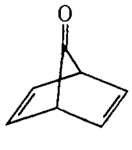
The Synthesis and Chemistry of Tricarbonyl(7-norbornadienone)iron[1]

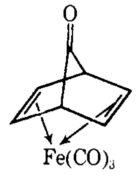
J. M. Landesberg* and J. Sieczkowski[2]

Contribution from the Department of Chemistry, Adelphi University, Garden City, New York 11530. *Received June 29, 1970*

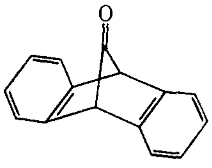
Abstract: The synthesis, physical properties, and chemical reactivity of tricarbonyl(7-norbornadienone)iron are described.

In general, metal carbonyl complexes containing an organic ligand have been of considerable interest in recent years. It is well documented that transition metal atoms can stabilize carbonium ions by their bonding to the metal; many of these π-dienyl metal complex cations, where iron is the transition metal, are more stable than their simple carbonium ion counterparts. Tricarbonyl(π-allyl)iron,[3] tricarbonyl(π-pentadienyl)iron,[4] tricarbonyl(π-cycloheptadienyl)iron,[5] and tricarbonyl(π-cyclooctadienyl)iron[6] are a few of the many examples in this category. In cases where the organic ligand is a neutral molecule which would be of unusually high instability in the uncomplexed state, the tricarbonyliron group renders the organic moiety stable and isolatable as the complex. Included in this class of compounds are tricarbonyl(cyclobutadiene)iron,[7] tricarbonyl(*o*-quinodimethane)iron,[8] and tricarbonyltris(methylene)methyliron.[9] Thus, highly elusive, unstable organic molecules containing π electrons can be stabilized and isolated by incorporating a transition metal into the system. In view of these past successes, it was hoped that the tricarbonyliron group could be used to stabilize the elusive 7-norbornadienone (**1**) and thus derive **2**. The premise that **2** should exist was based on a number of observations.


1

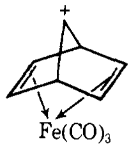


2

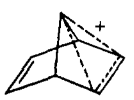

3

An article by Yankelevitch and Fuchs[10] presented evidence which discounted most previous claims of successful syntheses of substituted derivatives of **1**; only dibenzonorbornadien-7-one (**3**)[11] survived their critique. In attempting to analyze the instability of **1** (and derivatives), it was argued that the interaction of the π cloud of the carbon–carbon double bonds with that of the carbonyl leads to a net destabilizing effect. Compensation of this interaction by bending of the C_7=O bridge cannot occur in **1** as it can in 7-norbornenone.[10] As a result, **1** and its derivatives would rapidly decarbonylate to thermodynamically stable aromatic systems and carbon monoxide. This is demonstrated by the rapid formation of anthracene when solutions of **3** are warmed to room temperature.[11] This is also supported by the failure of the dimethyl ketal of **1**[12] (and similar derivatives[13]) to undergo acid hydrolysis to **1** and the failure of 7-norbornadienol[14,15] (and similar derivatives[16]) to undergo oxidation to **1**; aromatization results in all cases. Furthermore, extension of their argument suggests that if electron density can be decreased in the olefinic bonds, the unfavorable π-cloud interactions would be alleviated; this should lead to stabilization. The use of a tricarbonyliron group to achieve this end furthermore is based on some recent solvolysis results.

Lillya and coworkers[14] determined the solvolysis rate of tricarbonyl(7-tosyloxynorbornadiene)iron. Their experiments showed that this complex had low solvolytic reactivity when compared with corresponding uncomplexed materials. Thus, the tricarbonyl(7-norbornadienyl)iron cation (**4**) is a relatively destabilized system. This is in contrast to the stabilized 7-norbornadienyl cation (**5**), the stability of which is attributed to homoallylic interaction of at least one pair of π electrons with the carbonium ion at C_7.[17] It is apparent then that electron density is diminished on the exo side of the double bond in **4**; therefore, this reduces the interaction of the olefinic bonds with the positive charge at C_7. Thus, a net destabilization and a reduced solvolysis rate



4



5

---

[1] Preliminary communications are as follows: (a) J. M. Landesberg and J. Sieczkowski, *J. Amer. Chem. Soc.*, **90**, 1655 (1968); (b) J. M. Landesberg and J. Sieczkowski, *ibid.*, **91**, 2120 (1969).

[2] Abstracted from the Ph.D. Thesis of J. Sieczkowski, Adelphi University, 1970.

[3] G. F. Emerson and R. Pettit, *J. Amer. Chem. Soc.*, **84**, 4591 (1962).

[4] J. E. Mahler and R. Pettit, *ibid.*, **85**, 3955 (1963).

[5] J. D. Holmes, D. A. K. Jones, and R. Pettit, *J. Organometal. Chem.*, **4**, 324 (1965).

[6] W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 2162 (1963).

[7] G. F. Emerson, L. Watts, and R. Pettit, *J. Amer. Chem. Soc.*, **87**, 133 (1965).

[8] W. R. Roth and J. D. Meier, *Tetrahedron Lett.*, 2053 (1967).

[9] G. F. Emerson, K. Ehrlick, W. P. Giering, and P. C. Lauterbur, *J. Amer. Chem. Soc.*, **88**, 3172 (1966).

[10] S. Yankelevitch and B. Fuchs, *Tetrahedron Lett.*, 4945 (1967).

[11] J. Meinwald and E. G. Miller, *ibid.*, 253 (1961).

[12] D. M. Lemal, R. A. Lovald, and R. W. Harrington, *ibid.*, 2779 (1965).

[13] P. G. Gassman, D. H. Aue, and D. S. Patton, *J. Amer. Chem. Soc.*, **86**, 4211 (1964).

[14] D. F. Hunt, C. P. Lillya, and M. D. Rausch, *ibid.*, **90**, 2561 (1968).

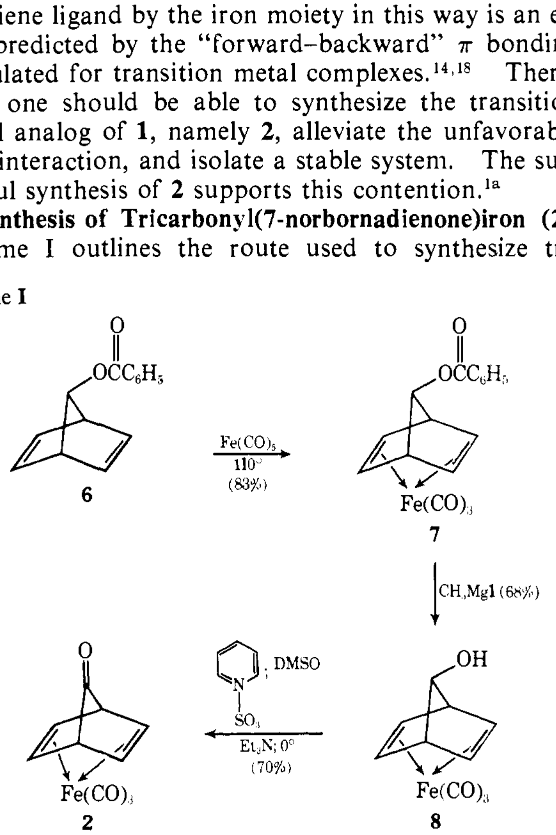
[15] (a) T. K. Hall and P. R. Story, *ibid.*, **89**, 6759 (1967); (b) W. C. Baird and M. Buza, *J. Org. Chem.*, **33**, 4105 (1968).

[16] P. D. Bartlett and W. P. Giddings, *J. Amer. Chem. Soc.*, **82**, 1240 (1960).

[17] S. Winstein and C. Ordronneau, *ibid.*, **82**, 2084 (1960).

is observed. It is rationalized that the iron of the tricarbonyliron group brings about a decrease in the electron density on the exo side of the olefinic bonds since a disproportionate amount of electron density is situated between the ligand and iron.[14] This "reduction" of electron density in the π-molecular bonding orbital of the diene ligand by the iron moiety in this way is an effect predicted by the "forward–backward" π bonding postulated for transition metal complexes.[14,18] Therefore, one should be able to synthesize the transition metal analog of **1**, namely **2**, alleviate the unfavorable π–π interaction, and isolate a stable system. The successful synthesis of **2** supports this contention.[1a]

Scheme I



Synthesis of Tricarbonyl(7-norbornadienone)iron (2). Scheme I outlines the route used to synthesize tricarbonyl(7-norbornadienone)iron (**2**). The key compound in this scheme is tricarbonyl(7-norbornadienol)iron (**8**);[19] modification of published procedures[14] (see Experimental Section) gives **8** in good yield. Oxidation leads directly to **2**. This is another example of a functional group interconversion that takes place in a system also possessing a tricarbonyldieneiron group.[19,20]

Of the oxidation procedures employed[21] only a modification of the Parikh and Doering procedure[23] was successful in oxidizing **8**. This mild oxidative method gave variable yields (50–70%) and seemed to depend on the quality of alcohol **8**—the purer the alcohol the higher the yield. No attempt was made to detect any other products (*e.g.*, benzaldehyde or benzene) in the oxidizing mixture, but apparently fragmentation or decomplexation is not facile under the conditions employed. Unpurified samples of **2** decompose quite rapidly to give a black residue. Purified ketone **2**, at room temperature or in solution (the ketone is soluble in most organic solvents), slowly darkens and deposits an insoluble red solid, which appears to be iron or iron oxide. When solid **2** is kept cold, it is stable for long periods; samples have kept for as long as 2 years at −5°. Ketone **2** is also acid sensitive and decomposes rapidly when in contact.[24] Therefore, knowing these properties, it is not unexpected that the results of oxidation at temperatures above 0° or in acid media give rise to decomposition.

