Reaction of Aryl Ketones with Cyclopentadienyl Sodium. Syntheses of Fulvenylmethanols

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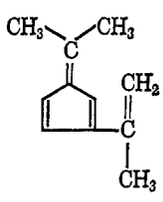
The reaction of 2-benzoylpyridine with cyclopentadienyl sodium in alcohol can be directed to give the expected 6-phenyl-6-(2-pyridyl)fulvene (**3**) as its dimer in 88% yield or the novel α-phenyl-α-[6-phenyl-6-(2-pyridyl)-2-fulvenyl]-2-pyridinemethanol (**4**) in 86% yield by varying the conditions. The reaction conditions which favor formation of **3** or **4** are discussed in terms of a mechanism for their formation. A variety of diaryl and alkyl aryl ketones, in which the aryl groups were phenyl, substituted phenyl, 2-, 3-, or 4-pyridyl, thienyl, or quinolyl, were allowed to react with cyclopentadienyl sodium. It was found that strongly electronegative aryl groups are required for conversion of diaryl ketones to 2-fulvenylmethanols. Aryl 2- (or 4-) pyridyl and di-2- (or 4-) pyridyl ketones form 2-fulvenylmethanols readily. Most diphenyl ketones do not form 2-fulvenylmethanols readily and alkyl pyridyl ketones give only trace amounts of fulvenylmethanols.

As part of our effort to synthesize 6,6-diarylfulvenes which are intermediates to bridged hydroisoindolines, 2-benzoylpyridine (**1**) was treated with cyclopentadienyl sodium (**2**) to give the anticipated 6-phenyl-6-(2-pyridyl)fulvene (**3**) (isolated as its maleimide adduct **5**)[1] and a 39% yield of orange crystals which we have identified as α-phenyl-α-[6-phenyl-6-(2-pyridyl)-2-fulvenyl]-2-pyridinemethanol (**4**). The formation of this unusual 2-fulvenylmethanol **4** led us to investigate the scope and limitations of the reactions of aryl ketones with cyclopentadienyl sodium. The cardiac antiarrhythmic activity of fulvenylmethanol **4** and α,α,6,6-tetra(2-pyridyl)-2-fulvenemethanol (**38**)[2] in dogs and the unique raticidal activity of the norbornenedicarboximide **6**[3] and its analogs[4] further stimulated our interest.

Evidence supporting the structure of the orange 2-fulvenylmethanol **4** consisted of the correct elemental composition (C, H, N, and O) and molecular weight. The ultraviolet spectrum was practically superimposable on that of 6,6-diphenylfulvene but exhibited a reversible bathochromic shift upon acidification. The presence of the hydroxyl group, evident from the infrared spectrum, was confirmed by alkylation of **4** to the corresponding O-methyl ether **8**.

Fulvenylmethanol **4** was obtained as a mixture of two geometric isomers[5] which were separated by fractional recrystallization. The *cis* isomer of the unsymmetrically substituted fulvene **4** is defined as that isomer in which the carbinol group and the 6-(2-pyridyl) group are on the same side of the fulvene nucleus (as illustrated in Chart I). Reaction of the individual isomers of **4** with maleimide gave isomeric mixtures of norbornenedicarboximides **6**, whose nmr spectra provided evidence that (a) the carbinol substituent of fulvenylmethanol **4** is located at position 2 rather than 1 since the vinyl resonance peak of **6** integrated for one proton and (b) the higher melting isomer of **4** possesses the *cis* configuration.[6]

Early workers[7] had considered the possibility of ring-substituted fulvenes, such as **9**, arising from reaction of acetone with cyclopentadiene in basic alcoholic solution. In 1963, after our structural proof was completed, two articles[8] appeared reporting the isolation of fulvenylmethanol **10** from the reaction of acetone and cyclopentadienyl sodium in <2% yield. We have converted the fulvenylmethanol **10** to its maleimide adduct **11**. The nmr spectrum of **11** verified the previous assignment[8b] of the carbinol group of **10** to the 2-position.



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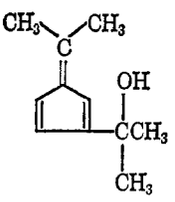

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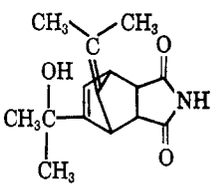

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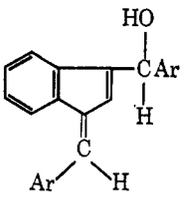


12

No other ketones have been reported in the literature to react with cyclopentadiene to give a fulvenylmethanol. It has been reported that indene condenses with aromatic aldehydes to give the related benzofulvenylmethanols (**12**) as very minor products.[9]

On further study of the reaction of 2-benzoylpyridine with cyclopentadienyl sodium, we found conditions which afforded almost exclusively either an 88% yield of the anticipated 6-phenyl-6-(2-pyridyl)fulvene (**3**) (condition B), which could not be isolated because of

(1) G. I. Poos, M. M. Lehman, E. B. Landis, and J. D. Rosenau, *J. Med. Pharm. Chem.*, **5**, 883 (1962).

(2) The initial observation and elaboration of the antiarrhythmic activity of fulvenylmethanols **4** and **38** were done by Dr. John Yelnosky of these laboratories. The latter compound is being considered for clinical trial.

(3) (a) A. P. Roszkowski, G. I. Poos, and R. J. Morhbacher, *Science*, **144**, 412 (1964); (b) A. P. Roszkowski, *J. Pharmacol. Exptl. Therap.*, **149**, 288 (1965).

(4) G. I. Poos, R. J. Mohrbacher, E. L. Carson, V. Paragamian, B. M. Puma, C. R. Rasmussen, and A. P. Roszkowski, *J. Med. Chem.*, **9**, 537 (1966).

(5) The mixture was shown to consist of only two isomers by phase solubility analyses using the method described by W. J. Mader, "Organic Analysis," Vol. 2, Interscience Publishers, Inc., London, 1954, p 253.

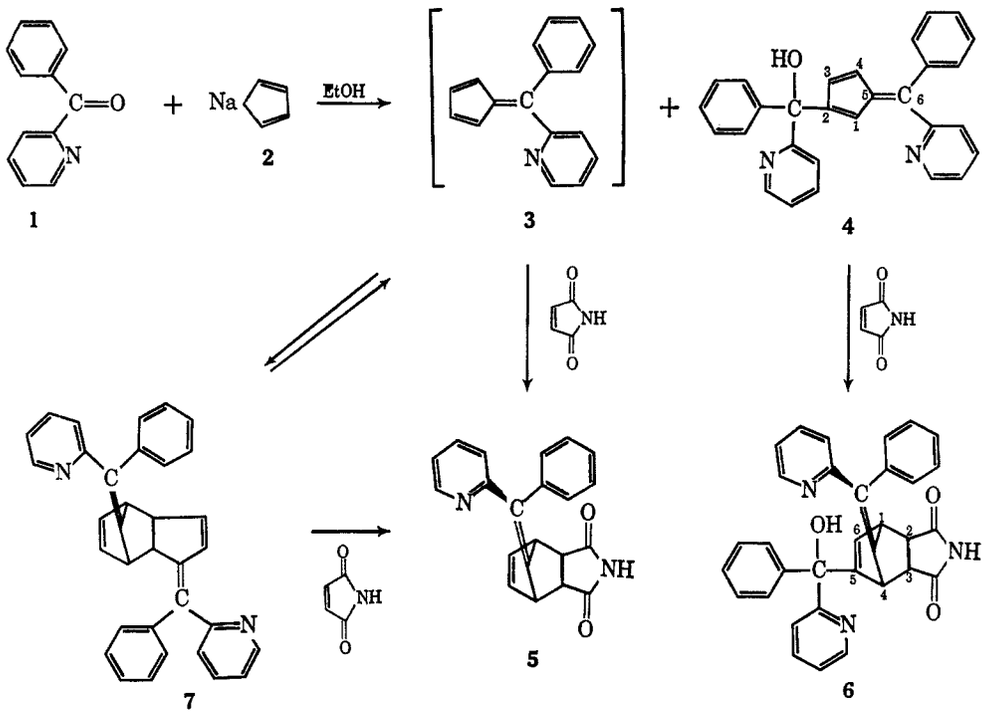
(6) R. J. Mohrbacher, H. R. Almond, Jr., E. L. Carson, J. D. Rosenau, and G. I. Poos, *J. Org. Chem.*, **31**, 2141 (1966).

(7) (a) J. Thiele and H. Balhorn, *Ann. Chem.*, **348**, 1 (1906); (b) C. Courtot, *Ann. Chim.* (Paris), **4**, 168 (1915); (c) K. Ziegler and F. Crossmann, *Ann. Chem.*, **511**, 89 (1934); (d) E. D. Bergmann, *Progr. Org. Chem.*, **3**, 81 (1955).

(8) (a) D. M. Fenton and M. J. Hurwitz, *J. Org. Chem.*, **28**, 1646 (1963); (b) W. B. Smith and C. Gonzalez, *ibid.*, **28**, 3541 (1963).

(9) (a) G. Kresze, H. Henkel, and H. Goetz, *Ann. Chem.*, **674**, 18 (1964); (b) J. Thiele, *Chem. Ber.*, **33**, 851 (1900); (c) C. Courtot, *Ann. Chim.* (Paris), **4**, 157 (1915).

CHART I



rapid dimerization to 7,[10] or an 86% yield of 2-fulvenylmethanol **4** (condition A). The product composition of this reaction was very sensitive to reaction conditions. A number of variations were studied; results, listed in Table I (p. 2152), are discussed below.

A mechanism for the reaction of aryl ketones with cyclopentadienyl sodium to form fulvenes **15** and/or 2-fulvenylmethanols **17** is shown in Chart II. Condensation of ketone **13** with cyclopentadienyl sodium could give, in several steps,[11] anion **14**. The intermediate anion **14** could either dehydrate irreversibly to fulvene **15** or undergo a second condensation with ketone **13**, analogous to the reaction of **13** with **2**,[11] to give anion **16**. Irreversible dehydration of **16** would give fulvenylmethanol **17**. Under similar conditions, certain ketones gave rise to isolable cyclopentadienedimethanols **18a** and **b** which were easily converted to fulvenylmethanols. The isolation of these diols (see below) supports the illustrated mechanism since they probably arise from protonation of anion **16**.

Apparently fulvenylmethanol **17** does not arise from fulvene **15**.[12] Several attempts to convert 6-phenyl-6-(2-pyridyl)fulvene **3** to fulvenylmethanol **4** failed.

In terms of the mechanism, the results of varying the reaction conditions (Table I) suggest that low reaction temperature and concentrated reaction medium favor a second condensation of 2-benzoylpyridine with **14** to give fulvenylmethanol **17**. Higher reaction temperature and dilute reaction medium favor expulsion of hydroxide ion from anion **14** to give fulvene **15**.

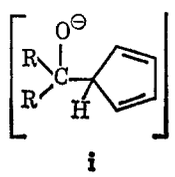
The reaction of a series of aryl ketones with cyclopentadienyl sodium was studied in an effort to define the structural parameters for the formation of fulvenylmethanols. Ketones which gave new fulvenes or fulvenylmethanols are listed in Table II in order of generally decreasing ease of fulvenylmethanol formation (see p. 2153).

