeds better in inert hydrocarbon solvents at higher temperatures (120–130°C.) at 30 atm. pressure over nickel. Less satisfactory is platinum oxide in ethyl alcohol at room temperature (22). The former conditions gave 38–55 per cent yields of isopropylcyclopentane, together with higher-boiling material, apparently a saturated polymer. Different temperatures and pressures had little effect on the results.

The fulvenes containing a phenyl group on the No. 6 carbon are reduced by aluminum amalgam, while dimethylfulvene is not (67). Dipropylfulvene is reduced to 4-cyclopentylheptane by sodium in ethyl alcohol (36).

The hydrogenation of methylpropylfulvene over nickel at 300°C. and 100 atm. pressure is complicated by isomerization and side reactions (33). Using copper-asbestos catalyst the reaction goes more smoothly, yielding chiefly 2-cyclopentylpentane.

The fulvenes made by condensing cyclopentadiene with β -ionone, α -ionone, and pseudoionone all add two moles of hydrogen rapidly and a third mole slowly (40).

Hydrogen and hydrogen halides add to those fulvenes which have three or four phenyl groups, but do not add to the fulvenes which have five or six phenyl groups (26).

C. Addition of halogens (see table 2)

Thiele and Balhorn (67) noted that the bromides of the fulvenes were easily made but could seldom be obtained pure enough for analysis. With diphenylfulvene, both a dibromide and a tetrabromide were isolated.

Dilthey and Huchtemann reported that the fulvenes add four atoms of chlorine, or two atoms of bromine, and do not add iodine at all. The first two atoms of chlorine, or the two atoms of bromine, add to the exo double bond;

in the case of the chlorine, the second pair is believed to add at the 1,4-positions. Chlorine adds in a matter of seconds, bromine in several hours. These colorless-to-yellow addition compounds on melting give up the halogen and regenerate the original fulvene.

Rather different results were reported by Bergmann and Christiani (9), who stated that diphenylfulvene reacts with excess bromine in chloroform solution to give a moderate yield of a tetrabromo derivative, bright blue in color. Their analysis showed a tetrabromo substitution product, rather than an addition product. They believed that no bromine adds to the exo double bond, by analogy with the results obtained by Staudinger (61) with the "open" fulvenes. Their argument that the characteristic No. 5 carbon of the fulvenes should have but little residual valence was borne out by later quantum-mechanical calculations.

TABLE 2
Halogen reaction products of some fulvenes

COMPOUND	COLOR	MELTING POINT	REFERENCE
		°C.	
Diphenylfulvene dibromide (addition product)	Light yellow tablets	102-102.5	(67)
Diphenylfulvene tetrabromide (addition product)	Yellowish tablets	123	(67)
Diphenylfulvene tetrabromide (substitution product)	Bright blue	190-191	(9)
1,2,3,4-Tetraphenylfulvene dibromide (addition product)	Lemon to brown	147-148	(26)
1,2,3,4-Tetraphenylfulvene tetrachloride (addition product)	Colorless	149	(26)

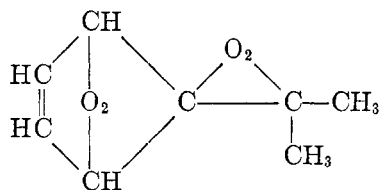
1,2,3,4,6,6-Hexachlorofulvene will add two atoms of bromine, or will add two or four atoms of chlorine. But when this fulvene is heated with bromine at 250-300°C. it gives an almost quantitative yield of hexachlorobenzene (52).

D. Addition of oxygen

The lower-molecular-weight fulvenes all react with atmospheric oxygen more or less rapidly to form solid products. The nature and extent of this oxygen absorption have received the attention of few investigators.

A benzene solution of dimethylfulvene shaken for 24 hr. turns cloudy, and at the end of 4-6 days gives a white granular precipitate of the diperoxide in good yield (28, 29). Both light and heat affect the rate of the reaction. The reaction in daylight is about twice as fast as in the dark. At higher temperatures, such as in boiling benzene, the product is not the insoluble and explosive diperoxide, but secondary products which are formed by the decomposition of the diperoxide above about 50°C. The reaction of dimethylfulvene with oxygen of the air yields the diperoxide, which explodes at 130°C., some polymer, and some unchanged fulvene. Ethylmethylfulvene absorbs oxygen at a slower rate, and methylphenyl-

fulvene very much more slowly. The structure of the diperoxide was believed to be as follows:

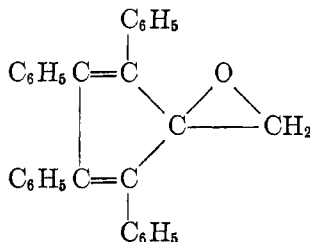


Dimethylfulvene diperoxide

Since cyclopentadiene adds only one mole of oxygen, the second mole absorbed by a fulvene may be attached to the exo double bond. The diperoxide can lose two atoms of oxygen, one from each peroxide group, spontaneously at room temperature and more rapidly when heated, to form the dioxide, which quickly polymerizes.