The structure of ketone **2** is based on its spectra and its decomposition products. The formula is established as $C_7H_6OFe(CO)_3$ by the elemental analysis and by its mass spectrum. The nuclear magnetic resonance spectrum is in accord with the assigned structure. The carbonyl stretching frequency is consistent with the values of known strained systems (Table I). Thermal, photochemical, and oxidative decomplexations lead to gas evolution and the formation of benzene. These observations leave little doubt concerning the identity of the product resulting from the oxidation of alcohol **8**.

Table I

Structure	$\nu_{C=O}$, cm^{-1}	Ref
3	1792	*a*
Quadricyclanone	1746	*b*
7-Norbornanone	1830, 1780, 1745	*c*
7-Norbornenone	1862, 1780, 1745	*c*
Nortricyclanone	1753	*d*
2	1860 (w), 1780 (s)	*e*

[a] See ref 11. [b] See ref 26. [c] P. G. Gassman and P. G. Pape, *Tetrahedron Lett.*, 9 (1963). [d] J. P. Schaefer, *J. Amer. Chem. Soc.*, **82**, 4091 (1960). [e] This work.

Chemistry of Tricarbonyl(7-norbornadienone)iron (2). The complexed ketone **2** is clearly a highly strained, reactive compound that is the simplest, stabilized derivative of the parent, 7-norbornadienone (**1**). Moreover, **2** is the precursor to the elusive **1**. Prior to the published photochemistry[1b] of **2** little evidence had been forwarded for the intermediacy of a 7-norbornadienone in a reaction system, even though the presence of such a system had been inferred from decomposition products.[12,13,16,25] Equations 2 and 3 (Scheme II) summarize the photochemical results. The finding of 9,10-diphenylanthracene in the trapping experiment (eq 2) and of quadricyclanone[26] in the experiment at liquid nitrogen temperature (eq 3) supports the contention that 7-norbornadienone (**1**) exists as a highly unstable, short-lived intermediate generated by photoinduced decomplexation[27] of **2**.

In some cases, the photochemical reactions were run with ketones (acetophenone, benzophenone, or acetone) present (as in the EPA glass at −196°). Their inclusion was based on two observations. Rapid ring closure of norbornadiene to quadricyclane occurred in the

---

(18) (a) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C71 (1951); (b) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953); (c) see also R. Pettit, G. F. Emerson, and J. E. Mahler, *J. Chem. Educ.*, **40**, 175 (1963).

(19) R. Pettit and G. F. Emerson, *Advan. Organometal. Chem.*, **1**, 1 (1964).

(20) G. O. Schenck, E. Koerner von Gustorf, and M.-J. Jun, *Tetrahedron Lett.*, 1059 (1962); these authors did functional group interconversions on compounds also possessing monoolefin-$Fe(CO)_4$ groups.

(21) Chromium trioxide–pyridine gave benzaldehyde and benzene (see also ref 14). Use of the Pfitzner–Moffatt procedure[22] gave no **2**; our conditions were such as to preclude isolation of any benzaldehyde or benzene.

(22) K. E. Pfitzner and J. G. Moffatt, *J. Amer. Chem. Soc.*, **87**, 5661 (1965).

(23) J. R. Parikh and W. von E. Doering, *ibid.*, **89**, 5505 (1967).

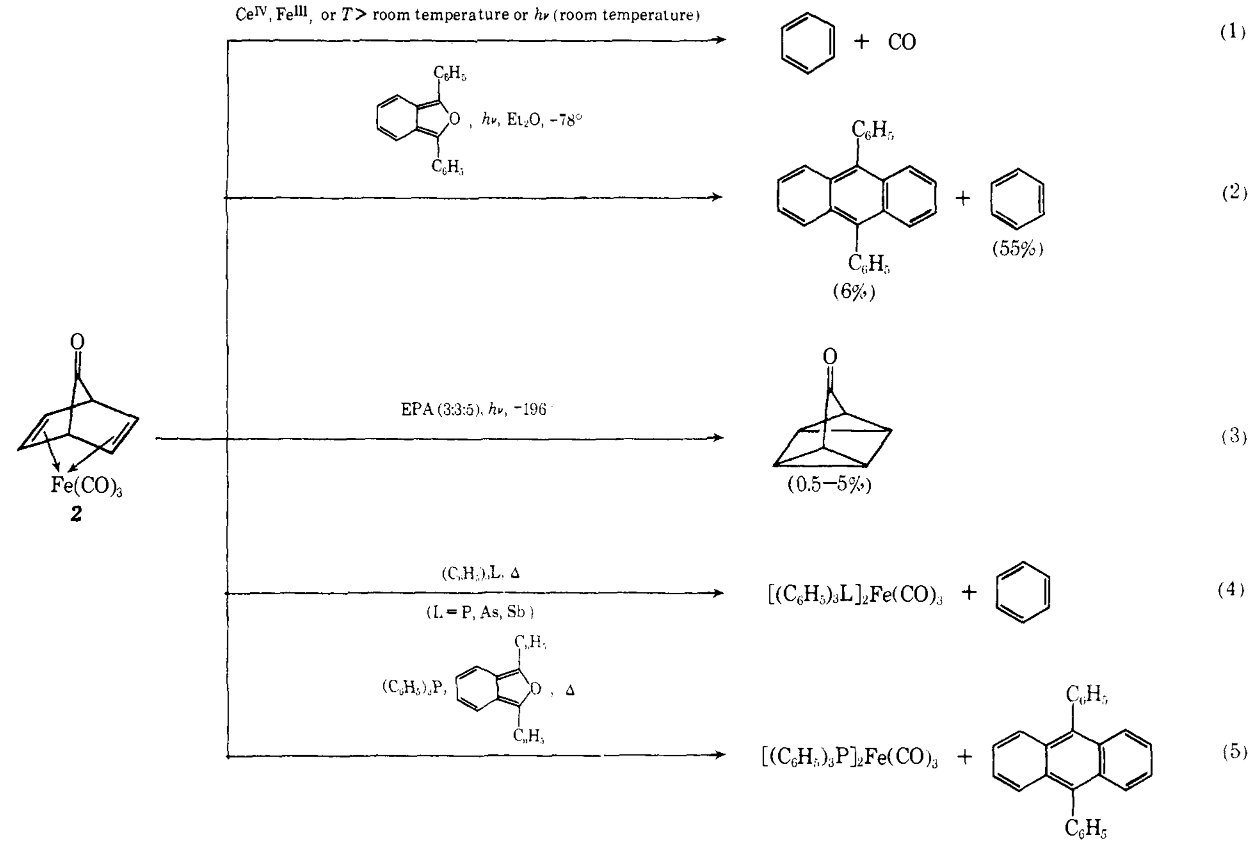
(24) Attempts to observe the nuclear magnetic resonance spectrum of **2** in FSO_3H–SbF_6–SO_2 at low temperature were unsuccessful; decomposition was too rapid to observe any cation formation. We thank Dr. Paul Clifford for running this experiment.

(25) (e) M. E. Kuehne and P. J. Sheeran, *J. Org. Chem.*, **33**, 4406 (1968); (b) J. W. Wilt and P. J. Chenier, *ibid.*, **35**, 1562 (1970); these are recent papers which infer substituted 7-norbornadienones as intermediates which give rise to aromatic product .

(26) P. R. Story and S. R. Fahrenholtz, *J. Amer. Chem. Soc.*, **86**, 1270 (1964).

(27) See ref 1b and references therein.

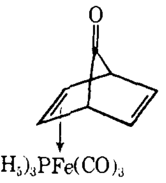
Scheme II



presence of acetone, acetophenone, or benzophenone.[28] Phosphorescence of naphthalene in a glass is photosensitized by ketones such as acetophenone or benzophenone.[29a] Thus it was hoped that in the EPA glass the intramolecular photodimerization of **1** to quadricyclanone could be improved. However, since the yields of quadricyclanone, with or without sensitizer, were variable and low, no conclusion could be drawn as to the photochemical processes or the influence of the ketones on the reaction.[29b]

Ketone **2** reacts with Lewis bases such as triphenylphosphine, triphenylarsine, or triphenylstibine (eq 4). Only organic ligand displacement resulted. Thus, with triphenylphosphine as reactant, tricarbonylbis(triphenylphosphine)iron[30] and benzene were found. When a trapping experiment was carried out with 1,3-diphenylisobenzofuran present in the reaction mixture, small quantities of 9,10-diphenylanthracene were isolated (eq 5). However, it is only speculative as to what was trapped; **1** or some other species, such as **9**, would lead to the same results.

It was of further interest to explore the behavior of ketone **2** toward various reagents. The reactions of this compound leading to the formation of C_7 derivatives are depicted in Scheme III.



9

The reduction of ketone **2** to alcohol **8** occurred readily with sodium borohydride. Attempts to carry out the reduction with lithium aluminum hydride gave extensive decomposition; none of **8** could be found in the reaction mixture, and no attempt was made to identify decomposition products.

The 2,4-dinitrophenylhydrazone (2,4-DNPH) derivative (**10**) could be formed as expected of a typical ketone. However certain problems removed this compound from the typical class. The 2,4-DNPH could be formed only under specific conditions, since it is destroyed under the usual conditions employed for hydrazone formation. Derivative **10** was prepared by using a procedure[31] in which the 2,4-DNPH completely precipitates as it is formed, and hence, minimizes decomposition in the acid medium.

