FULVENES AND SUBSTITUTED FULVENES

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CONTENTS

I. INTRODUCTION

The present review surveys the syntheses of fulvenes and their chemical reactions. It does not discuss the theoretical aspects, such as the electronic structure of the fulvenes and their analogs, or the theory of their absorption spectra, dipole moments, and other physical properties. These points have been reviewed elsewhere (27, 102, 153, 327), and some more recent papers on these subjects are listed in the References section (2, 10, 105, 224, 316, 460). It may only be recalled that cyclopentadiene tends to form a stable anion and cycloheptatriene a stable cation, both possessing a group of six π electrons. Therefore, the exocyclic double bond of the fulvenes (I) and heptafulvenes (II) is polar, the terminal carbon being positive in the former (I), negative in the latter case (II). The extent to which this is so can be calculated from the dipole moments of suitable substituted fulvenes (or their benzologs) or from the spectral shift as a function of the substituents (see, as an example, 224).

For reasons of symmetry, the above does not apply to the fulvalenes (III) and heptafulvalenes (IV), while obviously in the mixed fulvalenes (pentaheptafulvalenes) (V) the central double bond can be expected to be very highly polar. It is interesting to note that the central double bond in the best (and longest) known fulvalene, bis(biphenylene)ethene (VI), is characterized by high polarizability which expresses itself in an unusually large distortion polarization of the hydrocarbon (38).

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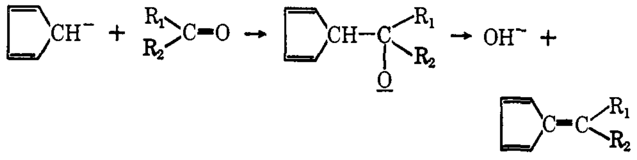
The recently discovered triafulvenes (VII) and triapentafulvalenes (VIII) represent an interesting addition to the fulvene series; their discussion will form part of this paper.

II. SYNTHESES

A. FULVENES

1. *Cyclopentadiene and Related Anions with Carbonyl Compounds*

The anions of cyclopentadiene and its benzologs, formed by the action of alcoholic alkaline hydroxides or alkoxides, aqueous or alcoholic ammonia, primary or secondary amines (124) such as piperidine (80, 83), ethylmagnesium bromide (92, 94), alkyl- or aryllithium compounds (62, 79, 97, 358), add to carbonyl compounds, giving a new anion which stabilizes itself by fulvene (I) formation.

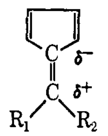


The ease of this reaction decreases with increasing annelation. While cyclopentadiene combines easily with ketones as well as with aldehydes, indene requires more stringent conditions for the reaction with ketones, and fluorene reacts with ketones only in the form of its bromomagnesyl or lithio derivatives, but not under the influence of alkoxides. No systematic studies of the behavior of the higher benzologs of fluorene have been carried out.

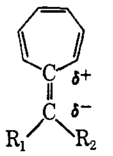
The influence, on the reaction with cyclopentadiene, of substituents in the benzaldehyde or benzophenone molecules has been investigated in detail (223, 225).

The reasons for this gradation of reactivity are probably manyfold. The anion of cyclopentadiene is the most stable of the three because of its symmetry and because the cyclopentadiene system shows the highest hyperconjugation effect (326); these factors also express themselves in the pK of the parent hydrocarbon (27) and in the increase in the wavenumber of the C–H frequency on going from cyclopentadiene to fluorene (183). However, there exists undoubtedly also a steric factor which affects the ease of fulvene formation and operates in the same direction as those mentioned above; it will cause the equilibrium in the above scheme to be shifted to the left. Reaction conditions in which the water liberated is removed from the equilibrium will thus favor the formation of fulvenes; one way of carrying this out is the condensation, under alkaline conditions, by azeotropic distillation with nonpolar, anhydrous solvents (249); another is the use of anionic exchange resins (270, 271, 349). Steric effects are probably also the reason that tri- and tetraarylcyclopentadienes condense with aldehydes, but not with ketones (107).

Aliphatic straight-chain aldehydes cause preparative difficulties, especially in the condensation with cyclopentadiene itself since these aldehydes are sensitive to alkaline conditions and also because fulvene and its 6-alkyl derivatives tend to form resins in the presence of oxygen. Of these fulvenes, therefore, only 6-ethylfulvene had been prepared until recently in pure form (112); the very unstable fulvene (410, 413) and 6-methylfulvene (411) have also been obtained, but difficulties have been experienced in repeating their syntheses (14), and the yield of pure fulvene prepared from cyclopentadiene and formaldehyde was only 0.6% (280). Two more expeditious methods have been used to replace the classical condensations: treatment of the mixture of 1- and 2-acetoxymethylcyclopentadienes (IX, X) with triethylamine gave pure fulvene in 74% yield (354), and the reductive deamination of 6-di-



I



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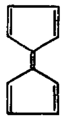

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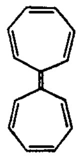

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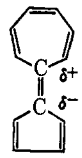

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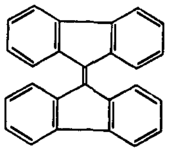

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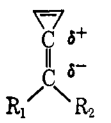

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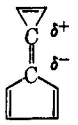

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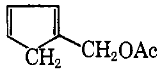

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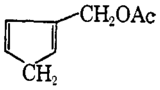

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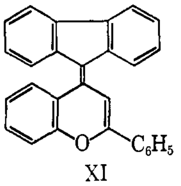

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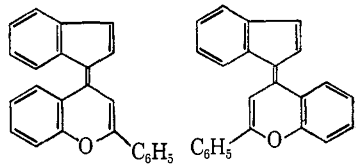

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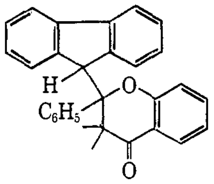
XII



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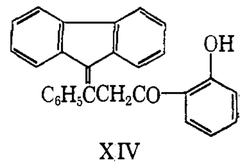

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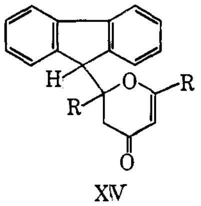
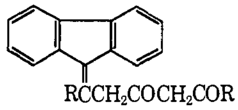


XIV



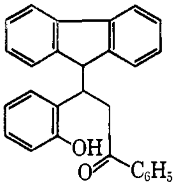
XVI

methylaminofulvene (see section III.A.10) with ethereal lithium aluminum hydride afforded an 80% yield of the yellow hydrocarbon (395).

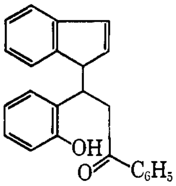
It seems that α-branched aldehydes react normally and give stable fulvenes (325, 375); equally tetraphenylcyclopentadiene yields a stable fulvene with formaldehyde (308).

Carbonyl compounds, which have recently been studied as partners in the preparation of fulvenes, include variously substituted benzaldehydes (19, 224), furfural [using diethylamine or sodium methoxide as condensing agents (339, 362, 363)], furyl ketones (339), the pseudo methyl ester of phthalaldehydic acid (216), α-tetralone (78), cycloalkanones (279), and dicyclopropyl ketone (160). Fulvenes derived from heterocyclic ketones, such as 4-(9-fluorenylidene)-2-flavene (XI) and 4-(1-indenylidene)-2-flavene (XII), can be obtained only indirectly (68, 70), as fluorenylsodium, *e.g.*, acts on flavone as well as on 2,6-dimethyl- and -diphenyl-γ-pyrone by 1,4 addition to the γ-pyrone ring, followed by opening of the heterocycles XIII and XV to give the substituted fulvenes XIV and XVI, respectively.

The *indirect* synthesis proceeds as follows: in the presence of potassium hydroxide in pyridine, indene and fluorene enter a Michael reaction with salicylideneacetophenone to give XVII and XVIII. The fluorene derivative XVII, upon treatment with chloranil in boiling xylene, is simultaneously cyclized, dehydrated, and dehydrogenated to XI. The indene derivative XVIII could not be transformed, by the analogous sequence of reactions, into XII; it gave with perchloric acid the flavylium salt XIX which yielded with base the red "anhydro base" XII. Obviously, in this stage a dehydrogenation takes place, the mechanism of which has not been elucidated (370).



XVII

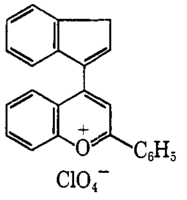


XVIII

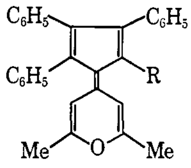
Equally curious, though not unexpected, is the formation of compounds of type XI and XII from 5-diazo-1,2,3-triphenyl- and -1,2,3,4-tetraphenylcyclopentadienes and dimethyl-γ-pyrone or dimethyl-γ-thiapyrone or the corresponding thioketones (256, 257). The tetraphenyl compound (XX, R = C_6H_5), *e.g.*, is isoelectronic with tetraphenylsesquifulvalene (see section II.F) and has, indeed, a very similar spectrum. Strong acids, such as perchloric or trifluoroacetic acid, form conjugate acids, for which the nuclear magnetic resonance spectrum indicates formula XXI (from XX, R = H). From these stable orange-colored salts, bases regenerate the fulvenes (such as XX), but if (and only if) the base has a p*K* of 5–10, the corresponding dihydropyridines (such as XXII, XXXV) are obtained.

Nitrogen and sulfur analogs of compounds such as XI and XII are accessible by a number of routes: cyclopentadienylsodium gives with 4-bromo-N-benzylpyridinium bromide 1-benzyl-4-cyclopentadienylidene-1,4-dihydropyridine (XXII) (47) and with 2-bromo-N-methylpyridinium bromide the analog XXIII (48). Likewise, 4-alkoxy- or -aryloxypyridinium salts react with cyclopentadiene in the presence of potassium *t*-butoxide (69). Also 9-(4-pyridyl)fluorenol (XXIV) can be transformed by alkylation plus dehydration and oxidation into compounds of type XXV (47).

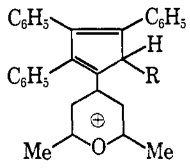
An analogous group of "heterosubstituted" fulvenes has been prepared by condensation of tetraphenylcyclopentadienyl- or fluorenylsodium with isotrithiones (XXVI) or 1,3-dithiolium salts (XXVII) (259; *cf.* also



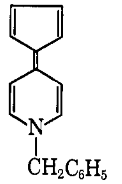
XIX



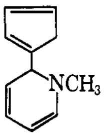
XX



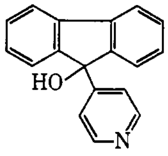
XXI



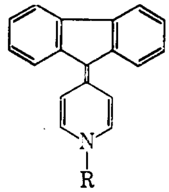
XXII



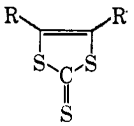
XXIII



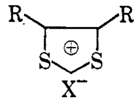
XXIV



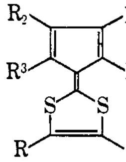
XXV



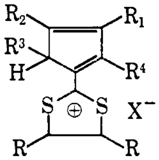
XXVI



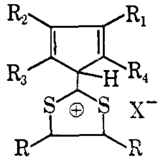
XXVII



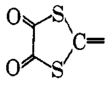
XXVIII



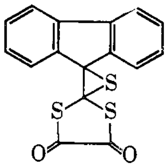
XXIX



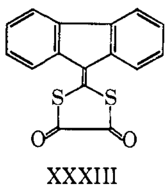
XXX



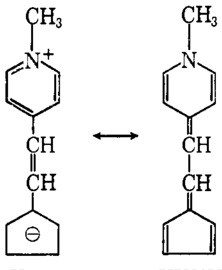
XXXI



XXXII



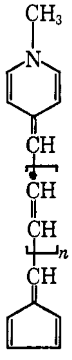
XXXIII



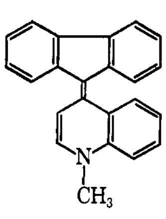
XXXIV XXXV

139). These compounds (XXVIII), too, are easily protonated, yielding salts of type XXIX or XXX. Into this series belong, at least formally, the sulfur compounds XXXIII obtained from diazofluorene (and analogous substances) and 4,5-dioxo-2-thiono-1,3-dithiolan (XXXI); in the first step the expected ethylene sulfide XXXII is formed; this loses the episulfide sulfur either on pyrolysis or by treatment with copper (368).

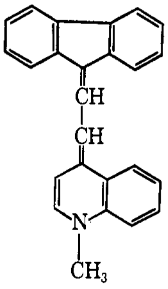
Of some interest are the vinylogs of these heterosubstituted fulvenes, which have recently found much attention. Cyclopentadienylsodium reacted with 4-(β-dimethylaminovinyl)-1-methylpyridinium salts normally by elimination of dimethylamine and formation of the compound XXXIV which is a resonance form of XXXV. The vinylogs XXXVI and XXXVII have been obtained analogously; they could only be prepared in solution, but were characterized by absorption at 584 and 602 mμ, respectively (in acetonitrile) (XXXV, 572 mμ). Equally, fluorenyllithium gave, with the appropriate quinolinium salts, the two series XXXVIII–XLV; the absorption spectra (in acetonitrile) are indicated with the formulas (187; *cf.* 227, 245, 246). Some other methods employed for the synthesis of compounds of these series deserve a brief mention (49): cyclopentadienylsodium gave, with compounds such as 2-halo-1-methyl- or -1-benzylpyridinium halides (XLVI), the heterosubstituted fulvenes XLVII, with liberation of 1 mole of cyclopentadiene. Cyclopent-2-en-1-one and 2-pyridyllithium afforded the tertiary alcohol XLVIII, the methosulfate of which gave by successive treatment with acid and alkali the fulvene XLVII (R = CH_3). Fluorenone reacted analogously with 2- or 4-pyridyllithium; the carbinols obtained (*e.g.*, XLIX) were reduced with hydriodic acid and the methosulfates or bromobenzylates of the reduction products (*e.g.*, L) were treated with alkali, thus affording compounds of type XXV (R = CH_3).



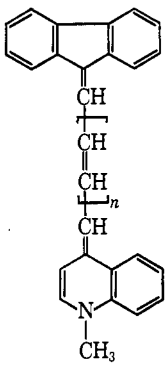
XXXVI, $n = 1$
XXXVII, $n = 2$



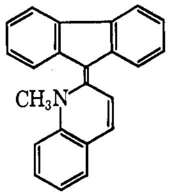
XXXVIII (λ 541 mμ)



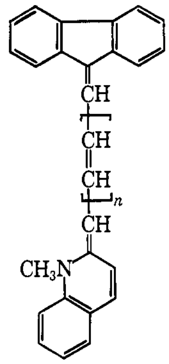
XXXIX (λ 547 mμ)



XL, $n = 1$ (λ 562 mμ)
XLI, $n = 2$ (λ 574 mμ)



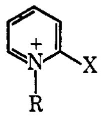
XLII (λ 523 mμ)



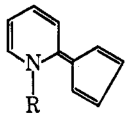
XLIII, $n = 0$ (λ 503.5 mμ)
XLIV, $n = 1$ (λ 539 mμ)
XLV, $n = 2$ (λ 552 mμ)

An interesting substance related to the above sulfur compounds is 5-(9-fluorenylidene)-2(5H)-thiophenone (LI) which has been obtained—in a not quite clear reaction—from 5-methoxythienyl-2-lithium and fluorenone (58).

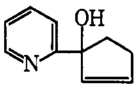
The reaction scheme outlined above for the synthesis of fulvenes indicates that an alternative way exists for the stabilization of the anionic adduct, *viz.*, its neutralization by a proton. Especially in the fluorene series, the dibenzofulvenes are accompanied by the corresponding (9-fluorenyl)carbinols (LII) (17, 28) which can then be dehydrated (343). In the cyclopentadiene and indene series, the initial formation of such alcohols is proven by the observation that compounds such as LIII and LIV are obtained, undoubtedly through rearrangement of the primarily formed alcohols LV and LVI to LVII–LX, respectively (93, 242, 414, 415, 418, 444) (see below).



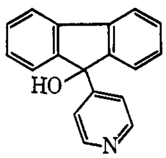
XLVI, R = CH_3, $CH_2C_6H_5$



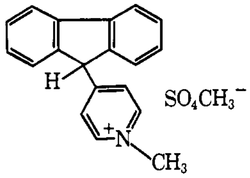
XLVII



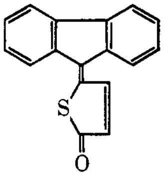
XLVIII



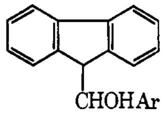
XLIX



L



LI



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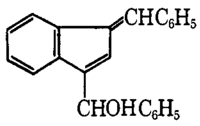

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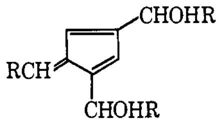

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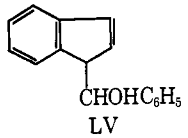

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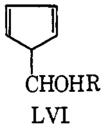

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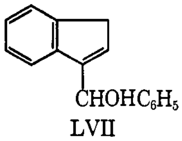

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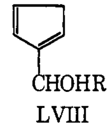
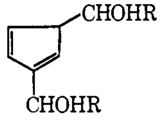


LVIII



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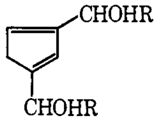
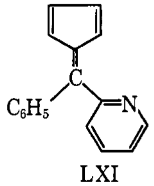
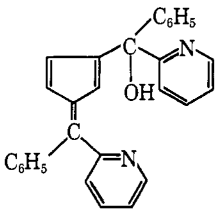


LX

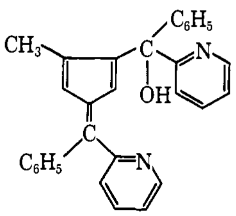


LXI

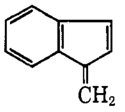
Systematic studies (274, 282, 283) have shown that diaryl ketones in which one aryl at least is heterocyclic (*e.g.*, 2-benzoylpyridine) tend to give significant amounts of stabilized carbinols ("fulvenemethanols") in the condensation with cyclopentadiene, especially at low temperature. 2-Benzoylpyridine gives, *e.g.*, both the fulvene LXI and the carbinol LXII. The direction which the condensation takes is not a function of the reactivity of the carbonyl group; both 2-acetylpyridine, which reacts very readily, and 2-butyl or cyclohexyl 2-pyridyl ketones, which are sluggish in their reaction, give only the fulvenes and not the fulvenemethanols. Methylcyclopentadiene condenses at 25° with 2-benzoylpyridine to the fulvene, while at 5° the fulvenemethanol LXIII is obtained. The important factor which favors the formation of the fulvenemethanols appears to be the electronegativity of the aryl or aryls; thus, nitrophenyl groups have an effect similar to that of pyridyl or quinolyl radicals.



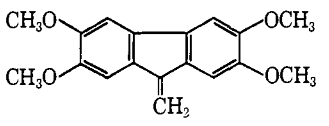
LXII



LXIII



LXIV



LXV

By dehydration of (1-indenyl)carbinol unsubstituted benzofulvene (LXIV) has been prepared (343); another more devious route, starting from 3-methyl-1-indanone, has also been suggested (55).

Analogously, halogenomethyl derivatives of cyclopentadiene and its benzologs can be dehydrohalogenated to fulvenes. In this way, 2,3,6,7-tetramethoxydibenzofulvene (LXV) has been prepared (263, 264).

The behavior of α,β-unsaturated aldehydes and ketones in the condensation with cyclopentadiene and its benzologs has been investigated in some detail (35, 218, 428, 432, 433, 451). These aldehydes appear to give fulvenes normally. Some recent examples are: acrolein (363), crotonaldehyde (124, 296), methacrolein (296), β-(2-furyl)acrolein, and 5-(2-furyl)pentadienal (363). Also compounds containing "potential" aldehyde groups, such as the perchlorates or fluoroborates of N,N′-dimethyl-N,N′-diphenylformamidine and its vinylogs, have been successfully employed, leading to fulvenes such as LXVI (185; *cf.* 405). The dimethyl acetal of N,N-dimethylaminoacrolein condenses smoothly with cyclopentadiene to give (3-dimethylaminoallylidene)cyclopentadiene (75).

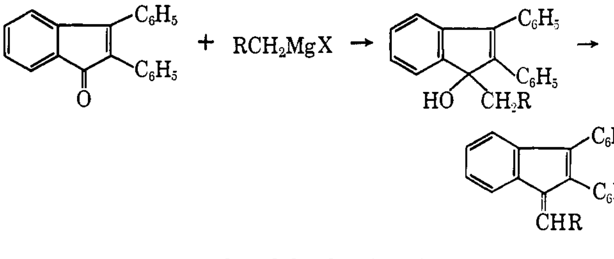
α,β-Unsaturated ketones, on the other hand, do not behave in uniform fashion. β-Ionone and methyl vinyl ketone (296) condense normally with cyclopentadiene in the presence of alkoxide, but 9-fluorenyllithium adds to mesityl oxide in a 1,4 manner (to give LXVII), whereas 9-fluorenylmagnesium bromide yields the tertiary alcohol LXVIII. 9-Fluorenyllithium also adds 1,4 to compounds of the benzylideneacetone and chalcone type (*e.g.*, to LXIX) and to fulvene ketones (cyclopentadienones, indones); the same is true for cyclopentadienyllithium and 1-indenyllithium, while from 1-indenylmagnesium bromide and 2,3-diphenylindone the tertiary alcohol LXX, the precursor of a fulvene, is formed. Recently, it has been shown that both the unsaturated aldehyde retinal (LXXI) and the unsaturated ketone retinylideneacetone (LXXII) condense normally with cyclopentadiene, substituted indenes, and fluorene, yielding some interesting fulvenic analogs of the carotenoids (145, 299).

It seems likely that these differences in behavior are due to the finer details of the mechanism by which organometallic complexes react with α,β-unsaturated carbonyl compounds (33, 260).

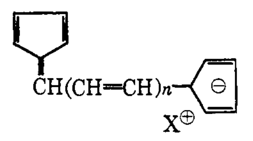
In a few cases, hydrocarbons of the cyclopentadiene type, if they have a sufficiently high boiling point, have been condensed with congeners of carbonyl compounds. Thus fluorene gives with dichlorodiphenylmethane at 320° 9-benzhydrylidenefluorene (and HCl) (191), and 2,3,4-triphenyl- and 2,3,4,5-tetraphenylcyclopentadiene behave analogously (107). 4,4′-Dimethoxythiobenzophenone gives with fluorene at 270° the corresponding fulvene (and H_2S), without external catalyst (366). The old observation that 9-benzhydrylidenefluorene is formed from fluorene, diphenylmethane, and sulfur at 290° (401) also points to the intermediate formation of either thiofluorenone or thiobenzophenone.

2. Cyclopentadienones and Related Ketones with Grignard Compounds, and Dehydration

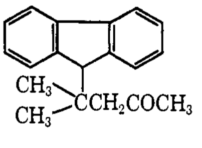
A second general and fairly obvious method for the synthesis of fulvenes consists in the reaction of fulvene ketones with Grignard compounds and dehydration of the tertiary alcohols formed, *e.g.*



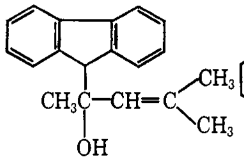
In many cases, the dehydration is spontaneous on contact with acid; otherwise, chemical methods usual for the dehydration of tertiary alcohols are applied, or the reaction is carried out catalytically in the vapor phase (92, 94, 121, 345). A specific example is the preparation of 9-allylidenefluorene (ω-vinyldibenzofulvene) (LXXIII) from fluorenone and allylmagnesium bromide (431).



