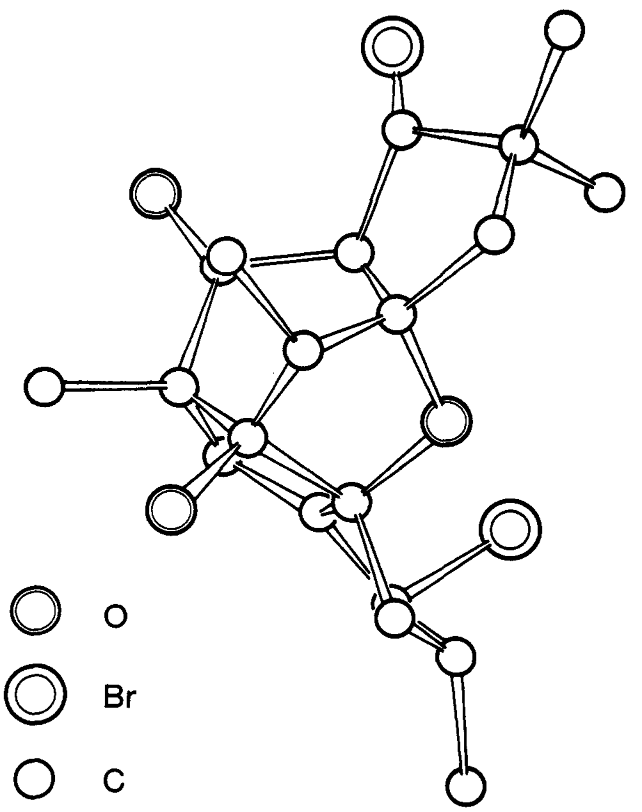

Figure 1. Model showing the absolute configuration of jatrophone dihydrobromide.

phone and the dihydrobromide adduct made the latter derivative an attractive target for X-ray crystallographic analysis.

Crystals of the dihydrobromide have orthorhombic symmetry with space group $P2_12_12_1$ and $a = 21.974$ (3), $b = 12.486$ (3), $c = 7.127$ (2) Å. On the basis of four formula units of $C_{20}H_{26}Br_2O_3$ in the unit cell, the calculated density is 1.610 g/cm^3, in reasonable agreement with the observed value of 1.61 (1) g/cm^3.

Intensity data were collected by diffractometry using monochromatic Mo Kα radiation, scintillation counting, and pulse height analysis.

The locations of the two bromine atoms in the unit cell were derived from a three-dimensional Patterson synthesis, and the carbon and oxygen atoms were found from two successive three-dimensional electron-density syntheses using the heavy atom method of phase determination. The approximate atomic parameters were refined by the block-diagonal least-squares method with individual isotropic thermal parameters to give $R = 0.104$, and with individual anisotropic thermal parameters to yield $R = 0.047$ and $R' = ([\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2])^{1/2} = 0.057$ for the 903 independent significant reflections measured. The molecular structure illustrated by Figure 1 is in the correct absolute configuration with respect to a right-handed coordinate system, as judged by independent least-squares refinement of the two possible enantiomeric structures taking into account the anomalous dispersion terms for the bromine atoms ($\Delta f' = -0.21$, $\Delta f'' = 2.68$). For the alternate configuration $R = 0.060$ and $R' = 0.074$.

From the spectral properties of jatrophone and its derivatives and the reversible interrelation with **3** it may be concluded that jatrophone has structure **1**. The ready formation of the dihydrobromide **3** is envisioned as a result of two novel transannular conjugate addition reactions: protonation of the C-14 ketone with nucleophilic attack by bromide ion at C-9 to form the 8,12 bond, followed by attack of a second bromide ion at C-3 in an acid-catalyzed ring closure of the 6,14 bond.

In view of the recent demonstration of the potential importance of nucleophilic additions to unsaturated systems for the tumor-inhibitory activity of other natural products,[4,9] investigations are in progress to determine the significance of various structural features in relation to the biological activity of jatrophone.

[9] S. M. Kupchan, D. C. Fessler, M. A. Eakin, and T. J. Giacobbe, *Science*, 168, 376 (1970).