Unfortunately, when tosylhydrazide is substituted in this procedure, the expected analogous derivative is not formed. Tosylhydrazide adds *twice* to ketone **2** (bisadduct **11**) as established by an elemental analysis for $C_{24}H_{24}N_4O_7S_2Fe$ and a molecular weight determination (osmometry). Heat instability and a low vapor pressure eliminated our obtaining a mass spectrum; the compound decomposed upon its introduction into the

---

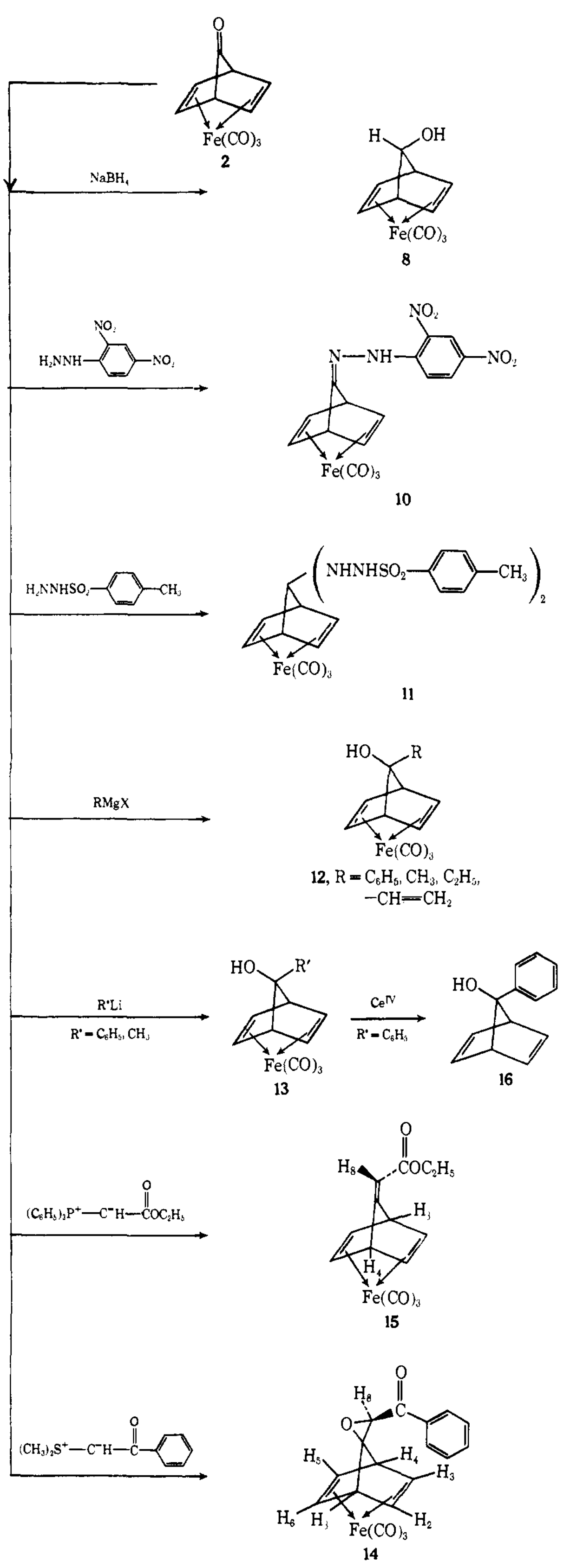
(28) G. S. Hammond, P. Wyatt, C. D. DeBoer, and N. J. Turro, *J. Amer. Chem. Soc.*, **86**, 2532 (1964); G. S. Hammond, N. J. Turro, and A. Fischer, *ibid.*, **83**, 4674 (1961).

(29) (a) A. Terenin and V. Ermolaev, *Dokl. Akad. Nauk SSSR*, **85**, 547 (1952); *J. Chim. Phys. Physicochim. Biol.*, 698 (1958); *Trans. Faraday Soc.*, **52**, 1042 (1956). (b) A referee has pointed out that since diffusion is essentially nonexistent in EPA at −196° and the lifetime of **1** is probably exceedingly short, there was probably little chance for sensitized quadricyclanone formation from **1** to occur. In the energy transfer experiments cited in (a), both donor and acceptor concentrations were near 1.0 *M*.

(30) A. F. Clifford and A. K. Mukherjee, *Inorg. Chem.*, **2**, 151 (1963).

(31) H. A. Iddles, A. W. Low, B. D. Rosen, and R. T. Hart, *Ind. Eng. Chem., Anal. Ed.*, **11**, 102 (1939).

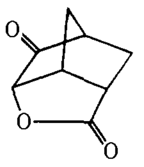
Scheme III



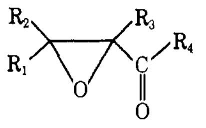
heated inlet system of the mass spectrometer. However, absorptions in the infrared spectrum at ν 2040 (sharp) and 1925 (broad) cm^{-1} (CS_2) show that the tricarbonyliron moiety is intact.[9,19] The nuclear magnetic resonance spectrum also is consistent with the bisadduct structure **11**: δ 7.90 (broad singlet, two protons corresponding to SO_2NHNH–), 7.53 [$(AB)_2$ pattern, eight protons corresponding to ArH], 4.67 (broad singlet, two protons corresponding to –NHNHR), 2.92 (broad, six protons corresponding to bridgehead and complexed vinyl), and 2.40 (singlet, six protons corresponding to $ArCH_3$). This evidence supports the assigned structure and discounts the possibility that the hydrazide added to a C≡O or displaced C≡O from iron.[32] The only reasonable conclusion is that C_7 has undergone attack by two molecules of tosylhydrazide to form a ditosyl hydrazoketal **11**. This product is unusual since there are no recorded examples of isolating a hydrazoketal. However, there is no *a priori* reason why this type of ketal cannot form.

There are examples in the literature of acetals related to bisadduct **11**, for example, $RORNCH_2NRNR_2$, RORNCHR'NROR, and $R_2NRNCH_2NRNR_2$ (where R and R' are alkyl).[33] Also hydrazine adds to aldehydes to form hexahydro-3,6-dialkyl-*S*-tetrazines.[34] Since there are no perfectly representative examples of bisadduct **11**, a discussion of the reason for its unexpected formation is in order.

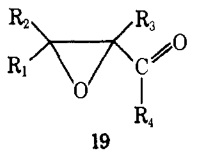
Even though ketone **2** does exhibit an infrared absorption that can be attributed to a strained ketone, an alternative proposal may account for the observed stretching frequency. Intramolecular dipolar interactions of a carbonyl with another polar group have been reported as influencing carbonyl stretching frequencies. For example, the high-frequency carbonyl absorption of **17** is attributed to a destabilizing dipolar interaction of the lactone and carbonyl.[35] A situation related to this arises in the case of α-epoxy ketones or esters.[36]



17



18



19

R_1, R_2, or R_3 = H or alkyl
$R_4 = C_6H_5$ or OC_2H_5

The cis orientation of the carbonyl groups and epoxy groups in **18** (or the analogous ester to **18**) effects a shift of the carbonyl stretching frequency; in the trans case, **19**, the destabilizing dipolar interaction is minimized and the effect on the carbonyl stretching frequency is negligible. Although ketone **2** can derive stability by the reduction of electron density on the exo side of the double bonds, the π clouds of the double bonds are still in proximity of the carbonyl π cloud, and this situation should be conducive to dipolar interaction.[14] However, the full extent of this interaction and its effect on the carbonyl stretching frequency cannot be ascertained without further study. The point to be made here is that

---

[32] J. Wender and P. Pino, "Organic Synthesis *via* Metal Carbonyls," Interscience, New York, N. Y., 1968, p 451; it is not usual for hydrazines to add to C≡O or to displace C≡O from tricarbonyliron complexes.

[33] (a) G. Zinner, W. Kliegel, W. Ritter, and H. Boehlke, *Chem. Ber.*, **99**, 1678 (1966); (b) G. Zinner and W. Ritter, *Angew. Chem.*, **75**, 640 (1963).

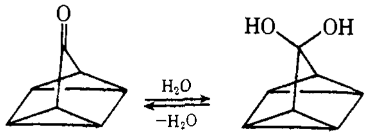
[34] T. Kauffman, G. Ruckelslauss, and J. Schulz, *ibid.*, **75**, 1204 (1963).

[35] R. M. Moriarty, C. R. Romain, and T. O. Lovett, *J. Amer. Chem. Soc.*, **89**, 3927 (1967).

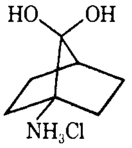
[36] H. O. House and J. W. Blaker, *ibid.*, **80**, 6389 (1958).

although ketone **2** exhibits a carbonyl stretching frequency of a strained system, the position of the stretching frequency may not be entirely due to strain in the bicyclic system.