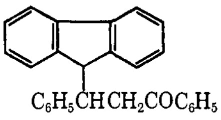
LXVI



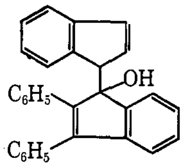
LXVII



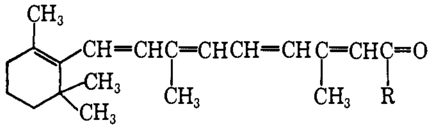
LXVIII



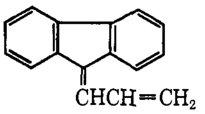
LXIX



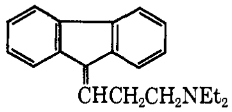
LXX



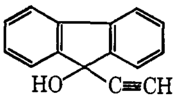
LXXI, R = H
LXXII, R = CH3



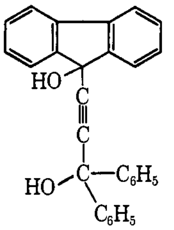
LXXIII



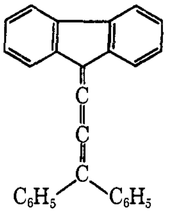
LXXIV



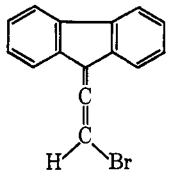
LXXV



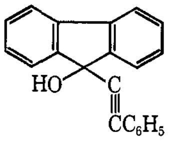
LXXVI



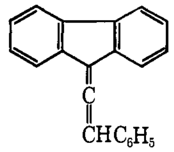
LXXVII



LXXVIII



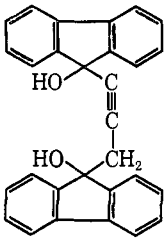
LXXIX



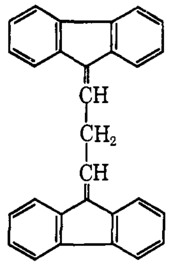
LXXX

In connection with pharmacological studies, Grignard reagents carrying basic substituents have been added to fluorenone (64–66). From the fulvene prepared with γ-diethylaminopropylmagnesium chloride (LXXIV), LXXIII has been made by Hofmann degradation. An alternative method utilizes the polar character of the fulvene system by adding dialkylamines to LXXIII, yielding compounds such as LXXIV (431). These basically substituted fulvenes as well as types LXI and LXII have been described variously as possessing antidepressant, thymoleptic, euphoric, antifibrillatory, anti-inflammatory, analgesic, and antiedema properties and as active against cardiac arrhythmia (*cf.* 384).

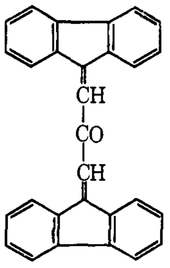
Considerable work has been devoted to the fulvenes derived from the condensation of fluorenone and ethynylmetal compounds. Ethynylmagnesium bromide gives with fluorenone the alcohol LXXV which reacts with, *e.g.*, benzophenone to give the diol LXXVI; its dehydroxylation leads to 1-biphenylene-4,4-diphenylbutatriene (LXXVII) (see section II.D) (86, 340). Analogously LXXV treated with phosphorus tribromide in acetic acid gave a 71% yield of the allene derivative LXXVIII (407), and 9-phenethynylfluorene (LXXIX) gave 1-biphenylene-3-phenylallene (LXXX) (238) under the influence of bases. With the bis(bromomagnesyl) derivative of propargyl bromide, fluorenone gives 1,5-dibiphenylene-2-pentyne-1,5-diol (LXXXI), from which by hydrogenation of the triple bond and dehydration the interesting 1,5-dibiphenylene-1,4-pentadiene (see section E) is obtained LXXXII (228, 232). The lithio derivative of LXXV can also condense with 1,3-bis(biphenylene)acetone (LXXXIII). The carbinol LXXXIV so obtained can be converted by successive reduction (with tin) and catalytic hydrogenation to the bright red fulvene LXXXV (116).



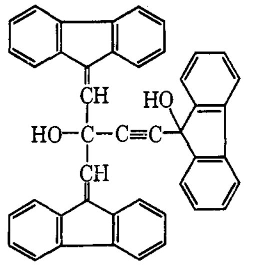
LXXXI



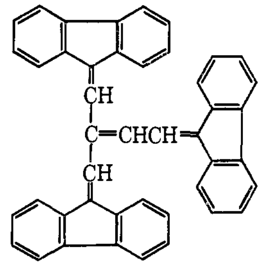
LXXXII



LXXXIII



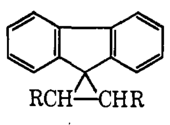
LXXXIV



LXXXV

3. *The Wittig Reaction*

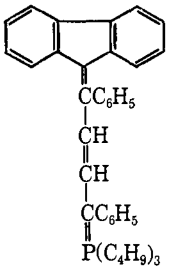
Fulvenes can also be obtained by the Wittig reaction, fluorenone being the only "fulvene ketone" studied so far. Fluorenone, it is true, gives with the usual substituted methylenetriphenylphosphines, not the ω-substituted methylenefluorenes, but by reaction with a second molecule of the phosphorus compound spirans



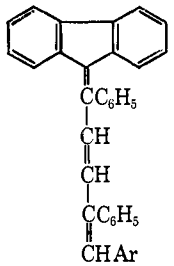
LXXXVI

of type LXXXVI (276), but diphenyl(dimethylaminophenyl)phosphinephenylmethylene yields benzylidenefluorene (427). Also from fluorenone and benzyldiphenylphosphinoxide, using potassium *t*-butoxide, a 43% yield of benzylidenefluorene is secured (113, 174). Obviously, the inverse reaction is also possible: triphenylphosphine- and trimethylphosphine-9-fluorenylidene and benzaldehydes or cinnamaldehydes give benzylidene- and cinnamylidenefluorenes (117, 178). Also from triphenylarsine-9-fluorenylidene and benzaldehyde, benzylidenefluorene was obtained (176, 180).

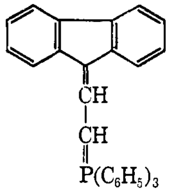
An extension of Wittig's method is based on the complex phosphorane (LXXXVII) which is formed from fluorene, triphenylphosphine, and diphenyldiacetylene. This reacts with aromatic aldehydes (as well as cinnamaldehydes and ketones) to yield compounds of the general formula LXXXVIII (388). Another useful Wittig compound is LXXXIX which is formed by the reaction of 9-(bromomethylene)fluorene and triphenylphosphinemethylene (116), or from fluorenone and triphenylphosphinebromomethylene in the presence of phenyllithium. Analogously, the vinylog XC gives with triphenylphosphinemethylene the Wittig compound XCI, and biphenyleneacrolein (XCII) with triphenylphosphinebromomethylene gives 1,1-biphenylene-4-bromo-1,3-butadiene (XCIII). In the latter reaction (and some analogous condensations), the (unexplained) formation of some 1,1-biphenylene-4,4-dibromo-1,3-butadiene (XCIV) has been observed.



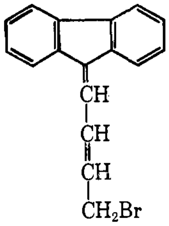
LXXXVII



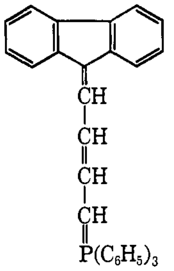
LXXXVIII



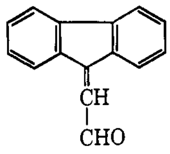
LXXXIX



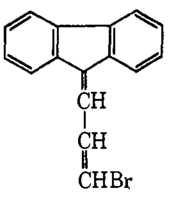
XC



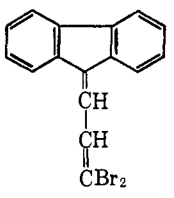
XCI



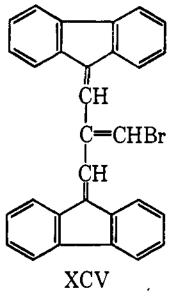
XCII



XCIII

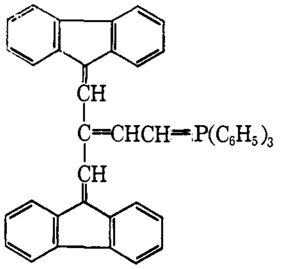


XCIV

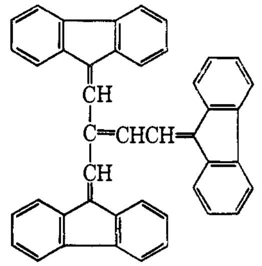


XCV

This scheme of reactions has been utilized for the preparation of some even more complex dibenzofulvene derivatives. Thus, reaction of 1,3-bis(biphenylene)-acetone (LXXXIII) with triphenylphosphinebromomethylene gave 1,3-bis(biphenylene)-2-bromomethylenepropane (XCV), which condensed with triphenylphosphinemethylene to the stable Wittig compound XCVI (116). The latter could not be induced to react with benzaldehyde but gave with fluorenone (at 230°(!)) 1,1-bis(biphenylenevinyl)-4-biphenylene-1,3-butadiene (XCVII).



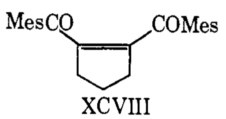
XCVI



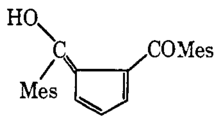
XCVII

4. *Dehydrogenation of Alkylcyclopentadienes and Their Benzologs*

A fourth general method which, however, has been applied only sporadically, consists in the dehydrogenation of suitable alkyl derivatives of cyclopentadiene and its benzologs, compounds which can be obtained by alkylation of the metal derivatives of these hydrocarbons. While bromine has been used successfully (91, 93), the method of choice seems to be the reaction with N-bromosuccinimide in the presence of peroxides or with the help of ultraviolet light (253). In this connection it is interesting to recall that 9-ethylfluorene is converted, by heating at 310° with mercuric oxide, into 9-ethylidenefluorene (267), that 9-methylfluorene is catalytically dehydrogenated to dibenzofulvene in the presence of a mixture of the oxides of iron, chromium, and potassium (385), and that 1,2-dimesitoylcyclopentene (XCVIII) is dehydrogenated by oxygen in the presence of alkali to the fulvene XCIX (128).



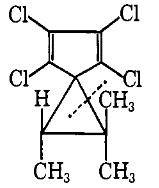
XCVIII

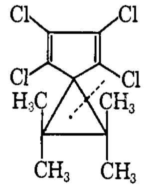


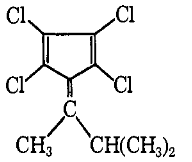
XCIX

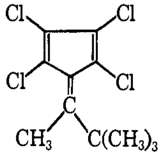
5. *Photochemical Methods*

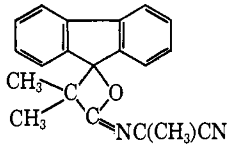
Benzene is isomerized to fulvene photochemically (13, 272) or radiochemically (439); similarly, cumene gives dimethylfulvene (13). Two other photochemical reactions have recently been used for the preparation of fulvenes. The photolysis of tetrachlorodiazocyclopentadiene in the presence of trimethylethylene or tetramethylethylene leads to the spirans C and CI. Upon heating, they isomerize to 6-isopropyl-6-methylfulvene (CII) and 6-*t*-butyl-6-methylfulvene (CIII), respectively, obviously by ring opening in the manner indicated in the formulas and subsequent migration of a hydrogen atom and a methyl group, respectively (268). The oxetane derivative CIV, obtained from fluorenone and dimethyl-N-(2-cyano 2-propyl)ketenimine, decomposes photochemically (or thermally) to 9-isopropylidenefluorene (380).


C


CI


CII

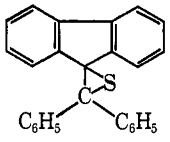

CIII


CIV

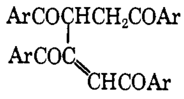
Another reaction which is conveniently mentioned here is the formation of benzhydrylidenefluorene from thiofluorenone and diphenyldiazomethane (247). In analogy with similar cases, the ethylene sulfide CV is the intermediate; it decomposes spontaneously.

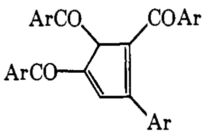
6. Cyclization Reactions

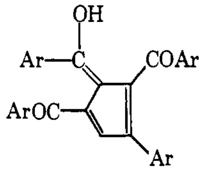
Some other methods yield fulvenes by more devious reactions, especially by cyclization of suitably constituted open-chain compounds. The dimers CVII of 1,2-diaroylethylenes (CVI) form, by elimination of water, triketones CVIII which are stable as the enol forms, *i.e.*, as highly substituted 6-hydroxyfulvenes (CIX) (127, 134, 461). Under the influence of phosphorus tribromide, 1,1,6,6-tetraphenyl-2,4-hexadiyne-1,6-diol (CX) isomerizes to a fulvene, *viz.* CXI. This formula is supported by the nmr spectrum and the nonreactivity of the bromine atom (407). Cycloisomerization of tetraarylbutatrienes (CXII) leads to 3-aryl-1-(diarylmethylene)indenes (CXIII) under the influence of acid, probably *via* an ion of the type CXIV.

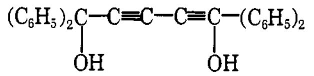

CV

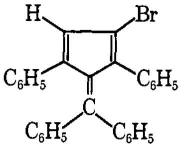
ArCOCH=CHCOAr
CVI

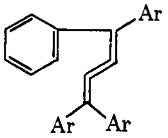

CVII

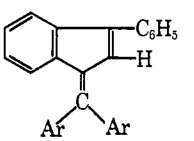

CVIII

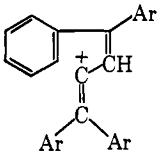

CIX

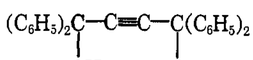

$$(C_6H_5)_2\underset{OH}{C}-C\equiv C-C\equiv C-\underset{OH}{C}-(C_6H_5)_2$$
CX

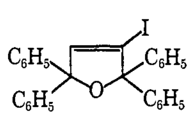

CXI


CXII

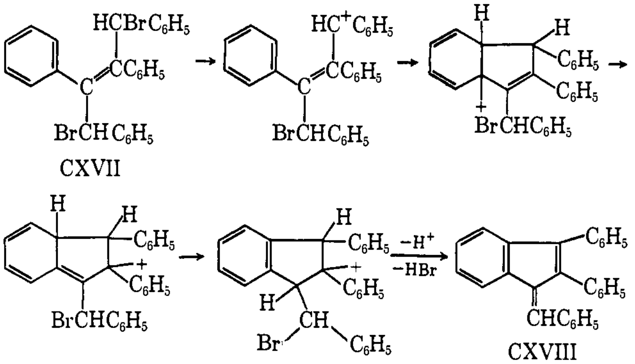

CXIII


CXIV

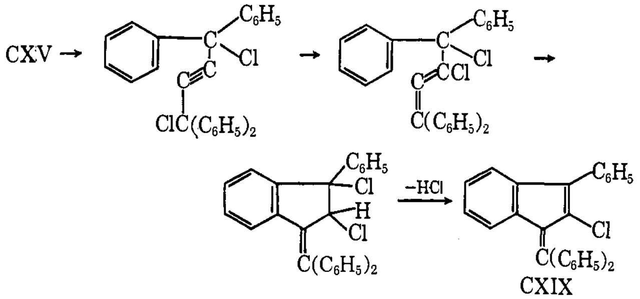

$$(C_6H_5)_2\underset{OH}{C}-C\equiv C-\underset{OH}{C}(C_6H_5)_2$$
CXV


CXVI

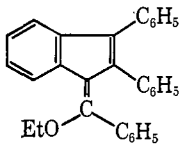
The transformation, into CXIII (Ar = C_6H_5), of 1,1,4,4-tetraphenylbutyne-1,4-diol (CXV) and 3-iodo-2,2,5,5-tetraphenyl-2,5-dihydrofuran (CXVI) under the influence of hydriodic acid (phosphorus tribromide in acetic acid reacts analogously (407)) can be rationalized by assuming the formation of CXII (Ar = C_6H_5) as an intermediate (71–74, 350–352). Analogously, the formation of 1-benzylidene-2,3-diphenylindene (CXVIII) from 1,4-dibromo-1,2,3,4-tetraphenyl-2-butene (CXVII) and alkali (302, 382) and of 1-benzhydrylidene-2-chloro-3-phenylindene (CXIX) from CXV and phosphorus pentachloride or acetyl chloride (34, 35, 446) can be explained by the mechanisms indicated.

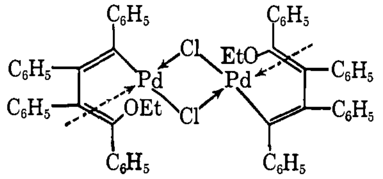

CXVII

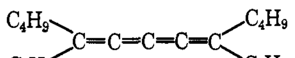
CXVIII

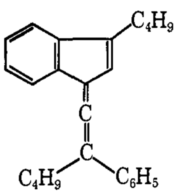

CXIX

Several analogous cases have been observed: tetraphenylbutatriene (CXII) yields with bromine 2-bromo-3-phenyl-1-benzhydrylideneindene (as CXIX, Br instead of Cl) (454), and tolan is converted by treatment with palladous chloride in ethanol into a mixture of CXVIII and 1-(α-ethoxybenzylidene)-2,3-diphenylindene (CXX), probably *via* a metalloorganic intermediate of the form CXXI (61). Equally, nickel bromide transforms tolan at 350° into CXVIII (275). A compound which had been expected to be 1,5-di-*t*-butyl-1,5-diphenylpentatetraene (CXXII) was shown to be the isomeric allenic benzofulvene CXXIII (239).


CXX

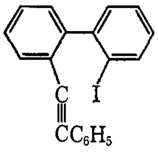

CXXI

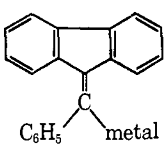

CXXII

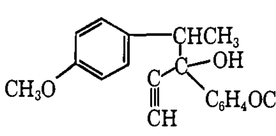

CXXIII

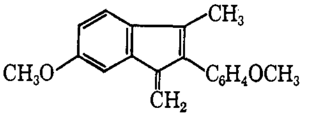
A formally similar route into the series of ω-substituted dibenzofulvenes, recently discovered (200), consists in the reaction of magnesium or *n*-butyllithium with 2-iodo-2′-phenylethynylbiphenyl (CXXIV); one obtains the metal derivative (CXXV) of benzylidenefluorene which opens many synthetic possibilities.

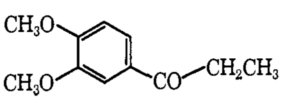
When 3,4-di-(*p*-methoxyphenyl)-1-pentyn-3-ol (CXXVI) was treated with phosphorus tribromide, 6-methoxy-2-methoxyphenyl-3-methyl-1-methyleneindene (CXXVII) was one of the products (379), and a similar reaction was observed (60) when diethylstilbesterol was treated with hydrochloric acid in dimethyl sulfoxide. Also the reaction of ethyl 3,4-dimethoxyphenyl ketone (CXXVIII) with phosphorus oxychloride led, after hydrolysis, to a fulvene, *viz.* 1-ethylidene-5,6-dimethoxy-2-methyl-3-veratrylindene (CXXIX) (461). In this connection, it may be recalled briefly that the oxide-catalyzed aromatization of paraffins leads partly to fulvenes by a similar cycloisomerization mechanism (168, 289, 402).

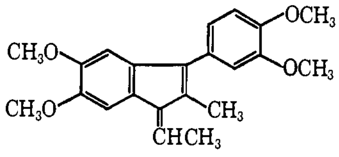

CXXIV


CXXV


CXXVI


CXXVII


CXXVIII


CXXIX

Another route by which a fulvene is obtained from an open-chain compound is the reaction of hexachloropropene with metallic aluminum, which leads to perchlorofulvene, probably *via* perchlorohexa-1,5-diene (CXXX) (346).

7. *Interconversions of Fulvenes*

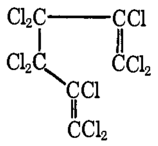
In ω-halogenofulvenes the halogen atom may be exchanged by an alkyl group when the compound is treated with a metalloorganic reagent. Thus, 9-chloromethylenefluorene and butyllithium give, among other products, a 17% yield of 9-pentylidenefluorene (98), and its 9-bromomethylene analog affords with β,β-diphenylvinylmagnesium bromide a 15% yield of 1-biphenylene-4,4-diphenylbutadiene (CXXXI) (87).

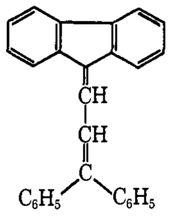
As mentioned above, the tendency to fulvene formation is so great that a 6-hydroxyfulvene is more stable than the corresponding nonfulvenoid keto form. In fact, every heteroatom in the 6 position that has a lone electron pair will stabilize the fulvene structure, as it will enhance the contribution of the dipolar form. It is therefore of interest that, recently, 6-hydroxy- and 6-aminofulvenes have become readily available. Cyclopentadiene condenses with diethoxy(dimethylamino)-methane (278) and cyclopentadienylsodium with the adduct (CXXXII) of dimethyl sulfate and N,N-dimethylformamide (159) to give 6-dimethylaminofulvene (CXXXIII) for which the resonance structure CXXXIV, which is not fulvenic, may also be written. The same product is formed when a mixture of phosphorus oxychloride and dimethylformamide reacts with cyclopentadiene; the reaction continues (see section III.A.10) and two formyl groups are introduced into the ring. Indene behaves analogously (151). Vinylogs of CXXXIII, such as CXXXVI, can be obtained by thermal rearrangement of the 1-alkyl-2-cyclopentadienyl-1,2-dihydropyridines (CXXXV) (146, 148).

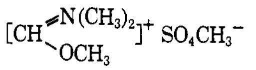
This synthesis can also be carried out indirectly, condensing, *e.g.*, 1-(N-methylanilino)-1,3-pentadien-5-al (CXXXVII) ("Zincke aldehyde," prepared by degradation of pyridine) (see also section III.A.7) with cyclopentadiene (147; *cf.* 226). Another compound of this type (CXXXVIII) is prepared from fluorene-9-carboxaldehyde, ethyl acetoacetate, and ammonia under the conditions of Hantzsch's dihydropyridine synthesis (425).

Pyrylium salts condense with cyclopentadienylsodium in the same way as the pyridinium compounds (154).

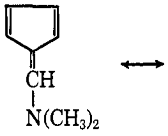
Formula CXXXIV explains best the reactions with nucleophilic agents, primary and secondary amines or the hydroxyl ion, which give other substituted 6-aminofulvenes and 6-hydroxyfulvene (CXXXIX), respectively. For CXXXIX several other formulas (CXL, CXLI) apart from the aldehyde form CXLII can be written which, however, do not appear to con-

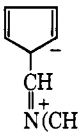

CXXX

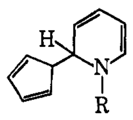

CXXXI

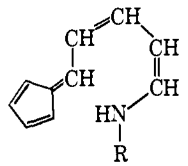

$\left[\mathrm{CH}\genfrac{}{}{0pt}{}{=\mathrm{N(CH_3)_2}}{-\mathrm{OCH_3}}\right]^+ \mathrm{SO_4CH_3^-}$

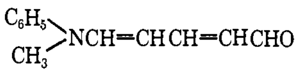
CXXXII


CXXXIII

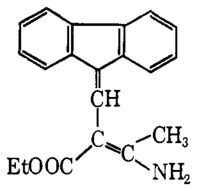

CXXXIV

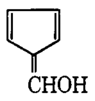

CXXXV

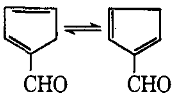

CXXXVI

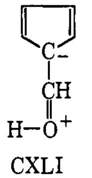

$\genfrac{}{}{0pt}{}{\mathrm{C_6H_5}}{\mathrm{CH_3}}{>}\mathrm{NCH{=}CHCH{=}CHCHO}$

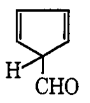
CXXXVII

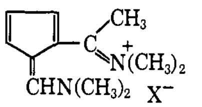

CXXXVIII

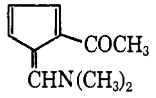

CXXXIX

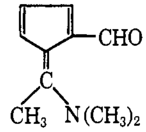

CXL

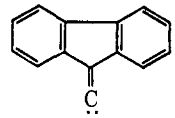

CXLI

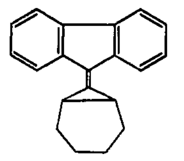

CXLII


CXLIII


CXLIV


CXLV


CXLVI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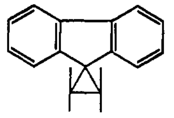
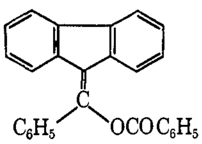
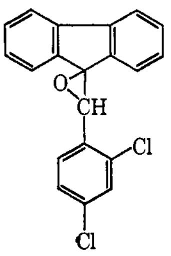
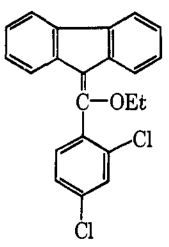
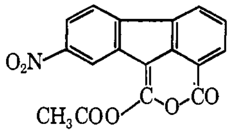
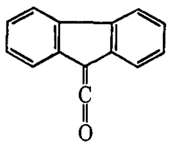

CXLVIII


CXLIX


CL


CLI


CLII

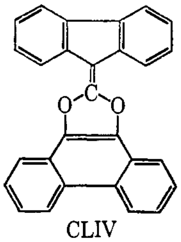

CLIII

tribute markedly to the actual structure of the molecule that is as acidic as phenol (153, 157).

