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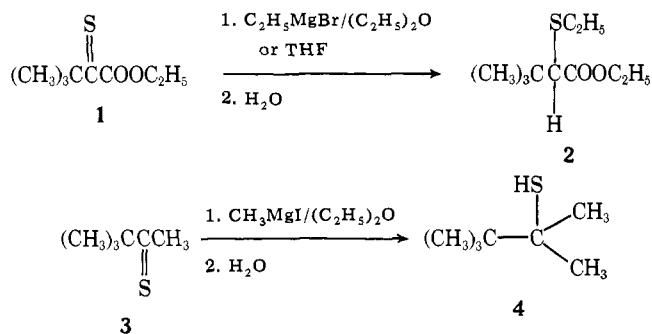
Synthesis of Fulvenes by Reaction of Thiobenzophenones with Cyclopentadienylmetal Carbonyl Anions under Anhydrous or Phase Transfer Catalyzed Conditions

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Abstract: Thiobenzophenones react with the cyclopentadienyliron dicarbonyl anion and the cyclopentadienylmolybdenum or tungsten tricarbonyl anion at room temperature to give fulvenes as the major product. Disulfides were also formed in some instances, along with the cyclopentadienylmetal carbonyl dimer. These reactions were effected under anhydrous (NaK or Na/Hg in tetrahydrofuran) or phase transfer catalyzed conditions [50% aqueous NaOH/C₆H₆/C₁₆H₃₃N(CH₃)₃⁺Br⁻ or 18-crown-6 as the catalyst], the highest yields being realized by the latter method. The reactivity of the anions toward the thioketones is C₅H₅Fe(CO)₂⁻ >> C₅H₅Mo(CO)₃⁻ ≈ C₅H₅W(CO)₃⁻. Reaction of a given thiobenzophenone with the methylcyclopentadienyliron or -molybdenum carbonyl anions gave the same ratio of isomeric fulvenes. An electron transfer mechanism is proposed for this novel desulfurization and coupling reaction.

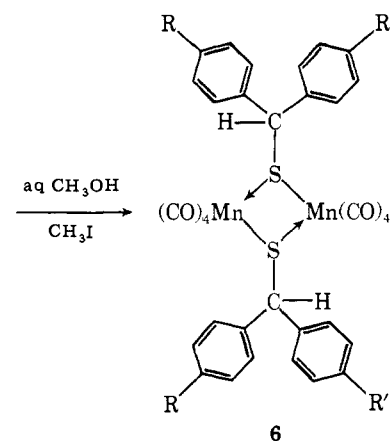
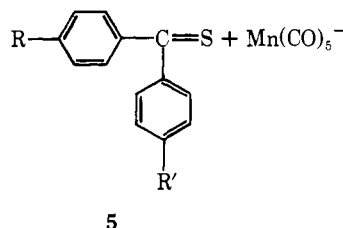
The reactions of thioketones with nucleophiles is a subject of considerable current interest.¹ Both thiophilic and carbo-philic additions have been reported in the literature. For example, ethylmagnesium bromide undergoes thiophilic addition to the α-thioketo ester, **1**, to give **2**,² while the thione **3** reacts with methylmagnesium iodide in ether to form the mercaptan, **4**.^{1b} Reaction solvents and the nature of the groups attached



to the thiocarbonyl carbon have an important influence in some, but not in all, of these reactions.

A systematic investigation of the reactions of thioketones with metal carbonyl anions was recently undertaken in our laboratories. Manganese pentacarbonyl anion undergoes formal thiophilic addition to thiobenzophenones (**5**) to give complexes of structural type **6**.³ A question arises as to what effect metal carbonyl nucleophilicity has on the reaction course.

