(29) P. F. Hollenberg and L. P. Hager, *J. Biol. Chem.*, **248**, 2630 (1973); P. M. Champion, E. Munck, P. G. Debrunner, P. F. Hollenberg, and L. P. Hager, *Biochemistry*, **12**, 426 (1973). It is of interest to observe that although the electronic spectra of certain high-spin modifications of chloroperoxidase are similar to those of **1** and oxidized P-450, the combination of experimental and calculated *g* values of the low-spin (native) enzyme (2.63, 2.26, 1.84) is in better agreement with data for **2** than for the latter species.

Stephen Koch, S. Conrad Tang, R. H. Holm*
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Richard B. Frankel
Francis Bitter National Magnet Laboratory
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

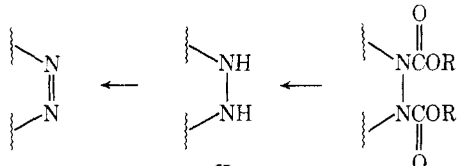
James A. Ibers
Department of Chemistry, Northwestern University
Evanston, Illinois 60201

Received October 21, 1974

1,2-Bis(β-tosylethoxycarbonyl)diazene. Its Application to the 2,3-Diazabicyclo[2.2.0]hexene System

Sir:

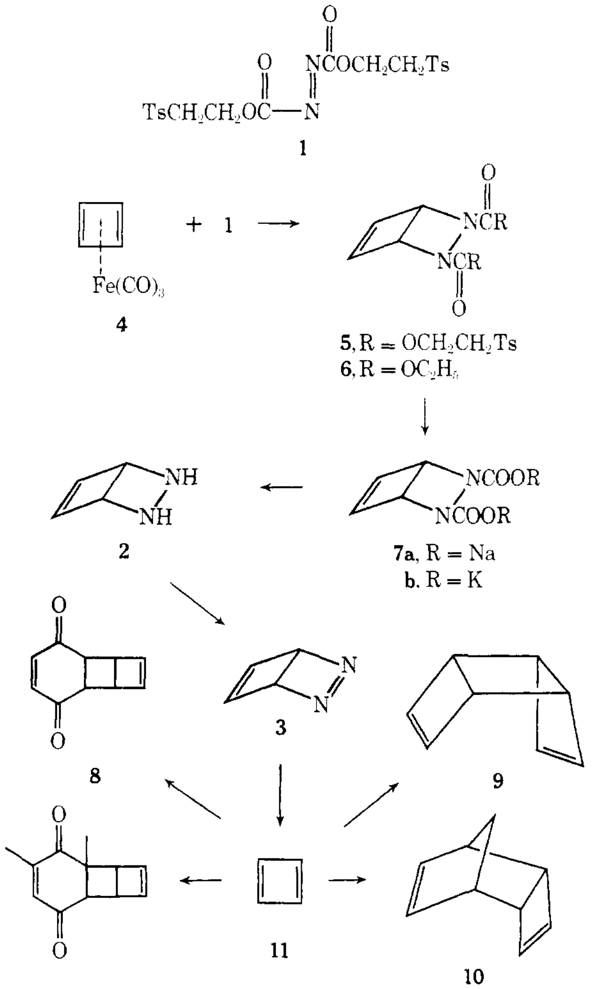
Use of the diazenediyl[1] (azo) group (I) in physical and synthetic organic chemistry is extensive for obvious reasons. Compounds containing this functional group serve as precursors for the study of important reaction intermediates such as trimethylene[2] and are also utilized to form a new carbon-carbon bond, as exemplified in the synthesis of prismane.[3] A general route leading to this functionality involves the oxidation of a 1,2-diazanyl[1] (hydrazo) derivative (II) which is generally prepared from the corresponding alkoxycarbonyl derivative (III). The condition normally required for the hydrolysis of III is rather severe,[4] and, not surprisingly, many functional groups and systems do not survive this operation. 1,2-Bis(β-tosylethoxycarbonyl)diazene (**1**), recently prepared in our laboratory, has overcome this difficulty, as applied to the synthesis of 2,3-diazabicyclo[2.2.0]hex-5-ene (**2**). We believe that this reagent is widely applicable to syntheses of sensitive systems and further report the intriguing behavior of 2,3-diaza-Dewar benzene (**3**) generated from (**2**).