Instead of dimethylformamide, other N,N-dialkylformamides may be employed in such syntheses. However, the amides of the homologs of formic acid are refractory (149, 150, 158, 159). On the other hand, 6-dimethylaminofulvene reacts not only with dimethylformamide and phosphorus oxychloride, but also with dimethylacetamide, yielding CXLIII which upon hydrolysis gives both the ketone CXLIV and the aldehyde CXLV (153).

ω-Aminodibenzofulvene has been known for some time; it is formed from 9-formylfluorene and ammonia. Recently, its reaction with isoamyl nitrite has been studied (99); it leads to the carbene CXLVI which can be used as starting point for a synthesis of the type of fulvenes depicted by formulas CXLVII (9-(bicyclo-[4.1.0]hept-7-ylidene)fluorene) and CXLVIII, which are the products of interaction of the carbene with cyclohexene and tetramethylethylene, respectively.

As pointed out above, hydroxyfulvenes are quite stable. Their ethers and esters are easily prepared: the anion of CXXXIX is O-acylated by ethyl chlorocarbonate or acetyl chloride (157); triphenylphosphinealkoxymethylenes give with fluorenone 9-alkoxymethylenefluorenes (453); the reaction of 9-benzoylfluorene with sodium ethoxide and isopropyl bromide gives a 70% yield of the C-isopropyl and a 15% yield of the O-isopropyl derivative (24, 348); and the reaction of benzoyl chloride with the potassium or sodium derivative of fluorene leads to the benzoate CXLIX of the enol form of 9-benzoylfluorene (357); an analogous observation has been recorded for indenylsodium (341). Similarly, the epoxide CL is transformed by successive treatment with ethanol and with phosphorus oxychloride in pyridine into the fulvenic enol ether CLI (179). A further example is the formation of CLII from 7-nitrofluorene-1,9-dicarboxylic acid and acetyl chloride (229). This substance in which the ω-carbon atom carries two (substituted) hydroxyl groups brings to mind a class of compounds which are obtained from biphenyleneketene (CLIII) and *o*-quinone diazides, *e.g.*, phenanthraquinone 9,10-diazide; in this case 2-(9-fluorenylidene)phenanthro[9.10]-1,3-dioxol (CLIV) was formed (336–338). It has been shown that the introduction of two aldehyde groups into the cyclopentadiene molecule on neighboring carbon atoms causes the aldehyde absorption to disappear. 6-Aminofulvenealdehydes behave similarly (155).

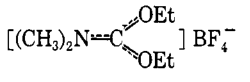

CLIV

8. *Miscellaneous Methods*

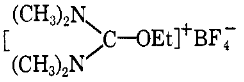
In a more general way, 6,6-dialkoxy-, 6,6-bis(dialkylamino)-, and 6,6-di(alkylthio)fulvenes and mixed types of such compounds have become available by classical reactions of cyclopentadienylsodium. It gives with the three fluoroborates CLV, CLVI, CLVII 6,6-diethoxy-, 6-ethoxy-6-dimethylamino-, and 6,6-bis(dimethylamino)fulvene (CLVIII, CLIX, CLX), respectively (157). Dialkyl trithiocarbonates, on the other hand, give upon treatment with cyclopentadienylsodium the anion CLXI, which can be alkylated to substances such as CLXII; all compounds of this type are red, polymerizable oils. While the ester amide CLXIII of trithiocarbonic acid, tetrasubstituted thioureas, and thioamides do not react with cyclopentadienylsodium, they can be "activated" by combination with methyl iodide. Thus, N,N-dialkyl-S,S′-dimethyldithiocarbamidium salts CLXIV and the compounds CLXV and CLXVI give the fulvenes CLXVII, CLX, and CLXVIII, respectively (162, 163). Also carbon disulfide can be employed; it gives with cyclopentadienylsodium the dianion CLXIX, which can be alkylated in the usual way (394). From the dipole moments of the compounds (which are appended to the formulas), one obtains a qualitative impression of the increasing contribution of dipolar forms to the ground state of the molecules.

$(C_2H_5O)_3C^+BF_4^-$

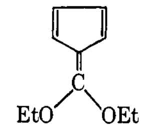
CLV

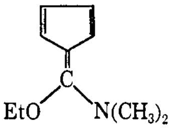

$[(CH_3)_2N{=}C(OEt)_2]\,BF_4^-$

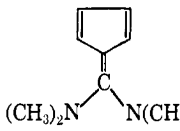
CLVI

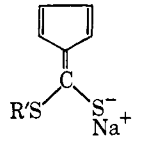

$[((CH_3)_2N)_2C{-}OEt]^+BF_4^-$

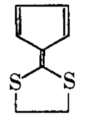
CLVII

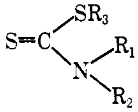

CLVIII ($\mu = 3.6$ D)

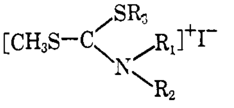

CLIX ($\mu = 4.5$ D)

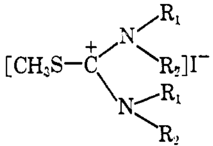

CLX ($\mu = 5.4$ D)

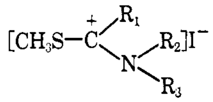

CLXI

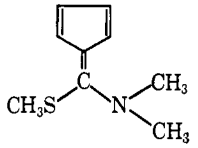

CLXII ($\mu = 3.75$ D)

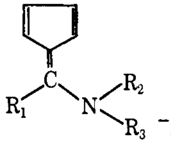

CLXIII

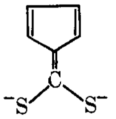

CLXIV

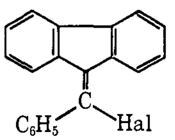

CLXV

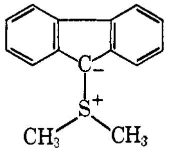

CLXVI


CLXVII ($\mu = 4.4$ D)


CLXVIII


CLXIX


CLXX

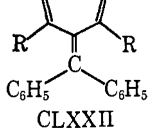

CLXXI

It is interesting to compare these compounds with fulvenes which are substituted on the exocyclic carbon atom with highly negative substituents. For example, the introduction of nitrile groups obliterates the fulvenic character; the dipole moment of the molecule is directed toward the negatively substituted exocyclic carbon atom. ω,ω-Dicyanodibenzofulvene has been obtained from malononitrile and 9,9-dichloro-, 9,9-dipiperidino-, or 9,9-dimorpholinofluorene (355, 371). Analogous condensations have been carried out with ethyl cyanoacetate, cyanoacetamide, and dibenzoylmethane (120, 371). Of interest is the 2,4,7-trinitro derivative of ω,ω-dicyanodibenzofulvene which is a powerful electron acceptor and can thus be used for the preparation of charge-transfer complexes (286).

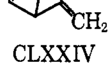
Of other fulvenes substituted in the ω position by polar substituents, 9-(nitromethylene)fluorene may be mentioned, which is formed from fluorenonimine and nitromethane (85). 9-(Halomethylene)fluorenes can be obtained in several ways: 9-ethynyl-9-fluorenol gives with concentrated hydrochloric acid or thionyl chloride 9-(chloromethylene)fluorene (166), and 9-diazofluorene reacts with dihalocarbenes and phenylhalocarbenes with evolution of nitrogen, yielding 9-(dihalomethylene)-fluorenes and 9-(α-halobenzylidene)fluorenes (CLXX) (333). Analogously, triphenyl- or tributylphosphine-fluorenylidene or the sulfur ylide CLXXI reacts with these carbenes (301), and also a mixture of fluorenone, triphenylphosphine, and carbon tetrachloride affords 9-dichloromethylenefluorene (329).

B. HEPTAFULVENES

Numerous attempts at the synthesis of heptafulvenes (II) and monobenzoheptafulvenes have failed (27). However, three representatives of the 7-benzhydrylidene-3,4-benzoheptafulvenes (CLXXII) have been known for a long time but appear to have been overlooked (see below) (393). Only recently (108, 109) has heptafulvene been obtained by decomposition of trimethyl(norcaradienyl)ammonium hydroxide (CLXXIII) at room temperature and under 1-mm pressure. It is a red, very unstable oil, showing the absorption spectrum of a planar, fully conjugated system; its structure follows from the hydrogenation to methylcycloheptane and the formation of formaldehyde upon ozonization. Also other methods have been devised

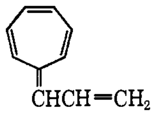

CLXXII


CLXXIII

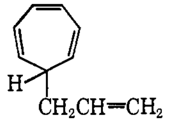

CLXXIV

for the preparation of heptafulvene, all of them giving only minute yields; thus the hydrocarbon is obtained by pyrolysis of 5-methylenebicyclo[2.2.1]heptane (CLXXIV; 0.05% yield) (266).

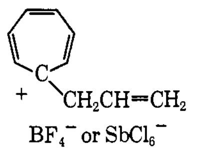
Extension of the conjugation in the vinylog CLXXV of heptafulvene does not stabilize the system; this red hydrocarbon could be prepared in solution only (52). To its preparation a method has been applied which is of general utility in the heptafulvene (and triafulvene) series and which is based on the tendency of the cycloheptatriene system to form the cycloheptatrienylium (tropylium) cation. 7-Allylcycloheptatriene (CLXXVI) gives with triphenylmethyl fluoroborate or hexachloroantimonate the corresponding (7-allyltropylium salt CLXXVII from which trimethylamine (in methylene chloride as solvent) eliminates a proton.



CLXXV



CLXXVI



CLXXVII

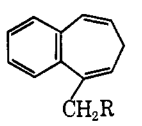
Somewhat greater is the stability of the benzo derivatives of heptafulvene (53). From 2-methyl- (or 2-benzyl-) 3,4-benzocycloheptatriene (CLXXVIII), by successive treatment with triphenylmethyl perchlorate (or hexachloroantimonate) and trimethylamine *via* the benzotropylium salt and a nitrogeneous intermediate CLXXIX, 1,2-benzoheptafulvene and its 8-phenyl derivative (CLXXX) were prepared. Both are oils, but the latter could be isolated and was stable for a few minutes, if kept under nitrogen. The same is true for 3,4-benzoheptafulvene (CLXXXII) which was prepared analogously from 7-methyl-3,4-benzocycloheptatriene (CLXXXI).

Also phenylation of the exocyclic carbon atom has—expectedly (see below)—a stabilizing influence on the heptafulvene system. The synthesis of (CLXXII, R = H) has been repeated (188). The product had a somewhat (30°) higher melting point than reported before (393). Tropone does not react analogously with diphenylketene, but gives a product of the probable structure CLXXXIII.

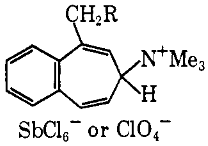
Much of the work done in this field relates to the heptafulvenes derived from 2,3,6,7-dibenzocyclohepta-2,4,6-triene and its higher benzologs. The tropone derivative CLXXXIV (37, 425) reacts normally with methylmagnesium iodide and benzylmagnesium chlorides; the alcohols so obtained are dehydrated to the heptafulvenes CLXXXV (*cf.* 121). The same applies to the benzologous ketones CLXXXVI–CLXXXVIII (28, 42). (Tropone itself reacts with Grignard compounds—as with diphenylketene (see above)—by 1,4, not 1,2, addition (298).) The dehydration of the tertiary alcohols is not always easy. In some cases, it is necessary to resort to thermolysis of the corresponding acetates.

The synthesis of the necessary "heptafulvene ketones" is simple: condensation of phthalic anhydrides with arylacetic acids leads to arylmethylenephthalides, which are reduced by phosphorus and hydriodic acid to dibenzyl-*o*-carboxylic acids; the latter are cyclized, *e.g.*, by means of polyphosphoric acid.

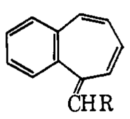
ω-Phenyl-2,3,4,5,6,7-tribenzoheptafulvene (CLXXXIX) has been obtained analogously from tribenzotropone (CXC). For the synthesis of the latter two conventional methods have been worked out (43, 128). A third, most elegant method is based on the ability of the dibenzocycloheptatrienone (CLXXXIV) system to form a benzyne-type derivative (CXC1), *viz.* by treatment of the 5-bromo drivative of CLXXXIV with potassium *t*-butoxide. This benzyne analog adds normally furan, and the adduct CXCII is converted by successive hydrogenation and dehydration into CXC (420, 421).



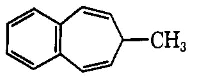
CLXXVIII, (R = H, C_6H_5)



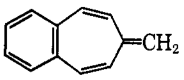
CLXXIX



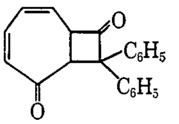
CLXXX



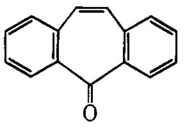
CLXXXI



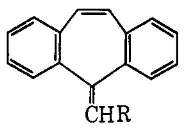
CLXXXII



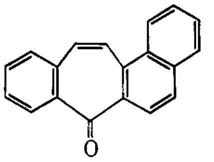
CLXXXIII



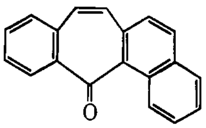
CLXXXIV



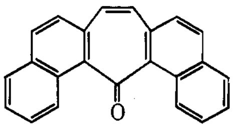
CLXXXV



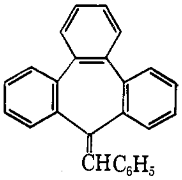
CLXXXVI



CLXXXVII



CLXXXVIII

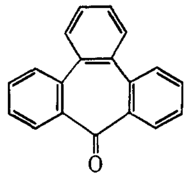


CLXXXIX

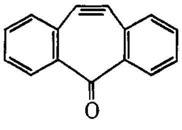
Obviously, the dibenzoheptafulvenes can also be obtained from 2,3,6,7-dibenzo-2,4,6-cycloheptatriene (CXCIII); this gives a 1-lithio derivative which reacts normally with aldehydes and ketones (28). For the synthesis of CXCIII or its substitution products, the solvolytic rearrangement of the 9,10-dihydroanthrylcarbinols (CXCIV) is most useful (45, 342, 409), as these carbinols are easily accessible by lithium aluminum hydride reduction of 9-acylanthracenes (or, for R = H, methyl anthracene-9-carboxylate) or of 9-acyl-9,10-dihydroanthracenes which are formed in a somewhat surprising manner by Friedel–Crafts reaction of 9,10-dihydroanthracene (295). It may be mentioned that CXCIII is also formed as one of the products of the interaction of anthracene with diazomethane (285).

An alternative method for the preparation of the heptafulvene CLXXXV (R = H) consists in the dehydrohalogenation of the dibenzocyclooctatriene derivative CXCV with boiling α-picoline. Possibly, the tropylium ion CXCVI is the intermediate (90).

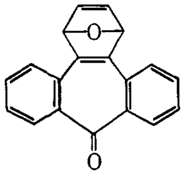
The dibenzotropone CLXXXIV has also been converted into basically substituted dibenzoheptafulvenes by reaction with basic Grignard reagents (3, 54, 173).



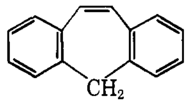
CXC



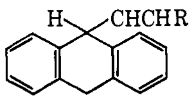
CXCI



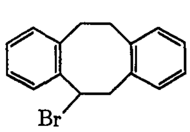
CXCII



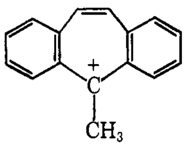
CXCIII



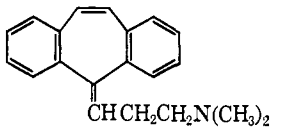
CXCIV



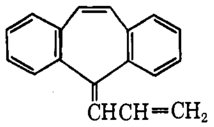
CXCV



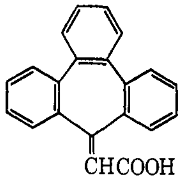
CXCVI



CXCVII



CXCVIII

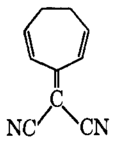


CXCIX

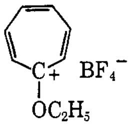
Thus, with γ-dimethylaminopropylmagnesium chloride the heptafulvene CXCVII has been obtained; Hofmann degradation converted it into ω-vinyl-2,3,6,7-dibenzoheptafulvene (CXCVIII) (173) (*cf.* section II.A.2). Many patents in the tranquilizer field have been based in recent years on compounds of this type.

The fact mentioned above that CXCIII gives a lithio derivative, *i.e.*, an anion, is surprising; it shows that in the benzologs of cycloheptatriene the specific properties of this system are obliterated or at least weakened. This is also evident from a comparison of the properties of the heptafulvenes with theory (326). As expected, heptafulvene is polar, and the direction of the dipole moment from the ring to the exocyclic carbon atom has been proven to be in accord with theory (42). Qualitatively, the hypsochromic effect of annellation has been predicted correctly by theory. However, in the spectra of the dibenzoheptafulvenes, no fulvenic characteristics can be detected; in fact they are the same as those of the 5,6-dihydro derivatives and of the corresponding substituted 1,1-diphenylethylenes. The suspicion is thus justified that the molecules are not planar. Indeed, it has been shown that the aminodibenzoheptafulvene CXCVII and the carboxytribenzoheptafulvene CXCIX can be prepared in optically active forms which racemize on heating. The activation energy of racemization (31 and 32 kcal/mole, respectively, at 139°) can be interpreted as the energy for the flipover of the boat form of the central ring (422, 423; *cf.* 110). In any event, it should be borne in mind that the nonannellated heptafulvene CC is planar in the solid state (378), and an attempt to evaluate the pseudoaromatic character of the dibenzoheptafulvene system by nuclear magnetic resonance spectroscopy should be mentioned (330).

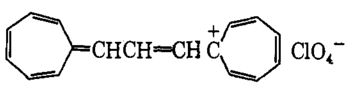
From the preceding consideration it will be obvious that the introduction of strongly negative substituents into the exocyclic methylene groups of heptafulvene will enhance the contribution of the dipolar form and thus increase the fulvenic character. A number of such substituted heptafulvenes has been described. Ethoxytropylium fluoroborate (CCI), formed from tropone and triethyloxonium fluoroborate, reacts with malononitrile in the presence of bases to give the orange ω,ω-dicyanoheptafulvene (CC) (156, 297), which, indeed, has the high dipole moment of 7.49 D), indicating a significant contribution of a dipolar structure. Equally, methyltropylium perchlorate (2 moles) and ethyl orthoformate condense in acetic anhydride to the deep blue [3-(cycloheptatrienylidene)allyl]tropylium perchlorate (CCII) (156). An alternative method consists in the dehydrogenation (with bromine, N-bromosuccinimide, or chloranil) of tropylmalononitrile, diethyl tropylmalonate and ethyl tropylcyanoacetate behaving analogously (297, 457). A number of analogs



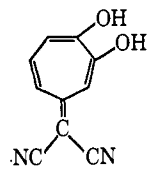
CC



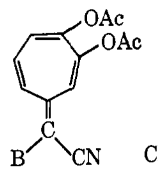
CCI



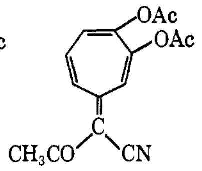
CCII



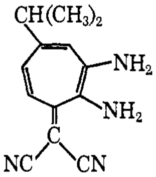
CCIII



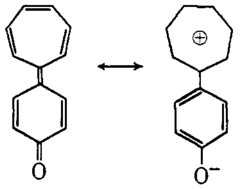
CCIV



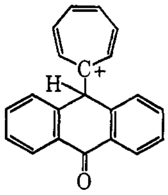
CCV



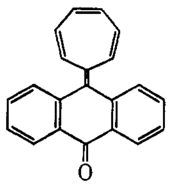
CCVI



CCVII



CCVIII



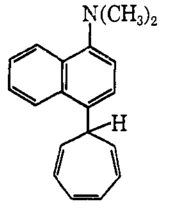
CCIX

of CC have been prepared, *viz.* CCIII (205), CCIV and CCV (206), and CCVI (207).

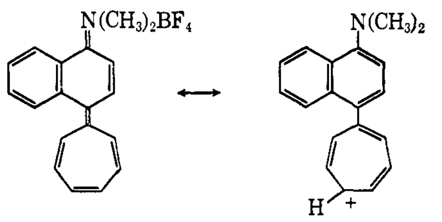
Another approach to the stabilization of the dipolar form was directed toward the system CCVII by treatment of *p*-tropylphenol with triphenylmethyl perchlorate (59). The deeply colored compound could not be isolated in pure crystalline form, but the contribution of the dipolar form to the ground state of the molecule is evident from its inability to react with 2,4-dinitrophenylhydrazine, methylmagnesium iodide, or the cyclopentadienide anion and from the absence of any infrared absorption in the range 1600–2850 cm^{-1} (for a dimethyl derivative of CCVII, see 434). Greater stability is imparted to the structure of CCVII by annellation: 7,7-dichlorocycloheptatriene (7-chlorocycloheptatrienylium chloride) reacts with anthrone to give the chloride of the cation CCVIII which could be deprotonated by triethylamine to the heptafulvene CCIX. 7,7-Dichloro-3,4-benzocycloheptatriene reacted analogously. The infrared absorption (1655 cm^{-1}) and the dipole moment (3.80 D) of CCIX indicate a fair contribution of a dipolar form to the ground state of the molecule (119). For comparison, the stable blue salt (CCXI) which has been obtained from 1-dimethylamino-4-tropylnaphthalene (CCX) and triphenylmethyl fluoroborate (258) should be mentioned. An elegant, but abortive, attempt has been made to synthesize compound CCXII by condensation of the dianion of cyclooctatetraene and tropylium bromide (291).

In conclusion, a study is reviewed (184) which has led to stable heptafulvene derivatives of the immonioalkenyl salt type (CCXIII) and vinylogs of CC. 7-Alkylcycloheptatrienes give with phosphorus pentachloride in methylene chloride the corresponding tropylium hexachlorophosphates which react with substituted formamides, CHO(CH=CH)NR′R″, to yield the immonium salts CCXIII (n = 0, 1, 2). Analogously, 7-methoxycycloheptatriene gave with 1,2,3-trimethyl-2-methyleneindoline in the presence of glacial acetic acid the crystalline 1,3,3-trimethyl-2-[(1,3,5-cycloheptatrien-7-yl)methylene]indoline (CCXIV) which could be dehydrogenated by chloranil to the salt CCXV. As expected, in the compounds of type CCXIII the NR_2 group is replaced by the dicyanomethylene group upon treatment of the salt with malononitrile. Thus, the vinylogs CCXVI and CCXVII of CC were prepared (longest absorption bands for CC, 405 (shoulder); CCXVI, 465; and CCXVII, 505 mμ (in ethanol)).

