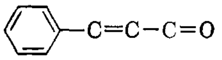
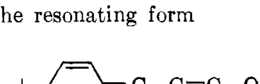
Bands were found at 3.425 and 6.00 μ for the chalcones which are regions of C—H and conjugated carbonyl absorptions, respectively. The enols absorbed at 2.95, 3.425, and 6.00 μ. The diketone (XXI)[11] which is 100% ketonic, adsorbed at 3.425, 5.85, and 5.95 μ. There was no band at 2.95 μ. These observations are in agreement with the findings of Barnes and Pinkney.[18] When the enols were converted to the allyl ethers, the band at 2.95 μ disappeared in each case. Upon equilibration of the enols with deuterium oxide, the band at 2.95 μ disappeared. This observation justified the assignment of this band to O—H stretching frequency.

Ferguson and Barnes[19] studied the ultraviolet spectra of some 1,3-diketones and related intermediates. They observed that the main chromophoric system in the chalcones is



probably due to the resonating form



They concluded that groups such as alkoxyl which readily accept a positive charge, will have a bathochromic effect while negative groups such as NO_2 will have the opposite effect.

Spectra in the ultraviolet region were obtained using the Beckman Model DU spectrophotometer with 95% ethanol as the solvent. The effects observed by Barnes and Ferguson[19] were also observed in the following cases with the exception of the *p*-nitrobenzalacetomesitylene (VI) and the α-hydroxy-*p*-nitrobenzalacetomesitylene (XX). Complete agreement with the observation was obtained in the allyl ethers of the enols. The completely ketonic glyoxal (XXI) absorbs at 255 mμ. (See Table III.)

TABLE III

WAVE LENGTH OF THE MAXIMUM ABSORPTION BANDS

		λ_{max}, (mμ)
I.	$C_6H_5CH{=}CHCOC_6H_5$	305 (313)[a]
II.	$C_6H_5CH{=}CHCO$ Mes	292
III.	o-$CH_3OC_6H_4CH{=}CHCO$ Mes	335
V.	o-$O_2NC_6H_4CH{=}CHCO$ Mes	250 (252)[b]
VI.	p-$O_2NC_6H_4CH{=}CHCO$ Mes	305
XVI.	$C_6H_5CH{=}\underset{\mathrm{OH}}{C}$ CO Mes	318
XVII.	o-$CH_3OC_6H_4CH{=}\underset{\mathrm{OH}}{C}$ CO Mes	345
XIX.	o-$O_2NC_6H_4CH{=}\underset{\mathrm{OH}}{C}$ CO Mes	295
XX.	p-$O_2NC_6H_4CH{=}\underset{\mathrm{OH}}{C}$ CO Mes	345
XXI.	Mes $CH_2COCOC_6H_5$	255
XXIV.	o-$CH_3OC_6H_4CH{=}\underset{\underset{\mathrm{Allyl}}{\mathrm{O}}}{C}$ CO Mes	335
XXVI.	o-$O_2NC_6H_4CH{=}\underset{\underset{\mathrm{Allyl}}{\mathrm{O}}}{C}$ CO Mes	265
XXVII.	p-$O_2NC_6H_4CH{=}\underset{\underset{\mathrm{Allyl}}{\mathrm{O}}}{C}$ CO Mes	275

[a] See ref. 20. [b] See ref. 19.

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[18] R. P. Barnes and G. E. Pinkney, *J. Am. Chem. Soc.*, **75**, 479 (1953).

[19] L. N. Ferguson and R. P. Barnes, *ibid.*, **70**, 3907 (1948).

[20] (a) D. Radulescu, *Ber.*, **64**, 2243 (1931); (b) A. Russell, J. Todd, and C. L. Wilson, *J. Chem. Soc.*, 1940 (1934); (c) V. Alexa, *Bull. Chim. Soc. Chim. Romania*, [2] **1**, 77 (1939).

Structures of Substituted Fulvenes. The Reaction Products from Acetone and Dimethylfulvene

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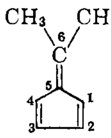
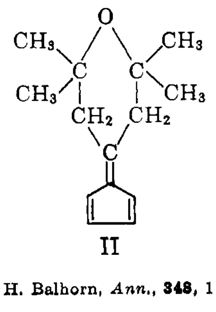
Acetone has been shown to substitute on to the ring carbons of 6,6-dimethylfulvene rather than the side-chain carbons. The structures of the mono-, di-, tri-, and tetrasubstituted 6,6-dimethylfulvenes are discussed. The presence of methanol in the reaction medium leads to the formation of ethers.