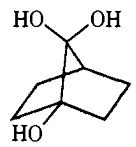
In any case, the addition of two tosylhydrazide molecules to C_7 does take place and the basic reason seems to point to relief of strain at the C_7 position. This behavior, quaternization of a strained carbonyl, appears to be common; *e.g.*, quadricyclanone is known to partially hydrate to a gem diol[26] and this fact is attributed to the relief of strain imposed by the trigonal carbonyl. Compounds **20**[37], **21**,[37] and **22**[37] have been isolated and



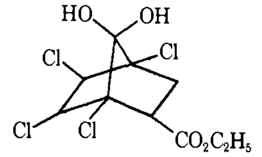
are the monohydrates of the corresponding ketones. From another point of view, ketal **23** could not be hy-



20

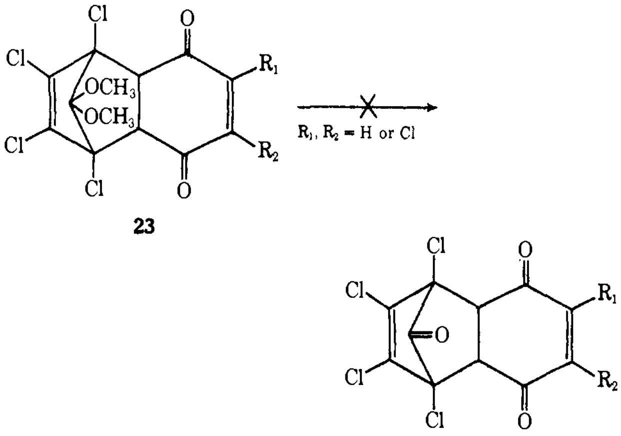


21



22

drolyzed under a variety of conditions to the respective ketone.[38] This behavior is consistent with the idea that



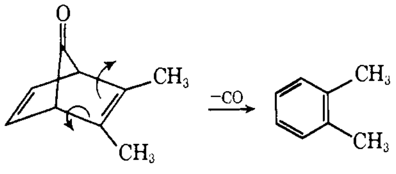
23

a carbonyl introduces strain into the system. In the light of these examples, ditosyl hydrazoketal **11** is not an unreasonable product to expect from ketone **2**. Although attempts to form the dimethyl ketal of **2** failed, this may be due to early decomposition of ketone **2** in the acid medium rather than any unreactivity of the carbonyl. Oxidative decomplexation of **11** by Ce^{IV} only gave decomposition products.

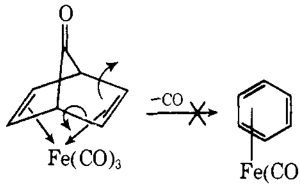
Ketone **2** acts as a normal ketone in its reactions with alkyl and aryl Grignard and lithium reagents (Scheme III). When **2** is treated with a lithium reagent, a short reaction time must be employed since long periods of mixing only give rise to decomposition. Apparently the lithium reagent or intermediate brings about decomposition[39] since the Grignard reagents did not cause extensive decomposition under similar conditions; no decomplexed alcohol was ever found in these decomposed solutions. Oxidative decomplexation of **12** ($R = C_6H_5$) with ceric salts gave 7-phenylnorbornadien-7-ol. Thus, an alternative route less tedious than the quadricyclanone path[40] is available to 7-substituted norbornadienes.

As illustrated in Scheme III, there was some success in having ketone **2** react with ylides. The formation of the simple 7-methylene or 7,8-epoxy compounds was not successful. These compounds are usually formed under strongly basic conditions (*e.g.*, NaH), and under these conditions (*i.e.*, strong base), ketone **2** decomposes. However, when ylides requiring weaker bases (*e.g.*, triethylamine) for their formation were used, products were formed: **14** and **15**. The effect of a strongly basic ylide may be to displace the organic ligand in **2** or to attack the carbonyls coordinated to iron.[39] In either case, decomposition is the end result. The structures of **14** and **15** are consistent with the observed elemental analyses and spectral characteristics (see Experimental Section).

In conclusion, it should be pointed out that the stability of **2** might be due to reasons other than those argued. Gassman[41] has pointed out that the orbital symmetry of ketone **24** is such that a concerted loss of carbon monoxide by a disrotatory transformation is allowed. Therefore, as a consequence of metal-olefin backbonding, population of the antibonding orbitals of the olefin may cause the analogous transformation of the complex **2** to be disallowed by symmetry,[42] hence, rendering **2** stable. It is hoped that experiments in progress may help to clarify this point.



24



Experimental Section

General. All melting points were taken in capillary tubes and are uncorrected. The infrared (ir) spectra were measured on Perkin-Elmer grating infrared spectrophotometers, Models 257 and 337; spectral calibrations were against the 1601-cm^{-1} band of polystyrene. Nuclear magnetic resonance (nmr) spectra were taken on a Varian A-60 spectrometer; measurements are expressed in parts per million (δ) downfield from tetramethylsilane used as an internal standard. Vapor phase chromatography (vpc) was carried

---

(37) D. E. Applequist and J. P. Klieman, *J. Org. Chem.*, **26**, 2178 (1961).

(38) H. Rakoff and B. H. Miles, *ibid.*, **26**, 2581 (1961).

(39) E. O. Fischer, V. Kiener, D. St. P. Bunbury, E. Frank, P. F. Lindley, and O. S. Mills, *Chem. Commun.*, 1378 (1968).

(40) A. F. Brezaeale, Ph.D. Thesis, University of Washington, Seattle, Wash., 1965.

(41) P. G. Gassman, D. H. Aue, and D. S. Patton, *J. Amer. Chem. Soc.*, **90**, 7271 (1968).

(42) (a) F. D. Mango and J. H. Shachtschneider, *ibid.*, **89**, 2484 (1967), and (b) H. Hogeveen and H. C. Vogler, *ibid.*, **89**, 2486 (1967), cite some possible examples of this effect. (c) This was also suggested by Drs. C. P. Lillya and D. F. Hunt in a private communication.

out isothermally on equipment as follows: (1) an F & M Model 720 thermal conductivity gas chromatograph using (a) a column 4 ft × 0.25 in. packed with 20% 1,2,3-tris(2-cyanoethoxy)propane (TCEP) on Chromosorb P (column 1a), (b) a column 4 ft × 0.25 in. packed with 20% ethylene glycol adipate on Chromosorb W (column 1b), (c) a column 2 ft × 0.25 in. packed with 20% methyl silicone rubber (General Electric) on Chromosorb W (column 1c); and (2) an F & M Model 810 flame ionization gas chromatograph using (d) a column 6 ft × 0.25 in. packed with 20% TCEP on Chromosorb P (column 2d), (e) a column 6 ft × 0.25 in. packed with 10% 1540 Carbowax on Chromosorb W (column 2e). The percentages of reaction products in mixtures were determined quantitatively by the internal standardization method. Relative percentages were determined from the vpc chromatograph by cutting out and weighing the paper under the curve drawn out by the recorder pen and comparing to mixtures of known composition (other methods used are indicated in appropriate places). Mass spectra were obtained on a Perkin-Elmer Hitachi RMU-6D mass spectrometer. Microanalyses were performed by Schwartzkopf Microanalytical Laboratory, Woodside, N. Y. Magnesium sulfate and sodium sulfate were anhydrous. Petroleum ether was low boiling (30–60°). A ratio of approximately 30 g of adsorbent to 1 g of organic material was used for column chromatography.

Preparation of Tricarbonyl(7-benzoyloxynorbornadiene)iron (7). 7-Benzoyloxynorbornadiene was prepared from norbornadiene in a manner similar to the method of Tanida and Tsuji.[43] The complexed ester **7** was obtained by modifying the procedure of Hunt, *et al.*[14] 7-Benzoyloxynorbornadiene (32.00 g, 150.8 mmol) was added to a fivefold excess of iron pentacarbonyl (115 ml). The reaction mixture was heated in an oil bath at 108–114° under nitrogen for 117–168 hr. It was necessary to control the temperature of the reaction to within ±3° of 111°. If the temperature of the reaction fell below 108°, then the reaction was not completed in the specified time. On the other hand, if the temperature was allowed to rise above 114°, only a finely divided precipitate of iron and carbonized starting material was isolated. Excess iron pentacarbonyl was removed *in vacuo* and the solid residue was dissolved in ether, filtered, and the ether removed *in vacuo*. The yield of dried crude tricarbonyl(7-benzoyloxynorbornadiene)iron (**7**) was 44 g (83%). Recrystallization from petroleum ether gave yellow needles, mp 102–103° (lit.[14] 100–101°).

Preparation of Tricarbonyl(7-norbornadienol)iron (8). Complex **8** was obtained by modifying a procedure of Hunt, *et al.*[14] Methylmagnesium iodide, prepared from methyl iodide (25.2 g, 0.178 mol) and magnesium metal (4.34 g, 0.178 g-atom) in ether, was added over 30 min under nitrogen to a stirred solution of tricarbonyl(7-benzoyloxynorbornadiene)iron (**7**) (25.0 g, 71.0 mmol) dissolved in a minimum amount of anhydrous benzene. The temperature of the reaction was controlled to 20–25° by means of a water bath. The reaction mixture was stirred an additional 90 min at room temperature. Ice water was poured into the reaction mixture and the organic layer was separated and dried over magnesium sulfate before filtering. Solvent was removed *in vacuo*, and the solid yellow mass was triturated with petroleum ether before filtering. The petroleum ether was saved and the solid alcohol **8** was recrystallized from petroleum ether–ether at −78°. The mother liquor from the crystallization and the petroleum ether from the filtration were combined and passed through an alumina column. Unreacted ester **7** and small amounts of side products were eluted with ether; subsequent elution with methanol afforded the product. The yield of tricarbonyl(7-norbornadienol)iron (**8**) was 12 g (68%, mp 89.5–94.0°). Recrystallizing from hexane gave yellow crystals: mp 100–100.2° (sealed, partially evacuated capillary tube) (lit.[14] 95–96.5°).

