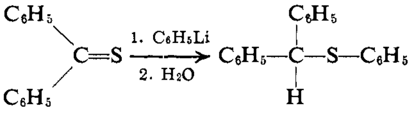
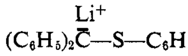
wish to report a reaction which illustrates both phenomena and reveals the possibility of inverse addition of organometallics to carbon–heteroatom multiple bonds.

Reaction of phenyllithium in ether–benzene with equimolar thiobenzophenone at −70 or 25° gives immediate decolorization of the blue thioketone solution. Aqueous quenching followed by extractive and triturative or chromatographic work-up gives a 30–40% isolated yield of benzhydryl phenyl sulfide (**1**).[3] Quenching the reaction solution immediately after disappearance of the blue color of thiobenzophenone with methanol-O-*d* (94 atom % *d*) gives **1** with 84% deuterium at the benzhydryl carbon, as shown by pmr and mass spectrometry, suggesting **2** as a reaction intermediate.



$$(C_6H_5)_2C{=}S \xrightarrow[2.\ H_2O]{1.\ C_6H_5Li} C_6H_5{-}C(C_6H_5)(H){-}S{-}C_6H_5$$

1



$$\overset{Li^+}{(C_6H_5)_2\bar{C}}{-}S{-}C_6H_5$$

2

$(C_6H_5)_3C{-}S^*$

3

$(C_6D_5)_2CHSC_6H_5$

4

The possibility that thiobenzophenone and phenyllithium react by initial addition to carbon to give the anion or radical **3** which rearranges to **2** or its precursor[4] is discounted by the observation that thiobenzophenone-d_{10} reacts with phenyllithium to give benzhydrylphenyl-d_{10} sulfide (**4**) containing less than 3% S-phenyl-d_5 material.[5] Reaction of thiobenzophenone with phenylmagnesium bromide produces **1** in 10% yield. *n*-Butylbenzhydryl sufide is obtained in 25% yield (glpc) by reaction of *n*-butyllithium with thiobenzophenone.

Although reports of the reactions of arylthioketones and organometallics usually stress the formation of tetraarylethylene sulfides and tetraarylethylenes,[6] products resulting from thiophilic attack on thiocarbonyls are precedented with organometallics,[7] radicals,[8] diazo compounds,[9] and other nucleophiles.[10, 11] It has been suggested that the polarization of a thiocarbonyl group is toward a negative carbon from a positive sulfur on the basis of dipole moment measurements.[12] The present results are consistent with initial thiophilic attack on sulfur by the organometallic to give an intermediate stabilized anion, but we cannot discount the prior intermediacy of radicals. The mode of addition is inverse to that usually observed for the reaction of carbon–heteroatom multiple bonds and organometallics. Further study of the scope[13] and mechanism of this reaction is in progress.

Acknowledgment. We are grateful to the Alfred P. Sloan Foundation and the Public Health Service (GM 12595) for support.

Helmkamp, and M. F. Rettig, *J. Amer. Chem. Soc.*, **91**, 5239 (1969); B. M. Trost, R. LaRochelle, and R. C. Atkins, *ibid.*, **91**, 2175 (1969); C. R. Johnson and J. J. Rigau, *ibid.*, **91**, 5398 (1969); R. Tang and K. Mislow, *ibid.*, **91**, 5644 (1969), and references cited therein.

(3) The product was unambiguously identified by spectral and melting point comparisons with authentic material prepared by the reaction of thiophenol and diphenyldiazomethane: A. Schoenberg, O. Schutz, and J. Peter, *Ber. Deut. Chem. Ges. B*, **62**, 1663 (1929).

(4) R. West and H. F. Stewart, *J. Amer. Chem. Soc.*, **92**, 853 (1970); E. Grovenstein, Jr., and Y. Cheng, *Chem. Commun.*, 101 (1970); H. E. Zimmerman and A. Zweig, *J. Amer. Chem. Soc.*, **83**, 1196 (1961).

(5) The location of the deuterated phenyl rings was determined by mass spectrometry. The fragmentation of 1 shows major peaks for $[C_6H_5S]\cdot^+$ and $[(C_6H_5)_2CH]^+$. The fragmentation of **4** shows the former peak unshifted and the latter peak 10 amu higher.

(6) E. Campaigne, "Chemistry of the Carbonyl Group," S. Patai, Ed., Interscience, New York, N. Y., p 942; the formation of the episulfides and ethylenes could involve intermediates analogous to **2**, as could a number of other reactions of thiocarbonyl compounds.