I II III

Preparation of 1. Reaction of β-tosylethoxycarbonyl chloride[5] with hydrazine in aqueous dioxane in the presence of magnesium oxide provided a near-quantitative yield of the corresponding 1,2-disubstituted diazane which in turn was oxidized with nitrogen oxide (chiefly N_2O_4) at 0°. The resulting yellow, low melting (ca. 5°) crystals (**1**) (A_2X_2, δ 3.56, 4.73),[6] obtained in 40–50% yield were shown to undergo a Diels-Alder reaction. Typically, a 1:1.5 mixture of **1** and cyclopentadiene provides at room temperature the expected adduct in more than 90% yield (Scheme I).

Scheme I



Preparation of 2. Slow addition of cyclobutadiene iron tricarbonyl (**4**)[7] (10.4 m*M*) in pyridine to a stirred mixture of lead tetraacetate (38.0 m*M*), reagent **1** (6.4 m*M*), and pyridine, produced an adduct (**5**) (AA′XX′, δ 4.97, 6.62 roughly doublets 3.5 Hz apart, A_2X_2, δ 3.47, 4.43) in 45% yield. Its ^{1}H NMR spectrum exhibits absorptions typical of symmetrically substituted cyclobutenes and observed in numerous bicyclo[2.2.0]hexenes, and virtually reproduces that of the ethoxycarbonyl derivative (**6**)[8] (AA′XX′, δ 5.15, 6.70), produced from **4** and diethoxycarbonyldiazene in a similar manner. Thus **5** is formulated as shown. Treatment of **5** with 2 equiv of alkali (sodium or potassium ethoxide) in ethanol at room temperature (or below) immediately and quantitatively generated the disodium or dipotassium salt of *N,N′*-dicarboxylate (**7a** or **7b**) AA′XX′ δ 5.01, 6.82, D_2O). Careful neutralization of these salts with trifluoroacetic acid provided carbon dioxide and an air-sensitive liquid (**2**) and its ^{1}H NMR spectrum (AA′XX′ $\delta \sim$ 5.1, 6.91) was consistent with the expected structure.[9,10]

Reactions of 2. Addition of benzoquinone to a methanolic (or tetrahydrofuran) solution of **2** either at −70 or 0° immediately induced gas evolution and provided *endo*-tricyclo[4.4.0.$0^{2,5}$]deca-3,8-dien-7,10-dione (**8**)[11] in ca. 50% yield but no trace of *syn*-tricyclo[4.2.0.$0^{2,5}$]octa-3,7-diene (**9**). With 2,6-dimethylbenzoquinone and DDQ, **2** behaved similarly to yield the corresponding adducts, respectively. Oxidation of **2** with aqueous sodium hypochlorite both heterogeneously (methylcyclohexane as solvent) and homogeneously (tetrahydrofuran) led to the formation of **9**. When cyclopentadiene was utilized as a trapping reagent in these experiments, the product was a 1:1 mixture of **9** and tricyclo[4.2.1.$0^{2,5}$]nona-3,7-diene (**10**)[12] but no anti isomer of **9**.[13]

A straightforward, yet the best interpretation of the above experiments is that mild oxidation of **2** leads to the formation of **3**, which undergoes a retro-Diels–Alder reaction to form cyclobutadiene (**11**) and nitrogen with great ease. The unique antiaromatic properties of **11** do not significantly retard the reaction that is observed with 2,3-diazabicyclo[2.2.2]octa-2,5-diene[14] and many other related systems. The facile ring opening that a Dewar pyridine, 2-azabicyclo[2.2.0]hexa-2,5-diene,[15] undergoes does not compete in the case of **3**. Thus the utility of **2** as a metal-free precursor of **11** is obvious. The exclusive formation of dimer **9** from **11** is in agreement with several independent experiments, using metal-free precursors,[16] but is (presumably insignificantly) inconsistent with an earlier report[12] that oxidation of **4** provides a 1:5 mixture of the anti and syn dimers.[17] Because of the reactivity (short lifetime), the pot-to-pot transfer of either **3** or **11** by means of vacuum distillation appears to be impossible.[16b,18]

Finally, it is emphasized that reagent **1** promises well for the synthesis of diazane derivatives that have heat-, acid-, and even alkali-sensitive functional groups (e.g., esters) and systems, since conditions even milder than those used in the present work easily bring about the cleavage, as already demonstrated in the synthesis of peptides and other systems.[5,19]

References and Notes

(1) J. H. Fletcher, O. C. Dermer, and R. B. Fox, "Nomenclature of Organic Compounds," American Chemical Society, Washington, D.C., 1974, Chapter 32.