The Oxidation[23] of Tricarbonyl(7-norbornadienol)iron (8) to Tricarbonyl(7-norbornadienone)iron (2). Chlorosulfonic acid (8.40 g, 72.0 mmol) was added over a period of 30 min to a solution of pyridine (12.0 g, 152 mmol) in carbon tetrachloride (15 ml) while cooled in an ice bath. Following completion of the addition, the white salts (pyridine hydrochloride plus pyridine–sulfur trioxide complex) that formed were washed with ether several times and dried by passing a stream of nitrogen over the salts. (The pyridine hydrochloride was not removed by washing with water as described in Fieser.[44]) A solution of these salts in dimethyl sulfoxide (80 ml) was then added dropwise over a period of 30 min to a mixture, stirred under nitrogen in an ice bath, of dimethyl sulfoxide (40 ml), triethylamine (66 ml), and tricarbonyl(7-norbornadienol)iron (**8**) (6.00 g, 24.4 mmol). The reaction mixture was stirred an additional period of 30 min. During this time the reaction mixture became a deep red slush. The reaction mixture was added to an ice-cold 10% sodium chloride solution (200 ml). Ether (100 ml) was added to the mixture, shaken in a separatory funnel, and then suction filtered through infusorial earth (white calcine, USP). The red ether layer was separated and the water extracted an additional two times with ether. The ether layers were combined and washed with three portions of 10% sodium chloride solution (100 ml). After the ether was removed *in vacuo* (on a rotary evaporator) at room temperature, a red oil remained. The oil (which solidified when cooled) was dissolved in pentane (~400 ml) at room temperature. The pentane solution was filtered into a flask that was immersed in a Dry Ice–acetone bath. Tricarbonyl(7-norbornadienone)iron (**2**) immediately crystallized from the cold pentane. The solution was quickly suction filtered to obtain 4.15 g (70%) of ketone **2**. Additional recrystallizations (2–3) were necessary to obtain the product with optimum stability and purity. An analytical sample was obtained from pentane: mp 93–95° (sealed, partially evacuated capillary tube).

Anal. Calcd for $C_{10}H_6O_4Fe$: C, 48.82; H, 2.46. Found: C, 48.89; H, 2.51.

The spectral characteristics of **2** are as follows: ir ν ($CHCl_3$) 2049 and 1956 ($C \equiv O$), 1864 (w) and 1775 (s) (ketone $C=O$), 1304, 1154, 1084, 924, 902, and 844 cm^{-1}; nmr δ ($CDCl_3$) 3.65 (q, 2, J = 2.5 Hz, bridgehead H) and 3.02 (t, 4, J = 2.5 Hz, complexed vinyl H); mass spectrum (10 eV) *m/e* (rel intensity) 246 (0.50), 218 (0.64), 190 (30), 162 (78), 134 (100), and 78 (36); mol wt calcd for $C_{10}H_6O_4Fe$: 246.

The 2,4-dinitrophenylhydrazone (**10**) was prepared by the method of Iddles, *et al.*[31] Tricarbonyl(7-norbornadienone)iron (**2**) (0.40 g, 1.6 mmol) in anhydrous ethanol (10 ml) was added dropwise to a saturated solution of 2,4-dinitrophenylhydrazine (0.51 g, 2.6 mmol) in 2 *N* hydrochloric acid (100 ml) at room temperature. Upon addition of ketone **2**, a precipitate formed. After the addition of 2 *N* hydrochloric acid (50 ml), the reaction mixture was filtered. The precipitate was dissolved in ether and the ether was washed with 5% sodium bicarbonate solution (50 ml). Finally, the ether solution was washed three times with water (50 ml), dried over magnesium sulfate, filtered, and the ether removed *in vacuo*. An analytical sample was prepared from the residue by recrystallization from dichloromethane–hexane, mp 164° dec.

Anal. Calcd for $C_{16}H_{10}N_4O_7Fe$: C, 45.10; H, 2.37; N, 13.15. Found: C, 45.30; H, 2.50; N, 13.27.

Reaction of Tricarbonyl(7-norbornadienone)iron (2) with Triphenylphosphine. Tricarbonyl(7-norbornadienone)iron (**2**) (0.2016 g, 0.8190 mmol) and triphenylphosphine (0.2267 g, 0.8650 mmol) were heated together in a partially evacuated (0.025 mm) sealed tube at 140° for 20 min (the contents were melted together at 100° before bringing to 140°).[45] The tube was cooled to −78° before it was opened. The decomposed black mass was extracted with ether (1 ml), and toluene[46] (79.6 mg) was added for an internal standard. The solution was examined by vpc (column 2e, 50°). Benzene was found in 92% yield. The residue was extracted with chloroform and the solution was passed through a basic alumina Woelm, activity I) column. Chloroform separated a yellow band of material which was collected. This yellow chloroform solution was chromatographed an additional two times before the chloroform was finally removed *in vacuo*. A solid remained which was washed with ether. This yellow solid was tricarbonylbis(triphenylphosphine)iron (0.075 g): mp 265–270° dec [lit.[30] mp 272° dec]; ir ν (CS_2) 1887 cm^{-1} ($C \equiv O$) (lit.[30] 1885 cm^{-1}).

Experiments with triphenylarsine and triphenylstibine led to similar results.

Attempts to Trap 7-Norbornadienone (1) in a Diels–Alder Reaction by Ligand Displacement from Tricarbonyl(7-norbornadienone)iron (2). Experiment A. Tricarbonyl(7-norbornadienone)iron (**2**) (0.2048 g, 0.8340 mmol), 1,3-diphenylisobenzofuran (0.2032 g, 0.7510 mmol), triphenylphosphine (0.2300 g, 0.8760 mmol), and benzene (6 ml) were placed in a tube and the tube was sealed and then heated at 80° for 12.5 hr. The tube was cooled to room temperature, opened, and the contents filtered. The crystalline solid

---

(43) H. Tanida and T. Tsuji, *Chem. Ind.* (*London*), 211 (1963).

(44) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath, Boston, Mass., 1955, p 337.

(45) G. F. Emerson, L. Watts, and R. Pettit, *J. Amer. Chem. Soc.*, 87, 131 (1965).

(46) Toluene is well separated from benzene and gave good reproducibility (±5%) with known benzene–toluene mixtures.

residue was identified as tricarbonylbis(triphenylphosphine)iron (0.1712 g, 31% based on ketone **2**). Benzene was removed *in vacuo* from the filtrate and a carbon tetrachloride solution of the residue was passed through a basic alumina (Woelm, activity I) column. The separation of 9,10-diphenylanthracene was followed with a uv light as it was washed off the column by carbon tetrachloride. Upon solvent removal, crystalline 9,10-diphenylanthracene (56 mg, 23% based on 1,3-diphenylisobenzofuran) was characterized by the similarity of its melting point, the identity of its R_f value by thin-layer chromatography (tlc), and the superimposability of its infrared spectrum (KBr) to commercially available material (K & K Laboratories).

Experiment B. Ketone **2** (0.2066 g, 0.8400 mmol), 1,3-diphenylisobenzofuran (0.2034 g, 0.7520 mmol), and triphenylphosphine (0.2274 g, 0.8670 mmol) were placed in a glass tube which was evacuated to 0.025 mm before sealing. The contents were melted at 100° and then heated at 140° for 20 min. The tube was cooled to −78°, opened, and the contents extracted with 1 ml of ether. Toluene[46] (627 mg) was added for an internal standard. An aliquot was examined by vpc (column 2e, 50°). Benzene was found in 98% yield. The entire reaction mixture was extracted with chloroform and the chloroform was removed *in vacuo*. The residue was thoroughly washed with ether. This residue was identified as tricarbonylbis(triphenylphosphine)iron (0.2070 g, 37% based on ketone **2**). The ether solution was added to an equal volume of carbon tetrachloride and the mixture was passed through a basic alumina (Woelm, activity I) column and washed with carbon tetrachloride. A fluorescent band was separated and was washed off the column. Solvent was removed *in vacuo* and the solid which remained was identified as 9,10-diphenylanthracene (22 mg, 10% based on 1,3-diphenylisobenzofuran). Thin layer chromatography on alumina (6062 Eastman Chromatogram sheets) showed a single fluorescent spot of identical R_f with that of commercially available material (K & K Laboratories).

No adducts were found in experiments using furan or cyclopentadiene as trapping agents. Only tricarbonylbis(triphenylphosphine)iron could be isolated.

Thermal Decomposition of Tricarbonyl(7-norbornadienone)iron (2). Tricarbonyl(7-norbornadienone)iron (**2**) (0.2055 g, 0.8350 mmol) was placed in a glass tube which was evacuated to 0.025 mm before sealing. The tube was placed in an oil bath at 140° and heated for 22 min. A sudden, violent pyrolysis took place after 2 min which left a black mass of material. The tube was cooled to −78° before opening. Ether (1 ml) was used to wash out the organic material and toluene[46] (651 mg) was added for an internal standard. An aliquot was examined by vpc (column 2e, 50°). Benzene was found in 79% yield. Insoluble organic material and iron residues remained in the tube.