(7) A. Schoenberg, E. Singer, E. Frese, and K. Praefcke, *Ber. Deut. Chem. Ges. B*, **98**, 3311 (1965), have reported that sodium acetylide and thiobenzophenone give 1,2-thiabenzhydrylacetylene.

(8) A. Ohno, Y. Ohnishi, M. Fukuyama, and G. Tsuchihashi, *J. Amer. Chem. Soc.*, **90**, 7038 (1968); K. Uneyama, T. Sadakaye, and S. Oae, *Tetrahedron Lett.*, 5193 (1969).

(9) A. Schoenberg, D. Cernik, and W. Urban, *Ber. Deut. Chem. Ges. B*, **64**, 2577 (1930); A. Schoenberg, B. Koenig, and E. Singer, *ibid.*, **100**, 767 (1967); W. J. Middleton, *J. Org. Chem.*, **34**, 3201 (1969).

(10) Noncarbon nucleophiles are reported to add to the sulfur of thiocarbonyls: W. J. Middleton and W. H. Sharkey, *ibid.*, **30**, 1384 (1965); G. H. Birum, U. S. Patents 3,116,335 (1963), *Chem. Abstr.*, **60**, 10549*d* (1964); 2,931,755 (1960), *Chem. Abstr.*, **54**, 15245*b* (1960); and 3,172,803 (1965), *Chem. Abstr.*, **62**, 14727*c* (1965).

(11) Analogous reactions between trivalent phosphorus nucleophiles and ketones which can stabilize a negative charge on carbon have been reported by Ramirez and coworkers. F. Ramirez, *Accounts Chem. Res.*, 1, 168 (1968), and references cited therein.

(12) R. H. Lumbroso and C. Andrieu, *Bull. Soc. Chim. Fr.*, 3201 (1966).

(13) Reaction of phenyllithium with carbon disulfide and subsequent hydrolysis with water and treatment of the resulting mixture with methyl iodide give 12% thioanisole as well as the expected methyl dithiobenzoate.[14] The carbon disulfide was purified by distillation and filtration through alumina.

(14) E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. IV, Chemical Publishing Co., New York, N. Y., 1962, p 38.

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Received March 26, 1970

Cycloaddition Reactions of Cycloheptatriene and 2,5-Dimethyl-3,4-diphenylcyclopentadienone[1]

Sir:

Following the prediction of concerted cycloadditions of order greater than [4 + 2] made by Woodward and Hoffmann in 1965,[2] several examples of the [6 + 4] cycloaddition reaction were discovered.[3] Although the [6 + 4] cycloaddition elucidated herein has been mentioned briefly,[3e,4] we wish to report preliminary evidence concerning the concertedness of this reaction, and, in addition, to outline the complexity of the reaction paths observed.

Cycloheptatriene and 2,5-dimethyl-3,4-diphenylcyclopentadienone (VII) form 1:1 adducts I, mp 145–146°, II, mp 171° (needles) and mp 196–197° (prisms), III, mp 199–200°, and IV, mp 158–159°, a decarbonylated 1:1 adduct V, mp 198–199°, and a 2:1 adduct VI, mp 225–226°.[5]

---

(1) Taken in part from K. N. Houk, Ph.D. Dissertation, Harvard University, 1968.

(2) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 2046 (1965).

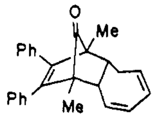
(3) (a) R. C. Cookson, B. V. Drake, J. Hudec, and A. Morrison, *Chem. Commun.*, 15 (1966); S. Itô, Y. Fujise, T. Okuda, and Y. Inoue, *Bull. Chem. Soc. Jap.*, **39**, 135 (1966); (b) T. Nozoe, T. Mukai, K. Takase, and T. Takase, *Proc. Jap. Acad.*, **28**, 477 (1952), isolated an adduct whose structure was proven by Cookson;[3a] (c) S. Ito, Y. Fujise, and M. C. Woods, *Tetrahedron Lett.*, 1059 (1967); (d) L. A. Paquette and J. H. Barrett, *J. Amer. Chem. Soc.*, **88**, 2590 (1966); (e) L. A. Paquette, J. H. Barrett, and D. E. Kuhla, *ibid.*, **91**, 3616 (1969), and references therein. (f) In modern terminology, these are all $[_\pi 6_s + _\pi 4_s]$ cycloadditions: R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

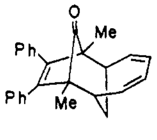
(4) (a) R. B. Woodward, *Chem. Soc., Spec. Publ.*, No. 21, 217 (1967); (b) H. Kwart and K. King, *Chem. Rev.*, **68**, 415 (1968); (c) G. B. Gill, *Quart. Rev., Chem. Soc.*, **22**, 338 (1968); (d) D. Seebach, *Fortsch. Chem. Forsch.*, 11, 177 (1968).