High yields of fulvenylmethanol were obtained from the dipyridyl (**19–23**) and phenyl 2- or 4-pyridyl (**1** and **24**) ketones. Phenyl 3-pyridyl ketone (**28**) and nitrobenzophenones **27** and **30** gave modest yields while benzophenone (**32**)[13] and several alkyl pyridyl ketones (**33–35**) did not form fulvenylmethanols to any appreciable extent.

It is apparent that among diaryl ketones only those with more electrophilic carbonyl groups are capable of forming fulvenylmethanols. An approximate parallel between the reactivity of diaryl ketones to cyclopentadienyl sodium and their ability to form fulvenylmethanols was observed. Thus, at 5°, di-2-pyridyl ketone and the three isomeric benzoylpyridines (**1**, **24**,

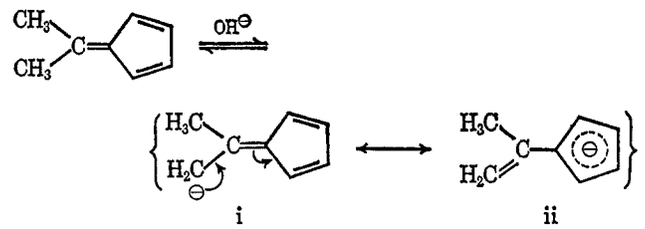
(10) An investigation of fulvene dimers is being carried out in these laboratories.

(11) The first intermediate is undoubtedly i, which could be converted to anion **14** by a number of routes. Intramolecular transfer of a cyclopentadienyl proton of i could give **14** directly. Anion i could also be protonated by the ethanol (pK_a = 17) or the available cyclopentadiene (pK_a = 15) [D. J Cram, *Chem. Eng. News*, **41**, No. 33, 92 (1963)] to give an intermediate carbinol which could be converted to anion **14** in the basic reaction medium.



i

(12) The formation of fulvenylmethanols from 6,6-dialkylfulvenes (see ref 8 and 9) probably occurs by the following mechanism which is unavailable to 6,6-diarylfulvenes. (See column 2.)

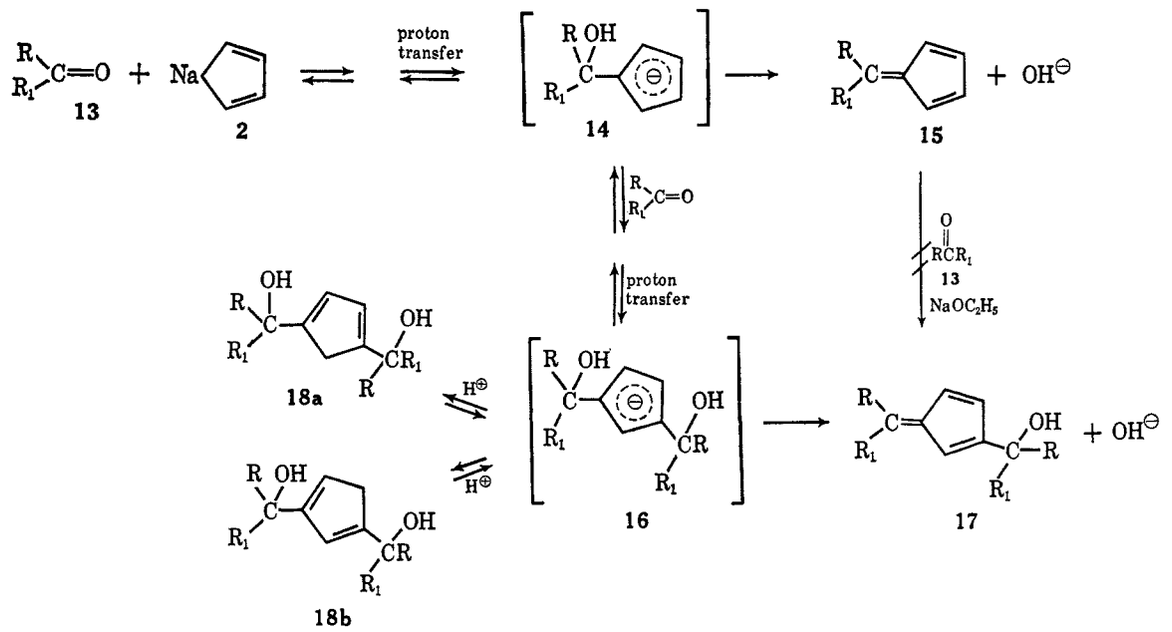


i ii

Anion ii could be alkylated further as is the case for **14** → **17**.

(13) Fulvenylmethanol **55**, from benzophenone, was prepared in 6% yield along with 60% diphenylfulvene using pyridine as solvent.

CHART II



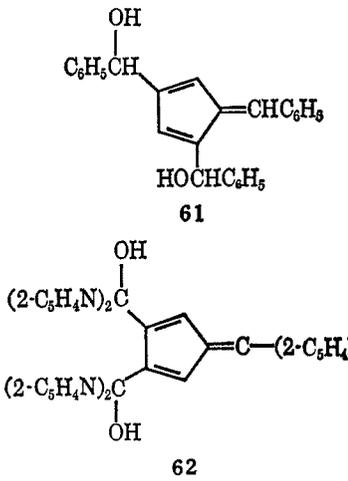
28) reacted completely after 35 min, while benzophenone was essentially unchanged after 18 hr.

In competitive experiments at 5° employing equimolar quantities of reagents, di-2-pyridyl ketone reacted completely in 5 min while 2-benzoylpyridine was unchanged. At higher temperatures (45°), benzophenone was completely reacted in 1 hr while *p,p'*-dimethoxybenzophenone was 90% unchanged. With both of these ketones, as well as *p,p'*-dibromobenzophenone, fulvenes were the only products.[14]

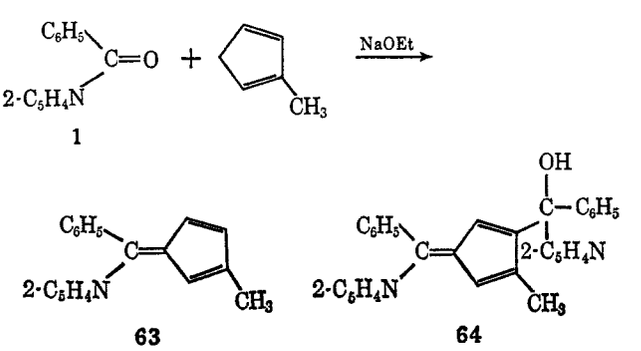
It appears that diaryl ketones which lack electron-withdrawing groups require higher temperatures to react with cyclopentadienyl sodium. At these temperatures, the irreversible dehydration of anion **14** supersedes the condensation with another molecule of ketone and subsequent irreversible dehydration to fulvenylmethanol.

However, the explanation of fulvenylmethanol formation may not rest solely on the basis of ketone reactivity in that 2-acetylpyridine reacted rapidly at 5° to give a good yield of fulvene **56** and only a trace of fulvenylmethanol **57**. At −30°, the product composition was the same although the yield was lower. In contrast to the reactivity of 2-acetylpyridine, two sterically hindered alkyl pyridyl ketones, cyclohexyl (**35**) and *t*-butyl (**34**), reacted slowly at 25° to produce only fulvenes. Similarly, 4-(N-methyl)piperidyl phenyl ketone (**36**) gave a low yield of fulvene while 2-(N-methyl)piperidyl phenyl ketone failed to react.

Two aldehydes were studied and found to be highly reactive. Pyridine-2-carboxaldehyde reacted rapidly with cyclopentadienyl sodium at −70°. Although fulvene products were evident in the reaction mixture, none could be isolated. Benzaldehyde reacted readily to 5° to produce, in addition to 6-phenylfulvene[15] as the major product, a low yield of fulvenyldimethanol **61**. A similar product, fulvenedimethanol **62**, was isolated in minor yield from the condensation of three molecules of di-2-pyridyl ketone with cyclopentadiene. Since the yields of fulvenedimethanols were low and the isolations were difficult, it is possible that other position isomers were present.



Reaction with Substituted Cyclopentadienes.—Methyl cyclopentadiene reacted with 2-benzoylpyridine at 25° to give fulvene **63**. At 5° the same ketone gave fulvenylmethanol **64** in 31% yield. Benzhydrylcyclopentadiene[16] and 2-benzoylpyridine gave fulvene **65** and by-product **66**. Fulvene **65** was converted to the dimethylenecyclopentene **66** by an irreversible base-catalyzed rearrangement.



(14) Kresze, *et al.* [*Ann. Chem.* **648**, 51 (1961)] isolated modest yields of fulvenes from *p,p'*-dimethoxybenzophenone and *p,p'*-dibromobenzophenone by reaction in refluxing methanol.

(15) J. H. Day and J. C. Lukman, *Ohio J. Sci.*, **52**, 335 (1952).

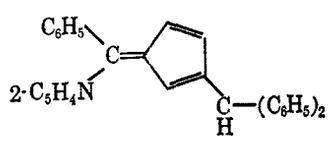
(16) K. Hafner, *Ann. Chem.*, **606**, 79 (1957).

TABLE I

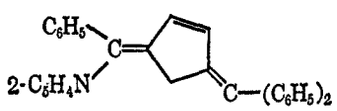
REACTION OF 2-BENZOYLPYRIDINE WITH CYCLOPENTADIENE

Condition	Molar ratio of reactants: Ketone	Cyclopentadiene	Sodium ethoxide	Order of addition[a]	Final concn of ketone/alcohol (w/v) %,	Reaction temp, °C	Time,[b] hr	Fulvene and fulvenylmethanol, % yield[c]	% ratio of fulvene/fulvenylmethanol[c]
A	2	1	0.1	Reverse	36	5	1.5	88[d]	10/90
A-1	2	1	0.1	Reverse	36	25	1	75	20/80
A-2	2	1	0.1	Reverse	3.6	5	18	8	20/80
A-3	2	1	0.1	Reverse	3.6	25	18	12	20/80
B	1	5	5	Normal	1.8	25	0.5	90	99/1
B-1	1	5	5	Normal	1.8	5	1	*Ca.* 95	80/20
B-2	1	2	2.1	Normal	1.8	25	0.5	*Ca.* 40	80/20
B-3	1	2	2.1	Normal	13	25	0.5	88	95/5

[a] Reverse addition, cyclopentadiene added to solution of ketone and base over 30-min period. Normal addition, ethanolic solution of ketone added to ethanolic solution of base and cyclopentadiene over 2-hr period. [b] Time between end of addition and work-up. [c] The yields and product composition (last column) are approximate. The yields were determined by separating and weighing the solid products (**4** and **7**). The mother liquors were then examined by tlc. If only one fulvene product (**3** or **4**) was present, an ultraviolet spectral assay of the mother liquor (ref 24) was used to estimate the quantity of fulvene present. In some cases (expt B-1, -2, and -3) samples of the mother liquors and measured quantities of fulvenylmethanol **4** were spotted on tlc plates. Comparison of the size and intensity of the spots gave an estimate of the amount of fulvenylmethanol **4** present in the mother liquors. For those experiments (A-2 and -3 and B-2) in which the yield of solid products was low, the mother liquors were shown to have appreciable quantities of ketone **1** by infrared spectra. [d] Yield of crystalline fulvenylmethanol isolated was 77%. Condition A, using 1 mole of sodium ethoxide, allowed isolation of an 86% yield of fulvenylmethanol (see above).