The fulvene made by condensing cyclopentadiene with α -ionone absorbs oxygen rapidly from the air (40). Pentamethylenefulvene in carbon tetrachloride absorbs oxygen to yield an amorphous peroxide (41).

1,2,3,4-Tetraphenylfulvene takes on only one atom of oxygen per molecule and becomes colorless and crystalline (26). This compound is definitely not the tautomeric aldehyde, and gives up its oxygen to regenerate the original fulvene when reduced with a Grignard reagent. The following formula is suggested:



The deep red 1,2,3,4,5,6-pentaphenylfulvene and the dark brown hexaphenylfulvene absorb oxygen in solution to become pale yellow oxy compounds. The tetraphenylfulvene oxide can also be made by oxidizing the fulvene with 3 per cent hydrogen peroxide in dioxane, alcohol, or acetone in the presence of potassium hydroxide.

1,2,3,4-Tetraphenylfulvene and 1,2,3,4,6-pentaphenylfulvene are effective in inhibiting the autoxidation of benzaldehyde. When the fulvene color has disappeared, the effectiveness of the fulvene has gone. The product from the fulvene is a resin, not a ketone (76).

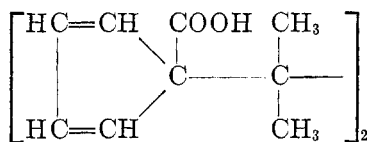
The fulvene from β -ionone and cyclopentadiene is oxidized by ozone to yield geronic acid (40).

E. Reaction with alkali metals and with phenyllithium

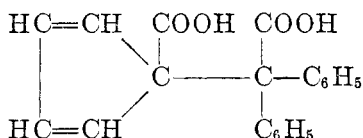
Alkali metals add to fulvenes, on the No. 5 carbon atom or on both the No. 5 and the No. 6 carbon atoms. The fulvene-sodium addition compounds then react further to yield the fulvene dimer, which contains two atoms of sodium.

The possible mechanism of this reaction has been studied in detail (54, 55, 56, 71, 77b).

Dimethylfulvene treated with sodium in ether yields a red precipitate which reacts with ethyl alcohol and carbon dioxide to give the following compound (56):

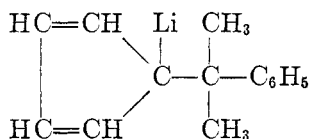


Diphenylfulvene treated with sodium in ether rapidly gives a clear red solution which is decomposed by ethyl alcohol to yield 3-benzohydrilcyclopentadiene, or by carbon dioxide to yield the acid.



Dimethylfulvene reacts with triphenylmethylsodium in ether to give triphenylmethane. Decomposition of the reaction products regenerates the original fulvene.

Dimethylfulvene adds phenyllithium to form a product believed to have the following structure (79):



This compound turns brown in air, and on hydrolysis yields a resin. Diphenylfulvene also adds phenyllithium; this result is remarkable, in that this addition is very slow, when it takes place at all, with other unsaturated hydrocarbons. This reactivity of the fulvenes resembles the behavior of the carbonyl double bond.

F. Polymerization

Diphenylfulvene when heated for 5 hr. at 140°C. in a bomb gives a yellow crystalline polymer which melts above 200°C. (1). In preparing large amounts of diphenylfulvene, there is also obtained a by-product dimer, which is yellow and crystalline and which on hydrogenation gives tetrahydrobisdiphenylfulvene.