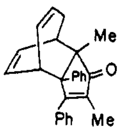
When equimolar amounts (0.5 M) of VII (as the dimer[6]) and cycloheptatriene were dissolved in tetrachloroethylene at 120°, nmr monitoring of the ensuing reaction revealed initial formation of the [4 + 2] adduct I and the [6 + 4] adduct II, while, after 7 hr, the amount of [4 + 2] adduct I began to decrease as the amount of III increased. After 30 hr, I had been consumed at the expense of III. Heating a pure sample of [4 + 2] adduct I at 120° resulted in its quantitative rearrangement to III in less than 30 hr. These results demonstrate that the initial cycloaddition gives only I and II, and I subsequently undergoes Cope rearrangement to III. Substantially the same rates of formation of I, II, and III were found in acetic acid-d_4, ruling out dipolar intermediates in their formation.[7]

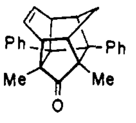
When VII and excess cycloheptatriene were heated together at 170° for 36 hr, II (32%), III (49%), IV (5%), and V (6%) were isolated by preparative layer chromatography. The Cope rearrangement product III was stable above 200°, while the [6 + 4] adduct II slowly and quantitatively rearranged to caged adduct IV at 170°.

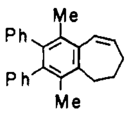
Unequivocal structural assignments were made for I–VI on the basis of spectral and chemical investigations. In particular, the [4 + 2] nature of I was concluded from the ir (CCl_4; 5.64 μ) and nmr ($CDCl_3$; 1.24 (3 H, s) and 1.38 ppm (3 H, s)), while spin decoupling experiments verified the presence of a 1,3-diene system. The *endo* nature of adduct I was demonstrated by its facile Cope rearrangement to III, which would be impossible for the analogous *exo* adduct.

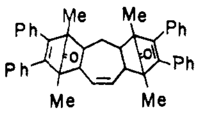

I

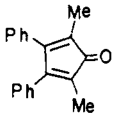

II


III


IV

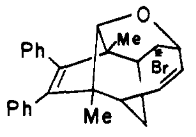

V

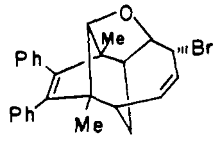

VI


VII

The 2:1 adduct VI, mp 225–226°, formed by heating I with excess VII, exhibited two sharp methyl resonances at 1.28 and 1.32 ppm in the nmr ($CDCl_3$). The equivalence of two pairs of equivalent methyl groups indicates the 2:1 adduct must be the result of two *endo* Diels–Alder additions, but VI may be either the *syn* or *anti* 2:1 adduct.

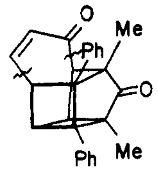
The structure of the [6 + 4] adduct II was shown by the ir (CCl_4; 5.69 μ) and the methyl singlet at 1.12 ppm and broad singlet for four olefinic hydrogens centered at 6.0 ppm in the nmr ($CDCl_3$). Catalytic reduction of II gave a tetrahydro adduct, mp 178–178.5°, which was different from the two Diels–Alder adducts formed on reaction of VII with cycloheptene.[8] The stereochemistry of the [6 + 4] cycloaddition was proven by lithium aluminum hydride reduction of II, which produced a single alcohol, VIII, mp 184.5°. Bromination of VIII gave a mixture of bromo ethers, IX, mp 140–141° (68%), and X, mp 124–126° (30%). IX was inert to both zinc in acetic acid and sodium iodide in acetone, while allylic bromide X was readily converted to alcohol VIII under these conditions, confirming the absence of skeletal rearrangements during bromination and proving the *exo* nature of the [6 + 4] cycloaddition.

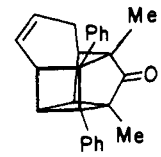

IX


X

The *endo* structure of III was confirmed by sequential N-bromosuccinimide bromination, silver oxide hydrolysis, photolytic cyclobutane formation, and Jones oxidation, which produced diketone XI, mp 238–240° (*syn* or *anti* carbonyls), in 40% overall yield from III. The presence of an α,β-unsaturated ketone (ir (CCl_4) 5.66, 6.00 μ) in XI requires that III be the *endo* structure shown. In addition, photolysis of III produced XII, mp 173–175°, in 80% yield.