65



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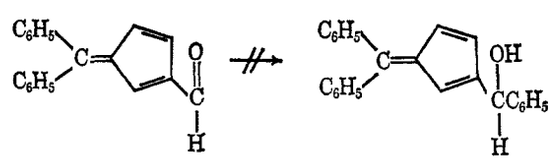
Isolation of Cyclopentadienedimethanols.—Several dipyridyl ketones reacted under condition A, except that less sodium ethoxide and lower temperatures (−5 to −10°) were employed, to give isolable diols.[17] Di-2-pyridyl ketone gave a 95% yield of an isomeric mixture of diols **67a** and **b** (Chart III). In contrast, 2-benzoylpyridine failed to react under the same conditions.

solution, diols **67a** and **b** were converted to fulvenylmethanol **38** in high yield.

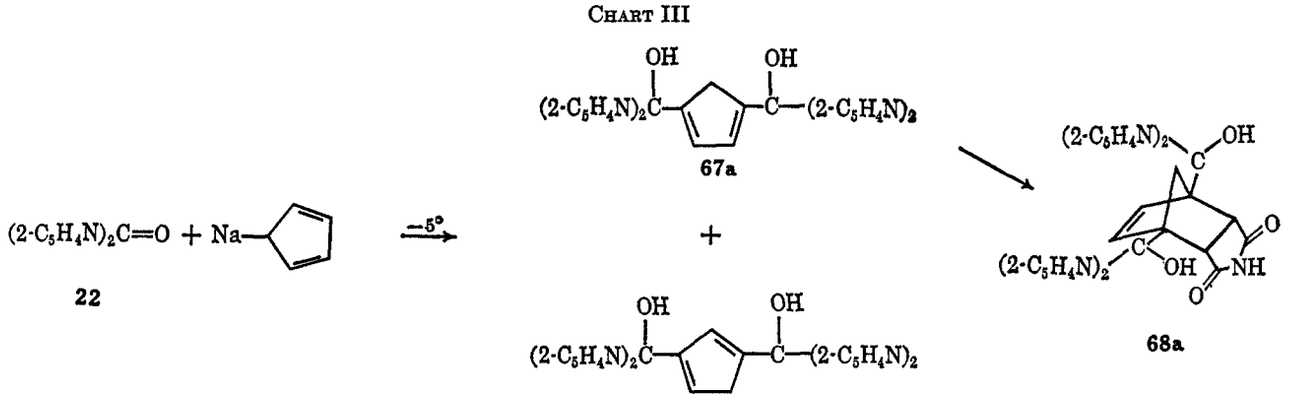
Other Attempts to Synthesize 2-Fulvenylmethanols. Attempts to convert 6,6-diphenylfulvene-2-carboxaldehyde (**69**)[19] to a fulvenylmethanol failed. Reaction of **69** with phenyl lithium under various conditions gave either unchanged aldehyde or intractable tars. Attempts to oxidize aldehyde **69** to the 2-carboxylic



69

acid, which could serve as an intermediate to fulvenylmethanols, failed. Oxidation with silver oxide,[20] chromic acid, alkaline permanganate in acetone, or

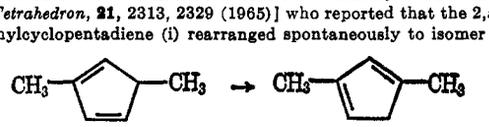
CHART III



Fractional crystallization of the isomeric mixture gave **67a** whose structure was confirmed by nmr analyses of it and its maleimide adduct **68a**. Although isomer **67b** has not been isolated, its maleimide adduct has been obtained and characterized. None of the third possible isomer of **67** was detected.[18] In warm basic ethanol

(17) An investigation of the conversion of ketones to cyclopentadienedimethanols is underway in these laboratories.

(18) This observation is in accord with that made by S. McLean and P. Hayes [*Tetrahedron*, **21**, 2313, 2329 (1965)] who reported that the 2,5 isomer of dimethylcyclopentadiene (i) rearranged spontaneously to isomer ii.



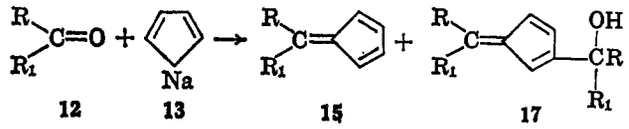
i ii

(19) K. Hafner and K. H. Vopel, *Angew. Chem.*, **71**, 672 (1959).

(20) E. Campaigne and W. M. LeSuer, *J. Am. Chem. Soc.*, **70**, 1555 (1948).

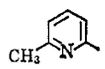
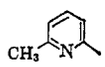
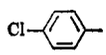
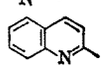
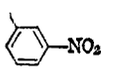
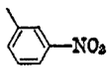
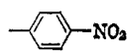
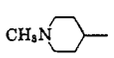
TABLE II

CONVERSION OF KETONES TO FULVENES AND 2-FULVENYLMETHANOLS



12 13 15 17

Fulvene (F) 2-Fulvenylmethanol (2-FM)

Ketone	R	R_1	Conditions[a]	Type of product[b]	Fulvene and fulvenylmethanol	Yield,[c] %
19			B	F	37	30
			A	2-FM	38	85
20			C	2-FM	39	59
21				2-FM	40	58
22			A	2-FM	41	35
23			A	2-FM	42	53
1			B	F	3	88
			A	2-FM	4	86
24			B	F	43	15
			C	2-FM	44	75
25			C	2-FM	45	73
26			C	2-FM	46	20
27			A	2-FM	47	25
28			B	F	48	35
			C	2-FM	49	20
29			C	2-FM	50	20
30				F	51	32
			A	2-FM	52	13
31				F	53	30
				(2-FM)[d]		(15)[d]
32			B	F	54	75
				2-FM	55	6
33	CH_3		C	F	56	50
				2-FM	57	1
34	$(CH_3)_3C$			F	58	14
35				F	59	15
36				F	60	15

[a] Condition A employed rapid addition of cyclopentadiene to 2 equiv of ketone in concentrated ethanol or ethanol–monoglyme solution containing 0.1–1 equiv of sodium ethoxide at 5°; condition B employed slow addition of a dilute solution of ketone to an ethanol or ethanol–monoglyme solution of 5 equiv of cyclopentadienyl sodium at 25°; condition C was the same as A except the reaction mixture was allowed to stand longer. Undesignated conditions are detailed in the Experimental Section. [b] The fulvene (F) and fulvenylmethanol (FM) structures were distinguished by nmr spectra or characterization of their maleimide adducts. [c] Yields were not necessarily maximal since some reactions were run only once. Noncrystalline products were characterized as their maleimide adducts (see Experimental Section). Low or modest yields of fulvenylmethanols were usually accompanied by substantial amounts of fulvenes. [d] Estimated from thin layer chromatography.

chromium trioxide in pyridine[21] gave either decomposition products or unchanged aldehyde. Attempts to reduce aldehyde **69** to the corresponding methanol with sodium borohydride in isopropanol gave intractable mixtures.

Experimental Section

All melting points are corrected and were taken in a stirred oil bath unless otherwise specified. Infrared spectra were obtained on a Perkin-Elmer Model 21 spectrometer and ultraviolet spectra on a Cary Model 14 spectrometer. The nmr spectra were determined on a Varian A-60 spectrometer at ambient temperature. The solutions, in $CDCl_3$ or DMF-d_7, were approximately 20% (w/v) or saturated. Tetramethylsilane was used as an internal standard. The chemical shifts are probably accurate to within $\delta \pm 0.03$.

***cis,trans*-α-Phenyl-α-[6-phenyl-6-(2-pyridyl)-2-fulvenyl]-2-pyridinemethanol (4).**[3a]—To a solution of 0.026 mole of sodium ethoxide (from 0.6 g of sodium) and 9.15 g (0.05 mole) of 2-benzoylpyridine (1) in 25 ml of absolute ethanol at 5° under nitrogen was added dropwise 1.72 g (0.026 mole) of freshly distilled cyclopentadiene over a 30-min period. The mixture was stirred under nitrogen for 1.5 hr at 10–13°, the red-orange crystalline product was collected by filtration, washed with cold alcohol, and dried to give 8.9 g (86%) of crystals: mp 160–175°; λ_{max}^{MeOH} 325 mμ (ε 22,800). Recrystallization from ethyl acetate gave a mixture of geometric isomers (mp 173–176°) of **4**, in which the more soluble *trans* isomer (mp 175–176°) and the less soluble *cis* isomer (mp 181–182°) were present in a ratio of about 4:6,[22] respectively: λ_{max}^{KBr} 2.96 (OH), 6.61 μ (aromatic); λ_{max}^{MeOH} 240 (ε 14,600), 262 (sh) (12,600), 267 (sh) (12,560), 323 mμ (24,300); $\lambda_{max}^{MeOH\text{-}HCl}$ 343 mμ (ε 22,300).

Anal. Calcd for $C_{29}H_{22}N_2O$: C, 84.03; H, 5.35; N, 6.76; O, 3.86; mol wt, 414.48. Found: C, 83.94; H, 5.46; N, 6.58; O, 4.00 (Unterzaucher); mol wt (isothermal distillation), *ca.* 412.

Fulvenylmethanol **4** was also formed under condition A using alcoholic solutions of other bases; *e.g.*, potassium hydroxide or Triton B in ethanol or potassium *t*-butoxide in *t*-butyl alcohol.

Phase solubility experiments[5] were conducted at 30° in ethyl acetate for 2 weeks. Quantitative analysis of the solutions were done gravimetrically.

The two geometric isomers of **4** were separated by fractional crystallization from ethyl acetate as described previously.[6]

Anal. Found for *trans*-**4** (mp 175–176°): C, 84.32; H, 5.69; N, 6.79. Found for *cis*-**4** (mp 181–182°): C, 84.17; H, 5.36; N, 6.68.

The nmr spectra ($CDCl_3$) of the isomers are shown in Table III. The three fulvenyl protons show an ABX pattern with

TABLE III

	Nmr Spectra (δ)					
Isomer	α-Pyridyl	Aromatic	1-Fulvenyl	3- and 4-Fulvenyl		Hydroxyl
trans	*Ca.* 8.6	*Ca.* 7.3	6.03	6.45	6.62	6.17
cis	*Ca.* 8.6	*Ca.* 7.3	6.08	6.37	6.59	6.17

J_{AB} = 5.3 cps and $J_{AX} \cong J_{BX}$ = 2.0 cps. Consequently,[23] the larger coupling (J_{AB}) is assigned to the vicinal coupling of the 3,4-protons and the smaller coupling constants (J_{AX}, J_{BX}) represent the long-range coupling of the 1-proton.