Pure dimethylfulvene, kept in a well-sealed and filled container, gives after 5 or 6 months bisdimethylfulvene, which when heated above the melting point regenerates dimethylfulvene. Light has no apparent effect on this reaction. Bisdimethylfulvene does not absorb oxygen from the air (67).

p-Bis(dimethylfulvenyl)benzene can be polymerized to a clear red resin melting above 200°C. This fulvene copolymerizes with acrylonitrile when heated, to yield a copolymer which is a liquid or a solid, depending on conditions and proportions. The polymerization times used were 24–168 hr. at 25–127°C. (68). The copolymer of the above-mentioned fulvene with styrene was either liquid

or solid, depending on the conditions of polymerization. A similar copolymer was formed with diallyl maleate. A petroleum ether solution of the above polymers used to impregnate wood flour molded at 5000 p.s.i. at a temperature of 130–160°C. gave strong hard discs. Methylphenylfulvene was found to copolymerize with the monomers of methyl acrylate, styrene, acrylonitrile, vinyl acetate, and polyolefinic hydrocarbons from gasoline sludge. The latter polymerization was begun at 25°C. and raised to 125°C. over a period of 36 days, using 0.5 per cent by weight of benzoyl peroxide as a catalyst. Emulsion polymerization also may be used.

Unpublished work by the author, which is continuing, shows that simple fulvenes may be made into hard resins by treatment with peroxides, with metal chlorides such as aluminum chloride, and with sulfuric or phosphomolybdic acid.

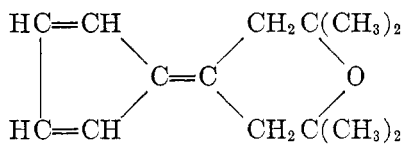
G. Color reactions with metal halides

The fulvenes develop new colors when treated with antimony trichloride. A 1 per cent solution of dimethylfulvene in chloroform when treated with dilute antimony trichloride gives a brown color which changes to red to deep violet. Only resinous products could be obtained (30). With ferric chloride a deep red color is generated. There is a dissociation equilibrium between the reactants and products which prevents isolation of the colored products.

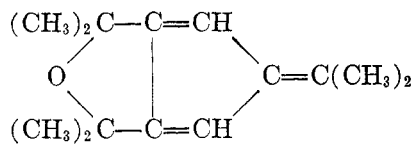
The fulvenes made from cyclopentadiene and α -ionone, β -ionone, or pseudoionone give a blue to blue-green solution when treated with antimony trichloride (40, 74).

H. Other reactions of the fulvenes

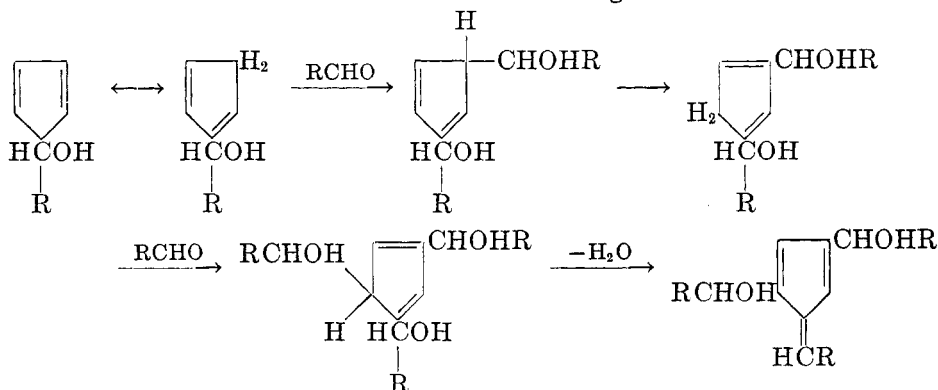
Cyclopentadiene can condense with one, two, or three moles of some aldehydes; hence dimethylfulvene will condense easily with a second mole of acetone