(2) E.g., R. J. Crawford, F. J. Dummel, and A. Mishra, *J. Am. Chem. Soc.*, **87**, 3023 (1965).

(3) T. Katz and N. Acton, *J. Am. Chem. Soc.*, **95**, 2738 (1973), and ref 7 quoted therein.

(4) For instance, the following conditions are recommended for the hydrolysis of diethyl 2,3-diazabicyclo[2.2.1]heptane-2,3-dicarboxylate: ca. 4 *N* KOH in ethylene glycol at 125–130° for 1 hr. P. G. Gassman and K. T. Mansfield, "Organic Synthesis," Coll. Vol. 5, Wiley, New York, N.Y., 1973, p 96.

(5) A. T. Kader and C. J. M. Stirling, *J. Chem. Soc.*, 258 (1964); A. W. Miller and C. J. M. Stirling, *J. Chem. Soc. C*, 2612 (1968). This functionality was originally devised to serve as a protecting group in peptide synthesis and has recently been utilized to generate selectively specific carboxylic groups in the synthesis of pyrenophorin. E. W. Colvin, T. A. Purcell, and R. A. Raphael, *J. Chem. Soc., Chem. Commun.*, 1031 (1972).

(6) Only important ^{1}H NMR signals are recorded in this note. Unless otherwise stated, $CDCl_3$ is used as solvent.

(7) G. F. Emerson, L. Watts, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 131 (1965); R. Pettit and J. Henery, *Org. Syn.*, **50**, 21 (1970).

(8) This compound (**6**) was previously prepared by photolysis of dimethyl 1,2-dihydropyridazine-1,2-dicarboxylate. L. T. Altman, M. F. Semmelhack, R. B. Hornby, and J. C. Vederos, *Chem. Commun.*, 686 (1968). The present method provides 50–60% yields of **6** and is synthetically preferred to the older route.

(9) Bis(β,β,β-trichloroethoxycarbonyl)- and bis(β,β,β-tribromoethoxycarbonyl)diazene (cf. R. B. Woodward, K. Heusler, J. Gosteli, P. Naegeli, W. Oppolzer, R. Ramage, S. Ranganathan, and H. Vorbrueggen, *J. Am. Chem. Soc.*, **88**, 852 (1966)), dicyanodiazene (C. F. D. Marsh and M. E. Harmes, *ibid.*, **87**, 1819 (1965)), and dibenzyloxydiazene all provided the corresponding cyclobutadiene adducts, but deblocking experiments consistently failed.

(10) After **2** was prepared in this way, we found that **6** could be hydrolyzed directly to give **2** under specified conditions.

(11) J. C. Barborak, L. Watts, and R. Pettit, *J. Am. Chem. Soc.*, **88**, 1328 (1966); L. Brener, J. S. McKennis, and R. Pettit, *Org. Syn.*, to be submitted for publication.

(12) L. Watt, J. D. Fitzpatrick, and R. Pettit, *J. Am. Chem. Soc.*, **88**, 623 (1966).

(13) Attempts to prepare the *N*-oxide of **3** have never been rewarded. Cf. J. P. Snyder, L. Lee, V. T. Bandurco, and C. Y. Yu, *J. Am. Chem. Soc.*, **94**, 3260 (1972).

(14) N. Riebu, J. Alberts, J. A. Lipsky, and D. M. Lemel, *J. Am. Chem. Soc.*, **91**, 5668 (1969).

(15) K. E. Wilzbach and D. J. Ransch, *J. Am. Chem. Soc.*, **92**, 2178 (1970).

(16) (a) S. Masamune, M. Suda, H. Ona, and L. M. Leichter, *J. Chem. Soc., Chem. Commun.*, 1268 (1972); (b) E. Hedaya, R. D. Miller, D. W. McNeil, P. F. D'Angelo, and P. Schissel, *J. Am. Chem. Soc.*, **91**, 1875 (1969); (c) E. Hedaya, I. S. Krull, R. D. Miller, M. E. Kent, P. F. D'Angelo, and P. Schissel, *ibid.*, **91**, 6881 (1969); (d) R. D. Miller and E. Hedaya, *ibid.*, **91**, 5401 (1969); (e) C. Y. Lin and A. Krantz, *J. Chem. Soc., Chem. Commun.*, 1111 (1972).

(17) A recent mechanistic study on this reaction of **4** concludes that the metal (Fe) is not close to the ligand (cyclobutadiene) and has little effect on the free ligand's electronic state when it reacts with trapping reagents. R. H. Grubbs and R. A. Grey, *J. Am. Chem. Soc.*, **95**, 5765 (1973).