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Isomer Distribution in the Aromatic Nitramine Rearrangement. Solvent Viscosity Effects within the Solvent Cage

Sir:

The composition of the product resulting from the acid-catalyzed nitramine rearrangement depends on the nature of the reaction medium. Thus, the yield of nitrated product from N-nitroaniline increases from 60 to 95% and the *ortho–para* isomer ratio changes from 3.5 to 19.0 as the concentration of the catalyzing acid is increased.[1] Similar results were obtained in the rearrangements of N-nitro-1-naphthylamine and its N-methyl derivative.[2] This behavior was attributed to the differential effect of the acid medium's basic strength on proton loss from the *ortho* and *para* positions. However, the data are poorly correlated by reference to either the water activity or the acidity function of the reaction solvent.

Interestingly, the published isomer ratios yield a smooth curve when plotted against the viscosity of the medium—results obtained in sulfuric, phosphoric, and perchloric acid falling along the same correlation line. The notion that the solvent viscosity determines the isomer distribution and the nitrated product yield in the nitramine rearrangement was pursued by rearranging N-nitro-N-methylaniline in a series of methanol–glycerol mixtures of different compositions and viscosities. This solvent pair was chosen because of the similar polar character of the components (Z (methanol) = 83.6 and Z (glycerol) = 85.3), but widely different viscosities (η (methanol) = 0.55 cP and η (glycerol) = 954 cP). Reactions were run both in the presence and absence of hydroquinone as scavenger. The results obtained are plotted in Figure 1. As the solvent viscosity was changed from 0.60 to 80.5 cP the total yield of nitrated product increased (from 34 to 90% in the presence of hydroquinone and from 76 to 100% in its absence) and the *ortho–para* isomer ratio was enhanced (from 1.30 to 18.5 in the presence of scavenger and from 1.23 to 13.7 in its absence).

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[1] D. V. Banthorpe, E. D. Hughes, and D. L. H. Williams, *J. Chem. Soc.*, 5349 (1964).

[2] D. V. Banthorpe and J. A. Thomas, *ibid.*, 7149 (1965).

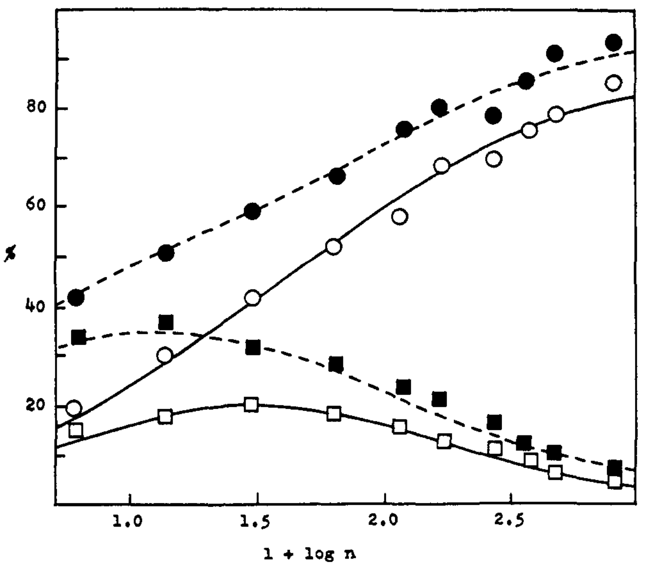
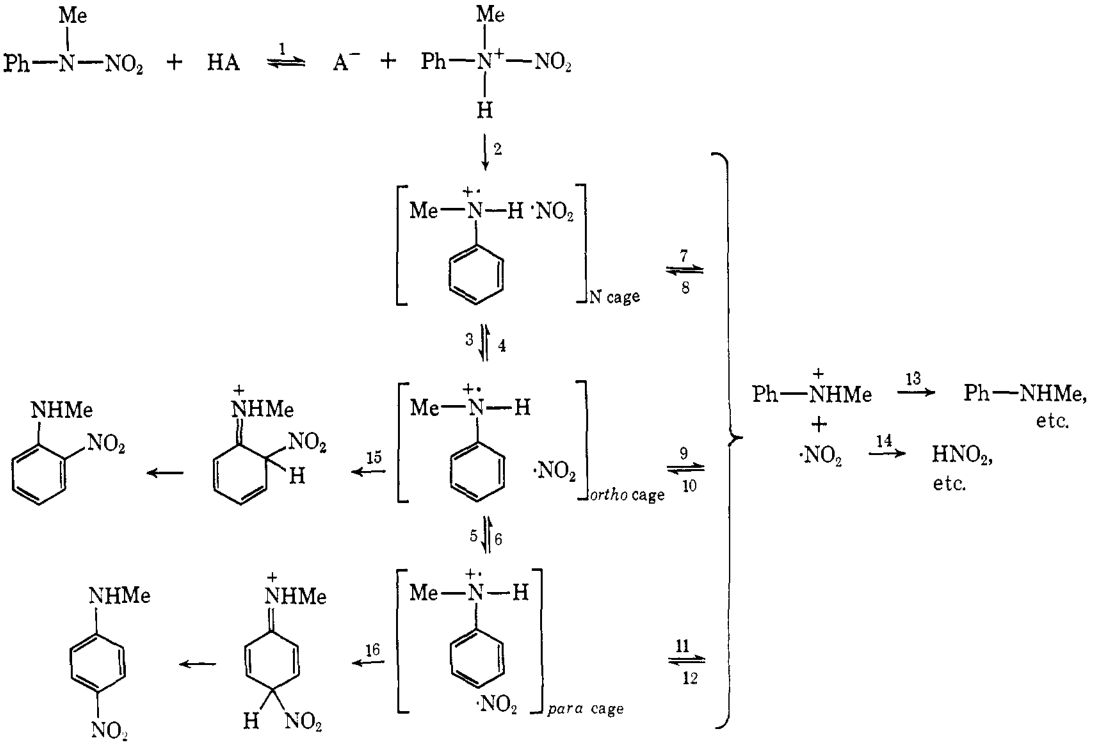