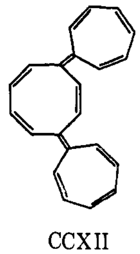
Another group of substances which is suitably discussed here are the "fulvalmixene-1,4-quinones" (209, 210); from cyclopentene-3,5-dione, tropylium bromide, and chloranil in xylene, in the presence of hydrogen bromide, the red CCXVIII has been obtained, undoubtedly *via* 2-tropylcyclopentane-1,3-dione. 1,2-Dichlorocyclopentene-3,5-dione reacts analogously 1,3-Diketohydrindene and tropylium bromide gave directly 2,2-ditropyl-1,3-diketohydrindene (CCXIX) which, upon pyrolysis, decomposed into cycloheptatriene and the red "2,3-benzofulvalmixene-1,4-quinone" (CCXX). The dipole moments of these "quinones" (2.85 and 4.91 D) indicate some measure of charge transfer from the seven- to the five-membered ring (190).



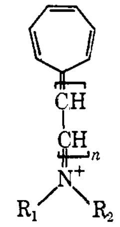
CCX



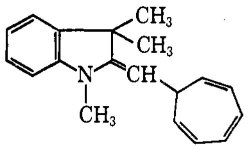
CCXI



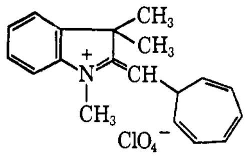
CCXII



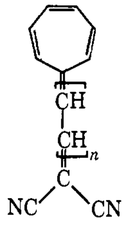
CCXIII, n = 0,1,2



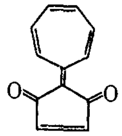
CCXIV



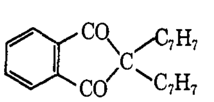
CCXV



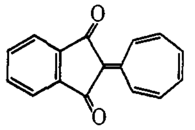
CCXVI, n = 1
CCXVII, n = 2



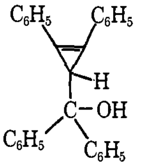
CCXVIII



CCXIX



CCXX



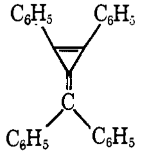
CCXXI

C. TRIAFULVENES

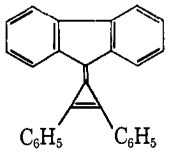
It has been predicted (27) that the electronic structure of the triafulvenes (VII) is analogous to that of the heptafulvenes. The name has been suggested by Bergmann and Agranat (29), while Chalvet, Daudel, and Kaufman (84) have suggested "triangle." The expectations of the theory seemed *a priori* justified when cyclopropenone (of which several disubstitution products have been prepared) was compared with tropone and the cyclopropenylium with the tropylium cation, both with regard to their physical and chemical properties (4, 118, 221, 222, 459). The theory predicts that hydrocarbons of triafulvene type would be unstable; indeed, no such compound has yet been synthesized. An attempt (76) to obtain 1,2,4,4-tetraphenyltriafulvene (CCXXII) by dehydration of the carbinol CCXXI led only to the formation of 1,2,4-triphenylnaphthalene and 1,2,3-triphenylazulene, and also reaction of diphenylcyclopropenone (77) and diphenylketene does not lead to the desired hydrocarbon CCXXII (28). Equally, from 1,2-diphenyl-2-(9-fluorenyl)-3-cyclopropenol, on dehydration, an isomer of the expected triafulvene CCXXIII was obtained (31). However, as in the heptafulvene series, the introduction of negative substituents on the exocyclic carbon atom increases the stability of the (dipolar form of the) triafulvenes, in which—as in the heptafulvene—the positive pole lies in the ring, the negative at the exocyclic carbon atom. The "quinocyclopropene" CCXXIV (195) has been prepared by treatment, with a tertiary amine, of 3-(3,5-dibromo-4-hydroxyphenyl)-1,2-diphenylcyclopropenium bromide (CCXXVII). The latter was obtained by addition of phenylchlorocarbene to 4-benzyloxytolane (CCXXV), pyrolytic debenzylation of the bromide of the cyclopropenium salt (CCXXVI) so obtained, and bromination with NBS. The bromine-free analog of CCXXIV could not be isolated in pure state; it, too, was an orange substance which regenerated the cyclopropenium system upon addition of strong acids.

A second compound of the same type has also been obtained by an unexpected, somewhat devious route: N,N-dimethyl-N′-(1,2-diphenylcyclopropenyl)-N′-nitrosourea (CCXXVIII) reacted with dimethyl fumarate in the presence of potassium *t*-butoxide in boiling heptane to give a 48% yield of the yellow dimethyl (1,2-diphenylcyclopropenylidene)succinate (CCXXIX), probably *via* the carbene CCXXX (181). A perhaps more rational approach consists in the reaction of diphenylcyclopropenone (77) with triphenylphosphinecarbethoxymethylene, leading to the bright yellow 4-carbethoxy-1,2-diphenyltriafulvene (CCXXXI), in 10–20% yield (23). In view of the experience in the heptafulvene series (section II.B), diphenylcyclopropenone was condensed with malononitrile in boiling acetic anhydride to give, albeit in 5% yield, 4,4-dicyano-1,2-diphenyltriafulvene (CCXXXII), which—like the corresponding heptafulvene—has a very high dipole moment (7.9 D) (29). The yield could be improved to 24% by addition of catalytic amounts of an amphoteric compound such as β-alanine (12; *cf.* 208 where a mixture of acetic anhydride and boron trifluoride was used as condensing agent). Also dipropylcyclopropenone reacted analogously with malononitrile (196), and ethyl cyanoacetate behaved like the dinitrile (12).

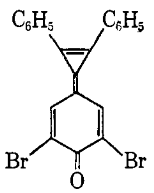
Another method for the preparation of electronegatively substituted triafulvenes uses the reaction of alkoxydiphenylcyclopropenium salts (CCXXXIII), easily accessible from diphenylcyclopropenone and trialkyloxonium salts, with "reactive methylene" compounds. As examples of the products formed, those obtained with phloroglucinol, 2,4,6-trinitrotoluene, and 1,3,3-trimethyl-2-methyleneindoline (CCXXXIV–CCXXXVI) are given (111); with anthrone, the interesting derivative CCXXXVII was obtained which by its high dipole moment (9.41 D) and low carbonyl frequency (1630 cm^{-1}) shows the extent to which a dipolar form contributes to the ground state of the molecule (compare CCIX). CCXXXVII could also be prepared from 3,3-dichloro-1,2-diphenylcyclopropene and anthrone: the fluoroborate (CCXXXVIII) of the primary product was deprotonated with triethylamine in acetonitrile. While the spectra of the product obtained by the two methods were identical, the melting



CCXXII



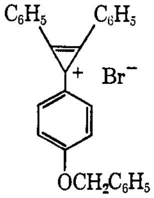
CCXXIII



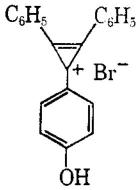
CCXXIV

$C_6H_5CH_2OC_6H_4C{\equiv}CC_6H_5$

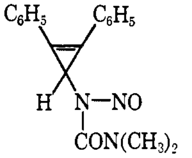
CCXXV



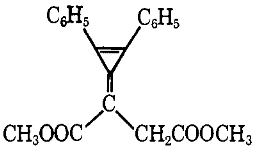
CCXXVI



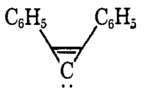
CCXXVII



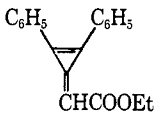
CCXXVIII



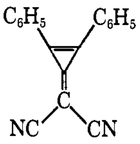
CCXXIX



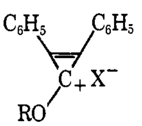
CCXXX



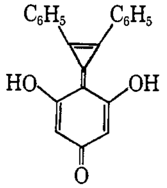
CCXXXI



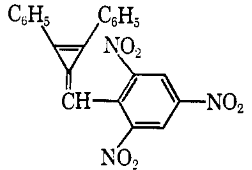
CCXXXII



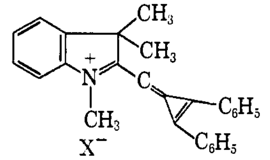
CCXXXIII



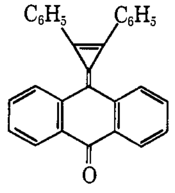
CCXXXIV



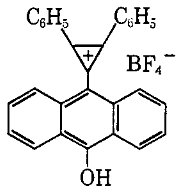
CCXXXV



CCXXXVI



CCXXXVII



CCXXXVIII

points (decomposition points) differed by 40° (118). In fact, there exist some uncertainties regarding this compound. From anthrone and diphenylcyclopropenylium perchlorate a different product, which was considered to be 2,3-diphenylallylideneanthrone (CCXXXIX) (119), has been obtained (118). Experiments (28) have shown, however, that neither this formula nor the isomeric CCXL (both compounds have been synthesized) represents the product obtained (incidentally, CCXXXIX and CCXL contain two hydrogen atoms more than CCXXXVII); it may be the benzanthrone derivative CCXLI. In any event, the physical constants of the product are not in disagreement with this formula.

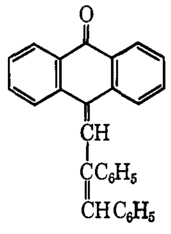
It is interesting to note, in conclusion, that when ethoxydiphenylcyclopropenylium fluoroborate (CCXXIII) was condensed with phenylmalononitrile, the reaction took place in the phenyl ring, leading to CCXLII (140).

D. FULVALENES

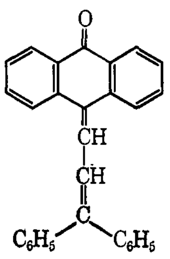
In principle, the methods used for the preparation of the fulvenes can also be applied to that of the fulvalenes (III). The condensation of cyclopentadiene and fluorenone in the presence of sodium ethoxide does not, it is true, give fluorenylidenecyclopentadiene (CCXLIII), but a dimeride (36), although the monomer has been briefly described as dark red (92, 94); however, cyclopentadienylmagnesium bromide gives with tetraphenylcyclopentadienone 1,2,3,4-tetraphenylfulvalene (CCXLIV); 1-indenylmagnesium bromide and 2,3-diphenylindone yield 7,8-diphenyl-1,2,5,6-dibenzofulvalene (CCXLV) (432, 433); and bis(2,3-diphenyl-1-indenyl) (CCXLVI) is dehydrogenated on heating with lead oxide to the fulvalene CCXLVII. CCXLV and CCXLVII occur in *cis–trans* isomeric forms which are easily interconvertible. An interesting substance which belongs into this series is the bis(diphenylene)-fulgide CCXLVIII, which is prepared from diethyl succinate and fluorenone in the presence of potassium *t*-butoxide (138).

For the preparation of symmetric fulvalenes some additional methods are available. The keto halides of fulvene ketones, as far as they exist, can be dehalogenated to fulvalenes by heating with metals, potassium sulfide (381), thioacetic acid (41), or iron pentacarbonyl (89). This method applies to the halides of fluorenones (9,9-dichlorofluorenes) and 1,1,3-trichloroindene (the keto chloride of the (unknown) 3-chloroindone); it appears that compounds of type CCXLIX are intermediates in this reaction as they can sometimes be isolated and lose the supernumerary halogen atoms only under more stringent conditions.

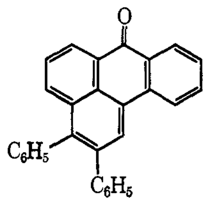
Variations of this method are the preparation of dibiphenyleneethene (VI) from fluorenoneketyl and titanium trichloride (169) or from fluorenone and chromium hexacarbonyl (16) and by photolysis or thermolysis (yield 91%) of biphenylenediazomethane (167). This reaction is also brought about by triphenylphosphine (137) and by acid chlorides (369) with the exception of oxalyl chloride which leads to CCL (392). It has been shown that the photolysis of diazocyclopentadiene gives fulvalene (III) itself (284) when carried out in a solid fluorocarbon–ether matrix at 77°K. Also 9-dimethylsulfonium fluorenylide (CLXXI) and 9-trimethylammonium fluorenylide (CCLI) give in their reactions as a by-product the red hydrocarbon (177, 179). Finally, the formation of 3,3′-diphenylbis(1,1′-diindenylidene) (CCLII) from 1,1-dibromo-3,3-diphenyl-2-propene (CCLIII) should be mentioned; it takes place in the presence of sodamide



CCXXXIX



CCXL



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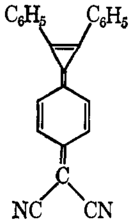

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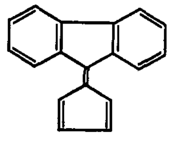
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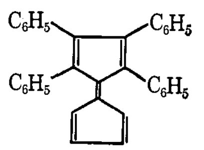

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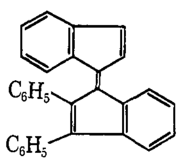

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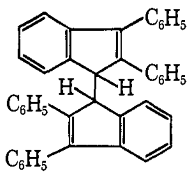

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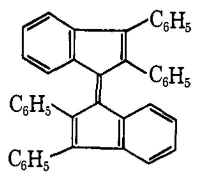

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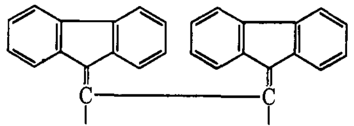

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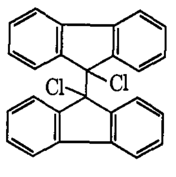

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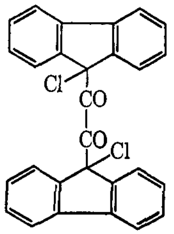
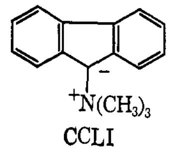


CCL



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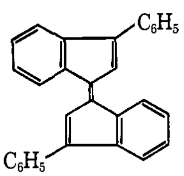

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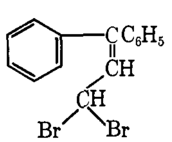

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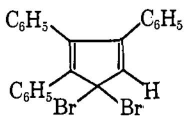

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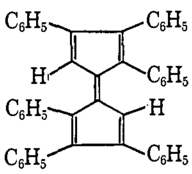

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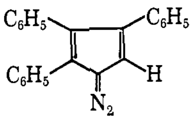
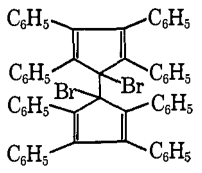


CCLVI



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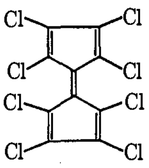

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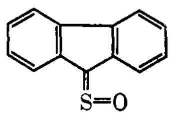


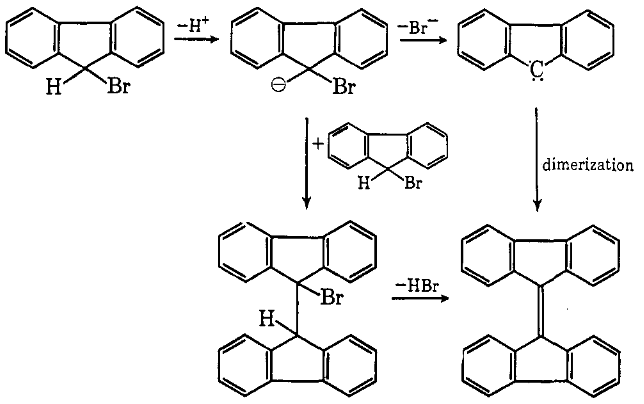
CCLIX

and combines the "dimerization" with a cycloisomerization reaction (see section II.A.6) (406, 408).

The "keto halide method" has also been successful in the preparation of some cyclopentadiene-derived fulvalenes. The 5,5-dibromo derivative CCLIV of 1,2,3-triphenylcyclopentadiene, upon reaction with iodine (Finkelstein reaction), gave the hexaphenylfulvalene CCLV which was also obtained from the diazo derivative CCLVI (306). However, the 5,5-dibromo derivative of 1,2,4-tri- and 1,2,3,4-tetraphenylcyclopentadiene yielded, upon dehalogenation (with zinc), only the 5,5′-dibromodicyclopentadienyls (*e.g.*, CCLVII) (307). For steric reasons, the formation of a monoplanar fulvalene appears to be impossible in these two cases, and the formula of CCLV is, therefore, probably correct also configurationally. Chlorine in these *ortho* positions does not have the same effect. Perchlorocyclopentadiene at 500° and under 0.1 mm pressure is dehalogenated by iron to give 48% of the blue perchlorofulvalene (CCLVIII) and 22% of its 5,5′-dichloride; in the absence of the metal, even at 700°, only traces (5%) of the latter compound and mainly perchloronaphthalene are obtained (136, 262, 269, 347). The reaction of triethyl phosphite with the 5,5′-dichloride of CCLVIII removes the supernumerary chloride atoms (262).

Another general method consists in the dehydrobromination of 1-haloindenes and 9-halofluorenes by bases. A recent example of this reaction is the formation of bis(biphenylene)ethene (XVI) from 9-chlorofluorene and alkali amide in liquid ammonia (164). A variation of this method consists in the reaction of a lithium derivative of cyclopentadiene and its benzologs with iodine. This was effected in the case of 1,2,3-triphenylcyclopentadiene (306), while (again) from 1,2,4-triphenylcyclopentadienyllithium only 1,1′-dihydrobis(triphenylcyclopentadienyl) and from 1,2,3,4-tetraphenylcyclopentadienyllithium only the 5-iodo derivative were obtained under these conditions (307).

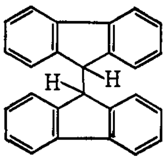
Two mechanisms appear possible, one involving a divalent carbon intermediate, the other the alkylation of the anion of the halogen compound.



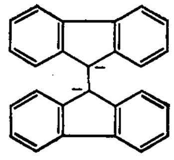
VI

A study of the reaction, using benzyltrimethylammonium hydroxide, has shown that the rate-determining step is bimolecular (in 9-bromofluorene), which is only possible if the first mechanism is accepted (56). However, when potassium *t*-butoxide was employed, first-order reactions were observed, *e.g.*, with 2-cyano- and 2-nitro-9-bromofluorene (57). Thus both mechanisms may be operative, and an old assumption of a carbene mechanism (39) appears to have been, at least partially, justified. A carbene mechanism has been suggested also for the pyrolysis of CLXXI and CCLI and is probably responsible for the formation of bis(biphenylene)ethene (VI) from fluorenylidene sulfine (CCLIX) (377). A carbene (CXLII) has, as mentioned before, been invoked in other reactions.

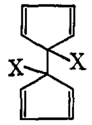
Fluorenes can be dehydrogenated with lead oxide, sulfur, or halogen at high temperatures (250–300°) to bis(biphenylene)ethenes (VI) (141–143, 161, 175), a reaction which undoubtedly also passes the stage of bis(biphenylene)ethane (CCLXII). The latter hydrocarbon is known to be dehydrogenated to VI by N-bromosuccinimide (397), lead dioxide, silver acetate in pyridine, quinone, iodine, or even air in the presence of alkali (436–438). Also manganese dioxide has been



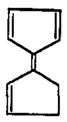
CCLXII



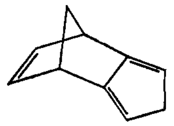
CCLXIII



CCLXIV



CCLXV



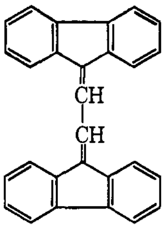
CCLXVI

used for this purpose (314). In some of these cases, undoubtedly the anion CCLXIII is responsible for the dehydrogenation step. A similar reaction is the formation of VI in 9% yield in the pyrolysis of di(9-fluorenyl) sulfide (26); simple pyrolysis of bis(biphenylene)ethane may well cause disproportionation and thus lead to VI and fluorene (189).

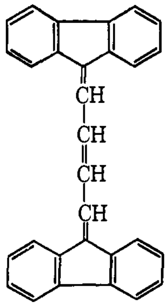
Cyclopentadiene can also be dehydrogenated to fulvalene (III), though indirectly: cyclopentadienylsodium is transformed by iodine into the dihydrofulvalene CCLXIV (X = H); its dilithio derivative (X = Li) is oxidized by oxygen and yields a solution of fulvalene (108). Incidentally, the physical data (spectra) reported for fulvalene by various authors are by no means identical.

Finally, it should be mentioned here that the simplest fulvalene (III) also has been prepared by autoxidation (catalyzed by silver oxide) of the dihydro derivative CCLXV, which in turn was formed when a mixture of 1-dicyclopentadienol and dilute hydrochloric acid was steam distilled, the hydrocarbon CCLXVI probably being the intermediate (356; *cf.* 84, 194, 219).

In this connection, a few words may be said of the vinylene homologs of VI and the corresponding cumulenes which all belong to the fulvalenes. 1,4-Bis(biphenylene)butadiene (CCLXVII) can be prepared by condensation of succinic acid with fluorenone in the presence of lead oxide and acetic anhydride (242); the use of dihydromuconic acid under the same conditions gives the higher vinylog 1,6-bis(biphenylene)hexatriene (CCLXVIII). CCLXVII is also obtained, somewhat unexpectedly, from the dibromide of 9-methylenefluorene and dimethylaniline (250, 447, 449), the latter possibly acting both as dehydrobrominating and debrominating agent.



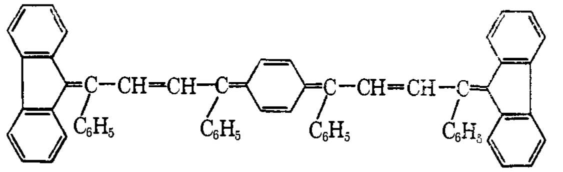
CCLXVII



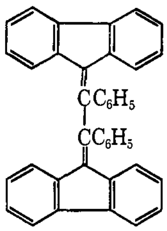
CCLXVIII

The Wittig reaction can be employed for the preparation of vinylogs of bis(biphenylene)ethene: the Wittig reagent LXXXIX gives with fluorenone CCLXVII and "dimerizes" on heating to CCLXVIII (116); the phosphorane LXXXVII yields with quinone the interesting polyene CCLXIX (388).

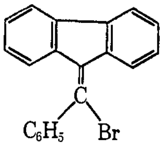
Other methods which may be capable of generalization have been employed in the synthesis of 2,3-diphenyl-1,4-bis(biphenylene)butadiene (CCLXX): the condensation of fluorene with benzil (220) and the dehydration of the pinacol of benzoylfluorene (387). Mechanistically less simple is the formation of CCLXX from the magnesium derivative of 9-(α-bromobenzylidene)fluorene (CCLXXI) with aromatic ketones (387); the system has obviously a high reducing power. Also with cuprous chloride does the magnesium derivative of CCLXXI (section II.A.6, CXXV) give CCLXX (200). Regarding this hydrocarbon, the literature contains some inconsistencies: in addition to the hydrocarbon, mp 302.5–303.5° (200, 387), one, mp 244°, has been obtained, among other products, from 9-chloromethylenefluorene and phenyllithium (100), and the product from benzil and fluorene (220) has been reported as having mp 369.3°. It would be worthwhile clarifying this point.



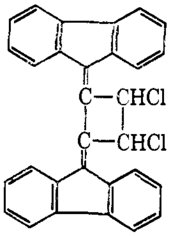
CCLXIX



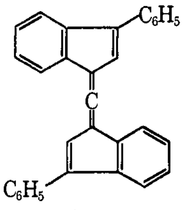
CCLXX



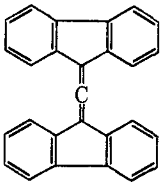
CCLXXI



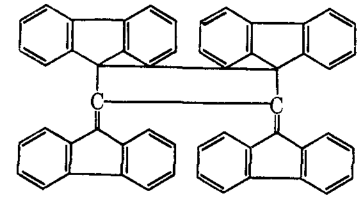
CCLXXII



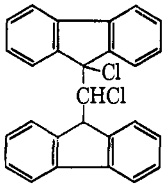
CCLXXIII



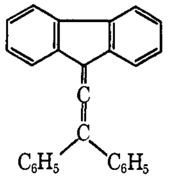
CCLXXIV



CCLXXV



CCLXXVI

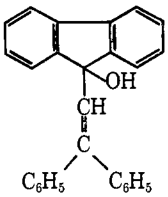


CCLXXVII

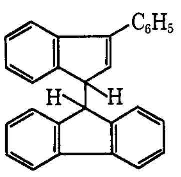
An interesting diene of this series is compound CCLXXII (and its bromo analog) which is formed from 9-ethynylfluorenol and thionyl chloride or hydrogen chloride (292).