Structure suggested by Thiele



Structure suggested by Ziegler and Crossman



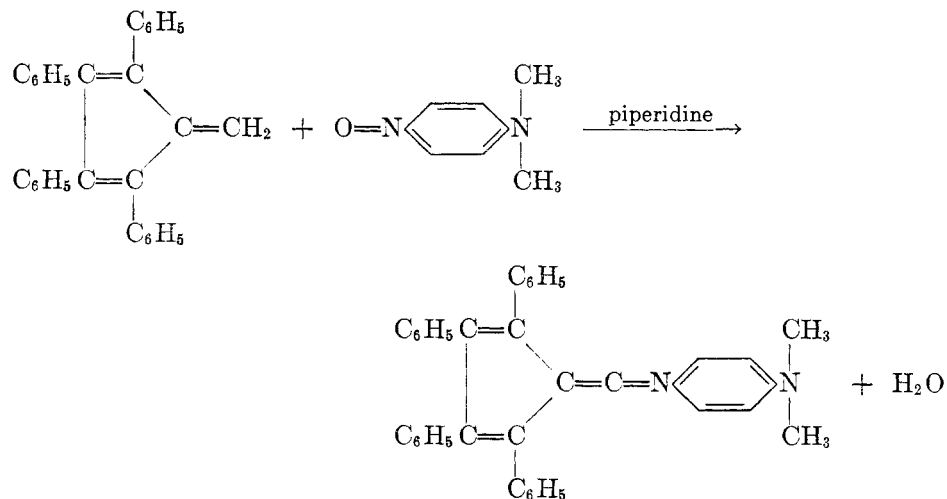
The mechanism according to Courtot

and also with a third (19, 67, 78). While several suggestions have been made as to the structure of the product, the most likely mechanism is that of Courtot. The suggested structures are listed on page 178.

Not all aldehydes will condense to the same extent; only two moles of anisaldehyde add to a mole of cyclopentadiene, and the proportions of mono- and dicondensation products are sensitive to concentrations and temperature. Their separation is difficult. Only one mole of cinnamaldehyde will condense with one mole of cyclopentadiene.

Ziegler and Crossman (78) found that anisaldehyde condenses readily with dimethylfulvene to give red crystals melting at 122°C.

The fulvenes which are unsubstituted on the No. 6 carbon atom condense easily with oxygen-containing groups, especially with nitroso compounds, in the presence of piperidine. Aldehydes and acid chlorides do not so add (26). For example:



The product is an intense black-violet in color and is very stable.¹

Pentamethylenefulvene on standing polymerizes to the dimer and yields the monomer on vacuum distillation (41).

The fulvenes do not rearrange to the isomeric benzene derivatives over alumina at 250°C. (8, 26).

One method of determining the amount of unsaturation of an oil sample is to shake it with a methanol solution of mercuric acetate. The unsaturated compounds react to form mercury compounds and acetic acid, which is determined by titration. Ethylmethylfulvene and diethylfulvene both react with mercuric acetate in this fashion (65).

The polyphenylfulvenes were found to have little or no carcinogenic activity (26).

¹Becker and coworkers (private communication) have shown that the condensation product of 1,2,3,4-tetraphenylfulvene with *p*-nitrosodimethylaniline is in reality the dimethylamino-anil of tetracyclone.

In general, the addition compounds of fulvenes with dienophiles, oxygen, and halogens tend to decompose at the melting or distillation temperature to regenerate the original fulvene, at least in part.

I. Polarography (see table 3)

A study of the reduction of fulvenes at the dropping mercury electrode shows that two electrons are involved in the first reduction wave (71). From this result it has been concluded that these fulvenes dimerize in the presence of sodium according to a mechanism suggested by Ziegler, Colonius, and Schafer (77b), with two atoms of sodium adding to the exo double bond, the addition compound then reacting with a second mole of olefin.

TABLE 3

Polarographic data for some fulvenes

Half-wave potentials and diffusion current constants in a 0.175 *M* solution of tetrabutylammonium iodide in 75% dioxane

COMPOUND	$\Pi_{1/2}$ vs. S.C.E.	i_d	<i>C</i>	$i_d/Cm^{3/2}t^{1/2}$
	volts	microamperes	millimoles/ liter	
Dimethylfulvene.....	-1.89	5.78	1.50	4.81
	-1.85*	3.82	0.97	4.92
Diphenylfulvene.....	-1.57	3.72	1.00	4.65

* In 0.175 *M* tetrabutylammonium iodide, 0.052 *M* tetrabutylammonium hydroxide, 75 per cent dioxane.

IV. PHYSICAL PROPERTIES OF FULVENES

A. Color

All of the fulvenes are deeply colored. Fulvene itself is bright yellow, and dimethylfulvene is yellow to yellow-orange; the color grows progressively darker with increasing molecular weight, phenylfulvene being red and diphenylfulvene intense red. The substitution of a phenyl group directly onto the ring is less effective in deepening the color than a phenyl group on the No. 6 carbon atom. The highly arylated fulvenes are darker still, hexaphenylfulvene being glittering black.

The color of the fulvenes is due to "crossed-conjugation," since the aromatic isomers themselves are colorless. The cyclic ring is not necessary to the color, since even the "open" fulvenes are yellow to gold in color (61), although the fulvenes are much deeper in color than the corresponding "open" fulvenes. A number of investigators have examined the problem of the color of fulvenes (21, 26, 64, 66). Quantum-mechanical calculations of the spectra of the fulvenes have been made with considerable success.