Figure 1. Yields of *o*- and *p*-nitro-N-methylanilines at various viscosities: ● and ■, *ortho* and *para* isomers, respectively, in the absence of hydroquinone; ○ and □, *ortho* and *para* isomers, respectively, in the presence of hydroquinone scavenger. Curves were calculated from the kinetics of the mechanism of Chart I using the rate constants listed in the text.

The data are readily interpreted and correlated in terms of the mechanism depicted in Chart I. Previous studies have demonstrated that the reaction is subject to specific acid catalysis[3a] and involves homolytic cleavage of the conjugate acid of the nitramine[3b] to give a pair of caged radicals which can undergo dissociation[3c] or associate to form intermediates leading to the nitroanilines.

Chart I



In the presence of hydroquinone scavenger, the dissociated radicals are destroyed ($k_{13} > k_8$, k_{10}, or k_{12} and $k_{14} > k_8$, k_{10}, or k_{12}) and do not contribute to the formation of nitrated products. Thus, the yield of nitroanilines is a measure of the extent of the intramolecular cage process. Since an increase in viscosity will impede dissociation, but not affect the rate of geminate recombination, the total of nitroanilines rises as the viscosity goes up. The change in the relative yields of the *ortho* and *para* isomers is explicable if the assumptions are made that: (1) there are at least three different cage species—one formed directly from the protonated nitramine, one that collapses to the *ortho* isomer, and one that yields the *para* compound,[4] and (2) the solvent interferes with the movement of the NO_2 radical from the locality of the amino nitrogen to the vicinity of the *ortho* position and, thence, to the *para* position. High solvent viscosities decrease the facility of migration so that the opportunity for the NO_2 radical to approach the *para* position before reaction has occurred at the nearer *ortho* position is lessened. Hence, the absolute and relative amount of the *ortho* isomer increases with viscosity. Interestingly, the yield of *para* isomer first increases and then declines as the solvent viscosity is raised. The initial enhancement is the result of reduced overall dissociation from the solvent cage. The ensuing decrease in *para* isomer yield is caused by solvent interference to the migration of the NO_2 radical to the *para* position.

The rate expressions derived from the above mechanisms permit a quantitative correlation of the ex-

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(3) (a) W. N. White, C. Hathaway, and D. Huston, *J. Org. Chem.*, **35**, 737 (1970); (b) W. N. White and J. R. Klink, *ibid.*, **35**, 965 (1970); (c) W. N. White and H. S. White, *ibid.*, **35**, 1803 (1970); W. N. White and J. T. Golden, *ibid.*, in press.