Methyl α-Phenyl-α-[6-phenyl-6-(2-pyridyl)-2-fulvenyl]-2-pyridylmethyl Ether (8).—A solution of 25 g (0.06 mole) of *cis,trans*-α-phenyl-α-[6-phenyl-6-(2-pyridyl)-2-fulvenyl]-2-pyridinemethanol (**4**) in 400 ml of anhydrous monoglyme was added dropwise over 40 min to a boiling suspension of 5.35 g of sodium hydride (54% in mineral oil, 0.12 mole, previously washed with anhydrous ether) in 100 ml of anhydrous monoglyme. After 1260 ml (84% of theoretical) of hydrogen had evolved, an additional 0.67 g of 54% sodium hydride was added; no further gas evolution was observed. The mixture was cooled and allowed to stand at room temperature overnight and then was treated with 8.52 g (0.06 mole) of methyl iodide in 15 ml of monoglyme. After 2 hr at room temperature, the mixture was refluxed for 30 min, cooled, and then treated with 15 ml of absolute ethanol. Addition of water was followed by evaporation to an oily sludge which was partitioned between water and chloroform. The chloroform layer was washed with water and with saturated brine. The dried solution was evaporated *in vacuo;* the tarry residue was triturated with hot ethyl acetate until most of the tar had dissolved. The supernatant solution was cooled to give 13.2 g of orange crystals (51.5%) which were recrystallized twice from ethyl acetate to give 6.2 g of crystalline **8**: mp 179–180°; λ_{max}^{MeOH} 243 (sh) (ε 13,500), 267 (sh) (11,200), 325 mμ (22,800); λ_{max}^{KBr} 6.34 μ.

Anal. Calcd for $C_{30}H_{24}N_2O$: N, 6.54. Found: N, 6.51, 6.69.

On thin layer chromatography (tlc) (alumina, ethyl acetate–cyclohexane, 1:8) compound **8** exhibited R_f 0.8, compound **4**, R_f 0.3. The nmr spectrum ($CDCl_3$) of **8** showed the 1,3- and 4-fulvenyl protons in an ABC pattern centered at δ 6.5 and a three-proton singlet at δ 3.24 (OCH_3).

3a,4,7,7a-Tetrahydro-1,8-bis(α-2-pyridylbenzylidene)-4,7-methanoindene (7).—To a solution of 900 ml of absolute ethanol containing 48 g (2.1 g-atoms) of dissolved sodium at ambient temperature was added 132 g (2 moles) of cyclopentadiene under a nitrogen atmosphere. To the resulting solution was added, with stirring, a solution of 183 g (1.0 mole) of 2-benzoylpyridine in 500 ml of absolute ethanol over a 2-hr period. A deep red color developed within a few minutes. The solution was allowed to stir an additional 15 min after the addition was completed. The solvent was removed *in vacuo* to give a semisolid mass. The residue was partitioned between water (*ca.* 200 ml) and ether (*ca.* 500–750 ml). The ether layer was washed with water and dried over potassium carbonate. The ether was removed *in vacuo* to give a red glass which, upon trituration with ether, afforded in four crops, 161 g (70%) of white solid. Recrystallization from ether afforded the pure dimer **7**: mp 116.5–132°; λ_{max}^{MeOH} 245 (ε 23,400), 280 (22,200) and 311 mμ (sh) (13,700); $\lambda_{max}^{CHCl_3}$ 6.30, 6.40 μ.

Anal. Calcd for $C_{34}H_{26}N_2$: C, 88.28; H, 5.67; N, 6.06. Found: C, 88.13; H, 5.72; N, 5.91.

The nmr spectrum ($CDCl_3$) exhibited complex multiplets centered at δ 8.56 (two α-pyridyl protons), δ 7.7–6.7 (16 aromatic protons), δ 6.08 (four vinyl protons), δ 4.43 (one aliphatic proton), and δ 3.47 (three aliphatic protons).

Tlc (alumina, ethyl acetate–cyclohexane, 1:5) showed three spots.

An additional 17.5% was isolated as its maleimide adduct, *endo*-7-(α-2-pyridyl)benzylidene-5-norbornene-2,3-dicarboximide **5**,[1,6] by refluxing a benzene solution of the mother liquor residue with maleimide. Dimer **7** reacted with maleimide in refluxing benzene to give a quantitative yield of **5**.

5-(1-Hydroxy-1-methylethyl)-7-isopropylidene-5-norbornene-2,3-dicarboximide (11).—A 4.8-g (0.029 mole) sample of α,α,6,6-tetramethyl-2-fulvenemethanol (**10**)[8b] and 3 g (0.031 mole) of maleimide in 40 ml of benzene was heated at reflux for 4 hr. After cooling, the separated solid was filtered and recrystallized from ethyl acetate–cyclohexane to give 1.45 g (19% yield) of white fluffy solid (**11**): mp 181–182°; λ_{max}^{KBr} 3.15, 5.67, 5.85 μ.

Anal. Calcd for $C_{15}H_{19}NO_3$: N, 5.36. Found: N, 5.46.

The nmr spectrum (dimethylformamide-d_7) exhibited singlets at δ 1.31 and 1.50 (12 methyl protons), multiplets at δ 3.60 and 3.83 (four alicyclic protons), a broad peak at δ 4.74 (one hydroxyl proton), and a quartet centered at δ 6.10 (one vinyl proton).

Attempted Conversion of Fulvene 3 to 2-Fulvenylmethanol 4.—A colorless solution of 2.3 g (0.005 mole) of 3a,4,7,7a-tetrahydro-1,8-bis(α-2-pyridylbenzylidene)-4,7-methanoindene (**7**) in 40 ml of absolute ethanol was heated to reflux. After 15 min of reflux an aliquot was withdrawn from the orange solution: λ_{max}^{MeOH} 315 mμ (ε 9100).[24] After an additional 80 min of reflux, an aliquot showed λ_{max}^{MeOH} 315 mμ (ε 11,500). An additional 2 hr of reflux caused no change in the ultraviolet spectra.[25]

(21) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 422 (1953).

(22) Estimated from qualitative paper strip chromatography as described in ref 6 (*n*-butyl alcohol–*n*-butyl acetate–concentrated hydrochloric acid–water, 75:25:6:100) in which the *trans* isomer runs at R_f 0.4 and the *cis* isomer runs at R_f 0.6.

(23) W. B. Smith and B. A. Shoulders [*J. Am. Chem. Soc.*, **86**, 3118 (1964)] observed $J_{3,4}$ = 5.17, $J_{1,3}$ = 1.38, and $J_{1,4}$ = 1.9 cps for diphenylfulvene.

(24) Calculated on the basis of the fulvene **3**. Since the phenylpyridylfulvenylmethanols exhibit molecular extinction coefficients (ε) of 23,000–24,000, an ε value of 11,500 was assumed to correspond to 50% conversion of dimer **7** to fulvene **3**.

Tlc (alumina, ethyl acetate–cyclohexane, 1:4) showed the three spots corresponding to dimer **7** and a fulvene spot[26] running ahead. Addition of 14 ml of absolute ethanol containing 0.006 mole of sodium ethoxide followed by 1 hr of reflux caused no change as determined by ultraviolet spectral assay.[27] After cooling to 5°, 0.87 g (0.0055 mole) of 2-benzoylpyridine (**1**) was added and the solution allowed to stand overnight at 0°. No change was observed as determined by ultraviolet spectra and tlc. In a similar experiment, 0.45 g (0.01 mole) of sodium hydroxide was employed with the same result.

Syntheses of Ketones. 2-Benzoylpyridine N-Oxide (29).—An 18.3-g sample (0.1 mole) of 2-benzoylpyridine (**1**) in 60 ml of glacial acetic acid was treated with 14.7 ml of 30% hydrogen peroxide at 60–80° with stirring for 12 hr. The reaction was then allowed to stir at room temperature for 16 hr.

The solvent was removed under reduced pressure and the residual oil was dissolved in chloroform and washed with potassium carbonate solution. Drying of the organic solution and concentration afforded the desired product which was recrystallized from ethyl acetate–ether to give 12.2 g (61%) of the white crystalline ketone **29**: mp 99–101°; λ_{max}^{MeOH} 257 mμ (ε 20,300); λ_{max}^{KBr} 2.80, 3.26, 5.95, 6.26, 6.31 μ.

Anal. Calcd for $C_{12}H_9NO_2$: C, 72.35; H, 4.55; N, 7.03. Found: C, 72.18; H, 4.67; N, 7.31.

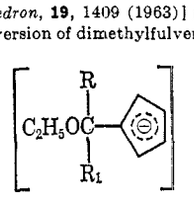
2-Pyridyl 2-Thienyl Ketone (31).—To a solution of 2-thiophene magnesium bromide, prepared from 100 g (0.61 mole) of 2-bromothiophene and 14.8 g (0.61 g-atom) of magnesium in 1000 ml of ether in the usual manner, was added dropwise and with stirring, 63.4 g (0.61 mole) of 2-cyanopyridine in 400 ml of ether. After the addition was complete, the reaction mixture was stirred for an additional hour, then hydrolyzed by treatment with aqueous ammonium chloride. The aqueous layer was then made weakly acidic with hydrochloric acid; the layers were separated and the aqueous layer was extracted with ether. The combined organic layers were dried and concentrated and the residual oil was distilled to give 77.7 g (67% yield) of ketone **31**: bp 148–153° (0.5 mm); λ_{max}^{MeOH} 240 (ε 5500), 278 (8800), 305 mμ (9300); $\lambda_{max}^{CHCl_3}$ 6.12 μ. Tlc (silica gel, cyclohexane–ethyl acetate, 1:1) showed the presence of minor amounts of two impurities.

Cyclohexyl 2-Pyridyl Ketone (35).—To a solution of cyclohexyl magnesium bromide prepared in the usual manner from 65 g (0.4 mole) of cyclohexyl bromide and 9.5 g (0.4 g-atom) of magnesium in ether was added 28 g (0.3 mole) of 2-cyanopyridine at 5°. The reaction mixture was stirred for 1 hr and then poured into a saturated ammonium chloride solution. The layers were separated, the aqueous layer was extracted with ether, and the combined organic layers were concentrated. The residue was hydrolyzed by stirring with 120 ml of 10% hydrochloric acid for 15 min. The solution was neutralized with sodium hydroxide and extracted with ether. Drying and concentration of the ether extracts left a residue which was distilled to give 22 g (23% yield) of cyclohexyl 2-pyridyl ketone (**35**) as a yellow liquid: bp 111–116° (0.8 mm). The ketone was characterized by conversion to its hydrochloride salt: mp 138–140°; $\lambda_{max}^{CHCl_3}$ 3.42, 3.50, 5.86 μ; λ_{max}^{MeOH} 230 (ε 7750), 267 mμ (4200).

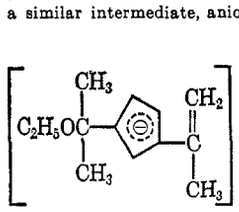
(25) A portion of the solution was allowed to cool to room temperature. After 2 hr an aliquot exhibited λ_{max}^{MeOH} 310 mμ (ε 10,000).