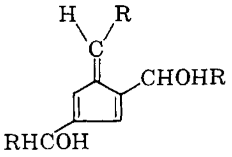
In 1906, Thiele[1] reported that, in addition to the production of 6,6-dimethylfulvene (I), the reaction of acetone and cyclopentadiene in a basic methanolic solution led to the formation of an ether whose analysis corresponded closely to that of $C_{14}H_{20}O$. A compound of very similar properties could be obtained after some purification from acetone and 6,6-dimethylfulvene in a basic alcoholic solution. The analysis, the typical fulvene physical properties of color and oxygen uptake, and the fact that the ether appeared to be composed of one cyclopentadiene and three acetone moieties led Thiele to postulate II for the structure of the ether. Courtot[2] speculated that compounds of structure III were possible when aldehydes (RCHO) reacted with cyclopentadiene under basic conditions. Ziegler[3] therefore considered II, IV, and V as possible structures for Thiele's ether and showed that the reaction product,



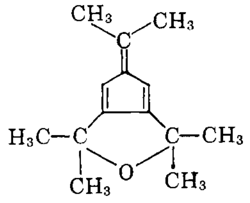
I



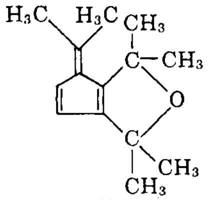
II



III



IV



V

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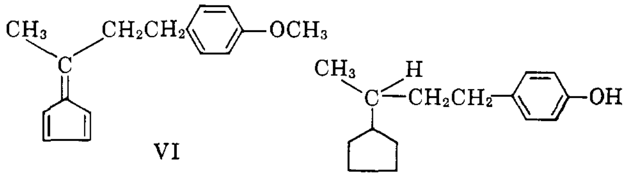
[1] J. Thiele and H. Balhorn, *Ann.*, **348**, 1 (1906).

[2] C. Courtot, *Ann. Chim.* (Paris) **4**, 168 (1915).

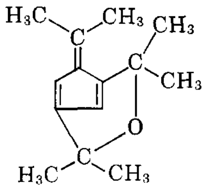
[3] K. Ziegler and F. Crossman, *Ann.*, **511**, 89 (1934).

VI, of β-p-anisylethyl methyl ketone and cyclopentadiene under basic conditions gave, after hydrogenation and cleavage, the phenol, VII, a compound which was quite different from the hydrogenated phenolic derivative of 6,6-dimethylfulvene and p-anisaldehyde. Therefore, the anisaldehyde skeleton had to be attached to a ring and not a side-chain carbon.



VI

VII



VIII

For this reason, structure II was considered unlikely, and emphasis was placed on structures IV and V as the permissible alternatives. More recently, Bergmann[4] has considered VIII as a possible structure for Thiele's ether.

In connection with other work in these laboratories, it was decided to elucidate further the structure of the more highly substituted products of 6,6-dimethylfulvene.

Discussion and Theory

Preliminary experiments showed that two compounds similar to Thiele's ether could be isolated from the reaction products when 6,6-dimethylfulvene and acetone reacted in a basic methanolic solution. One compound had the formula $C_{14}H_{20}O$ and will continue to be called Thiele's ether, while the other had $C_{15}H_{22}O$ and is possibly a methyl ether.[5]

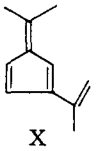
Because the solvent apparently entered into one of the reaction products, experiments were run without solvent in order to maximize the yield of Thiele's ether. However, when alcohols were omitted from the reaction media, only hydrocarbon products were isolated. Most of this report concerns the structure of these hydrocarbon products.

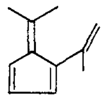
Five products were obtained by fractional distillation from the reaction mixture prepared from cyclopentadiene and acetone, with a less than stoichiometric amount of potassium hydroxide catalyst. All five products were hydrocarbons and their analyses indicated that they correspond to the addition and subsequent dehydration of first one, then two, three, four and, finally, five acetone moieties to one cyclopentadiene. When methanol was used as a solvent, the five products mentioned above were formed, in addition to the two products containing oxygen. The individual compounds are described in the following sections.

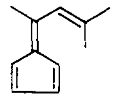
Table I

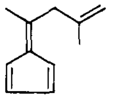
Thiele's product from methanol	Carbon	Hydrogen	Thiele's product from ethanol	Carbon	Hydrogen
Calcd. for $C_{14}H_{20}O$	82.35	9.80	Calcd. for $C_{14}H_{20}O$	82.35	9.80
Calcd. for $C_{15}H_{22}O$	82.51	10.16	Calcd. for $C_{16}H_{24}O$	82.70	10.41
Found	82.87	9.86	Found	82.95	10.18

Product $C_{11}H_{14}$(X).—The following four structures were considered for compound $C_{11}H_{14}$, X through XIII, and X was chosen to be the correct structure, based upon the following experiments.


X


XI


XII


XIII

The reaction of cyclopentadiene and diacetone alcohol under basic conditions led to the formation of a mixture of products from which 6,6-dimethylfulvene and compound $C_{11}H_{14}$ could be fractionally distilled. That this compound was really the same product obtained from the acetone reaction was indicated by the similarity of physical constants and the preparation of the same adduct with dimethyl acetylenedicarboxylate. Moreover, since some 6,6-dimethylfulvene was formed, the $C_{11}H_{14}$ compound could not be assigned structures XII or XIII unequivocally because prior dissociation into acetone was probable.