Compound IV, the product of thermal isomerization of [6 + 4] adduct II, was shown to be a caged adduct (ir (CCl_4) 5.66 μ; uv λ_{max} (95% EtOH) 255 nm (ϵ 800)) possessing two olefinic protons in the nmr. Double-resonance experiments verified the near symmetry of the cycloheptene ring, and the base peak due to VII in the mass spectrum verified the presence of the VII moiety intact in IV, leading to the structural assignment shown. The most reasonable mechanism for formation of IV involves a [1,3]-sigmatropic shift *via* diradical XIII,[9] followed by an intramolecular Diels–Alder reaction.


XI


XII

The structure of the decarbonylated product V was verified by the methyl resonances at 2.00 and 2.08 ppm and two olefinic hydrogens in the nmr ($CDCl_3$). Catalytic hydrogenation gave XIV, which was also obtained by thermolysis of the Diels–Alder adducts of VII and cycloheptene[8] followed by aromatization with bromine at room temperature. V must arise from the thermal decarbonylation of the bridged 3-cyclopentenone I,[10] followed by a sequence of 1,5-sigmatropic shifts of hydrogen.[11,3f]

I and II are formed by concerted cycloaddition of VII to cycloheptatriene. The lack of dependence of rate

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[5] All new compounds gave elemental and spectral analyses in accord with the assigned structures.

[6] C. F. H. Allen and J. Van Allan, *J. Amer. Chem. Soc.*, **64**, 1260 (1942); C. F. H. Allen and J. A. Van Allan, *ibid.*, 72, 5165 (1950).

[7] R. Gompper, *Angew. Chem., Int. Ed. Engl.*, 8, 312 (1969).

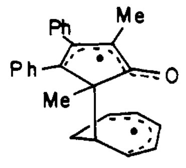
[8] VII and cycloheptene react at 140° to give a mixture of *exo* and *endo* adducts, one of which, mp 175–176°, was isolated in a pure state. This mixture cleanly decarbonylated at 210°, while tetrahydro-II was recovered unchanged under these conditions.

[9] Such intermediates are well documented in suprafacial [1,3] sigmatropic rearrangements: J. E. Baldwin and J. E. Brown, *J. Amer. Chem. Soc.*, 91, 3647 (1969).

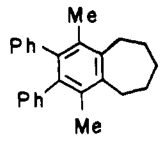
[10] B. P. Stark and A. J. Duke, "Extrusion Reactions," Pergamon Press, London, 1967.

[11] R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, 87, 2511 (1965).

on change in solvent polarity rules out a dipolar intermediate, while the potential diradical intermediate XIII is ruled out by the pyrolysis of II, which must proceed through XIII to IV without formation of I or III.



XIII



XIV

Since this is the first set of addends which give both [6 + 4] and [4 + 2] adducts simultaneously, it is of interest to note that, in this case, the Diels–Alder addition proceeds stereospecifically *endo*, while the [6 + 4] addition proceeds stereospecifically *exo*. This result is in agreement with considerations of secondary orbital interactions made by Hoffman and Woodward; that is, for [4 + 2] cycloadditions, secondary orbital interactions stabilize the *endo* transition state, while for [6 + 4] cycloadditions, secondary orbital interactions destabilize the *endo* transition state.[12,3f]

These results, combined with the nonselective [4 + 2] cycloaddition of VII to cyclopentene and cycloheptene,[8,13] appear to rule out the dominant influence of inductive forces[14] or angular dependence of overlap[15] on the stabilization of the *endo* transition state in Diels–Alder reactions and suggest that secondary orbital interactions are the primary influence in determination of product stereochemistry.

Acknowledgment. The financial support of the National Institutes of Health and the National Science Foundation (Harvard) and the donors of the Petroleum Research Fund, administered by the American Chemical Society (L. S. U.), is gratefully acknowledged.

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[12] R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, 87, 4388 (1965).

[13] K. N. Houk, *Tetrahedron Lett.*, in press.

[14] A. Wasserman, "Diels-Alder Reactions," Elsevier, London, 1965, and references therein.

[15] W. C. Herndon and L. H. Hall, *Tetrahedron Lett.*, 3095 (1967).