This paper describes the interesting reaction of thiobenzophenones (**5**) with the cyclopentadienylmetal carbonyl anions, C₅H₅M(CO)_n⁻ [(a) M = Fe; n = 2; (b) M = Mo, W; n = 3], and with several methylcyclopentadienylmetal carbonyl anion derivatives.⁴ Previous studies have indicated the following order of nucleophilicity of the cyclopentadienylmetal carbonyl an-



ions: C₅H₅Fe(CO)₂⁻ >> C₅H₅W(CO)₃⁻ > C₅H₅Mo(CO)₃⁻.^{5,6} The base strength of the cyclopentadienylmolybdenum tricarbonyl anion is approximately the same as that of the manganese pentacarbonyl anion.

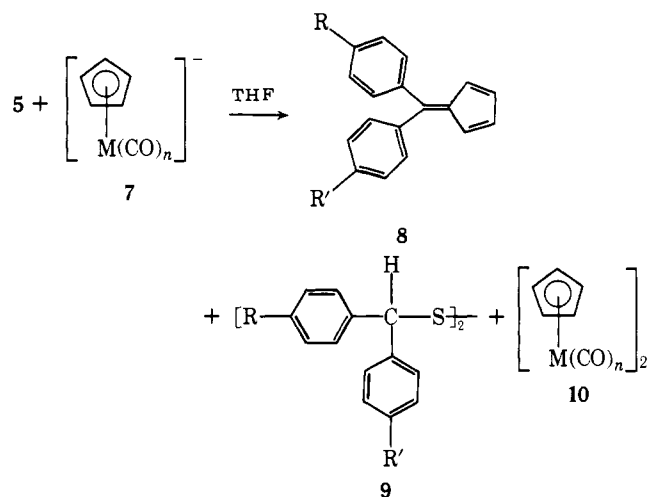
Results and Discussion

Reaction of a thiobenzophenone (**5**, R = R' = H, CH₃, OCH₃; R = OCH₃, R' = H) with the cyclopentadienyliron dicarbonyl anion (**7**, M = Fe, n = 2) in dry tetrahydrofuran (THF), at room temperature, affords fulvenes (**8**) via a novel desulfurization and coupling reaction. By-products of some

Table I. Products Obtained from Reaction of Thiobenzophenones with Cyclopentadienylmetal Carbonyl Anions

5, R =, R' =	Metal carbonyl anion	Method of generation ^a	Product	Yield, % ^b	Mp, °C	Lit. mp, °C	
H, H	7, M = Fe, n = 2	A	8	7.5	79-80	81.5-82.0 ^c	
			9	Trace	152-153	151-152 ^d	
		B	8	28			
			9	14			
			8	38			
	11, M = Fe, n = 2	C	9	13			
			12, 13 ^e	24			
		9	16				
			8	5.8	103-104	105 ^f	
			8	13			
CH ₃ , CH ₃	7, M = Fe, n = 2	A	8	5.8	103-104	105 ^f	
			9	5	149-150 ^g		
	7, M = W, n = 3	D	8	13			
			9	5			
	7, M = Mo, n = 3	A	8	18			
			9	6			
	OCH ₃ , OCH ₃	7, M = Fe, n = 2	A	8	8.2	108-109	108-109 ^c
				9	33		
			B	8	16	187-188	186-187 ^h
				9	46		
9				28			
7, M = W, n = 3		D	8	14			
			9	6			
		A	8	15			
			9	4			
			12, 13 ⁱ	18			
11, M = Fe, n = 2		A	9	5			
			12, 13	26			
		C	9	15			
			12, 13	15			
			9	9			
11, M = Mo, n = 3	A	12, 13	15				
		9	9				
	A	8	6.2	82-83	83.5-84.5 ^j		