Thiele had shown that the reaction of mesityl oxide and cyclopentadiene under basic conditions produced a typical fulvene color, but no products were isolated. This reaction was repeated and a product was isolated and is designated XII because of its physical constants and method of synthesis. XII is quite different from the $C_{11}H_{14}$ compound from acetone and further suggests that the fulvenes formed from diacetone alcohol under these conditions are the same as those from acetone. On standing, XII formed a new compound with a much higher boiling point, with a molecular weight of 260, but with the same analysis. The molecular weight of XII in refluxing benzene was found to be 230–240. It is probable that a reversible dimerization reaction occurs under these conditions.

When isopropylcyclopentadiene[6] reacted with acetone under basic conditions, a $C_{11}H_{16}$ compound was isolated. This compound must be either dihydro X or dihydro XI. Hydrogenation of the $C_{11}H_{16}$ compound produced a saturated hydrocarbon and a mixture of olefins. This same mixture of olefins was obtained when the $C_{11}H_{14}$ compound obtained from acetone was hydrogenated under similar conditions as determined by physical constants and gas–liquid chromatography (g.l.c.). Therefore, the product obtained from acetone had to be either X or XI.

Nametkin[7] has shown that under similar conditions the hydrogenation of 6,6-dimethylfulvene led to the production of isopropylcyclopentane, isopropylidenecyclopentane, and 1-isopropylcyclopentene. This work was repeated using platinum oxide as catalyst, and quite similar results were obtained. The hydrogenation of X, as stated before, led to the production of a mixture of olefins, of which one made up 75% of the product. However, in one run a diolefin was also pro-

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(4) E. D. Bergmann, J. Cook's "Progress in Organic Chemistry," Vol. 3, Butterworth Scientific Publications, London, 1955, p. 81.

(5) Reexamination of Thiele's limited data showed that his reaction product may also be interpreted as having either the formula $C_{14}H_{20}O$ or $C_{15}H_{22}O$. Similarly, Thiele's product from the basic ethanolic solution may be $C_{16}H_{24}O$, see Table I.

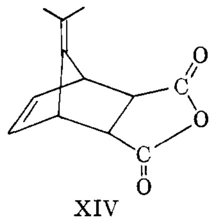
(6) K. Ziegler, H. Gellert, H. Martin, K. Nagel, and J. Schneider, *Ann.*, **589**, 91 (1954).

(7) S. S. Nametkin and M. A. Volodina, *Zh. Obshch. Khim.*, **21**, 331 (1951).

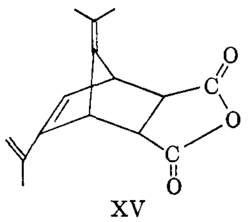
duced. The olefin mixture could not be hydrogenated with Raney nickel at 1000-p.s.i. hydrogen pressure at 100°, but the mixture did readily pick up bromine.

Hydrogenation of XII with a platinum dioxide catalyst gave a mono olefin which was quite different from those obtained from the hydrogenation of X.

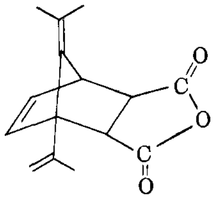
The $C_{11}H_{14}$ compound from acetone reacted with two equivalents of maleic anhydride to give a solid adduct. A consideration of the Diels-Alder reaction of 6,6-dimethylfulvene and maleic anhydride, which leads to the formation of XIV,[8] would indicate that XV and XVI would be the mono adducts from X and XI, respectively. Only XV contains a conjugated system and would be expected to react further to give a double adduct, XVII. Although there may be other structures present, X must be considered as the main constituent of the $C_{11}H_{14}$ fraction.



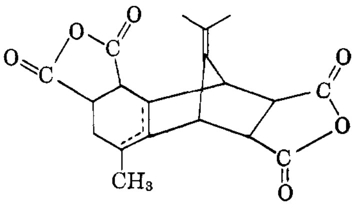
XIV



XV

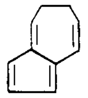


XVI

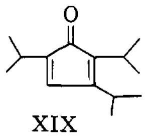


XVII

It was of interest to determine if a compound of type XI could be obtained under these basic conditions of fulvene formation. To this end, an aqueous glutaraldehyde solution was treated with a basic cyclopentadiene mixture. A very small amount of the fulvene XVIII was obtained. This dihydroazulene was readily dehydrogenated with chloranil to give azulene.

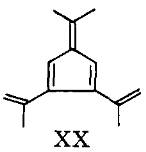


XVIII

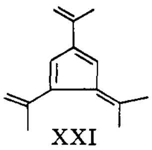


XIX

Product $C_{14}H_{18}$—The orange liquid, $C_{14}H_{18}$, rapidly picked up oxygen on exposure to air. This crude oxygenated product was hydrogenated on the Paar apparatus to give a bright red liquid, a fulvene ketone, $C_{14}H_{22}O$. Unsubstituted fulvene ketones are not stable because of dimerization reactions,[9] but tri- and tetra-substituted derivatives have been characterized.[10] The fulvene ketone $C_{14}H_{20}O$, in alcohol, would not form a 2,4-dinitrophenylhydrazone, possibly because of steric factors or because of redox reactions.[11] For these reasons, the most likely structure is XIX.