Attempt to Trap 7-Norbornadienone (1) in a Diels–Alder Reaction by Thermal Decomplexation of Tricarbonyl(7-norbornadienone)iron (2). Tricarbonyl(7-norbornadienone)iron (**2**) (0.1982 g, 0.8010 mmol) and 1,3-diphenylisobenzofuran (0.1984 g, 0.7340 mmol) were placed in a glass tube which was evacuated to 0.025 mm before sealing. The contents were melted at 100° and then heated at 140° for 20 min. The tube was cooled to −78°, opened, and the contents extracted with ether (1 ml). Toluene[46] was added (648 mg) for an internal standard and the mixture was examined by vpc (column 2e, 50°). Benzene was found in 86% yield. The ether solution along with a carbon tetrachloride extract of the residue was passed through a basic alumina (Woelm, activity I) column and the column was washed with carbon tetrachloride. A fluorescent band was separated and was washed off the column. The solvent was removed *in vacuo* and the solid which remained was identified as 9,10-diphenylanthracene (3 mg). Thin-layer chromatography on alumina (6062 Eastman Chromatogram sheets) showed a single fluorescent spot of identical R_f with that of commercially available material (K & K Laboratories).

Decomplexation of Tricarbonyl(7-norbornadienone)iron (2) with Ceric Ammonium Nitrate. Tricarbonyl(7-norbornadienone)iron (**2**) (0.500 g, 2.03 mmol), dissolved in acetone (50 ml), was treated with powdered ceric ammonium nitrate[47] (2.22 g) over a 4-min period. The mixture was stirred an additional minute and then poured into a saturated salt solution (50 ml). The acetone layer was removed and the salt solution was extracted with three portions of ether (10 ml). The organic layers were combined and dried over magnesium sulfate. The mixture was filtered and the magnesium sulfate was washed with three portions of ether (3 ml). Toluene[46] (165 mg) was added for an internal standard and the solution was examined by vpc (column 1b, 80°). Benzene was found in 104% yield (peak areas were determined by the method of approximate triangles and then determining the areas under the triangle).

Attempts to Trap 7-Norbornadienone (1) in a Diels–Alder Reaction during Oxidative Decomplexation. In two separate experiments tricarbonyl(7-norbornadienone)iron (**2**) (0.125 g, 0.508 mmol) and 1,3-diphenylisobenzofuran (0.138 g, 0.508 mmol) in acetone (10 ml) were treated with ceric ammonium nitrate[47] (1.00 g) at room temperature and at −78°. No 9,10-diphenylanthracene was found upon work-up at either temperature.

The Photolysis of Tricarbonyl(7-norbornadienone)iron (2) at Liquid Nitrogen Temperature, −196°. Experiment A. Tricarbonyl(7-norbornadienone)iron (**2**) (0.606 g, 2.46 mmol) and acetophenone (0.597 g, 4.97 mmol) were dissolved in 60 ml of a mixture of ether–pentane–ethanol (EPA, 3:3:5 ratio by volume); the resulting mixture was irradiated with a 450-W Hanovia lamp for 8 hr in a quartz tube immersed in liquid nitrogen. During this time the tube was rotated intermittently. The solution was then reduced to a small volume by means of a vacuum pump while maintaining the temperature at room temperature. Cyclohexanone[48] (0.0085 g) was then added for an internal standard. The mixture was examined by vpc (column 2d, 150°). A peak corresponding to quadricyclanone[26] (*vide infra* preparation of quadricyclanone) was found to be present in 2.0%. An aliquot of the photolysis mixture was examined on a preparative vpc (column 1a, 150°, retention time 24 min). A sample then was collected, after repeated injections, which had an infrared spectrum identical with quadricyclanone and which also gave a single vpc peak upon coinjection with quadricyclanone. Some starting ketone **2** was present after photolysis but was not recovered.

Experiment B. Ketone **2** (0.600 g, 2.44 mmol) and benzophenone (0.890 g, 5.44 mmol) were treated and analyzed as described above. Acetophenone[48] (0.100 g) was added to the residue for use as an internal standard.

The amount of quadricyclanone found was 0.77%. Starting ketone **2** was present after photolysis but was not isolated.

Experiment C. Ketone **2** (0.591 g, 2.40 mmol) and acetone (0.273 g, 4.70 mmol) were treated and analyzed as described in experiment A. Acetophenone[48] (0.0095 g) was used for an internal standard. Ketone **2** (0.273 g, 1.11 mmol) was recovered and the amount of quadricyclanone found (vpc column 2d, 150°), based on this recovery, was 5.32%.

Experiment D. Ketone **2** (0.600, 2.44 mmol) and furan (0.351, 5.15 mmol) were treated and analyzed as described in experiment A. Acetophenone[48] (0.0100 g) was used for an internal standard. Ketone **2** (0.320 g, 1.30 mmol) was recovered and the amount of quadricyclanone found (vpc, column 2d, 150°), based on this recovery, was 3.80%.

The Photolysis of Tricarbonyl(7-norbornadienone)iron (2) at Dry Ice Temperature, −78°. An ether solution of tricarbonyl(7-norbornadienone)iron (**2**) (0.151 g in 65 ml) was deoxygenated by bubbling through prepurified nitrogen before irradiating for 2 hr 54 min at −78° with a 450-W Hanovia lamp using a quartz tube. The mixture was filtered twice after the first hour and after the second hour of irradiation. Toluene[46] (450 mg) was added to the solution for use as an internal standard. Vpc (column 2d, 60°) showed benzene to be present in 56% yield. The ether was removed *in vacuo* and infrared spectral examination (neat) of the residue showed no carbonyl absorption due to quadricyclanone. Vpc examination of the residue at higher temperatures indicated no quadricyclanone was present.

Attempts to Trap 7-Norbornadienone (1) in a Diels–Alder Reaction during Photolytic Decomplexation. Tricarbonyl(7-norbornadienone)iron (**2**) (1.00 g, 4.07 mmol) and 1,3-diphenylisobenzofuran (1.00 g, 3.70 mmol) were dissolved in anhydrous ether (12.5 ml) and the solution was deoxygenated by passing a stream of nitrogen (prepurified) through the solution. The solution, in quartz glassware, was irradiated with a 450-W Hanovia lamp at a temperature of −78° for 105 min. Solvent was removed *in vacuo* and the

---

(47) L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Amer. Chem. Soc.*, 87, 3253 (1965).

(48) Retention time by vpc (column 2d, 150°): cyclohexanone 8 min, quadricyclanone 19 min; acetophenone 26 min. Known mixtures of ketone and quadricyclanone gave reproducible results to ±10%. The peak corresponding to quadricyclanone in the reaction mixtures was confirmed by coinjection of authentic quadricyclanone with an aliquot of the reaction mixture; no new peaks appeared and the peak assigned to quadricyclanone increased in size.

residue redissolved in carbon tetrachloride. This solution was passed through a basic alumina (Woelm, activity I) column and adsorbed material was eluted by washing with carbon tetrachloride. A light yellow band (which fluoresced under uv irradiation) was separated and was washed off the column with excess carbon tetrachloride (an additional 200 ml of carbon tetrachloride was used after the band appeared to have been removed). Removal of the solvent *in vacuo* gave 76 mg of 9,10-diphenylanthracene (6% based on 1,3-diphenylisobenzofuran), which was characterized by its identity (melting point and infrared spectrum) to commercially available material (K & K Laboratories). Methanol (100 ml) removed 475 mg of a mixture of dibenzoylbenzene[49] and 9,10-diphenylanthracene. The nature of this mixture was revealed by fluorescence under uv irradiation and examination of its infrared spectrum.

In a similar experiment ketone **2** (0.279 g, 1.14 mmol) and 1,3-diphenylisobenzofuran (0.280 g, 1.04 mmol), in anhydrous ether (70 ml), were irradiated as above for 12 hr 5 min (the mixture was filtered every 3 hr). Toluene[46] (0.103 g) was added for use as an internal standard and the mixture was examined by vpc (column 2e, 44°). Benzene was found in 44% yield. Column chromatography on basic alumina (Woelm, activity I) gave 9,10-diphenylanthracene (2 mg). Comparison to authentic material (K & K Laboratory) by thin-layer chromatography on silica gel (6061 Eastman Chromatograph sheets) gave an identical R_f value.

Preparation of Quadricyclanone.[26] Lithium aluminum hydride (2.01 g, 5.32 mmol) was added to an ether solution (20 ml) of 7-acetoxyquadricyclane[50] (8.00 g, 5.32 mmol). The mixture was stirred for 3.5 hr. Water addition followed by ether extraction was carried out. The ether was separated, dried over magnesium sulfate, and removed *in vacuo*. The crude 7-hydroxyquadricyclane[26,50] remained as an oil, 4.65 g (81%).

Pyridine–sulfur trioxide complex [prepared from chlorosulfonic acid (16.80 g, 144.0 mmol) and pyridine (24.00 g, 303.5 mmol) in carbon tetrachloride (*vide supra*)][44] in dimethyl sulfoxide (80 ml) was added dropwise, under nitrogen, to a solution of the crude 7-hydroxyquadricyclane (4.65 g, 42.0 mmol) in a mixture of triethylamine (132 ml) and dimethyl sulfoxide (10 ml).[22] The mixture was stirred an additional 2 hr at room temperature before adding 10% sodium chloride solution (500 ml); the resultant mixture was extracted with ether. The ether layer was washed several times with water before being dried over magnesium sulfate; removal of the ether *in vacuo* gave an oil. The oil was dissolved in pentane but pentane removal *in vacuo* only led to an oil. Pure quadricyclanone was isolated by preparative vpc (column 1c, 110°) of the crude product. The infrared spectrum was identical with that recorded by Story and Fahrenholtz.[26]

Reduction of Tricarbonyl(7-norbornadienone)iron (2) to Tricarbonyl(7-norbornadienol)iron (8). Sodium borohydride (15.5 g, 0.408 mmol) was added to a methanol solution (1 ml) of tricarbonyl(7-norbornadienone)iron (**2**) (0.200 g, 0.815 mmol) in an ice bath. The mixture was stirred for 10 min before pouring into ice water (20 ml). Product immediately precipitated. The mixture was extracted with ether and the ether extract dried over magnesium sulfate, filtered, and concentrated *in vacuo*. The yield of tricarbonyl(7-norbornadienol)iron (**8**)[14] was 0.15 g (75%).