(4) This is not meant to imply that there is only one caged species that leads to the *ortho* isomer and only one that produces the *para* product. It is likely that there are a variety of orientations of the two radicals for each mode of recombination. Thus, since *ortho* and *para* cage correspond to statistical distributions of radical pairs, the indicated rate constants for collapse, dissociation, and interconversion must be weighted averages of the true rate constants for these various processes as they apply to individual radical pair orientations.

perimental results. The solid and dashed lines in Figure 1 have been calculated using the following values for the pertinent rate constants in the mechanism of Chart I: $k_3 = 7.1k_7$, $k_4 = 16k_{15} - 8.1k_9$, $k_5 = 4.0k_{15}$, $k_6 = 5.1k_{16}$, $k_8 < 0.3\sqrt{k_{13}k_{14}}$, $k_{10} = 7.5\sqrt{k_{13}k_{14}}$, $k_{11} < 0.2k_{16}$, and $k_{12} = 2.5\sqrt{k_{13}k_{14}}$ (the overall rate constants of all of the steps in the mechanism except 1, 2, 15, and 16 have the form: $k_n' = k_n/\eta$).

The rearrangement of N-nitro-N-methylaniline has also been studied in a series of water–glycerol mixtures with similar results.

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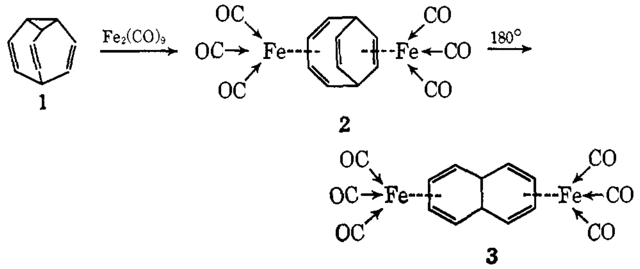
*Octahapto*bicyclo[4.2.2]deca-2,4,7,9-tetraenediiron Hexacarbonyl. The Structure of the Reaction Product of $Fe_2(CO)_9$ with Bullvalene

Sir:

The reaction of tricyclo[3.3.2.0^{4,6}]deca-2,7,9-triene (bullvalene) (**1**) with $Fe_2(CO)_9$ in boiling benzene yields a complex $C_{10}H_{10}Fe_2(CO)_6$ (**2**), mp 120°, which on heating to 180° in an autoclave was transformed into the known *octahapto*-9,10-dihydronaphthalenediiron hexacarbonyl (**3**).[1]



The nmr spectrum (Figure 1) of **2** as well as the facile conversion of **2** into **3** led to the postulate[1] of structure **2** for the complex, which thus would be the first example of a π complex of bicyclo[4.2.2]deca-2,4,7,9-tetraene (**4**), the remarkable $C_{10}H_{10}$ hydrocarbon first synthesized by Jones and Scott.[2] In the present communication we report the results of an X-ray structural analysis of **2** which confirms the previous structural assignments. The formation of **2** from bullvalene and $Fe_2(CO)_9$ is of particular interest in view of the demonstrated photorearrangement of **4** into **1**,[2] indicating that the reverse of a photochemical rearrangement process may be achieved thermally in the presence of iron carbonyl fragments.

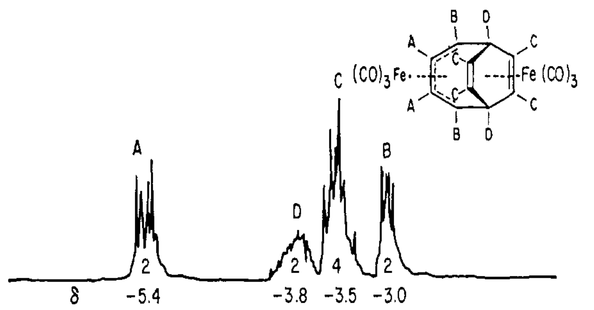


Figure 1. ^1H nmr spectrum of *octahapto*bicyclo[4.2.2]deca-2,4,7,9-tetraenediiron hexacarbonyl in $CDCl_3$ and suggested assignments.