^a A = dimer and NaK/THF; B = dimer and CTAB/50% NaOH/C₆H₆; C = dimer and 18-crown-6/50% KOH/C₆H₆; D = W(CO)₆ + C₅H₅Na. ^b Several of the fulvene yields reported in the preliminary communication are incorrect owing to typographical errors. ^c Reference 7. ^d Reference 1a. ^e Anal. Calcd for C₁₉H₁₆: C, 93.40; H, 6.60. Found: C, 93.42; H, 6.44 [E. W. Mueller and N. J. H. Small, German Patent 1 243 916 (July 6, 1967); *Chem. Abstr.*, **68**, 42032w (1968)]. ^f J. Altman and G. Wilkinson, *J. Chem. Soc.*, 5654 (1964). ^g Anal. Calcd for C₃₀H₃₀S₂: C, 79.25; H, 6.65. Found: C, 78.98; H, 6.71. ^h H. Alper and A. S. K. Chan, *J. Am. Chem. Soc.*, **95**, 4905 (1973). ⁱ Anal. Calcd for C₂₁H₂₀O₂: C, 82.86; H, 6.62. Found: C, 83.03; H, 6.38. ^j Reference 8.



of these reactions are disulfides (9), the cyclopentadienyliron dicarbonyl dimer (10, M = Fe, n = 2), and a sulfur-iron carbonyl complex of unknown structure. The yields and melting points for the reaction products are indicated in Table I. Pertinent ultraviolet,^{7,8} nuclear magnetic resonance, and mass spectral data for the fulvenes are listed in Table II.

The iron carbonyl anion 7 (M = Fe, n = 2) was generated in several ways. One method involves reaction of the dimer (10) with NaK in THF under rigorously anhydrous conditions. The ratio of thioketone (5)/10 (M = Fe, n = 2) used was 2:1.

Phase transfer catalysis provides a much more convenient method for effecting this reaction. Recent studies have demonstrated the utility of this technique, including the synthesis

Table II. Spectral Properties of Fulvenes

Fulvene	λ_{max} , nm ^a	NMR, δ , ppm ^b	Mass spectrum, M ⁺ , m/e
8, R = R' = H	248, 325	6.56 (2 H), 6.80 (2 H), 7.65 (10 H)	
8, R = R' = CH ₃		2.45 (6 H), 6.40 (2 H), 6.73 (2 H), 7.30 (8 H)	258
8, R = R' = OCH ₃	243, 352	3.90 (6 H), 6.35 (2 H), 6.67 (2 H), 7.00 (4 H), 7.36 (4 H)	290
8, R = OCH ₃ ; R' = H	242, 342	3.93 (3 H), 6.40 (2 H), 6.76 (2 H), 7.06 (2 H), 7.43 (7 H)	
12, 13, R = R' = H		2.08 (3 H), 2.11 (3 H), 6.09, 6.35-6.67 (6 H), 7.52 (20 H)	244
12, 13, R = R' = OCH ₃		2.15 (3 H), 2.18 (3 H), 3.97 (12 H), 6.21, 6.52, 6.63 (6 H), 7.10 (8 H), 7.50 (8 H)	304

^a Ultraviolet spectra were recorded using *n*-heptane as the solvent.

^b CDCl₃ solution with tetramethylsilane as internal standard.

of ortho-metalated,¹⁰ cluster,¹¹ π -allyl,¹¹ and substituted group 6 metal carbonyl complexes,¹² and in the iron carbonyl induced reduction of aromatic nitro compounds to amines.¹³

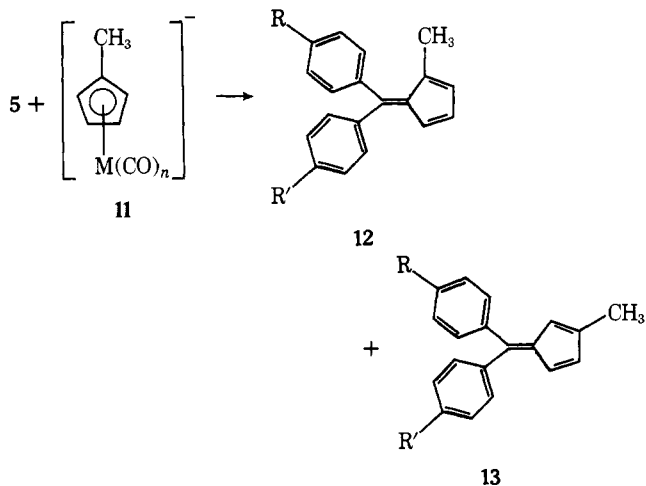
Treatment of a thione (5) with cyclopentadienyliron dicarbonyl dimer (10, M = Fe, n = 2), 50% sodium hydroxide, benzene, and the phase transfer catalyst, at room temperature,