B. Ultraviolet spectra

The ultraviolet spectra of some of the fulvenes have been measured (11, 23, 60). The fulvene structure is characterized by a strong absorption band at about

2700 Å. and a weaker band at about 3640 Å. The spectra of the simplest dialkylfulvenes are virtually identical.

Stark and Steubing report a not accurately located band in the short ultraviolet below 2300 Å., since light of such wave length excites in dimethylfulvene a blue-green fluorescence, which suggests a band in the region 1900–2030 Å. coupled with the band at 3640 Å. Interestingly enough, certain quantum-mechanical calculations predict a band in the 2300 Å. region (62). In the spectra of a series of fulvenes the absorption peaks progress toward the red with increasing molecular weight, and in diphenylfulvene an absorption peak becomes evident at 2480 Å. It has been suggested that this new peak may be the third, shortest-wave-length peak, brought into the range of ordinary ultraviolet spectrophotometry by the bathochromic effect, though it has also been attributed to the phenyl group (11).

The conjugation of the fulvene group at the 6-position with one phenyl group shifts the 2700 Å. band to about 300 Å. towards the red, and the presence of a second phenyl group shifts this band about 250 Å. farther, to 3280 Å. The effect of the added phenyl groups is not so marked when the phenyl groups are added onto the ring. For example, 2,3,4,5-tetraphenylfulvene has bands at 3330 Å. and 2500 Å.

Calculations of the spectrum of fulvene made by Sklar (59) predict a band at 3645 Å. as compared with experimental data for dimethylfulvene of 3650 Å.; calculation of the position of the other band leads to a result 600 Å. too low. Further calculations for fulvene by Sverdlov and Kovner (62) predict three bands, at 2300, 2700, and 3650 Å.; and calculations by Platt (44) predict bands at 2700, 3550, and 5400 Å.

1, 2, 3, 4, 6, 6-Hexachlorofulvene in benzene solution has an absorption maximum at 450 $m\mu$, the absorption falling slowly to near zero at 650. In hexane solution this fulvene has maxima at about 300 and 480 $m\mu$, with a minimum at about 350 (52).

C. Dipole moments

The dipole moment of fulvene has been calculated by the molecular orbital method by several investigators (6, 48, 53, 73). The particular value calculated depends on certain approximations in the calculation, but the most recent values are in good accord with experimental data obtained for the fulvenes listed in table 4.

In summation, it has been established that the fulvenes have a dipole moment of consequence, which has not been explained non-mathematically, in terms of resonating structures or otherwise. The ring part of a fulvene is negative, and the No. 6 carbon atom is quite positive.

D. Molar refraction

The molar refraction of some fulvenes has been calculated (table 5) and the values compared with experimental values. The fulvenes show a strong exaltation, amounting to 2 cc. or more (10, 33, 73, 75). The calculated values are arrived at in the usual way, by adding atom and bond refractivities.

The refraction and degree of exaltation vary with the wave length of the light used. For example, for methylpropylfulvene at wave lengths of 7065 Å. and 5875 Å. the molar refractions were 46.713 and 47.503, and the exaltations 2.44 cc. and 2.72 cc., respectively.

TABLE 4
The dipole moments of some fulvenes

COMPOUND	DIPOLE MOMENT		REFERENCE
	Experimental	Calculated	
	Debyes	Debyes	
Fulvene.....		1.2 4.7 1.1-4.7	(73) (53) (48)
Dimethylfulvene.....	1.44 ± 0.03		(73)
Diethylfulvene.....	1.44 ± 0.03		(73)
Isobutylmethylfulvene.....	1.43 ± 0.03		(10)
Diphenylfulvene.....	1.34 ± 0.04		(73)
	1.40 ± 0.03		(10)
6,6-Bis(<i>p</i> -chlorophenyl)fulvene.....	0.68 ± 0.1		(73)

TABLE 5
Molar refractions of some fulvenes for the sodium D line

COMPOUND	MOLAR REFRACTION		EXALTATION	REFER- ENCE
	Observed	Calculated		
	cc.	cc.		
Dimethylfulvene.....	38.20	35.54	2.66	(75)
Ethylmethylfulvene.....	42.75	40.16	2.59	(75)
	42.76	40.16	2.60	(7)
Methylpropylfulvene.....	47.493	44.779	2.714	(33)
Diethylfulvene.....	47.01	44.78	2.23	(7)
Isobutylmethylfulvene.....	51.01		1.6*	(13)
	51.3	51.5	0.2	(10)
Diphenylfulvene.....	77.2	71.2	6.0	(10)

* This calculation is different from the others in this table. The exaltation was calculated directly, from quantum-mechanical considerations, using the equation $E = \Delta R - \Delta R_0$, where $R = 1.80 \times 10^{10} \sum (f_{n \rightarrow v_j} / v_{n \rightarrow v_i}^2 - v^2)$, and $R_0 = m \Delta R_{C=C, f_{n \rightarrow v_i}}$ is the oscillator strength for a bond whose maximum is at v_j . v is the frequency at which the refraction is calculated, m is the number of double bonds, and $R_{C=C}$ is the value for an isolated double bond, taken as 1.8.