(18) W. J. R. Tyerman, M. Kato, P. Kebarle, S. Masamune, O. P. Strausz, and H. E. Gunning, *Chem. Commun.*, 497 (1967).

(19) The authors are grateful to the National Research Council of Canada for financial support.

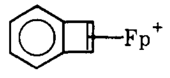
Satoru Masamune,* Nobuo Nakamura, J. Spadaro
Department of Chemistry, University of Alberta
Edmonton, Alberta, Canada

Received September 17, 1974

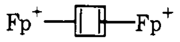
η^2 Cyclobutadienoid Transition Metal Complexes. The Generation and Trapping of a Cationic η^2-Cyclobutadiene Iron Complex

Sir:

Recently we reported the preparation of two reactive η^2 cyclobutadienoid transition metal complexes—a η^2-benzocyclobutadiene complex **1**[1] and a binuclear complex possessing a bridging cyclobutadiene ligand **2**.[2]



1



2

Fp = $Cp(CO)_2Fe^+$

We now report the trapping of the first cationic η^2 cyclobutadiene complex, η^2-cyclobutadiene-η^5-cyclopentadienyldicarbonyliron hexafluorophosphate (**3**), which is generated by chloride abstraction from η^1-4-(3-chlorocyclobutenyl)-η^5-cyclopentadienyldicarbonyliron (**4**). Complex **4**, is obtained by allowing an approximately equimolar tetrahydrofuran solution of *cis*-3,4-dichlorocyclobutene and NaCp-$(CO)_2Fe$ to stand at −78° for 16 hr followed by sequential warming to 0°, and rotary evaporation of the solvent. Extraction of the residue with petroleum ether and cooling (−78°) of the extract affords **4** as dark yellow crystals in 17% yield.[3] The NMR spectra and other physical data for all new compounds are presented in Table I. The structure of **4** was established by consideration of its spectroscopic properties and the quantitative thermal isomerization of **4** to the trans,trans chlorobutadiene complex **5**.

Although complex **4** fails to react with cyclopentadiene in methylene chloride at 25° over a 4-hr period, a rapid reaction ensues when a methylene chloride solution of **4** is added to a mixture of silver hexafluorophosphate and excess cyclo-

Table I. ^{1}H NMR and Ir for New Complexes[a]

4	Nmr (CS_2) τ 3.72 (m,[b] 1, H^1), 4.37 (m,[b] 1, H^2), 5.18 (s, 5, Cp, 5.59 (m,[b] 1, H^3), 6.17 (m,[b] 1, H^4); ir (Nujol) 2000, 1950 cm^{-1} ($C\equiv O$); mp 65–67°
5	Nmr (CS_2) τ 2.98 (d, 1, H^1, $J_{1,2}$ = 14.25 Hz), 3.81 (m, 2, H^2 and H^3), 4.35 (d, 1, H^4, $J_{3,4}$ = 12.75 Hz), 5.27 (s, 5, Cp); ir (neat) 2003, 1947 cm^{-1} ($C\equiv O$)
6	Nmr (CD_3COCD_3) τ 3.60 (m, 2, H^1), 4.20 (s, 5, Cp), 4.38 (s, 5, Cp 2, H^2), 7.01 (m, 2, H^3, $J_{3,4}$ = 3.8 Hz), 7.25 (m, 2, H^4), 8.09 (m, 1, H^5), 8.35 (m, 1, H^6); ir (Nujol) 2065, 2015 cm^{-1} ($C\equiv O$)
10	Nmr (CD_2NO_2) τ 4.21 (s, 4, H^1), 4.30 (s, 10, Cp), 7.05 (s, 4, H^2); ir (Nujol) 2080, 2035 cm^{-1} ($C\equiv O$)
13	Nmr (CS_2) τ 0.71 (d, 1, H^1, $J_{1,3}$ = 7.5 Hz), 3.06 (m, 1, H^2, $J_{2,3}$ = 15 Hz, $J_{2,4}$ = 9 Hz), 4.18 (m, 1, H^3), 5.25 (s, 5, Cp), 7.85 (d, 2, H^4); ir (neat) 2000, 1940 cm^{-1} ($C\equiv O$), 1648 cm^{-1} ($-CH{=}O$)

[a] All neutral complexes gave satisfactory analyses for carbon and hydrogen. Cationic olefin complexes were characterized by ir and NMR spectroscopy and by liberation and identification of the olefin ligand. [b] Narrow multiplet.