affords fulvenes in superior yields to those obtained by the NaK method (Table I). Furthermore, rigorously anhydrous conditions are not necessary, and reaction workup is exceedingly simple to effect. Cetyltrimethylammonium bromide (CTAB) and 18-crown-6¹⁴ are good catalysts for the reaction. Benzyltriethylammonium chloride, employed in other phase transfer catalyzed reactions,^{10,11} cannot be used here since the generated anion **7** ($M = Fe, n = 2$) undergoes benzylation by this quaternary ammonium salt.⁹

A 2:1 ratio of thione (**5**)/dimer (**10**, $M = Fe, n = 2$) was generally used for these phase transfer catalyzed reactions. Essentially the same results were obtained using a 1:1 ratio of the two reactants. Fulvene formation does not occur in the absence of the phase transfer catalyst. In addition, use of a 25% instead of a 50% hydroxide solution as the aqueous phase, and in the presence of 18-crown-6 or CTAB, does not give the fulvene. It is also noteworthy that alkylation does not occur when the nonaqueous reactions (i.e., NaK method) are effected in the presence of methyl iodide.

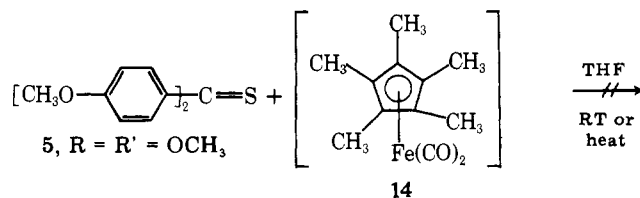
The group 6 metal carbonyl anions, $C_5H_5M(CO)_3^-$ (**7**, $M = Mo, W$), proved to be substantially less reactive toward thiobenzophenones than the cyclopentadienyliron dicarbonyl anion. Either of these group 6 anions, generated under anhydrous conditions, failed to react with thiobenzophenones at room temperature or in refluxing THF. However, reaction did take place at 110–120 °C in a Carius tube affording the fulvene (Table I).

Several thiobenzophenones were also reacted with the methylcyclopentadienylmetal carbonyl anions, **11**. Two fulvenes, **12** and **13**, may be formed by reaction of **5** with **11**.



Treatment of thiobenzophenone with **11**, $M = Fe, n = 2$ (generated under anhydrous or phase transfer conditions), gave **12** and **13** ($R = R' = H$) in a 1:1 ratio ($\pm 3\%$). Precisely the same ratio of isomeric fulvenes resulted using 4,4'-dimethoxythiobenzophenone (**5**, $R = R' = OCH_3$) as the substrate (phase transfer or anhydrous conditions), clearly indicating that the reaction is not sensitive to the nature of R, R' . Reaction of 4,4'-dimethoxythiobenzophenone (**5**, $R = R' = OCH_3$) with the methylcyclopentadienylmolybdenum tricarbonyl anion (**11**, $M = Mo, n = 3$) afforded **12** and **13** ($R = R' = OCH_3$) in the same ratio as in the case of the iron anion. The latter observation strongly suggests that, regardless of the reaction mechanism, cleavage of the metal-cyclopentadienyl bond is not involved in the rate-determining step of the reaction.