The molar polarization at infinite dilution has been found to be 95.1 cc. for methylisobutylfulvene and 120 cc. for diphenylfulvene, from data on dielectric constants measured by the heterodyne beat method (10).

E. Theoretical considerations

Fulvene has received unusual attention from those interested in calculating resonance energy, free valence, bond orders, and the like from quantum-me-

chanical considerations (6, 12, 15, 16, 24, 46, 47, 48, 49, 50, 51a, 53, 59, 72, 73). The special interest has lain in the fact that the method of molecular orbitals and the method of valence bonds give quite different values for fulvene, although these two methods generally agree for most common conjugated and aromatic systems.

This is not the place to discuss the various considerations that affect the two kinds of calculations. Because of the discrepancy in the results of the two methods, and the various values given by the molecular orbital method depending on the particular approximations used, it should be possible to distinguish between the reliability of the methods by an appeal to experiment. Unfortunately at the moment no data are available for fulvene itself, although some results are available for a number of fulvene derivatives.

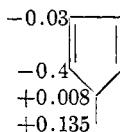
Some results of molecular orbital calculations are given below. The particular cases chosen are given for the sake of illustration only and must be read as selected examples rather than as finally definitive results.

Distribution of electronic charge

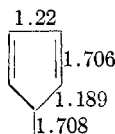
1. In terms of total π -electrons (48):



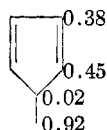
2. In terms of excess or defect of charge (net residual charge) (73):



Bond orders (73)



Free valence (16)



By comparison, the bond order in benzene is 1.67 and the free valence is 0.398. The total bond order indicates the degree of bonding; a bond order of 2 would represent a full double bond.

The "free valence" is defined as $F.V. = N - N_1$, where N is a constant taken as 4.698 (16), or more recently as 4.732 (51b), and N_1 is the sum of the indices of the corresponding sigma bonds. The sigma indices are taken as unity, and one obtains N_1 by adding 3 to the sum of the indices of the bonds about atom No. 1. The free valence should be a quantitative measure of the reactivity of the atom; it is a measure of the unsaturation of the atom.

TABLE 6
Physical properties of the fulvenes

COMPOUND	BOILING POINT °C.	COLOR	REFRACTIVE INDEX	DENSITY	ABSORPTION MAXIMA	REFERENCES
Fulvene.....	74/26 mm.	Yellow oil	$n_D = 1.5391$	0.8858	265, 357	(18, 67)
Methylfulvene.....	46/11 mm.	Yellow oil	$n_D = 1.5474$	0.881	270, 365	(28, 57)
Ethylfulvene.....	47/11 mm.	Yellow oil	1.5338			(28, 57)
Dimethylfulvene.....	45-47/12 mm.					(19, 22, 23, 32, 37,
	49-50/11 mm.					66, 67, 75)
	66-68/25 mm.					
	153-154/717 mm.					
	156-158/760 mm.					
	M. p., about 4					
	M. p., -13					
Ethylmethylfulvene.....	27-29/0.1 mm.	Orange-yel- low oil	$n_D = 1.5303$	0.878	268, 355	(7, 23, 29, 37, 67,
	62.5/13 mm.		1.5299	0.8772		75)
	62-65/13 mm.		$n_D = 1.5586$			
	67-70/25 mm.		1.5375			
	87.4-87.9/40 mm.		$n_D = 1.5370$			
	165-166/760 mm.		1.5374			
	185/760 mm.		1.5423			
Methylpropylfulvene.....	61-63/9 mm.	Orange	1.52-3	0.87518	270, 353	(10, 23, 33)
	177-178/760 mm.		1.5245			
Diethylfulvene.....	74.5-78.5/19 mm.	Orange	$n_D = 1.5234$	0.8812		(7, 37, 67)
	74-79/19 mm.		1.5218	0.878		
	96.8-97.2/40 mm.		$n_D = 1.5300$			
			1.5284			
Isopropylmethylfulvene.....	67-68/10 mm.	Orange	$n_D = 1.5325$		271, 354	(23, 36)
	181-182/760 mm.		1.5292			