(26) All fulvenes and fulvenylmethanols studied exhibited a dark blue fluorescence on tlc under long-wavelength ultraviolet light.

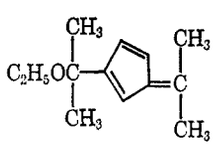
(27) These results indicate that addition of ethoxide or hydroxide to the 5,6 double bond of a fulvene to give an anion such as i does not apply to diaryl fulvenes. M. Shamma, J. P. Giannetti, R. B. Henry, and A. Melbardis [*Tetrahedron*, **19**, 1409 (1963)] proposed a similar intermediate, anion ii, in the conversion of dimethylfulvene to iii.



i



ii



iii

Anal. Calcd for $C_{12}H_{15}NO \cdot HCl$: C, 63.85; H, 7.15; N, 6.21. Found: C, 63.58; H, 6.91; N, 6.30.

1-Methyl-2-piperidyl Phenyl Ketone.—A mixture of 66 g (0.36 mole) of 2-benzoylpyridine (**1**) and 104 g (0.74 mole) of methyl iodide in 300 ml of methanol was allowed to stand at room temperature for 100 hr. It was then concentrated, diluted with water, and washed repeatedly with ether to remove unreacted ketone. The aqueous solution was then hydrogenated over 1 g of platinum oxide at an initial pressure of 53 psi at room temperature. After the hydrogen uptake had stopped (24 hr), the catalyst was removed by filtration and the filtrate was made basic with sodium hydroxide and extracted with ether. The organic layer was dried and the solvent was removed to leave 22.2 g of an oil. The oil, presumably containing the desired ketone and its corresponding alcohol, was oxidized by treatment with 9.1 g of chromium trioxide in 350 ml of acetic acid at 90° for 1 hr. The mixture was concentrated, diluted with water, made basic with sodium hydroxide, and extracted several times with ether. The combined organic extracts were dried and concentrated and the residual oil was distilled to give 12.5 g (14.5% from 2-benzoylpyridine) of a clear oil: bp 86–89° (0.1 mm). A hydrochloride salt was prepared and recrystallized from ethanol–ether to give a white solid: mp 171–172°; $\lambda_{max}^{CHCl_3}$ 3.40, 4.10, 5.93, 6.26 μ; λ_{max}^{MeOH} 246 (ε 12,500), 286 mμ (1220).

Anal. Calcd for $C_{13}H_{17}NO \cdot HCl$: N, 5.85. Found: N, 5.95.

Relative Reactivity of Ketones to Cyclopentadienyl Sodium. Reaction at 45°.—A solution of 0.004 mole of ketone, 0.004 mole of cyclopentadiene, and 0.004 g-atom of sodium in 20 ml of ethanol–monoglyme (50:50) was stirred at 40–45° and the ultraviolet spectra of aliquots, withdrawn at appropriate intervals, were measured. Aliquots were also worked up and the infrared spectra of the chloroform solutions of the products were measured as an estimation of the rate of disappearance of ketone which approximately paralleled the rate of formation of fulvene products.

Reaction at 5°.—Similar experiments were performed using 25 ml of ethanol as solvent.

Method A (General Conditions for Synthesis of Fulvenylmethanols).—To a solution of 0.01 mole of ketone in 5–10 ml of ethanol or ethanol–monoglyme at 5° containing 0.0005–0.005 mole of sodium ethoxide was added 0.005 mole of cyclopentadiene in 10 ml of ethanol over a period of 35 min. The mixture was allowed to stand for 90 min to 18 hr at 5°. The solid fulvenylmethanol was collected by filtration and recrystallized. Noncrystalline fulvenylmethanols (or fulvenes) were converted to their maleimide adducts.

Method B (General Conditions for Synthesis of Fulvenes).—An ethanol or ethanol–monoglyme solution (*ca.* 70 ml) of 0.01 mole of ketone was added dropwise over 2 hr to a solution of 0.05 mole of freshly distilled cyclopentadiene containing 0.05 mole of sodium ethoxide in 50 ml of ethanol at room temperature. The reaction mixture was stirred for 30 min and then concentrated under reduced pressure, diluted with water, and extracted with chloroform. Drying and removal of the solvent afforded the oily fulvene which was characterized as its crystalline maleimide adduct.

Method C (Conversion of Slower Reacting Ketones to Fulvenylmethanols).—A solution of 0.01 mole of cyclopentadiene, 0.01 mole of sodium ethoxide, and 0.02 mole of ketone in 60 ml of ethanol was allowed to stand for 24–60 hr at 5°. The solid fulvenylmethanol was filtered and recrystallized. Noncrystalline fulvenylmethanols were converted to their maleimide adducts.

Reaction of di-2-pyridyl ketone[28] (19) under condition B gave an impure oil containing 6,6-(di-2-pyridyl)-fulvene[29] (**37**) which was converted to its maleimide adduct (**72**) (Table IV) by allowing it to stand for 3 days with 1 equiv of maleimide in benzene solution. Reaction of ketone **19** under condition A gave orange crystals which were recrystallized from ethyl acetate to give **α,α,6,6-tetra(2-pyridyl)-2-fulvenemethanol (38)**: mp 147–148°; λ_{max}^{MeOH} 318 mμ (ε 24,800).

Anal. Calcd for $C_{27}H_{20}N_4O$: C, 77.86; H, 4.84; N, 13.45. Found: C, 77.89; H, 4.87; N, 13.44.

Reaction of di-4-pyridyl ketone[30] (20) under condition C gave orange crystals which were recrystallized from ethyl acetate to

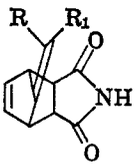
(28) Prepared in 85% yield following the procedure of H. R. Henze and M. B. Knowles [*J. Org. Chem.*, **19**, 1127 (1957)] except that 2-cyanopyridine was added in benzene solution.

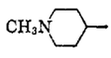
(29) Yield of this fulvene (Table I) is based on yield of maleimide adduct from starting ketone.

(30) J. P. Wibaut and L. G. Heeringa, *Rec. Trav. Chim.*, **74**, 1003 (1955).

TABLE IV

7-R,R$_1$-METHYLENE-5-NORBORNENE-2,3-DICARBOXIMIDES



Compd	R	R$_1$	Mp, °C	Solvent[a]	λ_{max}^{MeOH} mμ	ε	Calcd, % C	H	N	Found, % C	H	N
70			172–173	EA–C	225 263	9,850 7,100	76.81	4.91	8.53	76.51	4.79	8.75
71			212–213	EA–Me	225 242	14,000 14,000			8.53			8.73
72			216–217	D–Eth	241 271	14,700 11,200	72.93	4.59	12.76	72.63	4.53	12.70
73			191–192	EA	End absorption		75.83	6.94	8.04	75.79	6.68	7.99
74			214–215	PE–Cl	250 273	10,900 12,200	68.24	4.22	8.38	68.08	4.11	8.15
75	CH_3		159–160	EA–C	238 272 256	8,150[b] 5,200 3,900[d]					*c*	
76			200–201	EA	262 267 256	4,300 4,000 3,680[e]	75.42	6.63	8.38	75.33	6.58	8.11
77	$(CH_3)_3C$		248–249	Me	261 267	4,200 3,450	74.00	6.54	9.09	73.86	6.62	9.14[f]

[a] EA, ethyl acetate; C, cyclohexane; D, dioxane; Eth, Ether; PE, petroleum ether; Cl, chloroform; Me, Methanol. [b] In MeOH with HCl: 237 (4,850), 293 (6,700). [c] Both the analysis and the nmr spectrum of this substance show that it contains 1/3 to 1/2 molecule of cyclohexane of solvation per molecule of imide. [d] In MeOH with HCl: 261 (5,500). [e] In MeOH with HCl: 262 (6,200). [f] Calcd for $C_{19}H_{20}N_2O_2$: O, 10.38; mol wt, 308. Found: O, 10.43; mol wt, 328.

give **α,α,6,6-tetra(4-pyridyl)-2-fulvenemethanol (39)**: mp 236–238°; λ_{max}^{MeOH} 308 mμ (ε 25,000).

Anal. Calcd for $C_{27}H_{20}N_4O$: N, 13.45. Found: N, 13.29.[31]

Reaction of Di-3-pyridyl Ketone[32] (21).—To a solution of sodium ethoxide [prepared from 0.07 g of sodium (0.003 g-atom) in 175 ml of ethanol] containing 5.5 g (0.03 mole) of ketone (**21**) was added 2.2 g (0.033 mole) of cyclopentadiene and the resulting solution was stirred at 5° for 15 hr. The solid was filtered to give 3.6 g (58% yield) of orange crystalline solid which was recrystallized from ethyl acetate–methanol to give crystalline **α,α,6,6-tetra-(3-pyridyl)-2-fulvenemethanol (40)**: mp 219–220°; λ_{max}^{MeOH} 322 mμ (ε 25,000).

Anal. Calcd for $C_{27}H_{20}N_4O$: N, 13.45. Found: N, 13.47.[31]

Reaction of 2-pyridyl 4-pyridyl ketone[30] (22) under condition A gave orange crystals which were recrystallized from ethyl acetate to give **α-(2-pyridyl)-α-[6-(2-pyridyl)-6-(4-pyridyl)-2-fulvenyl]-4-pyridinemethanol (41)**: mp 133–145°; λ_{max}^{MeOH} 313 mμ (ε 23,800).

Anal. Calcd for $C_{27}H_{20}N_4O$:[33] C, 77.86; H, 4.84; N, 13.45. Found: C, 77.38; H, 4.94; N, 13.36.

Reaction of di(6-methyl-2-pyridyl) ketone[34] (23) under condition A gave orange crystals which were recrystallized from ethyl acetate to give **α,α,6,6-tetra-(6-methyl-2-pyridyl)-2-fulvenemethanol (42)**: mp 113.5–116°; λ_{max}^{MeOH} 325 mμ (ε 22,500).

Anal. Calcd for $C_{31}H_{28}N_4O$:[33] C, 78.79; H, 5.97; N, 11.86. Found: C, 78.27; H, 6.19; N, 11.74.

Reaction of phenyl 4-pyridyl ketone (24) under condition B gave an impure oil containing 6-phenyl-6-(4-pyridyl)fulvene[29] (**43**) which was converted to its maleimide adduct (**71**) (Table IV) in refluxing benzene.

Reaction of ketone **24** under condition C gave orange crystals which were recrystallized from ethyl acetate to give **α-phenyl-α-[6-phenyl-6-(4-pyridyl)-2-fulvenyl]-4-pyridinemethanol (44)**: mp 210–211°; λ_{max}^{MeOH} 325 mμ (ε 23,300).

Anal. Calcd for $C_{29}H_{22}N_2O$: C, 84.03; H, 5.35; N, 6.76. Found: C, 83.40; H, 5.55; N, 6.62.