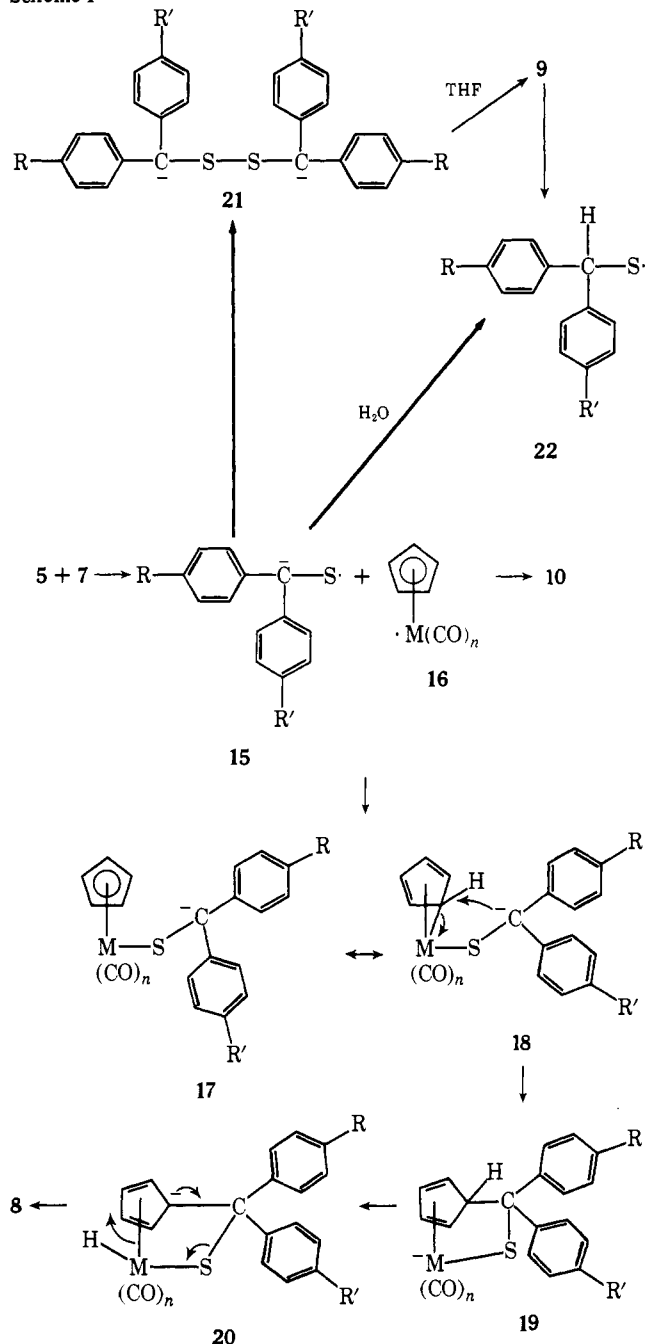
In an effort to isolate an organometallic intermediate in the thione-cyclopentadienylmetal carbonyl anion reaction, the pentamethylcyclopentadienyliron dicarbonyl anion (**14**) was prepared¹⁵ and treated with 4,4'-dimethoxythiobenzophenone (**5**, $R = R' = OCH_3$). The thioketone was recovered un-



changed when reaction with **14** was attempted at room temperature or in refluxing THF.

A possible pathway for the novel thioketone cyclopentadienylmetal carbonyl anion reaction is outlined in Scheme I.

Scheme I

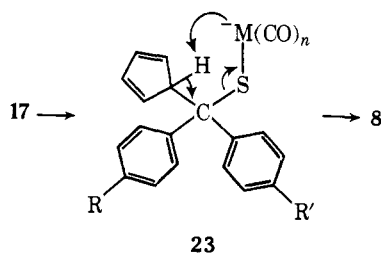


Electron transfer from the metal carbonyl anion to the thione would generate the radical anion **15** and the cyclopentadienylmetal carbonyl radical **16** (which can dimerize to **10**). Anion **17**, formed by coupling of **15** and **16**, can also be represented by the resonance contributor **18**. Intramolecular addition of the carbanion to the noted carbon atom of the cyclopentadienyl ring of **18**, and cleavage of the carbon-metal σ

bond, would afford **19**. Hydrogen transfer to give the metal hydride **20**, and subsequent elimination, would afford the fulvene (**8**). The disulfide **9** may be formed under anhydrous conditions by self-coupling of **15** to the dianion **21**, followed by hydrogen abstraction from the solvent. Using phase transfer catalyzed conditions, disulfide formation may occur via **21**, but protonation of **15** to **22** followed by dimerization is also conceivable.