For theoretical reasons, it is to be expected that these polyenes are most stable as *trans* compounds. However, *cis* forms have been prepared photochemically (261).

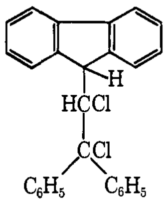
The simplest known cumulene of the fulvene series is the indene derivative CCLXXIII, which is formed from 1-(3-phenylindenyl)lithium and diethyl carbonate (63). The orange-yellow bis(biphenylene)allene (CCLXXIV) has been claimed to be formed in the interaction of quinoline with fluorene-9-carboxylic acid (391), probably *via* biphenyleneketene (CLIII), but recent work (115) has shown that the product was a dimer (possibly CCLXXV); it was also obtained when 1,2-dichloro-1,3-dibiphenylenepropane (CCLXXVI) was treated with quinoline, while the use of triethylamine in ethyl acetate permitted the isolation of the monomer. Similar observations were made in the case of the analogous allene CCLXXVII. The dehydration of 9-(β,β-diphenylvinyl)-9-fluorenol (CCLXXVIII) with hydrochloric acid (40) caused the allene CCLXXVII to isomerize (see section II.A.6) to the indene derivative CCLXXIX; only under special conditions did the dehydration of the tertiary alcohol give the desired allene. The latter could also be obtained from 1-biphenylene-2,3-dichloro-3,3-diphenylpropane (CCLXXX) with triethylamine. For the preparation of CCLXXX, 9-(β,β-diphenylethylidene)fluorene (CCLXXXI) was isomerized by means of potassium hydroxide in dimethylformamide to 9-(β,β-diphenylvinyl)-fluorene (CCLXXXII) and the latter chlorinated.



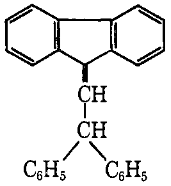
CCLXXVIII



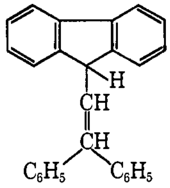
CCLXXIX



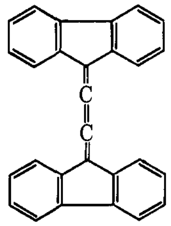
CCLXXX



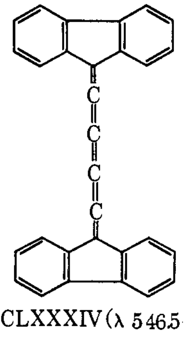
CCLXXXI



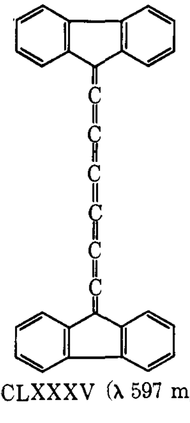
CCLXXXII



CCLXXXIII (λ 488 mμ)



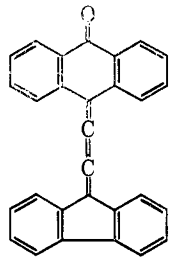
CCLXXXIV (λ 546.5 mμ)



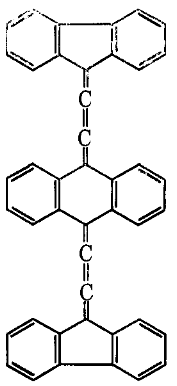
CCLXXXV (λ 597 mμ)

The three homologs (CCLXXXIII–CCLXXXV) of CCLXXIV were prepared from 1,4-bis(biphenylene)-2-butyne-1,4-diol, 1,6-bis(biphenylene)-2,4-hexadiyne-1,6-diol, and 1,8-bis(biphenylene)-2,4,6-octatriyne-1,8-diol, respectively, by reduction with hydriodic acid, diphosphorus tetraiodide, or stannous, chromous, or vanadous chloride (81, 234, 236, 240, 241, 243, 250, 340, 436–438). CCLXXXIII is also formed when 9-(bromomethylene)fluorene is treated with potassium amide in liquid ammonia (165) or when 9-(chloromethylene)fluorene reacts with phenyllithium (98).

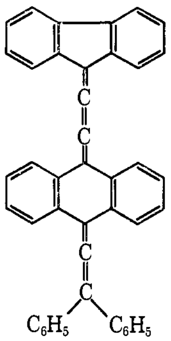
Three more complex types of cumulenes derived from fluorene may be mentioned in conclusion, *viz.* CCLXXXVI (335), CCLXXXVII (144, 335), and CCLXXXVIII (144).



CCLXXXVI



CCLXXXVII

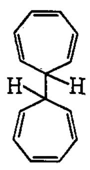


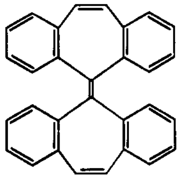
CCLXXXVIII

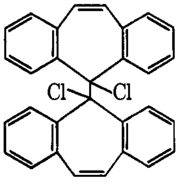
E. HEPTAFULVALENES

Only very recently (108, 109) heptafulvalene (IV) has been prepared as a fairly unstable but crystalline compound from tropylium bromide by reduction to the dihydroheptafulvene (CCLXXXIX) which could be dehydrogenated by successive treatment with bromine and trimethylamine. The first stable heptafulvalene was the tetrabenzo derivative CCXC (43) which, in analogy to the synthesis of symmetric fulvalenes, is formed from the keto chloride of CLXXXIV by heating it with copper in cymene, *via* the dichloro compound CCXCI. Also the Clemmensen reduction of CLXXXIV leads to CCXC, which does not show the properties expected of a heptafulvalene. By the keto chloride method hexabenzoheptafulvalene, mp 401–403°, has also been prepared (421).

A cumulene of the heptafulvalene series, *viz.* CCXCII, has been prepared in the usual manner (340), from the diol formed from CLXXXIV and diacetylenebis(magnesium bromide). In view of the unexpected lack of


CCLXXXIX


CCXC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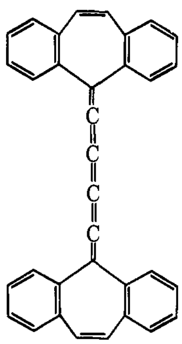
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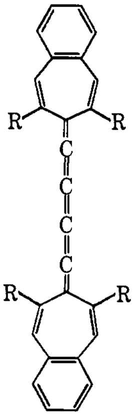
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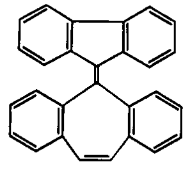
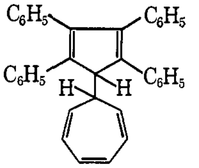

CCXCIV

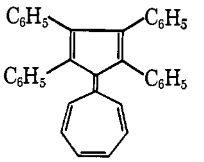
color in the other heptafulvalenes synthesized so far, the red color of this hydrocarbon is noteworthy. Analogously, two monobenzotropone derivatives (CCXCIII, R = H or CH_3) have been described, but they could not be isolated. Their color is also red.

F. PENTAHEPTAFULVALENES (MIXED FULVALENES, SESQUIFULVALENES)

In spite of the expected high stability of the pentafulvalene (V) system, in which the central linkage has been calculated to have the lowest bond order ever predicted for any "double bond" in such a system, only one representative of this group has been known for some time, *viz.* the tetrabenzo derivative CCXCIV. It is obtained by condensation of 9-fluorenyllithium and the ketone CCXXXIV (328); it has a finite dipole moment (0.83 D), but otherwise no outstanding properties of a fulvalene.

More recently, however, a number of somewhat simpler pentaheptafulvalenes have been described. Tetraphenylcyclopentadienylsodium gives with tropylium bromide the expected 1-tropyl derivative (CCXCV), which is dehydrogenated, *e.g.*, by chloranil, to tetraphenylsesquifulvalene (CCXCVI), green in the solid state and deep red in solution (315). When unsubstituted cyclopentadienylsodium was subjected to the same sequence of reactions, the product was too unstable to be isolated from its red solution (320). On the other hand, tetrachlorocyclopentadiene condensed with 3,4-benzotropone in methanol without added catalyst at room temperature and gave the violet tetrachlorobenzopentaheptafulvalene CCXCVII which has a fairly high dipole moment (5.20), as predicted by theory (212). Tropone does not behave analogously (211); when condensed with tetrachlorocyclopentadiene in ethanol it gave (instead of the expected $C_{12}H_6Cl_4$) two isomeric red compounds $C_{14}H_{11}Cl_3O$, and when methanol was used as solvent, two isomers $C_{13}H_9Cl_2O$; tetrabromocyclopentadiene yielded the bromine analogs of these products which had obviously formed by participation of the solvent. They were ordinary fulvenes of formula CCXCVIII (X = Cl or Br) in which the methoxy groups were either in the *ortho* or *para* positions of the benzene ring. Catalytic hydrogenation in the presence of sodium acetate caused both reduction and hydrogenolysis and led to *o*- and *p*-methoxybenzylcyclopentanes. The Japanese authors assume CCXCIX as an intermediate and point out that the reaction between pentabromocyclopentadiene and tropylium bromide also leads to benzylidenetetrabromocyclopentadiene.


CCXCV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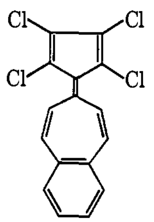
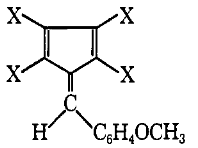

CCXCVII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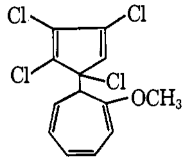
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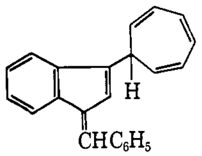
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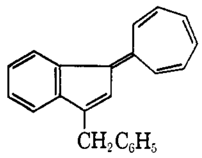
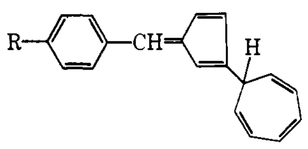
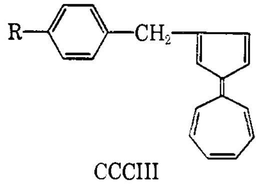
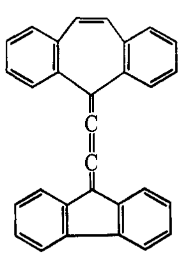
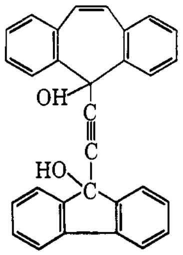

CCCI


CCCII


CCCIII


CCCIV


CCCV

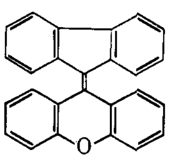
Tropylindene, prepared from indenylsodium and tropylium bromide, condenses with benzaldehyde, in the presence of sodium *n*-pentoxide, to 1-benzylidene-

3-tropylindene (CCC), which rearranges at elevated temperature to 8-benzyl-9,10-sesquifulvalene (CCCI) (322). In the same way, the tropylfulvenes CCCII are rearranged to benzylsesquifulvalenes CCCIII (320, 321).

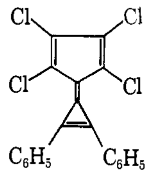
A cumulene derivative of this series, the red hydrocarbon CCCIV, has also been obtained from the acetylenic diol CCCV (340); vinylogous pentaheptafulvenes have not yet been synthesized, but some predictions as to their properties have been made (429); it may, however, be noted that some isoelectronic analogs of these vinylogs have been prepared and studied; most of them have been reviewed in section II.A.1. Here, it may be added that the xanthene system is also isoelectronic with 2,3,6,7-dibenzo-2,4,6-cycloheptatriene. Thus, CCCVI which is obtained from diazofluorene and 9,9-dichloroxanthene (367) can be considered a pentaheptafulvalene analog.

G. TRIAPENTAFULVALENES (CALICENES)

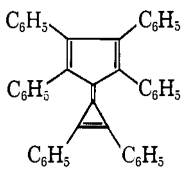
The expectation that the conjugation of a ring with the tendency to become negatively charged and one of opposite tendency would make the triapentafulvalenes (VIII) stable analogs of the pentaheptafulvalenes has been substantiated quickly in a number of laboratories; in fact, this field has been more fully developed than that of the pentaheptafulvalenes. The simplest representatives of this group are the yellow tetrachlorodiphenyl derivative CCCVII and the red hexaphenyltriapentafulvalene and the yellow tetraphenyldimethyl analogs CCCVIII and CCCIX, the only nonannellated hydrocarbons of the series. The first is obtained when tetrachlorocyclopentadiene and diphenylcyclopropenone are kept standing in methanol solution at room temperature (32, 288, 430); the second has been prepared by a more complex route which, however, opens many new applications: the lithio derivative of tetraphenylcyclopentadiene was condensed with 3,3-dichloro-1,2-diphenylcyclopropene; the primary product (CCCX) loses hydrogen chloride spontaneously (30). CCCIX has been prepared by a method used also in other series (see section II.A) and which has been particularly adaptable to triafulvene syntheses (318): tetraphenylcyclopentadienyllithium was condensed with 1,2-dimethylcyclopropenium fluoroborate and 3-tetraphenylcyclopentadienyl-1,2-dimethylcyclopropene so formed dehydrogenated by successive treatment with triphenylmethyl fluoroborate and triethylamine. Sodiotetrachlorocyclopentadiene reacted also with dipropylcyclopropenone to give CCCXI (199). The high dipole moments of the compounds CCCVII (8.1 D) and CCCVIII (6.3 D, which is the highest moment ever observed for a hydrocarbon) indicate a significant contribution of the dipolar form to the ground state of the molecule; in fact, the *hypsochromic* shift observed in most instances when the solvent changes from a nonpolar to a polar one proves that the ground state has a higher moment than the excited state. CCCVII is a base of about the strength of 2,4-dinitroaniline ($pK = \sim 4.7$); it is protonated by trifluoroacetic acid to CCCXII as indicated by the nmr and the ultraviolet spectra of its solution in that acid.



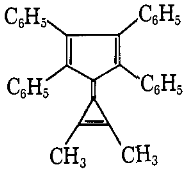
CCCVI



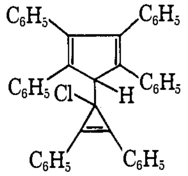
CCCVII



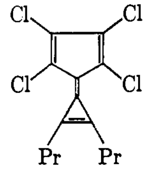
CCCVIII



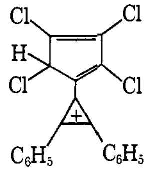
CCCIX



CCCX



CCCXI



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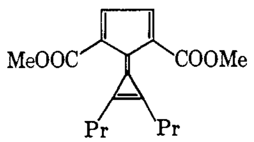

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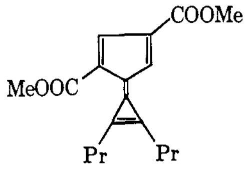
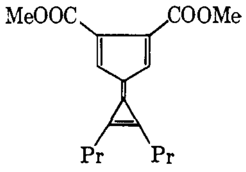
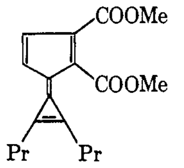


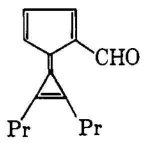
CCCXIV



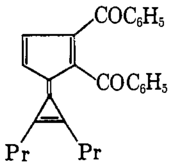
CCCXV



CCCXVI



CCCXVII



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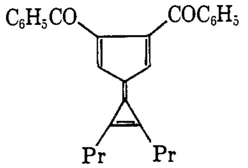
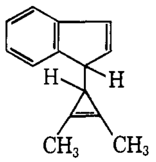
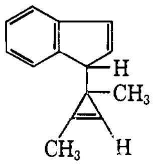


CCCXIX



CCCXX

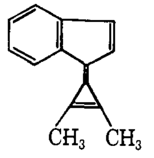


CCCXXI

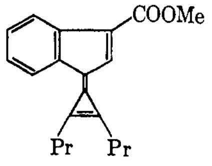
The analogous dehydrogenation of dimethylcyclopropenylcyclopentadiene, formed from cyclopentadienylsodium and 1,2-dimethylcyclopropenium fluoroborate, failed (317).

The introduction of electronegative substituents in the five-membered ring of the triapentafulvalenes will enhance the dipolar structure of the ring and stabilize the compounds formed. Thus, the condensation of the sodium derivative of "dimethyl cyclopentadienedicarboxylate" with dipropylcyclopropenone gave minute yields of the triapentafulvalenes CCCXIII and CCCXIV (197, 199), but, when instead of the ketone 1,2-dipropylcyclopropenium fluoroborate was used, a good yield (41%) of CCCXV together with some CCCXVI was obtained. 1,2-Diphenylcyclopropenium fluoroborate gave in 24% yield the diphenyl analog of CCCXV. A formyl or acyl group in the cyclopentadiene system has an analogous stabilizing effect. The sodio derivative of formylcyclopentadiene afforded at −10° CCCXVII, and the condensation of dipropylcyclopropenone with 1,5-dibenzoylcyclopentadiene, either in acetic anhydride or with sodium hydride, gave, albeit in small yield, CCCXVIII which in the latter case was accompanied by a 25% yield of CCCXIX. It is surprising that CCCXIX rearranges at 100° spontaneously to CCCXVIII.

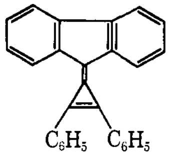
Annellation, too, stabilizes the calicene system; at the same time, as in the fulvene series and as predicted by theory, it causes a progressive hypsochromic shift of the longest absorption band of the system. A number of derivatives of indene have been studied. Indenylmagnesium bromide and 1,2-dimethylcyclopropenium fluoroborate gave a 5:1 mixture of the isomers CCCXX and CCCXXI. CCCXX was dehydrogenated in the usual manner to 5,6-dimethylbenzocalicene (CCCXXII), a hydrocarbon only stable in dilute solution (323). The same is true for the corresponding 5,6-diphenyl compound (182). In this series, too, the stabilizing effect of negative substituents in the indene nucleus has been studied. Methyl indene-3-carboxylate condenses with dipropylcyclopropenone in acetic anhydride at 120° in 15% yield to the triapentafulvalene CCCXXIII (182, 197) and the amide behaves analogously. It is interesting to note that indene itself does not undergo the analogous condensation under the conditions indicated.



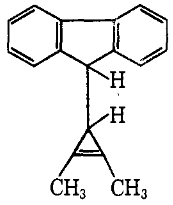
CCCXXII



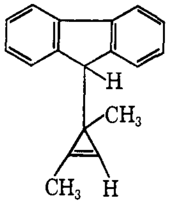
CCCXXIII



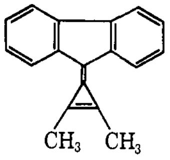
CCCXXIV



CCCXXV



CCCXXVI



CCCXXVII

Finally, fluorenyllithium was condensed with diphenylcyclopropenium fluoroborate and the product dehydrogenated to CCCXXIV, a red crystalline compound (182); analogously, dimethylcyclopropenium fluoroborate gave a mixture of the products CCCXXV and CCCXXVI; the former was converted by successive treatment with triphenylmethyl fluoroborate and triethylamine into the pale yellow CCCXXVII (318).

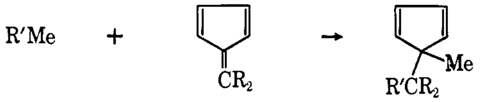
III. Chemical Reactions

A. FULVENES

The most unusual feature in the structure of the fulvenes is the polar character of the exocyclic double bond, which expresses itself in a number of unusual reactions. Furthermore, this double bond does not form an active conjugated system with either of the double bonds in the five-membered ring system of cyclopentadiene and indene. There exists thus a "natural" classification of the reactions of the fulvenes.

1. *Reaction with Metal Hydrides and Organometallic Compounds*

Metallorganic compounds and lithium aluminum hydride add to the exocyclic double bond in the expected manner, forming a carbon–metal bond (or a carbanion) at the central atom of the fulvene system.



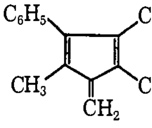
Me = metal

The study of the reactions of lithium aluminum hydride has been largely limited to fulvenes derived from fluorene (450); however, 1-methyl-2,3,4-triphenylfulvene (CCCXXVIII) has been reported to give with this reagent, 1,5-dimethyl-2,3,4-triphenylcyclopentadiene (CCCXXIX) (345). 9-Benzylidenefluorene leads to the addition product CCCXXX which gives upon hydrolysis 9-benzylfluorene and upon reaction with benzyl chloride 9,9-dibenzylfluorene. Obviously, CCCXXX is capable of many other reactions of synthetic interest (248, 249).

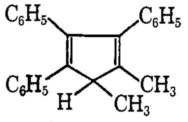
An interesting variant is the reaction of diisobutylaluminum hydride with dimethylfulvene. That the adduct is of the type CCCXXXI has been shown by its reaction with heavy water: the product contained a deuterium atom in the 1 position of the five-membered ring (458).

Analogous addition reactions of ethylidene- and benzylidenefluorene with phenylisopropylpotassium have been reported (463). In the same way (465), dimethyl- and diphenylfulvene and their benzo and dibenzo derivatives add phenyllithium. Also 9-methylenefluorene readily adds *n*-butyllithium, even at very low temperature; however, sterically more complicated organolithium compounds such as *sec*-butyllithium or CCCXXXII proved ineffective; in other cases, they led to complex secondary reactions (96). While this type of reactions with *alkali* organic compounds is not uncommon also for olefins which do not belong to the fulvene series, only fulvenes are capable, at least in a number of cases in which the 6 position is unsubstituted, of also adding *magnesium* organic compounds (67, 112, 129, 404).

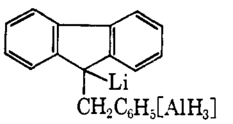
An important development of these addition reactions is the utilization of the adducts—which still contain the metal atom of the reagent—for the synthesis of ferrocenes (125, 214, 215, 217, 254, 255). The adduct CCCXXXIII of dimethylfulvene and phenyllithium, *e.g.*, gives with ferrous or ferric chloride the ferrocene CCCXXXIV (R = C_6H_5); the product of the reaction between dimethylfulvene and lithium aluminum hydride gives CCCXXXIV (R = H). A variant of this method is the reaction of ferrous chloride with the sodio *substitution* (CCCXXXV) product formed from dimethylfulvene and sodamide in liquid ammonia. Reaction with ferrous chloride gives diisopropenylferrocene (CCCXXXIV with side chains $-C(CH_3){=}CH_2$). In the same way, nickelocene derivatives have been obtained with the pyridine complex of nickel(II) chloride and cobalticene derivatives with cobalt(II) chloride (213). Also polar-substituted fulvenes behave analogously. Thus (dimethylaminomethylene)cyclopentadiene (CXXXIII) gives CCCXXXVI by successive treatment with methyllithium and ferrous chloride. In the benzofulvene series, too, successive treatment with lithium aluminum hydride and ferrous chloride gives dibenzoferrocenes (386). The "ferrocenylfulvenes" react, as the fulvenes do, with maleic anhydride and the cyclic imides of maleic acid (126, 303).