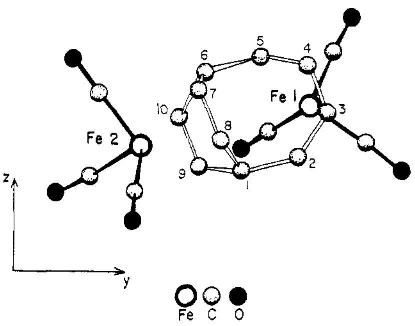


Figure 2. View of the complex along the *x* direction. The C–C bond lengths (Å, esd ± 0.02) are C_1–C_2 1.60, C_2–C_3 1.41, C_3–C_4 1.36, C_4–C_5 1.42, C_5–C_6 1.59, C_6–C_7 1.53, C_7–C_8 1.40, C_1–C_8 1.51, C_1–C_9 1.49, C_9–C_{10} 1.39, and C_6–C_{10} 1.51. The angles (deg) are $C_2C_1C_8$ 113, $C_2C_1C_9$ 118, $C_8C_1C_9$ 102, $C_1C_2C_3$ 125, $C_2C_3C_4$ 121, $C_3C_4C_5$ 121, $C_4C_5C_6$ 124, $C_5C_6C_7$ 115, $C_5C_6C_{10}$ 119, $C_7C_6C_{10}$ 101, $C_6C_7C_8$ 117, $C_1C_8C_7$ 117, $C_1C_9C_{10}$ 118, and $C_6C_{10}C_9$ 116.

The reddish-brown crystals of **2** belong to the orthorhombic system. Cell dimensions, as determined by a least-squares fit to the settings for 12 reflections on a Picker FACS-1 diffractometer (Mo Kα, λ 0.7107 Å), are a = 12.447 (6), b = 19.854 (9), and c = 12.443 (6) Å. The space group is Pbca and there are eight molecules of $C_{10}H_{10}\cdot Fe_2(CO)_6$ (mol wt = 409.9) in the unit cell. At the present stage of refinement,[3] the R factor on 1191 nonzero reflections collected on the diffractometer (Mo Kα) is 0.052. A view of the molecular structure is shown in Figure 2.

The standard deviations in the Fe–C lengths are 0.012–0.016 Å, while those of the C–C lengths are 0.02 Å, and those of the C–C–C angles are 0.6–0.7°. The agreement in the molecular dimensions related by a noncrystallographic mirror plane perpendicular to the C_3–C_4, C_7–C_8, and C_9–C_{10} bonds is well within these deviations. The mode of interaction of the $Fe(CO)_3$ group with the "butadiene" moiety of **4** (*i.e.*, C_2, C_3, C_4, C_5) is similar to that found in other π complexes of $Fe(CO)_3$ with 1,3-dienes.[4,5] The two $Fe_1\cdots C$ (outer) distances (2.100 (14) and 2.097 (14) Å) are slightly longer than the two $Fe_1\cdots C$ (inner) distances (2.038 (16) and 2.041 (15) Å). An unusual feature of the molecular geometry is the exceptional length (1.60 (2) and 1.59 (2) Å) of the C_1–C_2 and C_5–C_6 bonds. In view of the geometrical features of the π-complexed butadiene moiety (the distances C_2–C_3 and C_4–C_5 being somewhat longer than C_3–C_4) and the large $-\delta$ value of the A protons (attached to C_3 and C_4) in the nmr spectrum (Figure 1), the bonding

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[1] G. N. Schrauzer, P. Glockner, and R. Merényi, *Angew. Chem.*, **76**, 498 (1964); *Angew. Chem., Int. Ed. Engl.*, **3**, 509 (1964).

[2] M. Jones, Jr., and L. T. Scott, *J. Amer. Chem. Soc.*, **89**, 150 (1967); M. Jones, Jr., S. D. Reich, and L. T. Scott, *ibid.*, **92**, 3118 (1970).

[3] The temperature factors of all nonhydrogen atoms in the structure have been refined anisotropically.

[4] O. S. Mills and G. Robinson, *Acta. Cryst.*, **16**, 758 (1963).

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