An alternative pathway for fulvene formation (Scheme II)

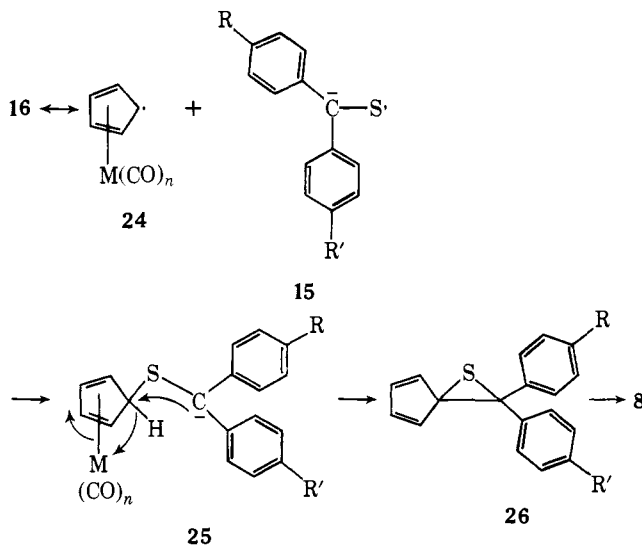
Scheme II



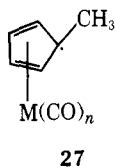
may involve cleavage of the π -cyclopentadienyl-metal bond of **17** to give **23**. An intramolecular hydrogen abstraction-elimination reaction would then afford **8**.

A third pathway (Scheme III), involving the delocalized

Scheme III



radical **24**, merits consideration. Coupling of the radical anion **15** with **24** would give **25**. Carbon-carbon bond formation and cleavage of the diene-metal bond of **25** would afford the episulfide **26**. Desulfurization of the latter by additional anion (**7**) would give the fulvene. Some evidence against this mechanism comes from the results obtained using the methylcyclopentadienylmetal carbonyl anions (**11**) where **27**, the analogue of



24, would be the most stable radical species derived from **11**. If **27** was important, the formation of nonmethylated fulvenes or other products was expected. However, such products were not obtained in these reactions.

In conclusion, a novel desulfurization and coupling reaction occurs on exposure of thioetheres to cyclopentadienylmetal carbonyl anions. The reactivity of the metal carbonyl anions towards thioetheres is $C_5H_5Fe(CO)_2^- \gg C_5H_5Mo(CO)_3^- \approx C_5H_5W(CO)_3^-$. Phase transfer catalysis is a technique of

considerable promise for the generation of the cyclopentadienyliron dicarbonyl anions, **7** and **11** ($M = Fe, n = 2$).¹⁶

Experimental Section

General. Melting points were determined using a Fisher-Johns apparatus and are uncorrected. A Perkin-Elmer 202 ultraviolet spectrometer was used for ultraviolet spectral determinations. Infrared spectra were recorded on a Beckman IR20A spectrometer, equipped with a calibration standard. ¹H NMR spectra were determined using Varian T60 and HA100 spectrometers. Mass spectral determinations were made on a Varian MS9 spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and by Drs. F. and E. Pascher, Bonn, West Germany.

The following compounds were commercially available and were used as received: cyclopentadienyliron dicarbonyl dimer, cyclopentadienylmolybdenum tricarbonyl dimer, tungsten hexacarbonyl, 4,4'-dimethoxythiobenzophenone, cetyltrimethylammonium bromide, benzyltriethylammonium chloride, and 18-crown-6. The procedures of Reynolds and Wilkinson¹⁷ were used to prepare methylcyclopentadienyliron dicarbonyl dimer (mp 97–98 °C, lit.¹⁷ mp 98–99 °C) and methylcyclopentadienylmolybdenum tricarbonyl dimer (mp 145–148 °C dec, lit.¹⁷ mp 146–147 °C dec). Pentamethylcyclopentadienyliron dicarbonyl dimer was synthesized from hexamethyl(Dewar benzene) according to the method of King and Efraty.¹⁵ Thiobenzophenone, 4-methoxythiobenzophenone, and 4,4'-dimethylthiobenzophenone were prepared by treatment of the corresponding ketone with P₄S₁₀ and base.¹⁸

Solvents were dried and purified by standard techniques. All reactions were run under a dry nitrogen atmosphere.