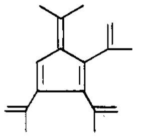
XX



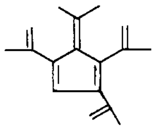
XXI

The $C_{14}H_{18}$ compound from acetone was hydrogenated to give a mixture of olefins and dienes. Although the carbon skeleton is indicated by the formation of the hindered fulvene ketone, both XX and XXI are consistent for the structure of the $C_{14}H_{18}$ compound. If Thiele's ether arises from the same sequence of reactions as does the $C_{14}H_{18}$ compound, then structure IV is quite possible for Thiele's ether. Structure VII would be unlikely because of special considerations.

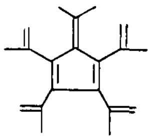
Structure of $C_{17}H_{22}$ and $C_{20}H_{26}$ Compounds—The orange-red liquid, $C_{17}H_{22}$, was hydrogenated to give a mixture of diolefins. By analogy with the $C_{14}H_{18}$ compound, this compound has either structure XXII or XXIII.



XXII



XXIII



XXIV

The dark red liquid, $C_{20}H_{26}$, was hydrogenated to give a mixture of dienes and trienes. Analogously to the other members in this series, only structure XXIV is possible.

Discussion of Experimental.—In the experiments leading to the formation of the fulvenes without the alcohol solvent, the base, potassium hydroxide, was mainly insoluble in reaction medium. However, after an induction period, during which some color formation was noted, an exothermic reaction ensued leading to the formation of a colored organic layer and an aqueous layer. External heating and the use of large amounts of acetone favored the production of the higher boiling compounds. Although the reaction was sometimes neutralized by the addition of acid to the basic mixture, in the case where ion exchange resins were used this step was certainly not necessary.[12]

If oxygen is allowed to enter into the reaction medium or come in contact with the fulvenes during isolation, a great deal of polymeric material is formed. If large amounts of oxygen are present, a very viscous pot residue, in some cases cross linked, will remain after distillation of the fulvenes. Special care was taken to prevent oxygen from contaminating the analytical samples, although the refractive indices were taken in the normal manner and may, therefore, be subject to some error.

TABLE II

Fraction	B.p., °C.	Color	Yield, g.	$n^{25}D$
1	30– 62 (0.6 mm.)	Yellow	25.3	1.5173
2	63– 71 (0.6 mm.)	Yellow-orange	14.2	1.5280
3[a]	72– 84 (0.6 mm.)	Orange	57.0	1.5458
4	85–105 (1.0 mm.)	Orange-red	5.6	1.5438
5	105–115 (1.2 mm.)	Red	6.4	1.5580
6	115–125 (1.2 mm.)	Red	24.9	1.5694

[a] Fraction 3 was redistilled to give Thiele's ether, b.p. 69–71° (1.0 mm.), 23.5 g., $n^{25}D$ 1.5261. *Anal.* Calcd. for $C_{14}H_{20}O$: C, 82.35; H, 9.80 Found: C, 82.96; H, 9.92. Methyl ether, b.p. 76–79° (0.6 mm.), orange, $n^{25}D$ 1.5281, 26.5 g. *Anal.* Calcd. for $C_{15}H_{22}O$: C, 82.51; H, 10.16; mol. wt., 218. Found: C, 82.40; H, 10.02; mol. wt., 219 ± 2.

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[8] K. Alder and K. Ruhmann, *Ann.*, **566**, 1 (1950).

[9] C. Depuy and C. Lyons, *J. Am. Chem. Soc.*, **82**, 631 (1960).

[10] C. Allen and J. Van Allan, *ibid.*, **72**, 5165 (1950); P. Pauson and B. Williams, *J. Chem. Soc.*, 4162 (1961).

[11] W. Josten, *Ber.*, **71**, 2230 (1938).

[12] G. McCain, *J. Org. Chem.*, **23**, 632 (1958).

TABLE III

					Calcd.		Found		Mol. wt.	
Compound	B.p., °C.	Color	Yield, g.	$n^{25}D$	Carbon	Hydrogen	Carbon	Hydrogen	Calcd.	Found
I, C_8H_{10}	56–60 (25 mm.)	Yellow	1003	1.5372	90.50	9.50	90.04	9.18		
$C_{11}H_{14}$	75–80 (10 mm.)	Yellow	30	1.5268	90.35	9.68	90.09	9.38		
$C_{14}H_{18}$	80–85 (1 mm.)	Yellow-orange	110	1.5372	90.26	9.74	90.29	9.50	186	193
$C_{17}H_{22}$[a]	105–110 (1 mm.)	Red	15	1.5476	90.20	9.80				
$C_{20}H_{26}$	134–138 (0.8 mm.)	Red	24	1.5635	90.16	9.84	90.50	9.68		
Pot residue		Red	91							

[a] This sample was very difficult to purify by repeated distillation and contained an oxygenated impurity.