Cycloaddition Reactions of Tropone and 2,5-Dimethyl-3,4-diphenylcyclopentadienone[1]

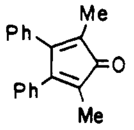
Sir:

In the accompanying communication, competition between *exo* [6 + 4] and *endo* [4 + 2] cycloadditions has been reported for the reaction of cycloheptatriene and 2,5-dimethyl-3,4-diphenylcyclopentadienone (I).[2] Tropone reacts readily with I to give an equally complex sequence of events, the preliminary studies of which are reported herein.[3]

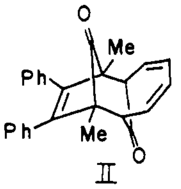
When tropone and I (as the dimer[4]) were heated together in a small amount of acetone or tetrahydrofuran at 60°, the [6 + 4] adduct II, mp 148–150°, crystallized in 95% yield after 8 hr.[5,6] The ir of II (CCl_4, 5.64, 5.77 μ) indicated the presence of two bridged carbonyl groups while the nmr ($CDCl_3$; 1.15 ppm (6 H); $A_2X_2Y_2$ spin system; A_2, 3.6 ppm, X_2Y_2, 5.9 ppm) demonstrated the symmetrical nature of the adduct and corresponded closely to the nmr of the [6 + 6] photodimer of tropone.[7]

Sodium borohydride reduction of II gave a single keto alcohol, III, mp 180.5–181.5° (ir (CCl_4) 5.77 μ), which underwent retro-[6 + 4] reaction to give tropone and 2,5-dimethyl-3,4-diphenylcyclopent-2-enone[8] upon pyrolysis at 200°. Bromination of III gave a mixture of bromo ethers IVa (ir (CCl_4) 5.81, 9.28 μ) and IVb (ir (CCl_4) 5.81, 9.41 μ) in a ratio of 2:1. While IVa was inert to zinc in hot acetic acid or sodium iodide in acetone, IVb was rapidly converted to III under these conditions, as was observed in the cycloheptatriene series.[2] Nmr spin-decoupling experiments confirmed the structures of IVa and IVb, and, therefore, the *exo* nature of [6 + 4] adduct II.

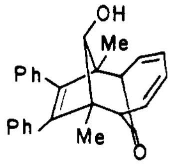
When a solution of tropone and I[4] in benzene was heated at 70° for 1 hr, II (46%) and Va (24%) were detected by nmr. After heating this solution 1 day at 70°, preparative layer chromatography gave II (53%) and light yellow Va, mp 123.5–124.0° (30%), along with recovered I-dimer. The [8 + 2] nature of Va was shown by ir (CCl_4; 5.84 μ) and nmr ($CDCl_3$; 0.75 (3 H, s), 2.00 (3 H, s), 2.5 (1 H, bd; J = 4.5 Hz), 4.9 (1 H, dd; J = 4.5 Hz, J = 9.0 Hz), 5.9–6.4 ppm (4 H, mm). The nmr of the tropone moiety is nearly identical with that of VI, obtained from diphenylketene and tropone.[9] The relative orientation of the addend fragments in the adduct has not been established as yet.



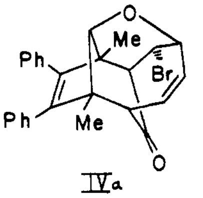
I



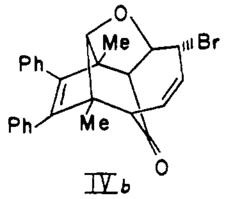
II



III



IVa



IVb

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[1] Taken in part from K. N. Houk, Ph.D. Dissertation, Harvard University, 1968.

[2] K. N. Houk and R. B. Woodward, *J. Amer. Chem. Soc.*, **92,** 4143 (1970).

[3] References to the [6 + 4] cycloaddition reported herein have been made; see ref 2, footnotes 3e and 4.

[4] C. F. H Allen and J. Van Allan, *J. Amer. Chem. Soc.*, **64,** 1260 (1942); C. F. H. Allen and J. A. Van Allan, *ibid.*, 72, 5165 (1950).

[5] All new compounds gave elemental and spectral analyses compatible with the assigned structures.

[6] The high yield of II obtained depends on the low solubility of II relative to Va and I-dimer.

[7] T. Mukai, T. Tezuka, and Y. Akasaki, *J. Amer. Chem. Soc.*, 88, 5025 (1966).

[8] Rearrangement of the initially formed dienol is perhaps quite common in the reduction of cyclopentadienones, although the literature on the latter subject is moderately confused: M. A. Ogliaruso, M. G. Romanelli, and E. I. Becker, *Chem. Rev.*, **65,** 261 (1965).

[9] C. Jutz, I. Rommel, I. Lengyel, and J. Feeney, *Tetrahedron*, **22,** 1809 (1966); R. Gompper, A. Studeneer, and W. Elser, *Tetrahedron Lett.*, 1019 (1968).