General Procedure for Reaction of Thiobenzophenones (5**) with Cyclopentadienyliron Dicarbonyl Dimer.** Using NaK (Method A). A mixture of cyclopentadienyliron dicarbonyl dimer (0.65 g, 1.84 mmol) and NaK (78% by wt of K) in THF (50 mL) was stirred at room temperature for 1 h. The bright red solution was filtered into a flask containing tetrabutylammonium perchlorate (1.30 g, 3.82 mmol) and the mixture was stirred for 20 min and then filtered (to remove KClO₄). To the filtrate of (C₄H₉)₄N⁺[C₅H₅Fe(CO)₂]⁻ (isolated⁹ first if desired) was added the thioether (3.3 mmol), and the solution was stirred overnight at room temperature. The solution was concentrated in vacuo, dissolved in the minimum amount of benzene, and then chromatographed on silica gel with petroleum ether (bp 60–80 °C). Elution with petroleum ether gave **10**, $M = Fe, n = 2$, followed by the fulvene (**8**).

Using CTAB (Method B). A mixture of the thiobenzophenone (**5**, 5 mmol), the dimer **10**, $M = Fe, n = 2$ (2.5 mmol), benzene (15–20 mL), NaOH (10 g/10 mL of H₂O), and CTAB (0.5 mmol) was vigorously stirred overnight at room temperature. The layers were separated (centrifuge), and the benzene layer was dried (MgSO₄), concentrated to approximately 5 mL, and then chromatographed on neutral alumina. Fulvenes (**8**) were isolated by elution with 5:1 to 10:1 benzene-hexane (any dimer was eluted with hexane). Disulfides, if formed, were isolated by further elution with benzene-hexane.

Using 18-Crown-6 (Method C). A solution containing the thioether (5 mmol), cyclopentadienyliron dicarbonyl dimer (2.5 mmol), 18-crown-6 (0.5 mmol), KOH (10 g) in H₂O (10 mL), and benzene (10 mL) was vigorously stirred overnight at room temperature, and then the product mixture was worked up as described in B.

Reaction of **5 ($R = R' = CH_3, OCH_3$) with the Cyclopentadienylmolybdenum Tricarbonyl Dimer and NaK (Method A).** A mixture of cyclopentadienylmolybdenum tricarbonyl dimer (1.25 mmol) and NaK (0.2 mL, 78% by wt of K) in THF (40 mL) was stirred for 2 h at room temperature. The resulting solution of K[C₅H₅Mo(CO)₃] was filtered into a Carius tube containing the thioether (2.50 mmol). The Carius tube was sealed, heated at 110–120 °C for 3 days, and then cooled. The tube was opened, the solution was filtered, and the filtrate was evaporated. The solid was dissolved in benzene and chromatographed on alumina. Elution with petroleum ether gave the dimer **10** $M = Mo, n = 3$. The fulvene (**8**) was isolated by elution with 10:1 petroleum ether-benzene. Further elution with petroleum ether-benzene afforded the disulfide.

Anion **11**, $M = Mo, n = 3$, was reacted with **5**, $R = R' = OCH_3$, by an analogous procedure.