COMPOUND	MELTING POINT °C.	COLOR	REFRACTIVE INDEX	ABSORPTION MAXIMA	REFERENCES
Isobutylmethylfulvene.....	98-100/22 mm.	Yellow-orange		270, 364	(10)
Amylmethylfulvene.....	213-214/760 mm.	Orange	1.5166	271, 360	(23)
Dipropylfulvene.....	92-93/10 mm.	Orange	1.5210	(36)	(28, 57)
Methyl(2-methyl-1-propenyl)fulvene.....	55-57/2 mm.	Orange	1.5472	270, 355	(23, 41)
6,6-Cyclotetramethylenefulvene.....	80-82/25 mm.	Yellow	1.5474	272, 352	(23, 41, 69)
6,6-Cyclopentamethylenefulvene.....	78-80/25 mm.	Bright yellow			
α-Furanylfulvene (furfurylidencyclopentadiene).....	80-83/25 mm.	low			
	70-72	Orange	1.5845	280, 345	(23)
Phenylfulvene.....	About 31	Deep red leaflets	1.5541	300	(23, 66, 69)
Methylphenylfulvene.....	3-5	Color of chromic acid	1.5596	302	(23, 66, 68)
Diphenylfulvene.....	B.p., 130.5/10 mm. B.p., 147-151/25 mm. 80-80.5	Red Ruby-red Crimson plates		243, 323 248, 328	(10, 19, 23, 32)
Styrylfulvene.....	81	Blue-red needles			(67)
2,3,4-Triphenylfulvene.....	82	Bright red needles			(26)
1,2,3,4-Tetraphenylfulvene.....	148	Red			(11, 26, 76)
	211-212	Orange			
	211	Fire-red		250, 333	
	204-206 (uncorr.)	Shiny brown-red needles			
1,3,4,6-Tetraphenylfulvene.....	156	Orange-brown needles			(26)
6-Methyl-1,2,3,4-tetraphenylfulvene.....	194-195	Orange-brown needles			(26)
1,2,3,4,6-Pentaphenylfulvene.....	199 (uncorr.)	Rust-red needles			(26, 42, 76)
	200-201	Deep red			
	204				

TABLE 6—Concluded

COMPOUND	MELTING POINT °C.	COLOR	REFERENCES
1,3,4,6,6-Pentaphenylfulvene.....	181	Little, violet-brown needles	(26)
1,2,3,4,6-Hexaphenylfulvene.....	301-302	Glittering, almost black needles	(26)
Biphenylenefulvene.....	133-135	Red to black prisms	(19)
Fulvene from α -ionone and cyclopentadiene.....	B. p., 107-109/5 mm.	Orange	(40)
Fulvene from β -ionone and cyclopentadiene.....	B. p., 111-113/0.5 mm.	Orange	(40, 74)
	B. p., 130.5/12 mm.	Red oil	
	B. p., 139-141/0.5 mm.	Red	(40)
Fulvene from pseudoionone and cyclopentadiene.....	172-172.5	Yellow needles	(68)
Methyl- <i>p</i> -(methylfulveno)phenylfulvene.....	164-165	Yellow needles	(31)
1,4-Di(<i>p</i> -tolyl)-2,6-di(<i>p</i> -tolyl)-6-hydroxyfulvene.....	164-165	Yellow needles	(31)
1,4-Dibenzoyl-2,6-diphenyl-6-hydroxyfulvene.....	197-198	Violet brown	(26)
6- <i>p</i> -Anisyl-1,2,3,4-tetraphenylfulvene.....	70	Red	(18, 32, 67)
<i>p</i> -Anisylfulvene.....			
2-[Hydroxy(<i>p</i> -methoxyphenyl)methyl]-6-(<i>p</i> -methoxy- phenyl)fulvene.....	129	Red prisms	(67)
Dioxydibenzylphenylfulvene.....	178-179	Red needles	(67)
Piperidinodimethylfulvene.....	B. p., 118-122/3 mm.	Golden oil	(58)
(Methylaminooethyl)phenylfulvene.....	B. p., 152-156/2 mm.	Dark yellow oil	(58)
(Diethylaminomethyl)methylfulvene.....	B. p., 105/3 mm.	Yellow needles	(58)
6-(<i>p</i> -Dimethylaminophenyl)-1,2,3,4-tetraphenylfulvene.....	207-210	Rust-red	(26)
(Isonitrosomethyl)methylfulvene.....	87	Reddish-brown needles	(67)
1,4-Di(<i>p</i> -chlorobenzoyl)-2,6-di(<i>p</i> -chlorophenyl)-6-hy- droxyfulvene.....	219-219.5	Orange needles	(31)
Dimethylaminophenylimine of 1,2,3,4-tetraphenyl- fulvene.....	217-218	Dark violet needles	(26)
6,6-Bis(<i>p</i> -chlorophenyl)fulvene.....	97-110 (est. 116)	Red plates	(73)
1,2,3,4,5,6-Hexachlorofulvene.....	153-154	Silky red needles	(52)
1,2,3,4-Tetrachloro-6,6-dianilinofulvene.....	Turns brown at 140; carbon- izes at 150-160	Gray-green crystals	(52)
1,2,3,4-Tetrachloro-6,6-bis(<i>p</i> -methylphenyl)fulvene.....	Carbonizes at 145-150	Yellow plates	(52)
1,2,3,4-Tetrachloro-6,6-bis(<i>o</i> -aminophenylamino)fulvene.....	Turns black at 150-170	Pale yellow-gray	(52)
Dimethyl 6,6-diphenyl-2,3-fulvencedicarboxylate.....	164-167	Brilliant red needles	(4)