Reaction of *p*-chlorophenyl 2-pyridyl ketone (25) under condition C gave a quantitative yield of an amorphous solid,[35] mp 90–108°, λ_{max}^{MeOH} 327 mμ (ε 17,300), containing **α-(*p*-chlorophenyl)-α-[6-(*p*-chlorophenyl)-6-(2-pyridyl)-2-fulvenyl]-2-pyridinemethanol (45)**, which was characterized as its maleimide adduct.[4]

Reaction of phenyl 2-quinolyl ketone[36] (26) under condition C gave orange crystals which were recrystallized from benzene–cyclohexane to give **α-phenyl-α-[6-phenyl-6-(2-quinolyl)-2-fulvenyl]-2-quinolinemethanol (46)**: mp 207°; λ_{max}^{MeOH} 338 mμ (ε 22,300).

Anal. Calcd for $C_{37}H_{26}N_2O$: C, 86.36; H, 5.09; N, 5.44. Found: C, 86.61; H, 5.26; N, 5.38.

Reaction of *m,m'*-dinitrobenzophenone[37] (27) under condition A using ethanol–monoglyme gave an oil which on purification gave both 6,6-di(*m*-nitrophenyl)fulvene[14] and an oil comprised mainly of **α,α,6,6-tetra(*m*-nitrophenyl)-2-fulvenemethanol (47)**: $\lambda_{max}^{CHCl_3}$ 2.80, 6.23, 6.56, 7.46 μ; λ_{max}^{MeOH} 251 (ε 28,800), 319 mμ (20,250). The nmr spectrum ($CDCl_3$) of fulvenylmethanol **47** exhibited multiplets at δ 8.13, 7.68 (aromatic) and δ 6.60, 6.35 (vinyl) in the ratio of 16:3.

Reaction of phenyl 3-pyridyl ketone (28) under condition B gave an impure oil containing 6-phenyl-6-(3-pyridyl)fulvene[29] (**48**) which was converted to its maleimide adduct (**70**) (Table IV) in refluxing benzene.

Reaction of ketone **28** under condition C gave, in addition to oily fulvene (**48**), orange crystals which were recrystallized from ether to give **α-phenyl-α-[6-phenyl-6-(3-pyridyl)-2-fulvenyl]-3-pyridinemethanol (49)**: mp 170–175°; λ_{max}^{MeOH} 327 mμ (ε 24,200).

Anal. Calcd for $C_{29}H_{22}N_2O$: N, 6.76. Found: N, 6.87.[31]

Reaction of 2-benzoylpyridine N-oxide (29) under condition C

(31) Erratic C and H values were obtained from independent laboratories. The structure was confirmed by the nmr spectra of the product and its maleimide adduct.[4]

(32) J. P. Wibaut, A. P. DeJonge, H. G. P. Van der Voort, and P. P. H. L. Otto, *Rec. Trav. Chim.*, **70**, 1054 (1951).

(33) Compound contains 2.5% of ethyl acetate as was determined by elemental analyses and its nmr spectrum.

(34) W. Mathes and W. Sauermilch, *Chem. Ber.*, **86**, 109 (1953).

(35) Estimated to be 73% pure assuming an ε value of 24,000 for pure fulvenes (see ref 24).

(36) V. Boekelheide and J. Weinstock, *J. Am. Chem. Soc.*, **74**, 660 (1952).

(37) E. Barnett and M. A. Matthews, *J. Chem. Soc.*, 767 (1924).

gave orange crystals which were recrystallized from ethanol–water to give **α-phenyl-α-[6-phenyl-6-(2-pyridyl)-2-fulvenyl]-2-pyridinemethanol di-N-oxide (50)**: mp 223–224°; λ_{max}^{MeOH} 322 mμ (ε 19,400).

Anal. Calcd for $C_{29}H_{22}N_2O_3$: C, 78.01; H, 4.97; N, 6.27. Found: C, 77.71; H, 4.92; N, 6.19.

Reaction of *p*-nitrobenzophenone (30) in ethanol–monoglyme under condition A gave an oil from which was separated **p-nitro-6,6-diphenyl fulvene (51)**. Recrystallization from hexane–cyclohexane gave orange crystals: mp 128–129°; λ_{max}^{MeOH} 280 (ε 19,600), 334 mμ (19,900).

Anal. Calcd for $C_{18}H_{13}NO_2$: N, 5.09. Found: N, 5.09.

The mother liquors from which fulvene **51** was isolated was evaporated to give an oil which was mainly *p*-nitro-[6,6-(*p*-nitrodiphenyl)-2-fulvenyl]diphenylmethanol (**52**): $\lambda_{max}^{CHCl_3}$ 2.79, 6.28, 6.61, 7.40 μ; λ_{max}^{MeOH} 277 (ε 23,500), 340 mμ (20,500). The nmr spectrum ($CDCl_3$) exhibited multiplets centered at δ 8.22, 7.45 (aromatic) and δ 6.2 (vinyl) in the ratio of 18:3.

Reaction of 2-Thienyl 2-Pyridyl Ketone (31).—To a sodium ethoxide solution prepared from 0.57 g (0.025 g-atom) of sodium in 100 ml of ethanol was added 9.45 g (0.05 mole) of ketone (**31**). The resultant solution was cooled to 5° and 1.65 g (0.025 mole) of cyclopentadiene was added. The entire mixture was stirred at 5° for 5 hr[38] and then poured into ice–water and extracted with benzene–ether. After washing with brine and drying, the organic layers were concentrated and the residual 6-(2-pyridyl)-6-(2-thienyl)fulvene (**53**), which was unstable at room temperature, was immediately converted to its maleimide adduct **74** (Table IV) by reaction with 1 equiv of maleimide in benzene at room temperature for 16 hr.

Reaction of benzophenone (32) under conditions A or B at 25° gave 75–80% yields of 6,6-diphenylfulvene (**54**).

Fulvenylmethanol **55** was prepared as follows. To a solution of 2.1 g (0.03 mole) of dry sodium ethoxide in 400 ml of pyridine was added 54 g (0.3 mole) of benzophenone. To this cooled (ice bath) solution was added 20 g (0.3 mole) of cyclopentadiene with stirring and the resulting red-brown solution was stirred at 25° for 24 hr. It was then concentrated, diluted with ether, and washed with dilute hydrochloric acid and water, dried, and concentrated. The residual red-brown oil in benzene was chromatographed on Woelm neutral alumina (activity grade I). After elution of 6,6-diphenylfulvene (~60% yield) and benzophenone with ether–petroleum ether (bp 30–60°) (1:1), the desired product was eluted with ether–chloroform (1:1) and amounted to 3.3 g (5.5% yield) of a red oil which crystallized. Recrystallization from cyclohexane gave **α,α,6,6-tetraphenyl-2-fulvenemethanol (55)** as orange crystals: mp 129–130.5°; $\lambda_{max}^{CHCl_3}$ 2.80, 6.27, 6.70, 6.92 μ; λ_{max}^{MeOH} 328 mμ (ε 25,000).

Anal. Calcd for $C_{31}H_{24}O$: C, 90.26; H, 5.86. Found: C, 89.96; H, 5.99.

The nmr spectrum (CCl_4) showed multiplets at δ 6.0, 6.2, 6.4 (three vinyl protons) and a resonance peak centered at δ 7.30 (20 phenyl protons).

Reaction of benzophenone and cyclopentadiene at 25° in the presence of Triton B[39] gave trace amounts of fulvenylmethanol **55** as determined by tlc. Other conditions to synthesize fulvenylmethanol **55** from benzophenone using preformed cyclopentadienyl sodium in monoglyme–pyridine (8:5) at 5°, or cyclopentadiene–potassium *t*-butoxide–dimethyl sulfoxide at 5°, were unsuccessful.

Reaction of 2-acetylpyridine (33) under condition C, except that the molar ratio of reactants was 1:1:1, gave an impure oil containing 6-methyl-6-(2-pyridyl)-fulvene (**56**):[29] λ_{max}^{MeOH} 292 mμ (ε 14,000). Fulvene **56** was converted to its maleimide adduct (**75**) (Table IV) in refluxing benzene.

Fulvenylmethanol **57** was prepared as follows. To a 25-ml solution of 18% cyclopentadienyl sodium (0.05 mole) in tetrahydrofuran was added 2-acetylpyridine (**33**) (6.0 g, 0.05 mole) dissolved in 50 ml of dry monoglyme. The resultant solution was allowed to stand at 5° for 21 hr. A 15 ml-portion was withdrawn and worked up by dilution with water and extraction with ether. Drying of the ethereal layer and removal of the solvent left an oil which was chromatographed on 40 g of Woelm neutral alumina (activity grade I). The fraction eluted with ether gave 70 mg of α-methyl-α-[6-methyl-6-(2-pyridyl)-2-fulvenyl]-2-pyridinemethanol (**57**) as a red oil: λ_{max}^{MeOH} 270 (ε 12,000), 293 mμ (13,000). This oil was treated with 28 mg of maleimide in 5 ml of benzene under reflux for 6 hr. Removal of the solvent and recrystallization of the residue from benzene–ether gave 53 mg of 5-[1-hydroxy-1-(2-pyridyl)ethyl]-7-[1-(2-pyridyl)ethylidene-norbornene-2,3-dicarboximide as an amorphous tan solid: mp 197–205°; λ_{max}^{KBr} 5.66, 5.82, 6.30 μ; λ_{max}^{MeOH} 262 mμ (ε 7,900).

The nmr spectrum ($CDCl_3$) of this imide exhibited resonance peaks at δ 6.73 (vinyl) and δ 8.9 (α-pyridyl) in the ratio of 1:2.

Reaction of *t*-Butyl 2-Pyridyl Ketone[40] (34).—A solution of 0.15 mole of cyclopentadienyl sodium and 17.1 g (0.1 mole) of ketone **34** in 120 ml of ethanol was allowed to stand at 25° for 65 hr. A 7.0-g sample of the oily product containing 6-(*t*-butyl)-6-(2-pyridyl)fulvene[29] (**58**) was chromatographed on 210 g of neutral alumina. The fractions eluted with 50% ether–petroleum ether were combined and concentrated. The residual light yellow oil was triturated with petroleum ether, the separated solid was filtered and recrystallized from petroleum ether to give 150 mg of white, crystalline **3a,4,7,7a-tetrahydro-1,8-bis[2,2-dimethyl-1-(2-pyridyl)propylidene]4,7-methanoindene (fulvene 58 dimer)**: mp 138–139°; λ_{max}^{MeOH} 256 (ε 18,200), 261 mμ (19,600).

Anal. Calcd for $C_{30}H_{34}N_2$: C, 85.26; H, 8.11; N, 6.63. Found: C, 85.21; H, 8.21; N, 6.58.

The nmr spectrum ($CDCl_3$) exhibited singlets at δ 0.8 and 1.2 (*t*-butyl groups), multiplets at δ 2.4, 2.8, and 3.1 (alicyclic), δ 5.83 and 6.10 (vinyl), δ 7.4 (vinyl and pyridyl), and δ 8.8 and 9.0 (α-pyridyl) corresponding to 18:4:3:7:2 protons, respectively.

The crude oil (before chromatography) containing fulvene **58** was treated with maleimide in benzene solution. After 18 hr at 25°, the solution was heated to reflux for 2 hr to give maleimide adduct (**77**) (Table IV).