The fulvenes could not be isolated by g.l.c. using a Tween 80 stationary phase column with helium as the carrier gas, although their hydrogenated derivatives were easily separated. The molecular weights were taken by ebulliometry using an internal standard.

Experimental

Reaction of 6,6-Dimethylfulvene and Acetone in Methanol.—To 166 g. (1.57 moles) of 6,6-dimethylfulvene were added 11.8 g. of potassium hydroxide, 190 g. (3.28 moles) of acetone and 150 g. of methanol. The mixture was magnetically stirred under nitrogen in a 1-l., three-necked, round-bottom flask equipped with a nitrogen inlet tube, a thermometer and a reflux condenser. The mixture reacted exothermically, the temperature rising to 31° and a red solution was formed. Heat was applied and the solution was refluxed for 4 hrs. After standing overnight, two 300-ml. layers had formed. The layers were not acidified but the water layer was washed with ether and the ether extract was added to the organic fraction. The combined organic fraction was washed with water and dried over magnesium sulfate. The dry organic liquid was fractionally distilled.

Reaction of Cyclopentadiene and Acetone without Added Solvent. A. With Stoichiometric Amounts of Acetone.—To 954.2 g. (14.4) moles of freshly distilled cyclopentadiene in a 5-l., three-necked flask equipped with a nitrogen inlet tube, thermometer, mechanical stirring apparatus and a reflux condenser were added 85 g. of XE-150, a mixed bed ion exchange resin manufactured by Rohm & Haas Co., and 840 g. (14.4 moles) of acetone. The mixture was heated and stirred under nitrogen to a temperature of 42°. Heating was discontinued as an exothermic reaction began. After 1 hr. at reflux, the now dark red mixture was cooled in an ice bath and allowed to stir at room temperature overnight. The resin was filtered and the filtrate separated into two layers. The water layer weighed 174 g. The red organic layer was fractionally distilled. See Table III.

B. With Excess Acetone.—To 20.0 g. of potassium hydroxide in a 1-l., three-necked flask equipped as described previously were added 100 g. (1.51 moles) of freshly distilled cyclopentadiene and 400 g. (6.88 moles) of acetone. The mixture was stirred and heated under nitrogen. Around 30° an exothermic reaction occurred which necessitated the use of an ice bath in order to control the reaction at gentle reflux. The base completely dissolved during this period and a bright red solution was formed. The exothermic reaction lasted for about 2 hr. and then an additional hour of heating at reflux was applied (61°). After standing overnight at room temperature, a solution of 40 ml. of concentrated hydrochloric acid in 250 ml. of water was slowly added to the stirred solution which was cooled in an ice bath. The organic layer was washed with water, dried over magnesium sulfate, and fractionally distilled.

TABLE IV

Fraction	B.p., °C.	$n^{25}D$	Yield, g.
1	62–64 (30 mm.)	1.5368	3.6
2	78–82 (20 mm.)	1.5281	3.1
3	100–106 (20 mm.)	1.5351	17.9
4	105–110 (1.2 mm.)	1.5468	10.2
5	120–125 (0.4 mm.)	1.5692	66.1
6	Pot residue		100

Reaction of Mesityl Oxide and Cyclopentadiene in Basic Methanol.—To 200 g. (2.02 moles) of mesityl oxide in a 2-l., three-necked flask equipped as described previously were added 130 g. (1.97 moles) of freshly distilled cyclopentadiene and 500 ml. of methanol containing 30 g. of sodium hydroxide. The solution was mechanically stirred under nitrogen and reacted exothermically to 60° and maintained this temperature for 2 hr. before cooling. The flask was refrigerated at 5° for 36 hr. and was then acidified with 50 ml. of glacial acetic acid. To the organic layer was added 500 ml. of ether and the ether solution was washed with water, dried over magnesium sulfate, and fractionally distilled. See Table V.

Dimerization of XII.—XII was stored in the refrigerator at 5° but after 7 months partial dimerization had occurred. The yellow liquid formed, b.p. 106–110° (0.5 mm.), $n^{25}D$ 1.5412, did not have the typical fulvene structure in the infrared but did have weak absorption in the conjugated diene region at 1660, 1630, and 1610 cm.$^{-1}$.

Anal. Calcd. for $C_{22}H_{28}$: C, 90.35, H, 9.65; mol. wt., 292. Found: C, 90.63; H, 9.72; mol. wt., 260.

The freshly distilled XII gave a molecular weight of 230–240 in refluxing benzene.

Reaction of Cyclopentadiene and Diacetone Alcohol.—In addition to 6,6-dimethylfulvene, there was a fraction isolated from the reaction of 100 g. of cyclopentadiene, 50 g. of potassium hydroxide and 126 g. of diacetone alcohol, which fraction was a yellow-orange liquid, b.p. 68–71° (9 mm.), $n^{25}D$ 1.5241, 12.3 g.