* The condensation product of cyclopentadiene with salicylaldehyde is green; that with citronellal is yellow; and that with vanillin is a yellow precipitate (69).

The bond order and free valence may be considered as reflecting the distributions of the electrons; the sum of the free valences, added to double the sum of the bond orders, should equal the total number of π -electrons in the molecule.

While the exact values of bond order and free valence are not known, the general results of these calculations agree in qualitative fashion. The five-carbon-atom ring is negative; the No. 6 carbon atom is positive. The prediction that fulvene and its derivatives should be quite reactive is borne out by the facts.

One estimate of the resonance energy of fulvene may be inferred in terms of the "resonance integral" β , as 0.64β , where β is believed to be about 17 kcal./mole (72). Heats of combustion or hydrogenation for fulvene or its derivatives have not yet been measured.

F. Table of physical properties of the fulvenes

Table 6 summarizes the physical properties of the fulvenes.

The author is greatly indebted to Dr. Tekla Hammer and Dr. Paul Krauss for help in translation of the original articles, and to Dr. Fred Tate and Dr. William Huntsman for criticisms of the manuscript.

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ADDENDUM

Several important papers have appeared since the body of this review was written, and some are in press.

Thompson, Bloch, and Bloch (82) have used methylphenylfulvene and diphenylfulvene as comonomers with styrene and with butadiene, to form copolymers varying from oils to solids, depending on the ratio of monomers and the polymerization conditions. Bulk or emulsion polymerization is effective, using typical initiators such as peroxides or potassium persulfate.

Fuson and York (80) have found that 1,2,3,4-tetraphenylfulvene reacts additively with *tert*-butylmagnesium chloride and with benzylmagnesium chloride. The adducts, which are themselves Grignard reagents, do not react with the fulvene. Water converts these adducts to the corresponding 5-alkyl-1,2,3,4-tetraphenylcyclopentadienes. The Grignard adducts also undergo alkylation with some halids. Attempts to prepare 6-vinyl-1,2,3,4-tetraphenylfulvene yielded only a polymer.

Rice and Starr (81) studied the hydrogenation of dimethylfulvene and diphenylfulvene in a low-pressure system, using palladium on charcoal as the catalyst. Dimethylfulvene was best hydrogenated in methyl alcohol with enough potassium hydroxide to neutralize the hydrogen chloride formed (by the reduction of palladium chloride). The only product was isopropylidene-cyclopentane. Diphenylfulvene gave a 95 per cent yield of cyclopentylidene-diphenylmethane. The exo bond was not reduced. Removal of the hydrogen chloride had no effect in this case.

Ernest I. Becker and coworkers have recently completed extensive and careful work with the fulvenes derived from tetraphenylcyclopentadiene. They have studied the methods of preparation of the substituted tetraphenylfulvenes, the addition of Grignard reagents to tetraphenylfulvene, and the ultraviolet spectra of these compounds. In the course of this work they have prepared a number of previously unreported fulvenes. The series of articles by Becker and coworkers will appear shortly in the *Journal of the American Chemical Society*.

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