Reaction of Cyclohexyl 2-Pyridyl Ketone (35).—A solution of 0.075 mole of cyclopentadienyl sodium and 9.45 g (0.05 mole) of ketone **35** in 70 ml of ethanol was allowed to stand at 25° for 100 hr. The oily product, which contained 6-cyclohexyl-6-(2-pyridyl)fulvene[29] (**59**) [λ_{max}^{MeOH} 268 mμ (ε 11,000)] was treated with maleimide in benzene solution. After 18 hr at 25°, the solution was heated to reflux for 2 hr to give maleimide adduct (**76**) (Table IV).

Reaction of 1-Methyl-4-piperidyl Phenyl Ketone (36).—A solution of 0.75 g (0.03 mole) of sodium, 2.9 g (0.04 mole) of cyclopentadiene, and 6.0 g (0.03 mole) of ketone **36** in 50 ml of ethanol was allowed to stand at 2° for 70 hr. The oily product, which contained 6-(1-methyl-4-piperidyl)-6-phenylfulvene[29] (**60**) [λ_{max}^{MeOH} 265 mμ (ε 12,000)], was converted to its maleimide adduct (**73**) (Table IV) in refluxing benzene.

The nmr spectrum ($CDCl_3$) of imide **73** exhibited peaks at δ 7.0 and 7.3 for five protons (phenyl) and at δ 6.25 for two protons (vinyl).

Reaction of *p,p'*-Dimethoxybenzophenone.[14]—Equimolar quantities of *p,p'*-dimethoxybenzophenone (1 g) and cyclopentadienyl sodium in 20 ml of ethanol-monoglyme (1:1) were stirred at 45° for 6 hr. Ultraviolet spectral assay of an aliquot indicated only 10% reaction while tlc (alumina, cyclohexane–ethyl acetate, 4:1) showed the presence of 6,6-(di-*p*-methoxyphenyl)fulvene as the only fulvene product.

Reaction of *p,p'*-Dibromobenzophenone.[14]—A solution of 3.4 g (0.01 mole) of ketone and 0.01 mole of cyclopentadienyl sodium in 40 ml of ethanol–monoglyme (1:1) was allowed to stand at 5° for 2 hr; reaction proceeded only slightly. After 3 hr at 25° all the ketone had reacted (infrared spectral assay) and tlc (as above) showed the presence of 6,6-(di-*p*-bromophenyl)fulvene as the only fulvene product.

1,3-Dis(α-hydroxybenzyl)-6-phenylfulvene (61).—To a solution of 6.9 g (0.3 g-atom) of sodium dissolved in 150 ml of absolute ethanol was added 21 g (0.32 mole) of freshly distilled cyclopentadiene. This solution, under nitrogen, was added dropwise over 30 min to a solution of 63.6 g (0.60 mole) of benzaldehyde in 450 ml of absolute ethanol at 0–3° with stirring. After stirring 3 hr at 3°, the mixture was filtered to give 11.9 g (17.1%) of orange crystals. Two recrystallizations from benzene gave 3.2 g of crystals: mp 180–182°; λ_{max}^{KBr} 2.98, 6.18 μ; λ_{max}^{MeOH} 316 mμ (ε 25,200).

Anal. Calcd for $C_{28}H_{22}O_2$: C, 85.21; H, 6.05. Found: C, 85.18; H, 5.79.

The nmr spectrum (dimethylformamide-d_7) exhibited singlets at δ 5.60, 5.88, 6.30, and 6.55 (four vinyl and methine protons)

(38) On tlc (alumina, ethyl acetate–cyclohexane, 1:5), in addition to the major spot of fulvene **53** (ref 26), a second spot estimated to account for a 15% yield of α-(2-thienyl)-α-[6-(2-pyridyl)-6-(2-thienyl)-2-fulvenyl]-2-pyridinemethanol was observed.

(39) E. Ghera and Y. Sprinzak, *J. Am. Chem. Soc.*, **82**, 4945 (1960).

(40) H. R. Henze and M. B. Knowles, *J. Org. Chem.* **19**, 1127 (1957).

and a series of multiplets from δ 7.0 to 7.62 (15 phenyl and 1 vinyl protons).

7-Benzylidene-1,5-bis(α-hydroxybenzyl)-5-norbornene-2,3-dicarboximide.—A solution of 2 g (0.00547 mole) of a 1,3-bis(α-hydroxybenzyl)-6-phenylfulvene (**61**) and 0.5 g (0.00515 mole) of maleimide in 100 ml of benzene was heated under reflux. A white solid began precipitating after 3.5 hr of heating. After heating for a total of 15 hr, the mixture was cooled to 5° and filtered to give 0.6 g of white solid. Recrystallization from methanol–water (1:3) gave 0.15 g of white crystals (fraction a): mp 207–208.5°; λ_{max}^{KBr} 2.9, 5.65, 5.87 μ; λ_{max}^{MeOH} 245 mμ (ε 14,500).

The filtrate of the 0.6 g of insoluble solid was evaporated to a gum which was dissolved in *ca.* 100 ml of ether. Filtration and dilution with hexane gave 0.57 g of white crystals. Two recrystallizations from methanol–water gave 0.34 g of white crystals (fraction b): mp 195–196°; λ_{max}^{KBr} 2.9, 5.68, 5.88 μ; λ_{max}^{MeOH} 248 mμ (ε 15,150).

Anal. Calcd for $C_{30}H_{25}NO_4$: C, 77.73; H, 5.44; N, 3.02. Found: C, 77.51; H, 5.44; N, 3.22.

On tlc (silica gel, ethyl acetate–cyclohexane, 4:1) fraction a exhibited R_f 0.71, while fraction b had R_f 0.8.

The nmr spectrum of fraction a in dimethylformamide-d_7 was consistent with the 1,5-bis(α-hydroxybenzyl)-5-norbornene-2,3-dicarboximide structure [from 1,3-bis(α-hydroxybenzyl)-6-phenylfulvene (**61**)] and exhibited an ABC pattern ranging from δ 3.2 to 4.08 (three aliphatic protons), a doublet at δ 5.15, a singlet at δ 5.75, and a singlet at δ 6.37 with integrated intensities of 1, 1, and 2, respectively (two unassigned methine and two unassigned vinyl protons). The aromatic region (δ 6.42–7.86) exhibited 15 protons.

The nmr spectrum of fraction b in dimethylformamide-d_7 indicated a complex mixture of isomers.

α,α,α′,α′,6,6-Hexa-(2-pyridyl)fulvene-2,3-dimethanol (62).—From the mother liquors of a number of large-scale syntheses of α,α-6,6-tetra-(2-pyridyl)-2-fulvenemethanol (**38**) there was collected a relatively insoluble orange solid which was recrystallized twice from ethyl acetate–chloroform (3:1) to give orange crystals of **62**: mp 234° dec; λ_{max}^{KBr} 2.98, 6.31 μ; λ_{max}^{MeOH} 262 (ε 21,000), 327 mμ (25,800).

Anal. Calcd for $C_{38}H_{28}N_6O_2$: N, 13.99. Found: N, 13.93.

The nmr spectrum ($CDCl_3$) exhibited a singlet at δ 5.95 (two fulvenyl protons), a multiplet from δ 6.7 to 7.9 (18 β, γ-pyridyl protons), and multiplets at δ 8.13 and 8.70 (six α-pyridyl protons).

5,6-Bis(α-hydroxy-α,α-di-2-pyridylmethyl-7-(di-2-pyridylmethylene)-5-norbornene-2,3-dicarboximide.—A mixture of 20 g (0.033 mole) of α,α,α′,α′,6,6-hexa-(2-pyridyl)fulvene-2,3-dimethanol (**62**) and 4.8 g (0.048 mole) of maleimide in 150 ml of xylene was stirred under reflux for 2.5 hr. The solid was collected by filtration and dissolved in hot chloroform. After removal of a small amount of insoluble material, the solution was diluted with petroleum ether to give 18 g of white, amorphous solid: mp 260–262° dec. The solid was redissolved in chloroform and the solution was diluted with petroleum ether. The first two fractions to precipitate exhibited identical infrared spectra and melting point and were combined to give 10 g of imide: mp 265° dec; $\lambda_{max}^{CHCl_3}$ 2.95, 5.66, 5.83 μ; λ_{max}^{MeOH} 262 mμ (ε 25,400).

Anal. Calcd for $C_{42}H_{31}N_7O_4$: N, 14.05. Found: N, 13.98.

The nmr spectrum ($CDCl_3$) exhibited singlets at δ 2.98 (two 2,3-*endo* protons) and δ 3.75 (two bridgehead protons), a multiplet from δ 6.8 to 7.9 (18 β, γ-pyridyl protons), and a multiplet at δ 8.31 (six α-pyridyl protons).

Reaction of Methylcyclopentadiene with 2-Benzoylpyridine.—To a sodium ethoxide solution, prepared from 1.2 g (0.05 g-atom) of sodium and 75 ml of ethanol, was added 2-benzoylpyridine (**1**) (18.3 g, 0.1 mole) dissolved in 80 ml of ethanol, followed by 8.0 g (0.1 mole) of methylcyclopentadiene dissolved in 15 ml of ethanol. The resulting solution was stirred at room temperature for 24 hr. It was concentrated to one-fifth its volume, diluted with ether, and washed with water. Drying and removal of the solvent left a red-brown oil containing 2-methyl-6-phenyl-6-(2-pyridyl)-fulvene (**63**). A 13-g portion of this oil and 4 g of maleimide in 75 ml of benzene was heated under reflux for 3 hr, then allowed to stand at room temperature for 60 hr. The precipitated tan solid was filtered and recrystallized twice from ethyl acetate to give 1.8 g of pure **5-methyl-7-(α-2-pyridylbenzylidene)-5-norbornene-2,3-dicarboximide** as white crystals: mp 210.5–211°; $\lambda_{max}^{CHCl_3}$ 2.96, 3.34, 5.65, 5.84, 6.30 μ; λ_{max}^{MeOH} 243 mμ (ε 15,500).

Anal. Calcd for $C_{22}H_{18}N_2O_2$: C, 77.17; H, 5.30; N, 8.18. Found: C, 76.98; H, 5.45; N, 8.19.

The nmr spectrum ($CDCl_3$) of the imide exhibited the following peaks: doublet at δ 1.88 (methyl), multiplets at δ 3.7 and 4.2 (ring protons), δ 5.98 (vinyl), δ 7.3 (phenyl and pyridyl), δ 8.9 (α-pyridyl) corresponding to 3:4:1:8:1 protons, respectively.

α-[3-Methyl-6-phenyl-6-(2-pyridyl)-2-fulvenyl]-α-phenyl-2-pyridinemethanol (64) (Isomers A and B).—To a sodium ethoxide solution, prepared from 2.4 g (0.1 g-atom) of sodium and 300 ml of ethanol was added 36.6 g of 2-benzoylpyridine (**1**) (0.2 mole) and 16 g (0.2 mole) of methylcyclopentadiene. The reaction mixture was allowed to stand at 4° for 3 days. The precipitated orange solid was filtered and amounted to 12.6 g (31% yield): mp 139–145°. Fractional crystallization from ethanol gave 3.2 g of **α-[3-methyl-6-phenyl-6-(2-pyridyl)-2-fulvenyl]-α-phenyl-2-pyridinemethanol (64, isomer A)** as orange crystals: mp 167–168°; $\lambda_{max}^{CHCl_3}$ 3.0, 3.37, 6.31, 6.7, 6.81 μ; λ_{max}^{MeOH} 245 (ε 14,400), 325 mμ (24,900).