Anal. Calcd. for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.30; H, 9.56.

A solution of 10.0 g. of this product, $C_{11}H_{14}$, and 10.0 g. of dimethyl acetylenedicarboxylate containing an inhibitory amount of phenothiazine was heated to 150° for 0.5 hr. under nitrogen. The yellow solution was distilled and the fraction boiling at 150–160° (0.35 mm.), $n^{25}D$ 1.5252, a very viscous orange liquid, was collected, 2 g.

Anal. Calcd. for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.66; H, 7.23.

The Reaction of the $C_{11}H_{14}$ Compound (from Acetone) and Dimethyl Acetylenedicarboxylate.—From a solution of dimethyl acetylenedicarboxylate and the $C_{11}H_{14}$ compound from acetone was isolated a viscous orange liquid, b.p. 150–154° (0.4 mm.), $n^{25}D$ 1.5248.

Anal. Calcd. for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.93; H, 7.05.

The infrared spectra of this adduct and that adduct from the fulvene from diacetone alcohol were virtually identical.

The Reaction of Maleic Anhydride and the $C_{11}H_{14}$ Compound From Acetone.—To 6.2 g. (0.042 mole) of compound $C_{11}H_{14}$ from acetone were added 9.0 g. (0.092 mole) of maleic anhydride and 50 ml. of xylene. This yellow solution was refluxed under nitrogen for 2 hr. On cooling, a yellow precipitate formed which was recrystallized from moist chloroform to give a light yellow solid. The infrared spectrum showed the presence of acid groups.

Anal. Calcd. for $C_{19}H_{22}O_8$: C, 60.31; H, 5.86. Found: C, 60.59; H, 5.73.

Preparation of Isopropylcyclopentadiene.—Following the procedure given by Ziegler,[6] the reduction of dimethylfulvene by lithium aluminum hydride gave a colorless liquid, b.p. 38–43° (14 mm.), $n^{25}D$ 1.4608 [reported b.p. 28–30° (18 mm.), $n^{25}D$ 1.4639]. After standing 1 month in a closed container the refractive index had changed, $n^{25}D$ 1.4862, indicating possible dimerization. This new material was cracked at a pot temperature around 210° to give the monomer back.

Condensation of Acetone and Isopropylcyclopentadiene.—To 92 g. (0.85 mole) of isopropylcyclopentadiene in a 500-ml. flask equipped with the usual attachments were added 50 g. (0.86 mole) of acetone and 20 g. of potassium hydroxide pellets. The mixture was stirred under nitrogen and heated to reflux for 1 hr.

TABLE V

Compound	Color	B.p., °C.	$n^{25}\text{D}$	Yield, g.	Calcd.		Found	
					Carbon	Hydrogen	Carbon	Hydrogen
XII	Orange	33–35 (0.5 mm.)	1.5185	176	90.35	9.65	89.00	10.20
Thiele's ether	Orange	59–61 (0.4 mm.)	1.5276	...	82.35	9.80	82.37	9.95
Methyl ether	Orange	70–72 (0.8 mm.)	1.5290	...	82.51	10.16	82.23	10.31

TABLE VI

Compound hydrogenated	Compounds formed	B.p., °C.	$n^{25}\text{D}$	Color	Calcd.			Found		Mol. wt.	
					Formula	Carbon	Hydrogen	Carbon	Hydrogen	Calcd.	Found
I	Alkane	126–128 (atm.)	1.4292	Colorless							
	Olefin	130–134 (atm.)	1.4334	Very light yellow							
$C_{11}H_{14}$	Olefin	178–180 (atm.) 50–53 (1.2 mm.)	1.4542	Very light yellow	$C_{11}H_{20}$	86.76	13.34	85.63	12.91		
$C_{14}H_{18}$	Diene	190–192 (atm.) 83–86 (25 mm.)	melting point 74–74.5°	Colorless	$C_{11}H_{18}$	87.93	12.07	88.46	11.94		
	Olefin	62–66 (0.5 mm.)	1.4762	Colorless	$C_{14}H_{24}$	86.51	13.49	86.07	13.11		
	Diene	230–234 (atm.) 61–64 (0.8 mm.)	1.4845	Very light yellow	$C_{14}H_{22}$	87.42	12.58	87.42	12.71		
$C_{17}H_{22}$	Diene	86–90 (1 mm.)	1.4913	Light yellow	$C_{17}H_{30}$	87.10	12.90	86.98	12.87	234	215
$C_{20}H_{26}$	Diene	116–120 (1.0 mm.)	1.4814	Light yellow	$C_{20}H_{36}$	86.86	13.12	86.88	13.32		
	Triene	134–138 (1.5 mm.)	1.4829	Light orange	$C_{20}H_{34}$	87.52	12.48	87.34	12.87	274	273
Thiele's ether	Saturated ether	52–55 (0.5 mm.)	1.4574	Colorless	$C_{14}H_{26}O$	79.93	12.46	80.20	13.03	210	211
Compound $C_{11}H_{16}$	Alkane	25–27 (0.7 mm.)	1.4380	Colorless	$C_{11}H_{22}$	85.63	14.37	85.94	14.05		
	Olefin	28–30 (0.7 mm.)	1.4531	Very light yellow							
XII	Olefin	180–182 (atm.) 68–72 (14 mm.)	1.4563	Colorless	$C_{11}H_{20}$	86.76	13.34	86.58	13.00		

After stirring overnight at room temperature, the mixture was cooled in an ice bath. A solution of 40 ml. of concentrated hydrochloric acid in 500 ml. of water was slowly added to the mixture. The organic layer was washed with water, dried over magnesium sulfate, and distilled to give three fractions.