Preparation of Tricarbonyl(7-methylnorbornadien-7-ol)iron. Procedure A. Tricarbonyl(7-norbornadienone)iron (**2**) (0.95 g, 3.9 mmol), in portions, was added to methylmagnesium iodide, prepared from methyl iodide (0.634 g, 4.46 mmol) and magnesium (0.118 g, 4.85 mg-atoms), in ether (10 ml) under a nitrogen atmosphere and in an ice bath. The mixture was stirred for 30 min before water (10 ml) was added to the mixture. The ether layer was separated, dried over magnesium sulfate, and filtered, and the ether was removed *in vacuo*. Recrystallization of the residual solid yielded 0.60 g (64%) of tricarbonyl(7-methylnorbornadien-7-ol)iron; 0.07 g of ketone **2** was recovered.

Procedure B. Methyllithium (Alfa Inorganics, 1.92 *M*, 2.50 ml, 4.80 mmol) in ether was added dropwise to a vigorously stirred ether solution (50 ml) of ketone **2** (1.00 g, 4.07 mmol) in an ice bath and under a nitrogen atmosphere. The mixture was stirred for 1 min before ice water (10 ml) was added to the mixture. The mixture was extracted with ether, the ether layer was separated, dried over magnesium sulfate, and filtered, and the ether was removed *in vacuo*. The residue was extracted with pentane, and the pentane solution cooled to −78° to give 0.22 g of alcohol. The residue (following pentane extraction) was taken up in carbon tetrachloride and the solution passed through a Florisil column. Impurities were eluted with carbon tetrachloride before yellow alcohol was eluted by benzene; benzene was then removed *in vacuo* and the solid was recrystallized from pentane to give an additional 0.21 g of product. Total recovered alcohol was 0.43 g (40%). The analytical sample prepared from pentane gave yellow needles, mp 78–79° (sealed, partially evacuated capillary tube).

Anal. Calcd for $C_{11}H_{10}O_4Fe$: C, 50.42; H, 3.85. Found: C, 50.04; H, 3.85.

The spectral characteristics of tricarbonyl(7-methylnorbornadien-7-ol)iron are as follows: ir ν ($CHCl_3$) 3594 (free O–H), 3559 (intramolecular O–H), 3434 (intermolecular O–H), 2934, 2874, 2045 and 1952 ($C\equiv O$), 1386, 1347, 1174, 1136, and 1076 cm^{-1}; nmr δ ($CDCl_3$) 3.04 and 2.97 (overlapping m, 6, bridgehead and complexed vinyl H), 2.37 (broad s, 1, O–H), and 1.17 (s, 3, $-CH_3$).

Preparation of Tricarbonyl(7-ethyl-7-norbornadienol)iron. Ethylmagnesium bromide, prepared from ethyl bromide (0.53, 4.9 mmol) and magnesium (0.12 g, 4.9 mg-atoms), in ether (10 ml) was added dropwise to tricarbonyl(7-norbornadienone)iron (**2**) (0.93 g, 3.8 mmol) in ether (10 ml) in an ice bath and under a nitrogen atmosphere. The mixture was stirred for 30 min before ice water (10 ml) was added and the mixture was extracted with ether. The ether was dried over sodium sulfate, filtered, and the ether removed *in vacuo*. The residue was distilled at 65° (0.025 mm) onto a cold finger. The yield of tricarbonyl(7-ethyl-7-norbornadienol)iron was 0.52 g (46%). An analytical sample obtained from pentane gave yellow needles, mp 56–57° (sealed, partially evacuated capillary tube).

Anal. Calcd for $C_{12}H_{12}O_4Fe$: C, 52.21; H, 4.38. Found: C, 52.17; H, 4.43.

The spectral characteristics of tricarbonyl(7-ethylnorbornadien-7-ol)iron are as follows: ir ν ($CHCl_3$) 3595 (free O–H), 3560 (intramolecular O–H), 3445 (intermolecular O–H), 2975, 2940, 2885, 2046 and 1906 ($C\equiv O$), 1320, 1175, 1143, 1067, and 993 cm^{-1}; nmr δ ($CDCl_3$) 3.05 and 3.00 (overlapping m, 6, bridgehead and complexed vinyl H), 2.15 (s, 1, O–H), 1.53 (q, 2, J = 7 Hz, $-CH_2CH_3$) and 0.84 (t, 3, J = 7 Hz, CH_2CH_3).

Preparation of Tricarbonyl(7-vinylnorbornadien-7-ol)iron. Tricarbonyl(7-norbornadienone)iron (**2**) (1.00 g, 4.07 mmol), dissolved in tetrahydrofuran (1.2 ml), was added to vinylmagnesium bromide, prepared from vinyl bromide (0.979 g, 9.15 mmol) and magnesium (0.122 g, 5.02 mg-atoms) in tetrahydrofuran (3.5 ml), in an ice bath and under a nitrogen atmosphere. The mixture was stirred for 30 min before ice water (10 ml) was added. The mixture was extracted with ether, the ether layer was separated, and the ether was removed *in vacuo*. The residue was extracted with pentane and the pentane solution was passed through a Florisil column. Benzene was used as eluent to separate a fast moving red band of ketone **2** (0.154 g) from a slower moving yellow band of tricarbonyl-(7-vinylnorbornadien-7-ol)iron (0.165 g, 18%). The analytical sample prepared from hexane gave yellow needles, mp 64.5–65.5°.

Anal. Calcd for $C_{12}H_{10}O_4Fe$: C, 52.59; H, 3.68. Found: C, 52.69; H, 3.78.

The spectral characteristics of tricarbonyl(7-vinylnorbornadien-7-ol)iron are as follows: ir ν ($CHCl_3$) 3582 (free O–H), 3562 (intramolecular O–H), 3432 (intramolecular O–H), 3077 (vinyl$=CH_2$), 2047 and 1952 ($C\equiv O$), 1175, 1007, 997, and 947 cm^{-1}; nmr δ ($CDCl_3$) 6.35–5.09, (complex ABX m, 3, $-CH=CH_2$), 3.07 (m, 6, bridgehead and complexed vinyl H), and 2.13 (s, 1, O–H).

Preparation of Tricarbonyl(7-benzoylmethylene-7,8-epoxynorbornadiene)iron (14). Dimethyl(benzoylmethyl)sulfonium bromide (3.18 g, 12.2 mmol), prepared from α-bromoacetophenone and dimethyl sulfide in a 0.83 : 1.0 molar ratio in benzene, was added as a solid to tricarbonyl(7-norbornadienone)iron (**2**) (1.00 g, 4.07 mmol), dissolved in triethylamine (11 ml) and dimethyl sulfoxide (20 ml) in an ice bath.[51] The mixture was stirred for 5.5 hr. Whenever the mixture solidified, it was removed from the ice bath, allowed to liquefy, and then placed back into the ice bath. Ice water (125 ml) was added to the mixture, then extracted with ether, and the ether was removed *in vacuo*. The residue was dissolved in a minimum amount of carbon tetrachloride and the solution was passed through a Florisil column. Carbon tetrachloride followed by benzene removed colored bands, which were not product. Tri-

---

(49) Oxidation of 1,3-diphenylisobenzofuran on the alumina column results in dibenzoylbenzene. Yellow solutions of 1,3-diphenylisobenzofuran decolorized rapidly on the support, and elution with polar solvents only gave dibenzoylbenzene.

(50) H. G. Richey, Jr., and N. C. Buckley, *J. Amer. Chem. Soc.*, **85**, 3057 (1963).

(51) (a) A. W. Johnson and R. T. Amel, *Tetrahedron Lett.*, 816 (1966); (b) K. W. Ratts and A. N. Yao, *J. Org. Chem.*, **31**, 1185 (1966).

carbonyl(7-benzoylmethylene-7,8-epoxynorbornadiene)iron (**14**), a light orange band, was washed from the column with chloroform. The chloroform was removed *in vacuo* and the residue recrystallized once from hexane to give light orange needles, mp 140–142°. The analytical sample was prepared from hexane, mp 145–147° dec.

Anal. Calcd for $C_{18}H_{12}O_5Fe$: C, 59.37; H, 3.32. Found: C, 59.34, H, 3.37.

The spectral characteristics of **14** are as follows: ir ν (CCl_4), 2070 and 1985 ($C\equiv O$), 1655 and 1650 (epoxy, phenyl $C=O$), 1610, 1575, 1455, 1395, 1340, 1235, 1050, 1030, and 980 cm^{-1}; nmr δ ($CDCl_3$) 7.50 (m, 5, Ar–H), 5.82 (s, 1, H_8), 5.44 (m, 2, J = 3.5 Hz, $H_{5,6}$, deshielding from 7,8-epoxide), 5.15 (center, dd, 1, J = 11 Hz, J = 3.5 Hz, H_2, deshielding from phenyl ketone), 3.37 (m, 2, $H_{1,4}$), and 3.00 (center, dd, J = 11 Hz, J = 3.5 Hz, H_3, complexed vinyl proton).