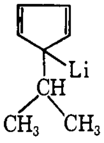
CCCXXVIII



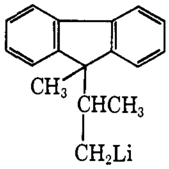
CCCXXIX



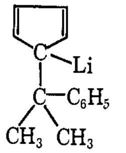
CCCXXX



CCCXXXI



CCCXXXII



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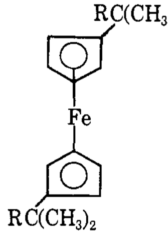
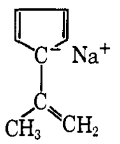


CCCXXXIV



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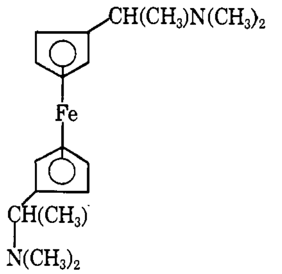

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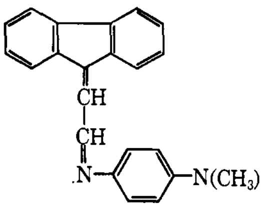

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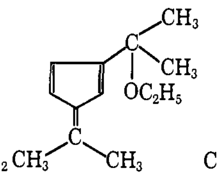

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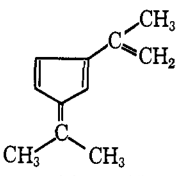
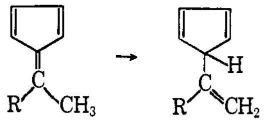


CCCXXXIX

2. Reactions of "Active" Methyl and Methylene Groups

The polarity of the exocyclic double bond of the fulvenes makes them analogs of the carbonyl compounds. One would thus expect that the methyl hydrogen atoms in 6-methylfulvenes are "active" in the same manner as in, *e.g.*, acetone. It is then not surprising that triphenylmethylsodium converts dimethylfulvene into an anion (CCCXXXV), as it converts acetone into its enolate ion (360). Equally, the methyl group in 6-methylated fulvenes can be condensed with aldehydes, ketones, and nitroso compounds in a reaction which is analogous to aldol condensation. Thus, ethylidenefluorene gives with benzaldehyde cinnamylidenefulvene (462) and with *p*-nitrosodimethylaniline the anil CCCXXXVII (394).

The mobility of the hydrogen atoms of methyl groups in the 6 position of the system is also responsible for the ability of such fulvenes to react in a tautomeric form



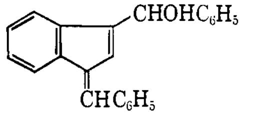
It is, then, understandable that in the condensation of cyclopentadiene and acetone in the presence of sodium ethoxide not only dimethylfulvene but also a 1:2 product is formed for which, in the course of time, various formulas have been proposed. The color indicates that it is a fulvene; recently, the structure CCCXXXVIII of 3-(dimethylethoxy)methyl-6,6-dimethylfulvene, which might be derived from the intermediate CCCXXXIX by addition of ethanol (114, 376, 383), has been proven. The formation of 3-(α-hydroxybenzyl)-1-benzylideneindene (CCCXL) as a by-product of the condensation of indene with benzaldehyde (414, 415) can be rationalized analogously. In this context, it should be mentioned that 3-alkyl-1-arylmethyleneindenes isomerize under the influence of base to 3-alkylidene-1-arylmethylindenes (46, 456). This type of reaction explains why dimethylfulvene is converted into di- and triisopropylcyclopentadienes by treatment with potassium hydroxide and isopropyl alcohol at 250° (under pressure) and that cycloalkylidenecyclopentadienes are transformed, under these conditions, into cycloalkylmono- and -diisopropylcyclopentadienes (125).

3. *Michael Reactions*

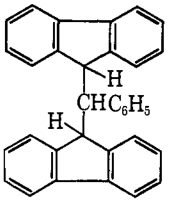
Fulvenes can act as acceptors in the Michael reaction. Thus, benzylidenefluorene adds fluorene (a solution of sodium hydroxide in aqueous pyridine serving as catalyst) and gives, in accordance with the direction of the polarity of the double bond, 1,3-bis(biphenylene)-2-phenylpropane (CCCXLI) (44). When in the condensation of butyraldehyde with fluorene, as in similar reactions, 1,1-di-(9-fluorenyl)butane (CCCXLII) is formed (18, 135, 389), it can be assumed that this compound is derived from butylidenefluorene by Michael addition of fluorene.

A formally analogous reaction takes place when fluorenol condenses with dibenzofulvenes, *e.g.*, benzylidenefluorenes, under *acidic* conditions, [(9-fluorenyl)-phenylmethylene]fluorenes, *e.g.*, CCCXLIII, being formed (441).

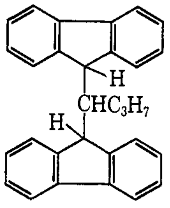
It is noteworthy that 6-furylfulvene does not act as acceptor for fluorene or diethyl malonate (364). On the other hand, an ω-aryl-ω-bromodibenzofulvene (CCCXLIV) reacts readily with fluorene in the presence of alkali giving, after acidification, a 1,3-bis(biphenylene)-2-aryl-2-bromopropane (CCCXLV); this easily loses hydrogen bromide, yielding a 1,3-bis(biphenylene)-2-aryl-1-propene (CCCXLVI) (235). The ability to undergo Michael reactions expresses itself also in the "mixed reductive coupling" which occurs when a mixture of, *e.g.*, benzylidenefluorene with an excess of acrylonitrile is subjected to electrolytic reduction. The dianion CCCXLVII, formed perhaps not in a single step, adds to 2 moles of acrylonitrile, giving CCCXLVIII which is protonated to 9-(β-cyanoethyl)-9-(γ-cyano-α-phenylpropyl)fluorene. With ethyl acrylate, benzylidenefluorene gave, under the same conditions, only a small amount of the "Michael product" CCCXLIX, the main product being 9-benzylfluorene. From 1-benzhydrylideneindene, the product obtained was CCCL, a result not wholly unexpected in view of the well-known susceptibility of indenes to polycyanoethylation (20).



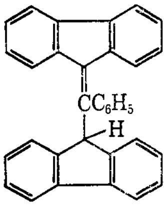
CCCXL



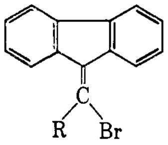
CCCXLI



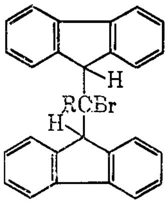
CCCXLII



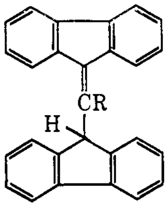
CCCXLIII



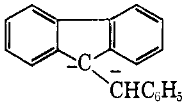
CCCXLIV



CCCXLV



CCCXLVI



CCCXLVII

4. *Reaction with Alkali Metals*

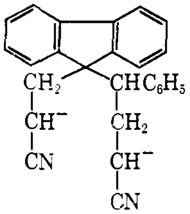
The well-known reaction of alkali metal with fulvenes may be considered as an additional chemical proof for the polar structure of these hydrocarbons. It is to be expected that the primary reaction would be the addition at the negative end of the dipole, *i.e.*, at the central atom of the cyclopentadiene ring. The radical so formed (*e.g.*, CCCLI) can then either dimerize to CCCLII or add a second atom of sodium (to CCCLIII), depending on the affinity of the radical to the metal. According to the first mechanism benzylidenefluorene gives the disodio derivative of 1,4-bis(biphenylene)-2,3-diphenylbutane (CCCLII, $R_1 = C_6H_5$; $R_2 = H$), while benzhydrylidenefluorene yields the disodio derivative of 9-benzhydrylfluorene (CCCLIII, $R_1 = R_2 = C_6H_5$) (359, 361).

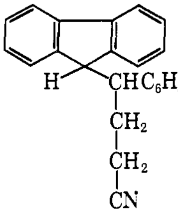
The same mechanism explains the "hydrodimerization" of benzylidenefluorene to 1,4-bis(biphenylene)-2,3-diphenylbutane (as CCCLII), when the compound is electrolyzed in dimethylformamide in the presence of quaternary ammonium salts. An intermediary red color appearing on the surface of the mercury electrode is undoubtedly due to the presence of an anion of type CCCLI (20).

It was to be expected that the sodium adducts of fulvenes would be capable of giving ferrocene derivatives in the same way as the adducts formed with lithium organic compounds or lithium aluminum hydride (see section III.A.1). Thus the metal compound CCCLIV formed from dimethylfulvene and sodium gives with ferrous chloride in tetrahydrofuran the ferrocene derivative CCCLV (324, 344). To the extent to which sodium metal does not add, but rather substitutes, the allyl isomeric form of the fulvene (*e.g.*, CCCLVI in the case of cyclopentylidenefulvene), a compound of type CCCXXXV, *viz.* CCCLVII, is formed (344).

5. *Reaction with Halogens*

The exocyclic double bond of the fulvenes appears to be refractory to halogen addition (461), recalling the behavior of highly arylated olefins: diphenylfulvene gives with chlorine a blue tetrachloro substitution product (CCCLVIII), and benzhydrylideneindene affords CCCLIX, which ultimately *adds* two chlorine atoms to give CCCLX. Bromine substitutes benzhydrylideneindene equally in the 2 and 3 position and


CCCXLVIII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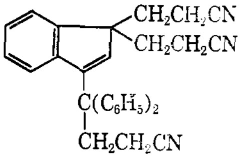
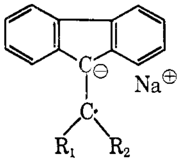

CCCL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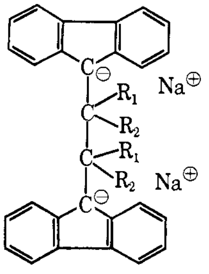
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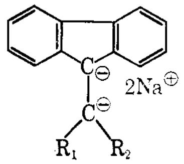
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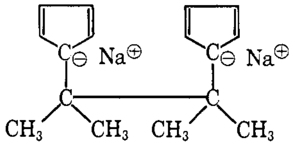
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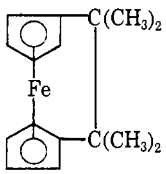
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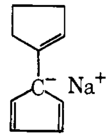
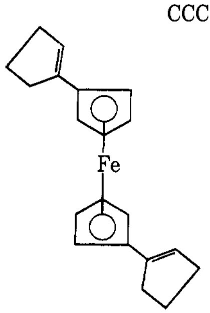

CCCLVI

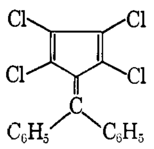

CCCLVII

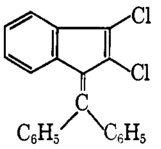
3-phenyl-1-benzhydrylideneindene first in the 2, then in the 6 position (to CCCLXI). Diphenyldibenzofulvene is brominated in the 2 and 7 positions. Also, 6-methylfulvene gives with bromine the 1,2,3,4-tetrabromo substitution product (412). However, addition products of the fulvenes have also been reported occasionally (103, 107, 416). In this connection, it is recalled that also diazocyclopentadiene is tetrasubstituted by N-bromosuccinimide (95).

6. *Reaction with Dienophiles*

Another reaction, which involves only the ring double bonds, is that of the fulvenes derived from cyclopentadiene with dienophiles. Fulvene itself and both dimethylfulvene and cyclopentylidenecyclopentadiene give adducts in the *endo* and the *exo* form, *e.g.*, with maleic anhydride CCCLXII or CCCLXIII (9, 98, 106, 450, 455). Diphenylfulvene forms only the *exo* configuration, while its reaction with maleimides, a very general reagent for fulvenes, is reported to yield only the *endo* compound CCCLXIV (313). The stability of the adducts (and their tendency to redissociate) depends on the substituents in the 6 position (225). Also dimethyl acetylenedicarboxylate (225, 307), tetracyanoethylene (225), and *p*-benzoquinone (7) have been employed. Benzynes, too, are useful dienophiles, giving compounds of type CCCLXV (287). Fulvenes derived from 2,3,4,5-tetrachlorocyclopentadiene do not react with dienophiles. In ω-(9-anthryl)tetrachlorofulvene only the anthracene moiety adds maleic anhydride (271).

On the other hand, diphenylfulvene also adds butadiene, yielding the hydrogenated fluorene derivative CCCLXVI (6), while the benzofulvenes do not seem to be able of reacting with dienes (28). It may be mentioned that in methylenefluorenes, as, *e.g.*, in methyleneanthrone (88), the exocyclic double bond forms a conjugated system with a neighboring benzene double bond and thus is capable of giving an adduct (CCCLXVII) with maleic anhydride (82); at the same time it gives the spiran CCCLXVIII with butadiene (448).


CCCLVIII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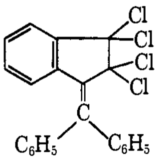
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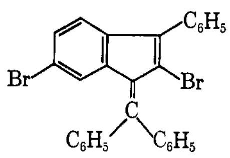
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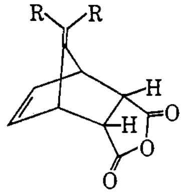
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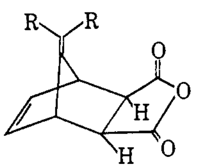
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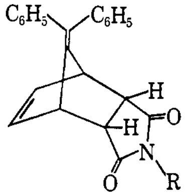
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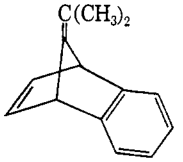
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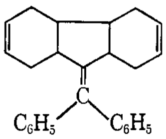
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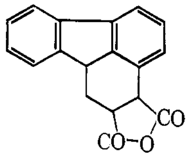
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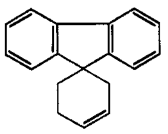
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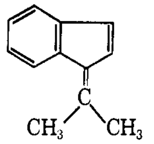
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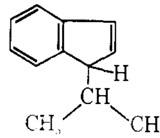
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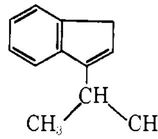

CCCLXXI

7. *Reduction*

In reduction reactions, the difference of the exocyclic and the ring double bonds is somewhat obliterated. Aluminum amalgam reduces the exocyclic double in diphenylfulvene, but leaves dimethylfulvene unchanged (416). Hydrogenation of both fulvenes with palladium as catalyst in methanol reduces only the ring double bonds (giving isopropylidene- and benzhydrylidenecyclopentanes, respectively) (334), and the same is true for 6-furylfulvene (364, 450). Sodium and alcohol as well as most other methods of catalytic hydrogenation give the fully reduced alkylated cyclopentanes (78, 193, 296, 364, 450).

It is noteworthy that the catalytic reduction of diphenylfulvene in the presence of *nickel* (not of palladium or platinum) proceeds in distinct steps, leading to benzhydrylidenecyclopentane and benzhydrylcyclopentane, respectively (192). Also, 2,3,4,5-tetraphenylfulvene is reduced by sodium and ethyl or butyl alcohol only at the exocyclic double bond (365); the same has been reported for the reduction of the fulvene CCCXXVIII when palladium in ethyl acetate was employed (345).

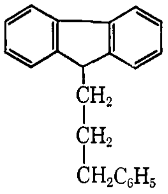
Elucidation of the reduction pathway of indene-derived fulvenes is complicated by the (already mentioned) fact that 1-alkylindenes rearrange easily to 3-alkylindenes. If, therefore, 1-isopropylideneindene (CCCLXIX) is reduced to 3-isopropylindene (CCCLXXI) by sodium and alcohol (419), it is not clear whether this is due to reduction of the exocyclic double bond (to CCCLXX) and rearrangement of the product or to direct 1,4 reduction of the conjugated system in CCCLXIX. Perhaps the latter is more likely as aluminum amalgam also reduces 1-benzylideneindene to 3-benzylindene under conditions which do not appear to favor prototropic rearrangement (417, 419). Hydrogenation of 1-cyclopentylideneindene leads directly to 1-cyclopentylhydrindene (424).

The double bond in benzhydrylidenefluorene is reduced by sodium and ammonia (290), and the same reduction takes place when dibenzofulvenes are treated with higher sodium alkoxides, such as the benzylate, $C_6H_5CH_2ONa$. Thus, benzylidenefluorene gives 9-benzylfluorene, cinnamylidenefluorene gives 9-(γ-phenylpropyl)fluorene (CCCLXXII), and bis(biphenylene)ethene gives bis(biphenylene)ethane (365, 390).

8. *Miscellaneous Addition Reactions*

Some other reactions of the fulvenes which appear to be of general applicability may be mentioned. Fulvenes derived from cyclopentadiene add diazomethane at one of the endocyclic double bonds, forming CCCLXXIII or CCCLXXIV which rearranges gradually at room temperature to the fulvene derivatives CCCLXXV or CCCLXXVI (5). Recently, however (305), the formation of a spiropyrazoline has been reported from diphenylfulvene and 2 moles of diazomethane, one molecule adding at a ring, the other on the exocyclic double bond.

Oxygen, in the presence of light, acts on 2,3,4,5-tetraphenylfulvene by epoxidation of the two endocyclic bonds and scission of the exocyclic double bonds (to CCCLXXVII) (21). A more detailed study has revealed the existence of two intermediate steps, CCCLXXVIII and CCCLXXIX, the former due to a photosensitized reaction, the second to a nonsensitized photochemical isomerization (22). Another type of oxidation of fulvenes is exemplified by the reaction of benzylidenefluorene with benzoyl peroxide and iodine, which leads to the benzoate of 9-fluorenylphenylmethanol (CCCLXXX) (133).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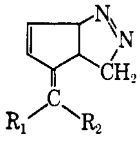
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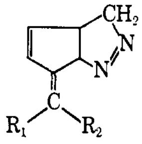
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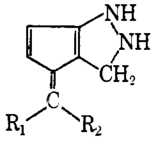
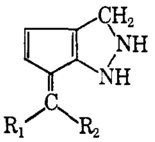

CCCLXXV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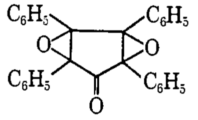
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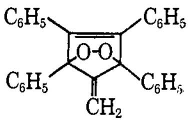
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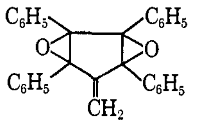
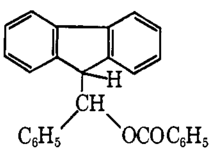
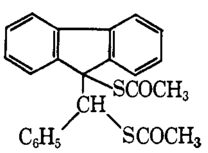

CCCLXXIX


CCCLXXX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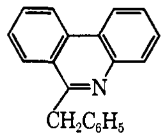
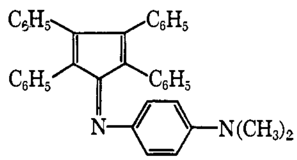

CCCLXXXII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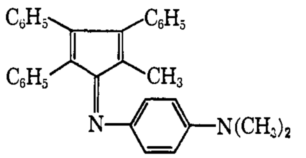
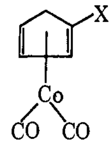
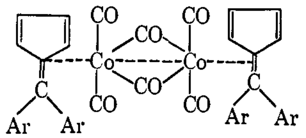

CCCLXXXIV


CCCLXXXV, X = $C\begin{smallmatrix}{=}CHR\\ CH_2R\end{smallmatrix}$

CCCLXXXVI, X = $CH(CH_2R)_2$


CCCLXXXVII

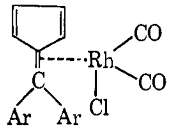
The fulvenic double bond, not unexpectedly, adds mercapto compounds in the presence of oxygen (*i.e.*, sulfur radicals). Thus benzylidenefluorene gives with thiolacetic acid CCCLXXXI, and bis(biphenylene)-ethene (VI) reacts analogously (281). The same point of attack offers itself to hydrogen azide, which converts 9-benzylidenefluorene into 9-benzylphenanthridine (CCCLXXXII) (15). Another type of addition reaction which is made possible by the polar character of the fulvenes is the addition of amines. This reaction, known for some time in the case of bis(biphenylene)-ethene (see section III.B), has been studied only cursorily (431). Thus 9-allylidenefluorene (LXXIII) adds dimethylamine or diethylamine to give compounds of type LXXIV.

The formation of fulvenes, *e.g.*, 2,3,4,5-tetraphenylfulvene, is reversed by treatment with piperidine (244). If this compound is treated with nitrosodimethylaniline and piperidine, the *p*-dimethylamino anil of the corresponding cyclopentadienone (CCCLXXXIII) (and formaldehyde) is obtained; even more surprisingly, 2,3,4-triphenylfulvene gives under these conditions the *p*-dimethylamino anil (CCCLXXXIV) of 2,3,4-triphenyl-5-methyl-cyclopentadiene.

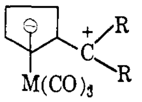
9. *Reaction with Metal Carbonyls*

It is not altogether unexpected that fulvenes are capable of forming π complexes with iron carbonyls (443) and molybdenum hexacarbonyl (213). A study of the reaction of several fulvenes with dicobalt octacarbonyl has revealed a series of possible pathways. Fulvene and 6-methyl-, 6,6-dimethyl-, and 6,6-dipropylfulvenes give an 1:1 mixture of an unsaturated and a saturated derivative of π-cyclopentadienyldicarbonylcobalt (CCCLXXXV, CCCLXXXVI) (11), oxygen-sensitive red oils which could not be separated from each other. During the transition state of the reaction, disproportionation by hydride transfer takes place. When 6,6-diarylfulvenes were treated with the same cobalt carbonyl, two carbonyl moieties were replaced by fulvene molecules, and brown compounds of type CCCLXXXVII were formed; the presence of both terminal and bridging CO units was indicated in the infrared spectrum. The rhodium carbonyl $[Rh(CO)_2Cl]_2$, on the other hand, gave with diarylfulvenes blue π complexes of the general formula CCCLXXXVIII, while the products formed from dialkylfulvenes were polymeric.

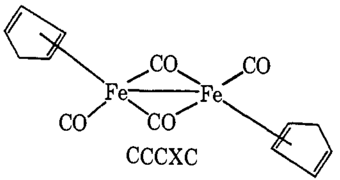
As it has been assumed that the formation of dimerides in the reaction of molybdenum or chromium hexacarbonyl (1) is due to the reactivity of the positively charged carbon atom in the primary product CCCLXXXIX, the stabilization of this positive charge by substituents which would delocalize it was attempted (204). Indeed, 6-dimethylamino- and 6,6-bis(dimethylamino)-fulvene gave both monomeric and dimeric derivatives with the two hexacarbonyls. With iron pentacarbonyl, 6-dimethylaminofulvene gave two "dimeric" isomers. Their ultraviolet spectra were similar to that of the cyclopentadienyl derivative CCCXC, but reduction by sodium amalgam did not cleave the dimer to two monomeric molecules, as in the case of CCCXC. Therefore, and on the strength of nmr measurements, formula CCCXCI (the two carbon atoms of the C–C chain are asymmetric, thus permitting two isomers), which with sodium amalgam would simply give a dianion, was suggested. Methylation, indeed, gave a dimethyl derivative of the dimer.



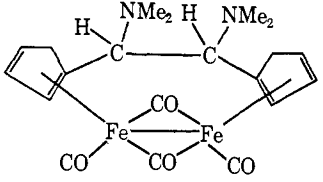
CCCLXXXVIII



CCCLXXXIX



CCCXC

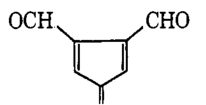


CCCXCI

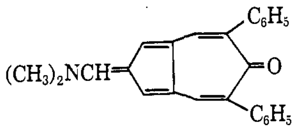
Also 9-(dicyanomethylene)fluorene gives a nickel(0) complex with nickel carbonyl; the complex is converted by intramolecular electron transfer into the nickel (dicyanomethylene)fluorene dianion (372). (For the reaction of fulvenes with free radicals, see 201, 202, 251, 403.)