Fraction 1, b.p. 45–48° (0.9 mm.), yellow liquid, $n^{25}\text{D}$ 1.5219, 64 g.

Anal. Calcd. for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 88.80; H, 9.55.

Fraction 2, b.p. 79–81° (0.9 mm.), $n^{25}\text{D}$ 1.5029, yellow-orange.

Fraction 3, b.p. 110–115° (0.9 mm.), $n^{25}\text{D}$ 1.5308, orange-red.

Preparation of 5,6-Dihydroazulene (XVIII).—To 800 g. (2.0 moles) of a 25% solution of glutaraldehyde in water in a 3-l., three-necked flask equipped as described were added 140 g. (3.9 moles) of freshly distilled cyclopentadiene, sufficient ethanol to give a cloudy dispersion, and 50 g. of potassium hydroxide pellets. The mixture, which was slightly exothermic was stirred overnight under nitrogen. The mixture was acidified with acetic acid. Water and ether were added until two layers easily formed. The ether layer was washed with water and then it was concentrated at aspirator pressures. Hexane was added to the viscous concentrate and the mixture was stirred until no more concentrate was seen to dissolve. The hexane solution was distilled and the red liquid collected, b.p. 38–40° (2 mm.), 3.6 g., which crystallized on cooling into a red solid, m.p. 46–50°.

Anal. Calcd. for $C_{10}H_{10}$: C, 90.91; H, 9.09. Found: C, 90.76; H, 9.09.

Dehydrogenation of XVIII.—To 2.5 g. of the crude XVIII was added 5 g. of chloranil in ethanol. The solution was heated to reflux and turned a dark green-blue. The concentrated solution was chromatographed on alumina with a hexane eluent. Azulene was isolated as dark blue plates, m.p. 98–101°, 1.3 g. (reported m.p. 98.5–99°[13]).

Anal. Calcd. for $C_{10}H_8$: C, 93.71; H, 6.29. Found: C, 93.47; H, 6.43.

Oxidation and Hydrogenation of the $C_{14}H_{18}$ Compound from Acetone.—After standing in contact with air for 35 days, 21 g. of the $C_{14}H_{18}$ compound, now a very viscous red liquid was hydrogenated in an ether solution utilizing platinum dioxide as catalyst on the Paar hydrogenation apparatus. The initial hydrogen pressure was 50 p.s.i. and after 3 hr. at room temperature the pressure had dropped to 38 p.s.i. No more hydrogen was absorbed after this time. The mixture was filtered and the filtrate distilled. After a forerun, a red liquid was collected, b.p. 110–112° (0.3 mm.), $n^{25}\text{D}$ 1.5026, 1.7 g. The infrared spectrum showed a strong band at 1715 cm.$^{-1}$ and a weak but very broad band at 1610–1650 cm.$^{-1}$. The reported band range for the carbonyl of fulvene ketones is 1697–1736.[14]

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[13] P. Plattner and S. T. Ptau, *Helv. Chim. Acta,* **20**, 224 (1937).

[14] E. D. Bergmann, see ref. 4, p. 118.

Anal. Calcd. for $C_{14}H_{20}O$: C, 81.50; H, 10.75. Found: C, 81.53; H, 10.84.

Several attempts were made to prepare a 2,4-dinitrophenylhydrazone but none was successful.

Hydrogenation Studies.—The data (see Table VI, p. 1650) describes the hydrogenation on the Paar apparatus at a maximum hydrogen press of 50 p.s.i. at room temperature with a platinum dioxide catalyst. The mixtures were mechanically shaken until no more hydrogen was consumed.

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The Preparation of Dodecamethylcyclohexasilane

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Directions are given for an improved method of preparation of dodecamethylcyclohexasilane; a proposed mechanism of catalysis by triphenylsilyllithium in this synthesis is considered.

The reaction of dichlorodimethylsilane with sodium at temperatures above 100° in hydrocarbon solvents has been shown to lead to an insoluble polymer as the principal product, with dodecamethylcyclohexasilane (I) being obtained in a low, unspecified yield.[1] It has been reported recently that the yield of I is only 0.05%, when the reaction mixture was worked up by methanol extraction rather than by the vacuum distillation procedure used by Burkhard, and that the use of lithium and tetrahydrofuran at high temperatures increased the yield to 2.5%.[2] Low yields of I also have been obtained from the treatment of dichlorodimethylsilane with sodium[3] and lithium[4] upon extended refluxing in tetrahydrofuran. In the latter case,[4] the yield of dodecamethylcyclohexasilane was 33%, even when dichlorodimethylsilane was added to the lithium at a slow rate.