Anal. Calcd for $C_{30}H_{24}N_2O$: C, 84.08; H, 5.65; N, 6.54. Found: C, 84.20; H, 5.70; N, 6.41.

From the mother liquors of the 12.6 g of orange solid was isolated 4.6 g of **α-[3-methyl-6-phenyl-6-(2-pyridyl)-2-fulvenyl]-α-phenyl-2-pyridinemethanol(64, isomer B)** as orange crystals: mp 147–148°; $\lambda_{max}^{CHCl_3}$ 3.0, 3.37, 6.30, 6.70, 6.81 μ; $\lambda_{max}^{CH_3OH}$ 245 (ε 14,700), 325 mμ (24,900).

Anal. Calcd for $C_{30}H_{24}N_2O$: C, 84.08; H, 5.65; N, 6.54. Found: C, 84.11; H, 5.71; N, 6.48.

Nmr analyses of the maleimide adducts of isomers A and B indicated that the fulvenylmethanols are geometric isomers.

2-Diphenylmethyl-6-phenyl-6-(2-pyridyl)fulvene (65) and 1-Diphenylmethylene-4-(α-2-pyridylbenzylidene)-2-cyclopentene (66).—To a solution of sodium ethoxide, prepared from 0.1 g (0.004 g-atom) of sodium and 100 ml of ethanol, was added 10 g (0.04 mole) of benzhydrylcyclopentadiene[16] and 7.16 g (0.04 mole) of 2-benzoylpyridine and the resulting mixture was heated under reflux for 30 min. It was then poured into ice–water containing dilute hydrochloric acid and extracted with ether. The ether layer was washed with water and dried. Concentration left a red oil (15 g). An 8.3-g sample of this oil was extracted with three 250-ml portions of boiling petroleum ether. On cooling the extracts, 1.49 g (17% yield from the ketone) of **2-diphenylmethyl-6-phenyl-6-(2-pyridyl)fulvene (65)** crystallized as orange needles: mp 134–136°; λ_{max}^{KBr} 6.25, 6.33, 6.40 μ; λ_{max}^{MeOH} 323 mμ (ε 19,200).

Anal. Calcd for $C_{30}H_{23}N$: C, 90.64; H, 5.83; N, 3.52. Found: C, 90.49; H, 5.85; N, 3.77.

The nmr spectrum ($CDCl_3$) exhibited resonance peaks at δ 5.25 (one benzhydryl proton), δ 6.02 and 6.48 (three vinyl protons), δ 7.1–7.8 (18 aromatic protons), and δ 8.67 (one α-pyridyl proton).

The petroleum ether-insoluble residue of the 8.3-g extraction was dissolved in hot benzene, filtered, and the filtrate was diluted with hexane. Cooling gave crystals which were recrystallized from ether then ether–petroleum ether to give yellow crystalline **1-diphenylmethylene-4-(α-2-pyridylbenzylidene)-2-cyclopentene (66)**: mp 149–164°; λ_{max}^{KBr} 6.35 μ; λ_{max}^{MeOH} 257 (ε 16,150), 364 mμ (31,000).

Anal. Calcd for $C_{30}H_{23}N$: C, 90.64; H, 5.83; N, 3.52. Found: C, 90.64; H, 6.04; N, 3.56.

The nmr spectrum ($CDCl_3$) exhibited singlets at δ 3.55 and 3.97 (methylene protons of *cis* and *trans* isomers), a series of overlapping multiplets starting at δ 6.56 and continuing into the aromatic region δ 7.12–7.42, and a multiplet at δ 8.60 (α-pyridyl). Within the multiplet from δ 6.56 to 7.12 two AB patterns were observable, $J_{2,3\ trans\ (or\ cis)}$ = 5.8 cps and $J_{2,3\ cis\ (or\ trans)}$ = 5.5 cps. The ratio of protons in the aromatic and vinyl region to those in the methylene region was 21:2. The ratio of integrated intensities of the methylene singlets at δ 3.55 and 3.97 was 4:6, indicating a 4:6 ratio of *cis–trans* isomers.

An ethanolic solution of **66** and sodium ethoxide was refluxed overnight; no fulvene **65** was detected. A benzene solution of **66** and maleimide was refluxed overnight in benzene with no evidence of reaction (ultraviolet spectral assay).

α,α,α′,α′-Tetra-2-pyridyl-1,3-cyclopentadiene-1,4-(and 1,3-)dimethanol (67a and b).—A stirred solution of 18.4 g (0.1 mole) of di-2-pyridyl ketone in 150 ml of absolute ethanol containing 0.002 mole of sodium ethoxide (equivalent to 0.05 g of sodium) was cooled to about −5° and treated with 3.6 g (0.055 mole) of

cyclopentadiene which was added over a few minutes. The temperature was maintained at 0 to −7°.

Precipitation of the product usually occurred within 1 hr. The mixture was stirred for an additional hour, after which the product was filtered off giving 20 g (95%) of dimethanol **67**: mp 120–123°. Nmr analysis indicated an isomeric mixture of **67a** and **b** with the symmetrical isomer **67a** predominating by a ratio of 3:1. Repeated recrystallization from methylene chloride eventually raised the melting point to 133–135°. By nmr analysis, this material was almost pure α,α,α′,α′-tetra-2-pyridyl-1,3-cyclopentadiene-1,4-dimethanol, *i.e.*, the symmetrical isomer **67a**.

The nmr spectrum of **67a** ($CDCl_3$) exhibited a triplet centered at δ 6.00 (vinyl protons), a triplet centered at δ 3.18 (methylene protons), and a series of multiplets ranging from δ 6.9 to 8.55 aromatic protons) with integrated intensities of 2:2:16, respectively.

Characterization was done on a mixture of the two isomers (**67a** and **b**): $\lambda_{max}^{CHCl_3}$ 3.0, 6.32, 6.40 μ; λ_{max}^{MeOH} 262 (ε 20,800), 267 (sh) mμ (18,300).

Anal. Calcd for $C_{27}H_{22}N_4O_2$: C, 74.63; H, 5.10; N, 12.90. Found: C, 74.57; H, 5.21; N, 12.77.

The nmr spectrum ($CDCl_3$) of the mixture of **67a** and **b** showed two quartets at δ 5.90 and 6.22 (vinyl protons of unsymmetrical isomer **67b**), a triplet centered at δ 6.00 (vinyl protons of symmetrical isomer **67a**), a triplet centered at δ 3.18 (methylene protons of **67a**), and a triplet at δ 3.13 (methylene protons of **67b**).

1,4-Bis(α-hydroxy-α,α-di-2-pyridylmethyl)-5-norbornene-2,3-dicarboximide (68a, b).—A solution of 5 g (0.012 mole) of the isomeric mixture of diols **67a** and **b** and 1.1 g (0.012 mole) of maleimide in 25 ml of benzene was heated under reflux for 4 hr. The filtered product weighed 3.1 g (51%): mp 240° dec. One recrystallization from dimethylformamide–water solution gave white crystalline isomer **68a**: mp 240° dec; λ_{max}^{KBr} 3.04, 5.65, 5.86, 6.32, 6.40 μ; λ_{max}^{MeOH} 255 (sh) (ε 12,900), 260 (14,200), 266 (sh), mμ (10,900).

Anal. Calcd for $C_{31}H_{25}N_5O_4$: C, 70.04; H, 4.74; N, 13.18. Found: C, 69.81; H, 4.94; N, 12.95.

The benzene mother liquors of the first crop slowly deposited additional crystalline material which was extracted with boiling benzene. Filtration removed the less soluble **68a** and cooling of the filtrate gave white crystals. One recrystallization from benzene gave crystalline isomer **68b**: mp 155–160°.

Anal. Found: N, 12.88.

Tlc (silica gel, cyclohexane–ethylacetate–methanol, 6:4:1) showed isomer **68b** running faster than **68a**.

The nmr spectrum ($CDCl_3$) of isomer **68a** showed resonance peaks at δ 6.63 (sharp singlet, 5,6-vinyl protons), δ 3.72 (sharp singlet, 2,3-protons), and δ 2.05 (AB quartet, 7-protons). The proton integration ratio was 2:2:2.

The nmr spectrum ($CDCl_3$) of isomer **68b** showed resonance peaks at δ 6.57 (sharp singlet, 6-vinyl proton), δ 3.75 (multiplet, 4-proton), δ 3.25 (multiplet, 2,3-protons), and δ 1.83 (unresolved AB pattern, 7-protons). The proton integration ratio was 1:1:2:2.

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Vibrational Spectra and Structure of Substituted Unsaturated Carbonyl Compounds. IV. Infrared and Raman Spectra of Methyl β-Chlorovinyl Ketone and Its Deuterated Derivatives

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Infrared and Raman spectra revealed that the title compounds exist in two conformational forms: *s-cis* and *s-trans*. A number of bands due to those forms have been assigned.

Infrared spectra of various β-substituted α,β-unsaturated ketones are characterized by considerable displacement of the $\nu_{C=O}$ and $\nu_{C=C}$ absorption bands to lower frequencies[1-6] resulting from equalization of the single and double bonds in the mesomeric system O=C—C=C—X. Consequently, the remaining stretching skeletal vibrations of this system are expected to shift to higher frequencies.[2] These vibrations, however, appear in the fingerprint region and there are serious difficulties with their assignment. Further complications may arise in connection with rotational isomerism and Fermi resonance which may increase the number of absorption bands to be assigned. This is presumably the cause why most interpretations are restructed to the 1500–1700-cm^{-1} spectral region. For this reason, it is important to obtain more spectral information on substituted unsaturated carbonyl compounds which play an important role both in spectroscopy[6] and in organic chemistry.

In the present investigation methyl β-chlorovinyl ketone (I) was studied. This compound has the advantage of showing a relatively simple infrared spectrum thus enabling to assign most of the essential frequencies with a high degree of certainty. The interpretation is based on comparisons with infrared spectra of three differently deuterated methyl β-chlorovinyl ketones (II–IV) and with Raman spectra of two of them (I and III). (See Figures 1–6.) The assignment thus derived may be of value in many other cases since compounds I–IV are related to various unsaturated ketones.

$^4CH_3{}^3CO{}^2CH=\,^1CH—Cl$ (I) $CD_3COCH=CH—Cl$ (II)

$CH_3COCD=CD—Cl$ (III) $CD_3COCD=CD—Cl$ (IV)

Recently Benson and Pohland[7] reported the $\nu_{C=O}$, $\nu_{C=C}$, vinyl γ_{C-H}, and ν_{C-Cl} frequencies of methyl β-chlorovinyl ketone and a series of its homologs; however, the resolution of the apparatus used was ap-

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