Preparation of Tricarbonyl(7-carbethoxymethylenenorbornadiene)iron (15). Carbethoxymethyl(triphenyl)phosphonium bromide (5.22 g, 12.2 mmol), prepared from ethyl α-bromoacetate and triphenylphosphine in a 1.0:0.95 mole ratio in benzene, was added as a solid to tricarbonyl(7-norbornadienone)iron (**2**) (1.00 g, 4.07 mmol), dissolved in triethylamine (11 ml) and dimethyl sulfoxide (20 ml) at ice bath temperature.[52] The mixture was stirred an additional 5.5 hr. Whenever the mixture solidified, it was removed from the ice bath, allowed to liquefy, and then placed back in the ice bath. Ice water (125 ml) was added to the mixture and then extracted with ether. The ether layer was separated and the ether was removed *in vacuo*. The residue was extracted with pentane and the pentane was removed *in vacuo*. This extraction process was repeated an additional two times before the residue was dissolved in cyclohexane. The cyclohexane solution was passed through a Florisil column (8 g). Elution with cyclohexane (250 ml) yielded 0.60 g of tricarbonyl(7-carbethoxymethylenenorbornadiene)iron (**15**) (mp 56–56.5°); further elution with benzene (30 ml) gave an additional 0.14 g. The total amount of **15** was 0.74 g (58%). An analytical sample prepared from hexane gave beige crystals, mp 56–56.5°.

Anal. Calcd for $C_{14}H_{12}O_5Fe$: C, 53.20; H, 4.08. Found: C, 53.14; H, 3.96.

The spectral characteristics of **15** are as follows: ir ν ($CHCl_3$) 2946, 2906, 2876, 2040 and 1948 ($C\equiv O$), 1706 (conjugated ester $C=O$), 1679, 1374, 1344, 1289, 1275, 1186, 1103, and 1036 cm^{-1}; nmr δ ($CDCl_3$) 4.80 (s, 1, H_8), 4.64 (m, 1, J = 2.5 Hz, H_1), 4.12 (q, 2, J = 7 Hz, OCH_2CH_3), 3.58 (m, 1, J = 2.5 Hz, H_4), 3.14 (t, 4, J = 2.5 Hz, $H_{2,3,5,6}$), and 1.27 (t, 3, J = 7 Hz, CH_2CH_3).

Preparation of Tricarbonyl(7-phenylnorbornadien-7-ol)iron. Procedure A. Tricarbonyl(7-norbornadienone)iron (**2**) (1.00 g, 4.07 mmol) in ether (15 ml) was added dropwise to phenylmagnesium bromide, prepared from bromobenzene (0.80 g, 5.1 mmol) and magnesium (0.12 g, 4.9 mg-atoms) in ether (15 ml) in an ice bath and under a nitrogen atmosphere. The mixture was stirred for 45 min before ice water (10 ml) was added. The mixture was extracted with ether, the ether layer was separated, and the ether was removed *in vacuo*. The residue was dissolved in carbon tetrachloride and passed through a Florisil column; the column was washed with carbon tetrachloride until a small red band separated from a large yellow band. Benzene was then used to remove both bands from the column. The material making up the red band (after benzene was removed *in vacuo*) was ketone **2** (0.13 g). The material from the yellow band (after benzene was removed *in vacuo*) yielded 0.42 g (37%) of tricarbonyl (7-phenylnorbornadien-7-ol)iron.

Procedure B. Phenyllithium (Alfa Inorganics, 1.91 *M*, 2.50 ml, 4.77 mmol) in benzene–ether (70:30) was added dropwise to ketone **2** (1.00 g, 4.07 mmol) in benzene–ether (70:30, 50 ml) in an ice bath and under a nitrogen atmosphere. The mixture was stirred for 5 min before ice water (10 ml) was added. The mixture was extracted with ether; the ether layer was separated and the ether removed *in vacuo*. The residue was dissolved in a minimum of carbon tetrachloride and the solution passed through a Florisil column. The column was washed with carbon tetrachloride until a light gray band separated from a yellow band and finally was eluted from the column. This band contained biphenyl.[53] The yellow band was eluted with benzene. The benzene was removed *in vacuo* and the residue was recrystallized once from pentane to yield 0.72 g (55%) of product. The analytical sample prepared from hexane gave yellow needles, mp 92–93° (sealed, partially evacuated capillary tube).

Anal. Calcd for $C_{16}H_{12}O_4Fe$: C, 59.15; H, 3.97. Found: C, 59.02; H, 3.72.

The spectral characteristics of tricarbonyl(7-phenylnorbornadien-7-ol)iron are as follows: ir ν ($CHCl_3$) 3585 (free O–H), 3550 (intramolecular O–H), 3420 (intermolecular O–H), 3070 (aromatic C–H), 2044 and 1949 ($C\equiv O$), 1447, 1349, 1173, 1060, and 912 cm^{-1}; nmr δ ($CDCl_3$) 7.29 (m, 5, Ar-H), 3.42 (m, 2, J = 2.5 Hz, bridgehead H), 3.08 (t, 2, J = 2.5 Hz, complexed vinyl H), 2.77 (t, 2, J = 2.5 Hz, complexed vinyl H), and 2.50 (s, 1, O–H).

Decomplexation of Tricarbonyl(7-phenylnorbornadien-7-ol)iron to Give 7-Phenyl-7-norbornadienol (16). Ceric ammonium nitrate (2.00 g, 3.65 mmol) was added to tricarbonyl(7-phenylnorbornadien-7-ol)iron (0.410 g, 1.27 mmol) in acetone (50 ml) at room temperature.[47] The mixture was stirred for 2 min before adding it to a saturated salt solution (50 ml). The mixture was extracted with ether and the ether layer was extracted with water. The ether layer was dried over sodium sulfate, filtered, and the ether removed *in vacuo*. A light yellow oil remained. A pentane solution of the oil was dried over sodium sulfate, filtered, and the pentane removed *in vacuo* to give 0.20 g (85%) of 7-phenylnorbornadien-7-ol (**16**), a light yellow oil. The infrared spectrum and nuclear magnetic resonance spectrum were identical with those reported in the literature.[40]

Attempted Preparation of the Tosylhydrazone of Tricarbonyl(7-norbornadienone)iron (2). Tricarbonyl(7-norbornadienone)iron (**2**) (1.6 g, 6.5 mmol), in ethanol (10 ml, 95%), was added dropwise to a vigorously stirred solution of *p*-toluenesulfonylhydrazide (2.0 g, 11 mmol), in 2 *N* hydrochloric acid (25 ml) in an ice bath. Almost immediately a light yellow precipitate formed. The mixture was stirred for 2 hr before filtering. The yellow precipitate was washed with water and was air dried. The solid was purified by dissolving in dichloromethane, adding hexane until a light precipitate developed, and then cooling to 0°. The yield of product was 1.7 g.

The same material can be formed by adding *p*-toluenesulfonylhydrazide (0.834 g, 4.48 mmol), dissolved in 2 *N* hydrochloride acid (12 ml), dropwise to a vigorously stirred solution of ketone **2** (1.00 g, 4.07 mmol) in ethanol (12 ml, 95%) in an ice bath. The yield of product prepared in this manner was 0.90 g. An analytical sample was prepared by recrystallizing from dichloromethane–hexane, mp 143° dec. Attempts to prepare an analytical sample by sublimation or column chromatography on alumina or Florisil only resulted in decomposition.

Anal. Calcd for tosylhydrazone of ketone **2**, $C_{17}H_{14}N_2O_5SFe$: C, 49.30; H, 3.41; N, 6.76; mol wt, 414. Calcd for 2:1 addition of *p*-toluenesulfonylhydrazide to ketone **2**, $C_{24}H_{24}N_4O_7S_2Fe$: C, 48.01; H, 4.03; N, 9.33; mol wt, 600. Found: C, 48.17, 47.93; H, 4.15, 4.09; N, 9.09; 9.36; mol wt, 607 (osmometry, dioxane).

The spectral characteristics of the bisadduct **11** are as follows: ir ν (CS_2) 3310, 3252, 3230, 2040 and 1925 ($C\equiv O$), 1342, 1318, 1310, 1215, 1160, 1148, 820, and 768 cm^{-1}; nmr δ (DMSO-d_6), 7.90 [broad s, 2, SO_2NHNH–), 7.53 [$(AB)_2$, 8, Ar–H], 4.67 (broad s, 2, SO_2NHNH–), 2.92 (broad s, 6, bridgehead and complexed vinyl H), and 2.40 (s, 6, $ArCH_3$). Any attempt to obtain a parent peak by mass spectrometry was not successful. The low vapor pressure of the sample coupled with its heat sensitivity caused extensive decomposition in the ionizing chamber before a parent peak resulted.

Attempts to isolate the organic moiety of the bisadduct **11** were not successful. Oxidative decomplexation with ceric ammonium nitrate[47] or ferric chloride[47] gave resinous material; small quantities of the tosylhydrazone of acetone were isolated.

Further work on bisadduct **11** to remove a mole of *p*-toluenesulfonylhydrazide only led to decomposition.

Acknowledgment. We gratefully acknowledge financial support by the Petroleum Research Fund, administered by the American Chemical Society (1061-G1), the Research Corporation, and the National Science Foundation (GP-7924).

---

[52] S. Tripett and D. M. Walker, *J. Chem. Soc.*, 1266 (1961).

[53] Biphenyl was found to be an impurity in the phenyllithium.