If the reaction with lithium in the presence of tetrahydrofuran is allowed to proceed in the presence of silyllithium compounds, we have found that the yields of dodecamethylcyclohexasilane are increased significantly to the range of 60–70%.

Initially, dichlorodimethylsilane in tetrahydrofuran is added to lithium in the presence of a small amount of triphenylsilyllithium. Thereafter, the addition of dichlorodimethylsilane is controlled such that silyllithium compounds are present in the reaction mixture throughout the course of the reaction.

The proposed mechanism of catalysis by triphenylsilyllithium is illustrated in the following equations.

$$(C_6H_5)_3SiLi + ClSi(CH_3)_2R \longrightarrow (C_6H_5)_3Si\text{-}Si(CH_3)_2R \xrightarrow{2Li} (C_6H_5)_3SiLi + \underset{\text{II}}{LiSi(CH_3)_2R}$$

(R is Cl, $Si(C_6H_5)_3$, or $[Si(CH_3)_2]_nR$)

Chlorosilanes may then react with either triphenylsilyllithium or with intermediates such as II. Triphenylsilyllithium can also be regenerated by reactions joining dimethylsilylene units, as shown in the following example.[5]

$$R(CH_3)_2Si\text{-}Li + R(CH_3)_2Si\text{-}Si(C_6H_5)_3 \longrightarrow R(CH_3)_2SiSi(CH_3)_2R + (C_6H_5)_3SiLi$$

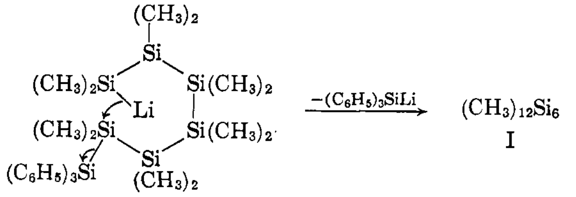
(R is Cl, $Si(C_6H_5)_3$, or $[Si(CH_3)_2]_nR$)

These reactions are supported by the observation that 2,2-dimethyl-1,1,1,3,3,3-hexaphenyltrisilane, upon treatment with lithium in tetrahydrofuran, afforded good yields of dodecamethylcyclohexasilane and triphenylsilyllithium, with the latter forming a derivative with chlorotrimethylsilane. In this case, by means of the cleavage reactions shown in the preceding equations, the formation of the observed products may be illustrated by the following mechanistic pathway. The

$$6(C_6H_5)_3SiSi(CH_3)_2Si(C_6H_5)_3 + 6Li \xrightarrow{-6(C_6H_5)_3SiLi}$$

$$3(C_6H_5)_3Si[Si(CH_3)_2]_2Si(C_6H_5)_3 \xrightarrow{4Li,\ -4(C_6H_5)_3SiLi}$$

$$(C_6H_5)_3Si[Si(CH_3)_2]_6Si(C_6H_5)_3 \xrightarrow[-(C_6H_5)_3SiLi]{2Li}$$



cyclization reaction given here undoubtedly occurs in the reaction involving dichlorodimethylsilane. However, other ring-closure reactions cannot be discounted.

The proposed mechanism of catalysis is further supported by the reaction of five molar equivalents of dichlorodimethylsilane with two equivalents of triphenylsilyllithium in the presence of the calculated amount of lithium. From this reaction, dodecamethylcyclohexasilane was isolated in a 25% yield; there were also obtained crystalline solids which apparently are mixtures of polydimethylsilanes containing terminal triphenylsilyl units. However, only 2,2-dimethyl-1,1,1,3,3,3-hexaphenyltrisilane could be separated in a pure state.

The formation of substituted-dimethylsilylithium intermediates may also occur by the lithium cleavage of tetramethyldisilanyl units. This was demonstrated by allowing the mixture obtained from the triphenyl-

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[1] C. A. Burkhard, *J. Am. Chem. Soc.*, **71**, 963 (1949).

[2] (a) E. Hengge and H. Reuter, *Naturwissenschaften*, **49**, 514 (1962); (b) See, also, the report which just appeared by U. Graf zu Stolberg, *Angew. Chem.*, **75**, 206 (1963).

[3] R. P. Anderson, private communication.

[4] H. Gilman and G. L. Schwebke, unpublished studies.

[5] The formation of hexaethyldisilane upon treatment of 1,1,1-triethyl-2,2,2-triphenyldisilane with lithium in tetrahydrofuran has been proposed to occur by a similar mechanism. See, H. Gilman and H. J. S. Winkler, "Organosilylmetallic Chemistry," in H. Zeiss, Ed., "Organometallic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1960, p. 277; and H. Gilman, G. D. Lichtenwalter, and D. Wittenberg, *J. Am. Chem. Soc.*, **81**, 5320 (1959).