10. *Miscellaneous Reactions*

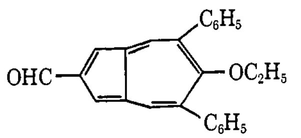
In conclusion, attention is drawn to the fact that the fulvenealdehydes derived from cyclopentadiene and indene (see section II.A.7) represent valuable starting points for the synthesis of azulene derivatives. Thus, 6-dimethylamino-2,3-diformylfulvene (CCCXCII) condenses with dibenzyl ketone to CCCXCIII which by O-alkylation and hydrolysis gives azulene derivatives of type CCCXCIV (149). (With compounds having only one reactive methylene group, the two aldehyde functions react separately (265, 300).) The product CCCXCV obtained from cyclopentadiene and "Zincke's aldehyde" (section II.A.7) cyclizes after shift of the double bonds in the five-membered ring to azulene in 60% yield when heated at 200–250° *in vacuo* (197, 226), and homologs of the aldehyde lead analogously to 5- and 6-methylazulene (152, 464), N-methylaniline being eliminated in this reaction. Indene gives 1,2-benzazulene in the same sequence of reactions (146). Analogously, the perchlorate CCCXCVI condenses with cyclopentadienylsodium at −40° to the interesting



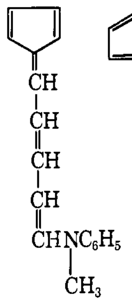
CCCXCII



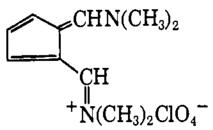
CCCXCIII



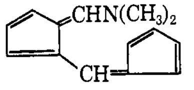
CCCXCIV



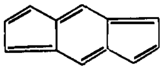
CCCXCV



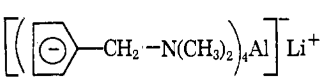
CCCXCVI



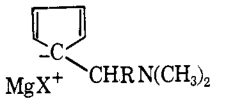
CCCXCVII



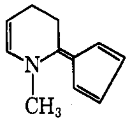
CCCXCVIII



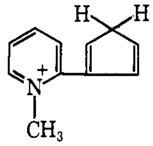
CCCXCIX



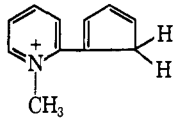
CD



CDI



CDII



CDIII

6-(6-dimethylamino-2-fulvenyl)fulvene (CCCXCVII), which cyclizes quickly to the unstable "dehydro-*s*-indacene" CCCXCVIII (153).

The reactions of 6-heterosubstituted fulvenes (see section II.A.1) deserve special review. 6-Dimethylaminofulvene (CXXXIII) behaves toward lithium aluminum hydride and alkyllithium compounds as β-dialkylamino α,β-unsaturated aldehydes and ketones do: the dimethylamino group is replaced by hydrogen or alkyl, respectively (395). The initial complex formed with lithium aluminum hydride has formula CCCXCIX and is hydrolyzed to 5-(dimethylaminomethyl)cyclopentadiene. This is transformed into fulvene (see section III.C) either by heating at 100° under high vacuum, or by passing it through a column of alumina, or by dry distillation of the corresponding methiodide under reduced pressure. It can be assumed that the reaction of CXXXIII with lithium alkyls also proceeds *via* an intermediate of formula CD. In a more complex representative of this class, N-methyl-2-cyclopentadienylidene-1,2-dihydropyridine (XXIII), lithium aluminum hydride reduces first one of the double bonds of the pyridine moiety, giving a product like CDI, and only then attacks the fulvenic bond (49). Compound XXIII is protonated on a carbon, and not on the nitrogen atom; its solution in trifluoroacetic acid contains both ions CDII and CDIII (49). These properties as well as the dipole moments and the ultraviolet spectra are in fair accord with calculation: in spite of significant bond alternation, there is a substantial charge separation in the ground state (50, 51).

B. FULVALENES

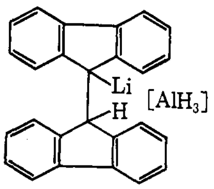
Obviously, the symmetry of the fulvalene system demands that the central double bond has no dipole moment; however, it would equally be expected that it has unusual properties. Indeed, the bond index of that linkage is very low for a double bond, and, taking bis(biphenylene)ethene as an example, the linkage has an unusually high polarizability that expresses itself, *e.g.*, in a very high exaltation of the molecular refraction of the molecule, an unusual behavior on polarographic reduction (170–172), and in a number of reactions which resemble those of the fulvenes.

On the other hand, it has to be taken into consideration that bis(biphenylene)ethene (VI) is not planar, due to the mutual interference of the four hydrogen atoms in the 1,1′,8,8′ positions. A nuclear magnetic resonance study has recently shown (329; *cf.* also 331) that in spite of the twist there is still a significant interaction between these hydrogen atoms. Yet, the problem of the actual conformation of the bis(biphenylene)ethene molecule has not yet been solved.

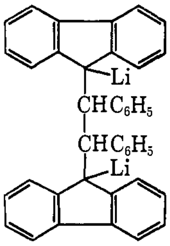
Lithium aluminum hydride adds to bis(biphenylene)ethene to give CDIV and, after hydrolysis, bis(biphenylene)ethane (249). 1,4-Bis(biphenylene)-1,3-butadiene reacts as a "double fulvene," adding two molecules of the reagent and giving, after hydrolysis, 1,4-bis(biphenylene)butane (250). 1,4-Bis(biphenylene)butatriene behaves analogously (230). Bis(biphenylene)ethene also adds phenyllithium (8) and methyllithium (25) as well as benzyl- and *t*-butylmagnesium chloride (130, 131), and 1,4-bis(biphenylene)-1,3-butadiene again reacts with two molecules of phenyllithium to give CDV (382). From bis(biphenylene)allene, on the other hand, and from 1,1-biphenylene-3,3-diphenylallene and phenyllithium, 1,3-bis(biphenylene)-2-phenyl-1-propene and 9-(triphenylvinyl)fluorene were obtained, respectively (116).

The peculiar electronic and steric structure of the bis(biphenylene)ethene system has recently been thrown into relief by the observation that 1,2,1′,2′,7,8,-7′,8′-tetrabenzobis(biphenylene)ethene (CDVI) exists partially in a form which is paramagnetic, while the formula, obviously, is that of a diamagnetic compound. From the temperature dependence of the equilibrium, the energy difference between the two forms is 3–4 kcal/mole (123).

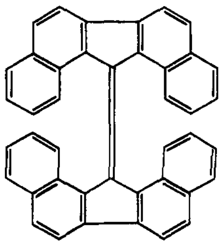
A study has been made of the use of bis(biphenylene)ethene as an acceptor in Michael reactions (309, 310,



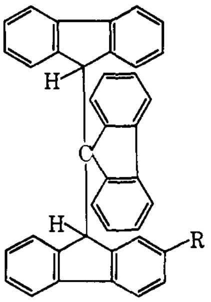
CDIV



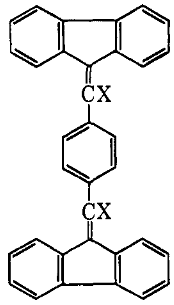
CDV



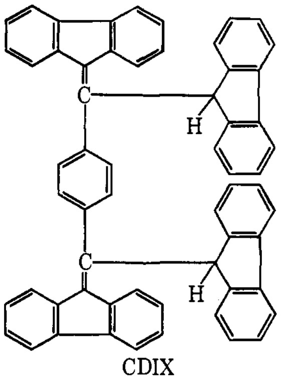
CDVI



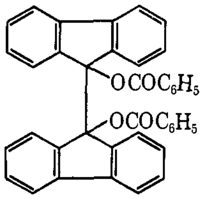
CDVII



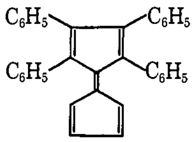
CDVIII



CDIX



CDX



CDXI

312): fluorene gives tris(biphenylene)propane (CDVII, R = H), and substituted fluorenes react analogously (396, 398–400). The reaction is reversible; therefore, alkali treatment of CDVII (R = Br), obtained from bis(biphenylene)ethene and 2-bromofluorene, both reproduces these two starting materials and gives fluorene and 2-bromobis(biphenylene)ethene (398). Fluorene adds, in the presence of alkali, to both polar bonds of the vinylog CDVIII (X = Br) of bis(biphenylene)-ethene and gives, with accompanying loss of two molecules of hydrogen bromide, after acidification, the tetrafluorenyl compound CDIX (235).

Even amines add to the highly polarizable central double bond of bis(biphenylene)ethene: with methylamine, the stable 9-methylaminobis(biphenylene)ethane is obtained, while the N-methyl-free compound disproportionates spontaneously into fluorene and fluorenone imine (310).

The addition of halogen and of metallic sodium to bis(biphenylene)ethene proceeds normally, as most of the classical reactions do. Also, compounds such as CDVIII (X = H) add normally 2 molecules of bromine; however, the tetrabromide loses, upon heating in glacial acetic acid, 2 molecules of hydrogen bromide and gives CDVIII (X = Br) (235). Benzoyl peroxide radicals, generated from silver benzoate and iodine, add to give CDX (445).

Interesting observations have been made in the hydrogenation of cumulenes derived from fluorene (230). Bis(biphenylene)allene (CCLXXIV) is reduced by means of the Lindlar catalyst to 1,3-bis(biphenylene)-propene (116), and the blue-violet bis(biphenylene)-hexapentaene (CCLXXXIV) gives, upon hydrogenation in tetrahydrofuran, the orange *cis*-1,6-bis(biphenylene)-1,3,5-hexatriene, which is transformed by light in the presence of iodine into the corresponding *trans* compound. Bis(biphenylene)ethene is quite sensitive to autoxidation (304, 452). It also decomposes (at 460°) to give fluorene, tetrabenzonaphthalene, which is an isomer of the starting material (also obtained by rearrangement of fluorenonepinacol), and more highly condensed products (252).

Finally, it might be mentioned that the fulvalene CDXI which contains an unsubstituted cyclopentadiene system gives an adduct with maleic anhydride which is red and, therefore, contains a fulvene system. Structure CDXII is most likely for this adduct (373). Equally, fulvalene itself reacts with two molecules of tetracyanoethylene and gives the adduct CDXIII (108).

C. HEPTAFULVENES, HEPTAFULVALENES, AND PENTAHEPTAFULVALENES

As already pointed out, most of the studies in this field have been concerned with the higher benzologs of the heptafulvene system. In these compounds, the reactions of the exocyclic double bond are those of normal olefins. In particular, they do not react with lithium aluminum hydride.

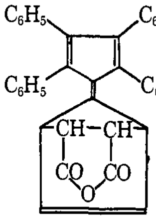
The recently discovered heptafulvene also shows the reactions of most cyclic olefins (108, 109). It does not react with phenyllithium or other nucleophiles; with dimethyl acetylenedicarboxylate (no other dienophile being sufficiently reactive) it gives a colorless adduct which oxidizes in air to dimethyl azulene-1,2-dicarboxylate and is, therefore, probably CDXIV.

Also the heptafulvene derivatives which carry polar substituents in the methylene group (see section II.B) react normally under hydrogenating conditions, 3 or 4 moles of hydrogen being absorbed without any break in the rate curve (406).

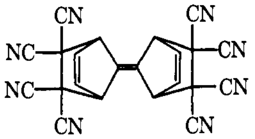
Still less is known about any particular reactions of the known tetrabenzoheptafulvalene CCXC and of the mixed fulvalene CCXCIV.

One should have expected interesting properties of the mixed fulvalene; it was pointed out before that the central linkage has the lowest bond order ever observed for a "double bond" in a conjugated system. The observations recorded so far in this field may be summarized as follows: the simplest mixed fulvalene reacts with tetracyanoethylene only in the cycloheptatriene ring, giving the normal adduct CDXV (315). The hydrocarbon CDXVI (see section III.F) reacts with butyllithium; for the adduct the summary formula CDXVII can be written (321). Also trifluoroacetic acid gives a salt-like adduct with CDXVI (321). (For free-radical reactions of 1,2,6,7-dibenzoheptafulvalene, see 203.)

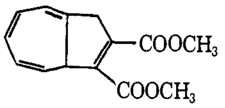
A more complete study of the mixed fulvalenes and their vinylogs (see section III.F) may be of theoretical interest.



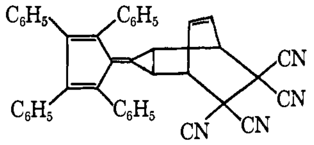
CDXII



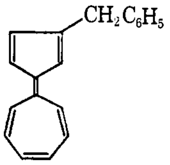
CDXIII



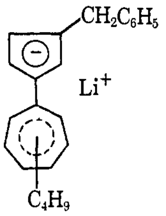
CDXIV



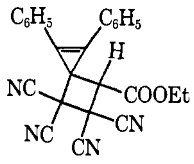
CDXV



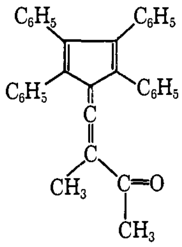
CDXVI



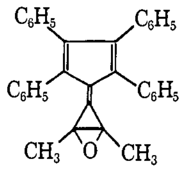
CDXVII



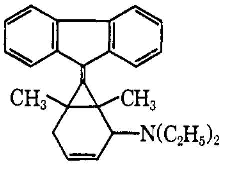
CDXVIII



CDXIX



CDXX



CDXXI

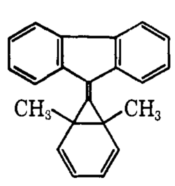
D. TRIAFULVENES AND TRIAPENTAFULVALENES

The chemical reactions of the triafulvenes (VII) have not yet been studied fully. The dibromodiphenylquinocyclopropene (CCXXIV) is reconverted to a salt of the corresponding cyclopropenium ion (as CCXXVII) by trifluoroacetic acid (450). The same is true for 4-carbethoxy-1,2-diphenyltriafulvene (CCXXXI) and fluoroboric acid (in acetonitrile as solvent) (23), while 4,4-dicyano-1,2-diphenyltriafulvene (CCXXXII), according to the nmr spectrum, is unaffected by this highly acidic compound (28). On the other hand, CCXXXII heated with 90% sulfuric acid gives the corresponding diamide which *adds* one molecule of the acid, forming a compound $C_{18}H_{16}N_2O_6S$. Also the 2,4-dinitrophenylhydrazone of diphenylcyclopropenone gives stable addition products with the acid used in its preparation (sulfuric, hydrochloric, perchloric acids, etc.) (195). The carbethoxy compound CCXXXI adds tetracyanoethylene and forms an adduct which shows the typical infrared spectrum of the diphenylcyclopropenes and is thus most probably CDXVIII. Compound CCXXXI and its analogs add chlorine at the fulvenic bond; the chlorine is easily removed again (12).

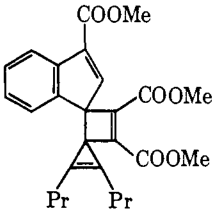
In the triapentafulvalene (calicene) series, too, the number of chemical reactions studied is yet small. It has been shown that, *e.g.*, the tetraphenylcyclopentadiene derivative CCCIX reacts rapidly with oxygen to give the allene ketone CDXIX. The mechanism of its formation would probably lead through an adduct of oxygen at the cyclopropene ring (CDXX) (318).

Another interesting reaction is that between the fluorene derivative CCCXXVII and N,N-diethyl-1-amino-1,3-butadiene, which takes place in boiling benzene and yields a compound to which formula CDXXI has been assigned. *In vacuo* at 160–180°, the trifluoroacetate of this base splits off diethylamine and gives the dibenzofulvene CDXXII. The physical and chemical properties of this compound, *e.g.*, its spectrum, its ozonization to fluorenone, and its complex formation with tetracyanoethylene, support the presence of both a fulvene and a norcaradiene system (319). This reaction recalls the formation of 3-diethylamino-1,2,4-triphenylcyclopentadienone from diphenylcyclopropenone and (diethylamino)phenylacetylene (122).

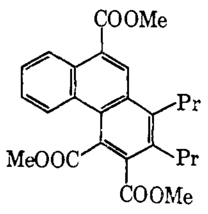
The calicene derivative CCCXXIII derived from methyl indene-3-carboxylate and dipropylcyclopropenone reacts with bromine by substitution, probably in the 2 position of the indene ring (see section III.A.5). With tetracyanoethylene, it gives an unstable deep blue complex, while with dimethyl acetylenedicarboxylate it leads to a mixture of two isomeric compounds CDXXIV and CDXXV which can be derived from a primary adduct of type CDXXIII by shift of a vinyl or an aryl group, respectively (198). The acetylene derivative, thus, would add initially at the fulvenic double bond. The same seems to be true for carbenes. In any event, the formation of phenyl-(α-chloro-α-propenyl)cyclopropenone (CDXXVII) from 1-phenyl-1-butyne and dichlorocarbene is explained by the addition of the carbene to an intermediate (CDXXVI) formed by elimination of hydrogen chloride from the normal addition product, accompanied or followed by hydrolysis of the olefinic chlorine atom (104). The



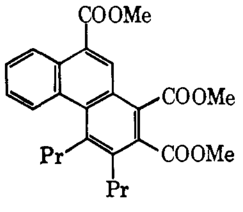
CDXXII



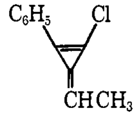
CDXXIII



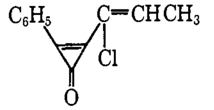
CDXXIV



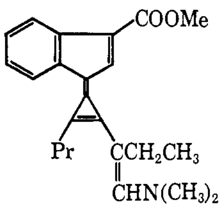
CDXXV



CDXXVI



CDXXVII



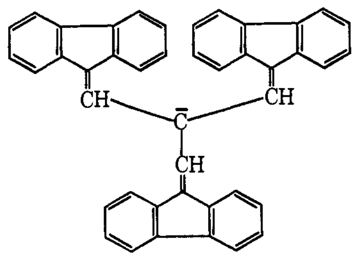
CDXXVIII

Vilsmeier reagent, phosphorus oxychloride in dimethylformamide, on the other hand, substitutes a methylene of one of the propyl groups in CCCXXIII, leading to CDXXVIII.

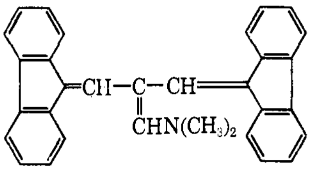
E. HIGHLY ACIDIC HYDROCARBONS

A recent series of studies (see, *e.g.*, 186, 233, 237) has added a new interesting aspect to the chemistry of the fulvenes, more especially of the dibenzofulvenes: certain biphenylene-substituted alkenes are highly acidic compounds, the negative charge of the anion being distributed over a large number of carbon atoms. This explains the observation that the acidity rises with the number of biphenylene units and that benzologs of fluorene give more acidic hydrocarbons than fluorene itself. Thus, in the "tris(dibenzofulvenyl)-methyl" anion (CDXXIX), the charge is delocalized over 40 carbon atoms. For the preparation of the hydrocarbon corresponding to this anion, the 3-lithio derivative of 1,5-bis(biphenylene)penta-1,4-diene (LXXXII), itself a highly acidic hydrocarbon, was condensed with 9-bromomethylenefluorene; an alternative method for the synthesis of this hydrocarbon is the reaction of 9-fluorenyllithium with the enamine CDXXX. (It is obvious that the anions of isomeric hydrocarbons of the types of 9-styrylfluorene and 9-β-phenylethylidenefluorene are identical.) Finally, one can apply to these syntheses the reaction of Wawzonek and Dufek (441) who have condensed 9-styrylfluorenol with 9-methylfluorenol in the presence of acid to give 3-phenyl-1,5-bis(biphenylene)penta-1,4-diene (as LXXXII). The hydrocarbon corresponding to CDXXIX could analogously be prepared from 9-methylfluorenol and 1,5-bis(biphenylene)-2-pentene-1,5-diol (CDXXXI). The hydrocarbon, corresponding to the anion, is more acidic than that belonging to the anion of LXXXII; the most acidic compounds so prepared are CDXXXII and CDXXXIII. It is interesting that anion formation from these hydrocarbons is usually slow; this has been ascribed to the necessity for the elaboration of richer energy conformations of the hydrocarbons, leading to deformation of the tetrahedral structure; only if the (planar) anion is preformed will the proton be extruded.

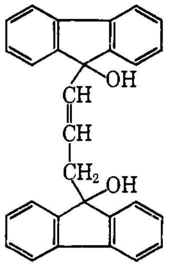
In conclusion, it may be predicted that the many interesting theoretical problems arising from the specific structures discussed in this review will find increasing attention. One of the most intriguing questions is whether the derivatives CDXXXIV of cyclononatetraene will be analogous to the fulvenes. It is also likely that the fulvenes will find practical applications. It has already been mentioned (section II.A.2) that some basically substituted dibenzofulvenes have interesting pharmacological properties. Not only the similarity of these dibenzofulvenes with the well-known derivatives of 2,3,6,7-dibenzocyclohepta-2,6-diene and -2,4,6-triene leads one to hope that tranquilizers may be



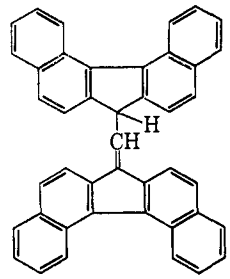
CDXXIX



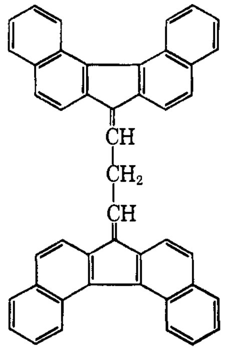
CDXXX



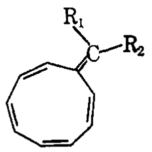
CDXXXI



CDXXXII



CDXXXIII



CDXXXIV

found in this series (see, *e.g.*, 101), but also in a small number of cases (19, 117) antitumor activity of fulvenes has been reported.

IV. ADDENDUM

Since the completion of this review, a fairly large number of pertinent publications has appeared, which are reported in the sequence used in the review.

I.—Among these publications one finds a brief survey (495) and several ones of theoretical interest. It has been proposed that the aromaticity of a system such as the fulvenes may be defined by the variation in length of the "peripheral" bonds (500); this approach is of interest in the case of the pentatriafulvalenes (V) as recently the bond length in several of them has been calculated (522, 524) and measured (503, 543); the same applies to pentaheptafulvalenes (V) (511, 525). For other papers of theoretical interest, see ref 475, 485, 489, 497, 533.

II.A.1.—In addition to dicyclopropyl ketone (505) and β-phenylcinnamaldehyde (470), carbonyl compounds have been condensed with cyclopentadienes which would enhance the tendency of the 6 substituent to accept a positive charge. Thus, cyclopentadienylsodium gives with compound CDXXXV the yellow fulvene (CXXXVI) (494), and the negatively substituted tetrachloro- and tetracarbethoxycyclopentadienes condense easily with γ-pyrones in boiling acetic anhydride to the deep-colored cyclopentadienylidene-γ-pyrans of type XXI (541).

The stabilization of the fulvene system by negative substituents in the five-membered ring is shown by the observation that tetrachlorocyclopentadiene condenses with aromatic aldehydes in refluxing alcohol in good yield (up to 50%) *without* alkali which attacks the tetrachloro compound (521).

A more detailed study of the fact that fluorene and *o*-chlorobenzaldehyde, in the presence of sodium ethoxide, give largely *o*-chlorocinnamylidene- and not -benzylidenefluorene (496) has been carried out.

A new type of fulvenes, similar to XXI, namely the olive-green 4-(tetraphenylcyclopentadienylidene)-1,2,6-triphenylphospha-2,5-cyclohexadiene P-oxide (CDXXXVII), has been obtained by heating tetraphenylcyclopentadiene with 4,4-dichloro-1,2,6-triphenylphospha-2,5-cyclohexadiene P-oxide (519).

II.A.2.—The reaction of fluorenone with β-phenylethylmagnesium bromide, followed by dehydration of the carbinol obtained, gave the expected (β-phenylethylidene)fluorene. This compound was also obtained by base-catalyzed isomerization of 9-*trans*-styrylflurene which was synthesized by decomposition of the xanthate (CCXXXVIII) of 2-(9-fluorenyl)-1-phenylethanol (469, 478). A similar isomerization is observed for 9-(β,β-diphenylvinyl)fluorene (478, 513, 540).

The use of ethynylcarbinols for the synthesis of fulvenoid cumulenes has proven effective in the reactions of acetylenes with fluorenone, 3,4,5,6-dibenzofluorenone, and tetraphenylcyclopentadienone (489). From the last ketone, *e.g.*, *via* the reaction with a metal derivative of phenylacetylene, the cumulene CDXXXIX has been prepared (537).

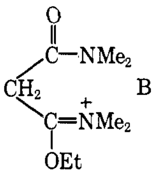
II.A.5.—Some additional studies on the photochemical transformation of benzene into fulvene have been carried out (476, 477, 552); it appears that a diradical (CDXL, "profulvene") is an intermediate in this reaction.