Reaction of **5 ($R = R' = CH_3, OCH_3$) with the Cyclopentadienyltungsten Tricarbonyl Anion.** Sodium sand (0.103 g, 4.3 mmol) was reacted with freshly prepared cyclopentadiene (5 mL) to form a so-

lution of sodium cyclopentadienide. The latter was added to THF (50 mL) containing tungsten hexacarbonyl and the mixture reacted for 12 h. The resulting solution of $\text{Na}[\text{C}_5\text{H}_5\text{W}(\text{CO})_3]$ was filtered into a Carius tube containing the thione. The Carius tube was sealed, heated at 110–120 °C for 3 days, and then cooled. The tube was opened and the reaction mixture was worked up as described for the reaction of **5** with **7**, $M = \text{Mo}$, $n = 3$.

Reaction of Thiobenzophenones (5) with the Methylcyclopentadienyliron Dicarboxyl Anion (11, $M = \text{Fe}$, $n = 2$). Using NaK (Method A). A solution of methylcyclopentadienyliron dicarbonyl dimer (1.15 g, 3.0 mmol) in THF (50 mL) was stirred with NaK (0.3 mL) at room temperature for 1 h. The solution of $\text{K}[\text{CH}_3\text{C}_5\text{H}_4\text{Fe}(\text{CO})_2]$ was filtered and the filtrate was reacted with the thiobenzophenone (6 mmol) for 16 h at room temperature. Workup was effected in the same manner as that described for reaction of **5** with **7**, $M = \text{Fe}$, $n = 2$.

Using 18-Crown-6 (Method C). The procedure described for the reaction of **5** with the cyclopentadienyliron dicarbonyl dimer was utilized here.

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A Comparison of the Photoaddition Reactions of Nucleic Acid Nitrogen Bases and Cyclohexenones with Isobutylene. The Role of Rigidity in Product Formation

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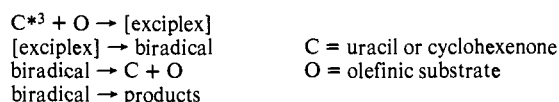
Abstract: The acetone-sensitized photoaddition of uracil, thymine, 6-methyluracil, and their 1,3-dimethyl derivatives to isobutylene has been studied and compared with analogous reactions with cyclohexenones. For the nitrogen base systems little regioselectivity was noted since mixtures of cis-fused 7,7-dimethyl- and 8,8-dimethyl-2,4-diazabicyclo[4.2.0]octa-3,5-dione derivatives were formed in good yields. The results for these systems contrast markedly with those for the photoadditions of the analogous cyclohexenones to isobutylene which often yield complex product mixtures. Labeling studies using isobutylene-1,1- d_2 establish that the ene products formed from the additions of cyclohexenone to isobutylene do not proceed via a symmetrical allylic species. The differences between these two systems are related to the flexibility of the ring systems rather than a marked change in the mechanism of the reaction.

Introduction

The similarity of the photochemistry of nucleic acid nitrogen bases and cyclic enones, while noted by several investigators,^{2a,b} was placed on a firm experimental basis by Wagner and Bucheck.^{2c} These workers established that the dimerization of cyclohexenone and uracil both proceeded from a triplet state ($E_T \sim 70$ kcal/mol) and followed similar kinetic schemes. Furthermore, they proposed that interaction of the triplet state of the nitrogen base or cyclic enone with a ground state molecule initially produces an exciplex. The exciplex subsequently collapses to give a biradical prior to product formation. This scheme is generalized below. More recently the cycloaddition of triplet 1,3-dimethyluracil to oxygenated olefins has been shown to proceed in a regiospecific manner, a behavior again paralleling that of cyclohexenone.³ Supporting this formal similarity between the excited state reactions of uracil and

cyclohexenone are recent calculations which reveal that the uracil $\pi-\pi^*$ transition is largely localized in the enone moiety and that the uracil $\pi-\pi^*$ state might best be viewed as an enone-like excited state.⁴

Scheme I. Abbreviated Mechanism for Photochemical Cycloaddition



Our motivation in initiating a study of the cycloaddition reactions of uracil, thymine, and 6-methyluracil to isobutylene was twofold. First, we hoped to utilize analogous photoaddition reactions in the synthesis of modified pyrimidine and nucleoside derivatives.⁵ In this context, the complex photoaddition mixtures and low yields of products obtained in irradiations