II.A.6.—*o*-Di(phenylethynyl)benzene (CDXLI) gives with bromine one of the possible isomers of CDXLII, which isomerizes under the influence of more bromine. Iodine reacts analogously, and hydrogen bromide cyclizes to CDXLIII, which by successive treatment with butyllithium and acid is debrominated to 1-benzylidene-2-phenylindene, the less stable of the two isomers which are formed simultaneously from 2-phenylindene and benzaldehyde and are interconvertible (with potassium ethoxide) (554). This is one of the few cases in which isomeric fulvenes have been isolated.

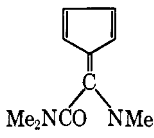
II.A.8.—A method for the preparation of polar-substituted dibenzofulvenes, which is perhaps of general utility, consists in the reaction of diazofluorene with carbenes such as phenylthio- and chloro(phenylthio)carbene; they give CDXLIV (535). There are several isolated cases of fulvene formation or synthesis: the deacetoxylation of 5-(α-acetoxyallyl)cyclopentadiene (CDXLV) with tertiary amines gave vinylfulvene (539); the decomposition of dimethyl 1,2,7-trimethylazepine-3,6-dicarboxylate (CDXLVI) in boiling benzene led to 2-carbomethoxy-3,4,6-trimethyl-6-(methylamino)fulvene (CDXLVII) (481); and methyllithium transformed the halogenated cyclopropane derivatives CDXLVIII and CDXLIX into 3,6- and 2,3-dimethylfulvene, respectively (544).

II.B.—For the preparation of two simple heptafulvenes (CDL, CDLI), methods were employed which had been applied before in the triafulvene and fulvene series, respectively. Photolysis of the sodium salt of tropone tosylhydrazone, in the presence of dimethyl fumarate, gave the spiran CDLII, which was isomerized in the presence of acid catalysts to CDL (499). Dichloroketene gave with tropone the yellow-orange heptafulvene CDLI (482); the chlorine-free parent substance had been prepared before (538). In the dibenzoheptafulvene series, the 1-(β-phenylcinnamylidene)-2,3,6,7-dibenzocyclohepta-2,4,6-triene has been synthesized by conventional methods (470), and for the synthesis of tribenzoheptafulvene (as CLXXXIX) two methods have been worked out, both starting with the corresponding tribenzotropone (523).

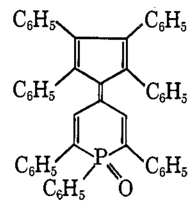
The relatively stable, orange 1-dimethylaminoheptafulvene (CDLIV) has been obtained by decomposition



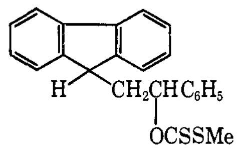
CDXXXV



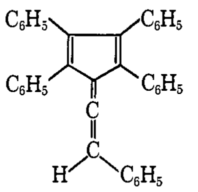
CDXXXVI



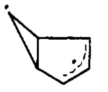
CDXXXVII



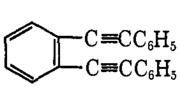
CDXXXVIII



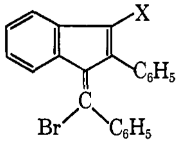
CDXXXIX



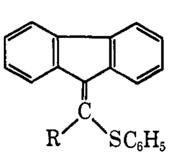
CDXL



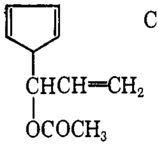
CDXLI



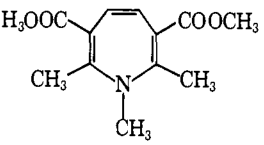
CDXLII, X = Br
CDXLIII, X = H



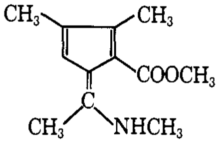
CDXLIV, R = H, Cl



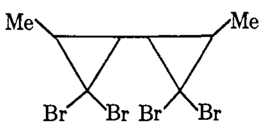
CDXLV



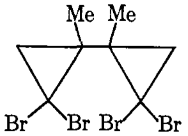
CDXLVI



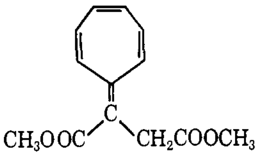
CDXLVII



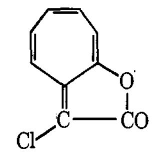
CDXLVIII



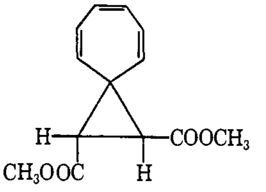
CDXLIX



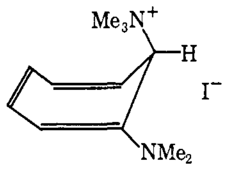
CDL



CDLI



CDLII



CDLIII

of the methiodide CDLIII; its structure was proven by hydrogenation to methylcycloheptane (551).

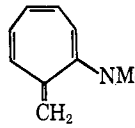
II.C.—The formation of 4,4-dicyano-1,2-diphenyltriafulvene (CCXXXII) is so much favored that it is formed, though in low (6%) yield, on prolonged (100 hr) refluxing of the reactants in methanol (28). The reaction of active methylene compounds with alkoxydiphenylcyclopropenium salts (CCXXXIII) has been extended to include β-diketones, β-oxoaldehydes, and β-oxoamides (487). The condensation with anthrone has been proven, in the meantime, to lead indeed to the benzanthrone derivative CCXLI (490). While CCXXXIII did not react with other phenols, 3,3-dichloro-1,2-diphenylcyclopropene did, and some of the hydroxyarylcyclopropenium salts so obtained could be deprotonated to triafulvenes analogous to CCXXIV (491).

A reaction analogous to the formation of CCXLI has been observed when diphenylcyclopropenone was treated with the phosphorane (CDLV) derived from 2-(bromomethyl)naphthalene. The product was 1,2-diphenyl-3-(β-naphthylmethyl)phenanthrene (CDLVI) (466).

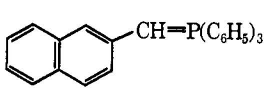
II.D.—In the Clemmensen reduction of 2- and 3-bromofluorenone, the alcohols CDLVII are formed which are dehydrated by alkali to the corresponding dibromobis(biphenylene)ethenes (549, 550). The "dihalide" method for the preparation of fulvalenes has been employed for the preparation of octabromofulvalene (CDLVIII), which is dark blue (see section III.A.5 for the color of tetrabromodiphenylfulvene); hexabromocyclopentadiene was treated with cuprous bromide in aqueous dimethoxyethane. X-Ray diffraction has shown that, probably for steric reasons, the two rings are twisted against each other (517). The corresponding octachlorofulvalene has been described before (492, 520).

In a variation of the dihalide method bis(biphenylene)ethene was obtained from 9,9-dibromofluorene and methyllithium (451). The dehydrobromination of 1-haloindenes and 9-halofluorenes as a method for fulvalene synthesis has been studied in a number of cases (480, *cf.* 468, 472). The most interesting among them is the preparation of diindenylene (CDLIX) by successive treatment of the photodimer (CDLX) of indene with N-bromosuccinimide and potassium amide (468). For the autoxidation of cyclopentadiene to fulvalene in alkaline solution, see ref 473. A method hitherto unemployed for the direct transformation of fluorenes into bis(biphenylene)ethenes uses the treatment of the ketones with triethyl phosphite at 150–180°; the yields were small (474).

In the series of vinylogs and cumulenes of fulvalenes, the following observations deserve mention. Bis(biphenylene)butadiene (CCLXVII) was prepared from fluorene and (9-fluorenylidene)acetaldehyde (CDLXI) for which several methods of synthesis have been worked out (470). A vinylog of CCLXVII is the product (CDLXII) that is obtained from fluorene and terephthaldehyde; the conjugation is disturbed by the intercalation of the $=CHC_6H_4CH=$ moiety (470). Ethynylcarbinols have been used for the preparation of cumulenes such as CDLXIII and CDLXIV (489, 534).



CDLIV



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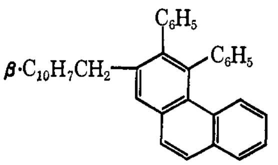

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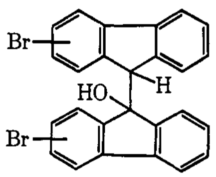

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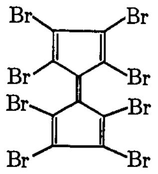

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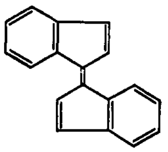

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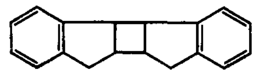
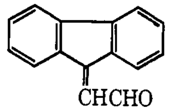


CDLX



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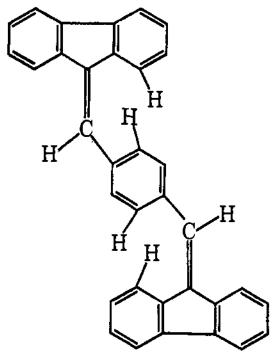

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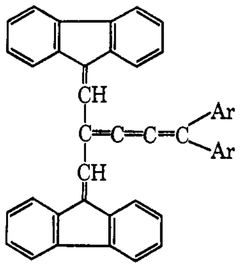

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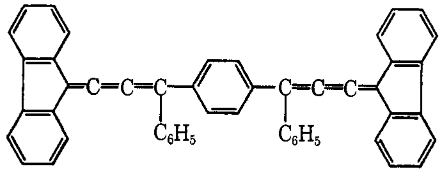

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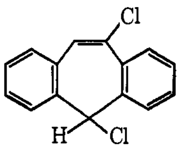

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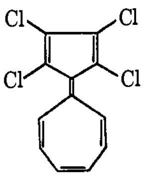
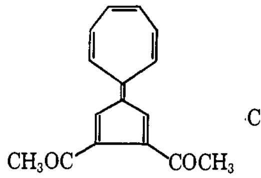


CDLXVI



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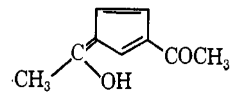


CDLXVIII

II.E.—New studies (518, 545, 546) on the reaction of the ketone CLXXIV with phosphorus pentachloride have led to an improvement in the preparation of the heptafulvalene CCXC (471). The keto chloride was found to isomerize at 160° to 1,4-dichloro-2,3,5,6-dibenzocyclohepta-2,4,6-triene (CDLXV). Clemmensen reduction of the ketone CLXXIV leads to the dihydro derivative of CCXC (28).

II.F.—Cyclopentadiene and tropone in benzene undergo a Diels-Alder reaction (498); tetrachlorocyclopentadiene, on the other hand, in acetic anhydride condenses with tropone to the sufficiently stabilized tetrachloropentaheptafulvalene (CDLXVI), which is theoretically interesting because the six hydrogen atoms in the molecule appear to be almost equivalent. Equally stabilized is the dark red diacetylpentaheptafulvalene (CDLXVII), which was obtained by the reaction between 3,4-diacetylcyclopentadiene in its tautomeric form CDLXVIII with tropylium bromide and treatment of the product (CDLXIX) with silver carbonate (493). As usual, benzologs and polyphenyl derivatives of pentaheptafulvalene are also fairly stable. 9-Tropylfluorene and 1-tropyl-2,3,4,5-tetraphenylcyclopentadiene could be dehydrogenated either directly (with halogenoquinones) or indirectly to the hydrocarbons CDLXX (orange-red) and CDLXXI (dark red in solution). The 1-tropylcyclopentadiene derivative isomerizes easily to 2,3,4,5,6-pentaphenylfulvene (531). Derivatives of benzylpentaheptafulvalene (CDLXXIII) are also available by prototropic rearrangement of 3-(2,4,6-cycloheptatrien-1-yl)-ω-arylbenzofulvenes (CDLXXII); the equilibrium lies entirely on the side of CDLXXIII, as hydrogen-deuterium exchange experiments have shown (530).

A vinylog (CDLXIV) of the pentaheptafulvalene CCXCIV has been prepared by condensation of fluorene with 2,3,6,7-dibenzocyclohepta-2,4,6-trienylideneacetaldehyde (CDLXV); comparison of the spectra of CCXCIV and CDLXIV shows that in the former steric hindrance twists the two halves of the molecule out of the common plane (470).

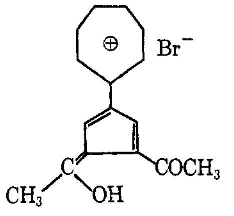
II.G.—Another preparation of CCCVII has been described (512).

III.A.1.—Titanocene dichlorides were obtained from fulvenes (548).

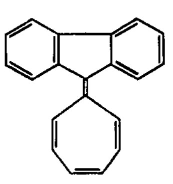
III.A.5.—The "pseudo-halogens" dinitrogen tetroxide and tetrafluorohydrazine add to the five-membered ring of diphenylfulvene; the former also causes some substitution (479, 542). The latter gives a mixture of *cis*- and *trans*-4-benzhydrylidene-3,5-bis(difluoroamino)cyclopentene (CDLXXVI), the former *cis*-4-benzhydrylidene-3,5-dinitrocyclopentane, together with 2-nitro- and 2,5-dinitrodiphenylfulvene, polymerization and oxidation also taking place to a considerable extent.

III.A.6.—The formation of 5-norbornene derivatives from fulvenes and maleic anhydride or maleimide has been studied (527, 547). 2,3,4,5-Tetraphenylfulvene reacts as a dienophile with 1-methoxybutadiene, 2-methyl-1,3-pentadiene, and 2,4-hexadiene; the compounds are considered as spirans, but no proof has been offered for this structure (488).

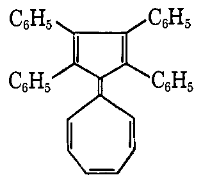
III.A.7.—While catalytic reduction of 9-(β-phenylethylidene)fluorene gives the expected 9-(β-phenylethyl)-fluorene (478), Raney nickel can carry the reduction of 9-arylmethylenefluorenes further, leading *via* 9-arylmethylfluorenes to 9-arylmethyl-1,2,3,4,4a,9a-hexahydrofluorenes (526). Also diborane reduces 9-benzylidene and 9-benzhydrylidenefluorenes to 9-benzyl- and 9-benzhydrylfluorenes, while bis(biphenylene)ethene (VI) is not attacked (533).



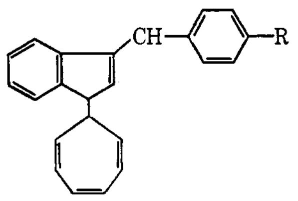
CDLXIX



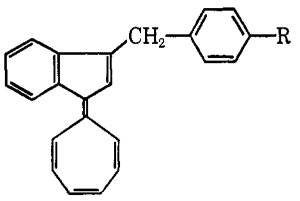
CDLXX



CDLXXI

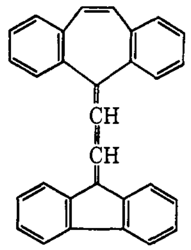


CDLXXII

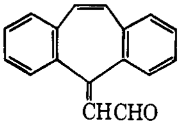


CDLXXIII

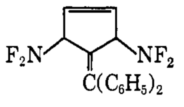
$R = H, Cl, OCH_3, N(CH_3)_2$



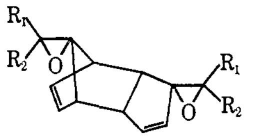
CDLXXIV



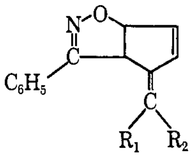
CDLXXV



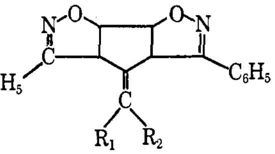
CDLXXVI



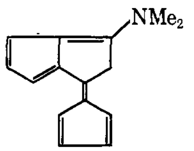
CDLXXVII



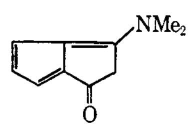
CDLXXVIII



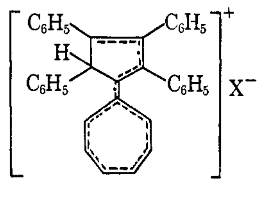
CDLXXIX



CDLXXX



CDLXXXI



CDLXXXII

III.A.8.—6,6-Disubstituted fulvenes are epoxidized at the exocyclic double bond, the epoxides dimerizing to compounds of type CDLXXVII (467); with benzonitrile oxide, these fulvenes give isoxazolines (CDLXXVIII, CDLXXIX) (532). Dialkyl phosphites and dihexyl phosphinoxide yield adducts of unelucidated structure (484).

III.A.9.—For the reaction of 6-dimethylaminofulvene with tris(acetonitrile)tungsten tricarbonyl, see ref 506.

III.A.10.—The fulvene CDXXXVI forms with cyclopentadienylsodium the red fulvene CDLXXX, while elimination of dimethylamine leads to the potential pentalene derivative CDLXXXI, from which 1,3-bis(dimethylamino)pentalene has been prepared (494).

The photooxidation of 2,3,4,5-tetraphenylfulvene has been described (536).

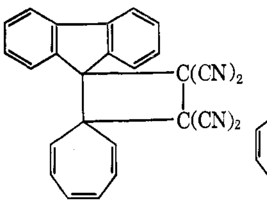
III.C.—Substituents (halogen, OCH_3) in the seven-membered ring of ω,ω-dicyanoheptafulvenes are exchanged by nucleophilic reagents (501, 507, 509, 510). Grignard reagents, however, do not exchange the methoxy group in 1-methoxy-ω,ω-dicyanoheptafulvene, but the alkyl group of the reagent enters the 3 position (508).

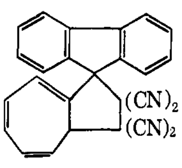
Systematic studies of the reactions of pentaheptafulvalenes have been carried out (530, 531). Tropylidenefluorene is protonated at the 9 position of the fluorene system, while from tropylidenetetraphenylcyclopentadiene CDLXXXII is formed. Lithium aluminum hydride gives mixtures of partially hydrogenated derivatives (after hydrolysis). With tetracyanoethylene, tropylidenefluorene gives *via* a red π complex an adduct for which structures CDLXXXIII or CDLXXXIV are possible; tropylidenetetraphenylcyclopentadiene gives probably CDLXXXV. The compound CDLXXIII is protonated at the 1 position of the indene moiety; with lithium aluminum hydride a red lithium salt is obtained, while catalytic hydrogenation adds 2 moles of hydrogen, the first slowly, the second much more quickly. Tetracyanoethylene gives, again by 1,8 addition, CDLXXXVI, while maleic anhydride leads, in independent reactions, to the two adducts CDLXXXVIII.

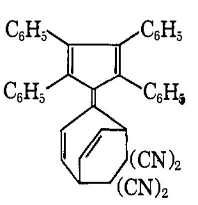
III.D.—Triapentafulvalenes, carrying negative substituents in the five-membered ring, are substituted by electrophiles in that ring. Thus CCCXV is mononitrated by benzoyl nitrate, substituted by the *p*-nitrophenylazo group, formylated by the Vilsmeier reaction, and diacetylated by means of acetyl chloride and stannic chloride; in CCCXIV, bromine substitutes both free positions in the ring (504).

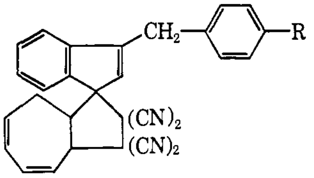
The triafulvene CCXXXII is attacked at the endocyclic double bond by 1-diethylaminobutadiene, forming in 1,4 fashion the orange-colored XDIX (483). This has the very high dipole moment of

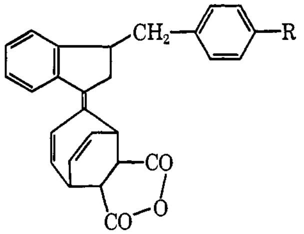
11.8 D. (466), indicating a significant contribution of a dipolar form. Similarly, 1-pyrrolidino-2-methyl-1-propene (XD) yields XDI (528). On the other hand, N-phenacylpyridinium salts attack 4,4-diacyl-1,2-diphenyltriafulvenes by opening an *ethanic* bond in the three-membered ring, giving, with elimination of pyridinium salt, pyran derivatives of formula XDII (diphenylcyclopropenone reacts analogously). Zwitterions of type XDIII (such as the corresponding benzothiazole and 3,3-dimethylindolenine derivatives) give with diphenylcyclopropenone substances of type XDIV (486).


CDLXXXIII


CDLXXXIV


CDLXXXV


CDLXXXVI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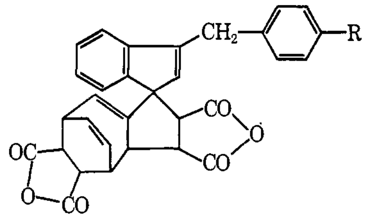
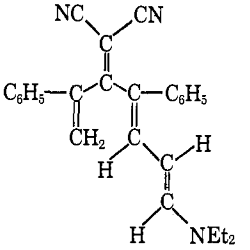
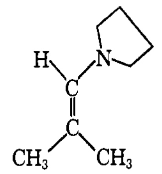
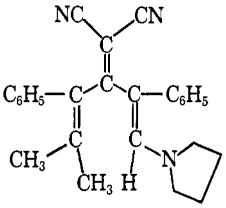

CDLXXXVIII


CDLXXXIX


XD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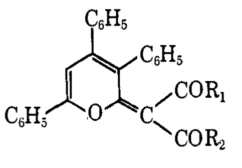
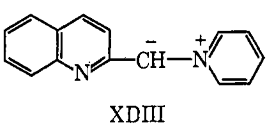
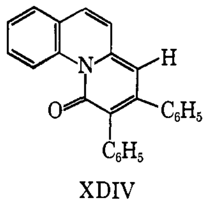
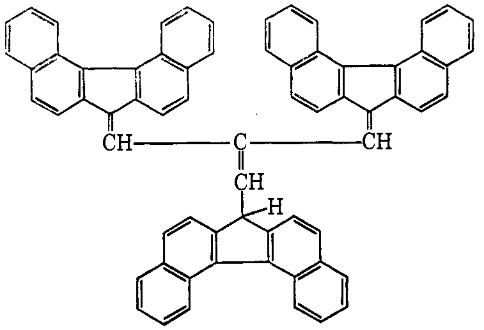

XDII

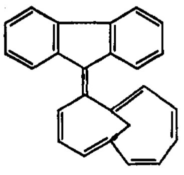

XDIII

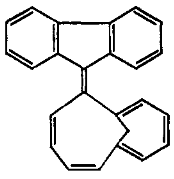

XDIV

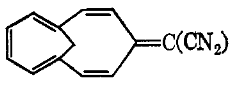
III.E.—In continuation of the study of highly acidic hydrocarbons, tris(7H-dibenzo[*e.g*]fluorenylidenemethyl)methane (XDV) has been prepared which gives a deep green anion (λ 697 mμ) and, by oxidation of the anion, a radical (λ 860 mμ). The hydrocarbon XDV is the most acidic known so far (p$K = 5.9$, while the pK of CDXXXIII is only 8.2). For the chemistry of the fulvenes it may be of interest that 1,2,7,8- and 3,4,5,6-dibenzofluorenes are more acidic; the 2,3,5,6 isomer is less acidic than fluorene. Only [*b*] annellation continues the acidity decrease known in the series cyclopentadiene–indene–fluorene (514–516).

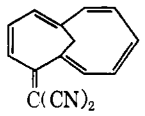
As predicted, the anion of cyclononatetraene (*cf.* 502) gives with *p*-dimethylaminobenzaldehyde a crystalline derivative, which is thought to be the fulvene CDXXXIV ($R_1 = H$; $R_2 = 4\text{-}N(CH_3)_2C_6H_4$) (466). In one step further, the pentahendecafulvalenes XDVI and XDVII have been described, in which the eleven-membered unsaturated ring takes the place of the seven-membered one in pentaheptafulvalene: fluorenyllithium was condensed with bicyclo[5.4.1]dodecapentaenylium fluoroborate, and the mixture of hydrocarbons was dehydrogenated with chloranil. Analogously, the two ω,ω-dicyanohendecafulvenes (XDVIII, XDIX) have been reported (529).


XDV


XDVI


XDVII


XDVIII


XDIX

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