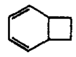
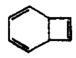
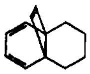
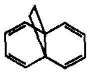
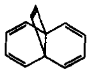
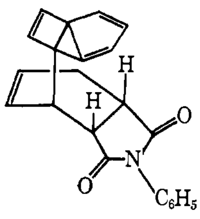
Table I. Ultraviolet and Chemical Shift Data for Selected 1,3-Cyclohexadienes

Compound	λ_{max} (ϵ)	Solvent	Olefinic protons (δ)	Pattern	Ref
	274 (3340)	Cyclohexane	5.62	Multiplet	*a*
	273 (3100) 277 (3000)	(unspecified)	5.63	Multiplet	*b*
	268 (2400) 276 (sl infl, 2100)	Isooctane	5.53	A_2B_2	*c*
	235 (4700) 285 (2600)	Cyclohexane	5.50	A_2B_2	*d*
	247 (2500) 290 (2100)	Isooctane	5.68	A_2B_2	*e*

[a] A. C. Cope, P. T. Moore, and W. R. Moore, *J. Am. Chem. Soc.*, **80**, 5505 (1958). [b] E. Vogel, H. Kiefer, and W. R. Roth, *Angew. Chem. Intern. Ed. Engl.*, **3**, 442 (1964). [c] Reference 1. [d] References **8a** and **8b**. [e] This work.

The even number of suprafacial components required for fragmentation of **1** to naphthalene and acetylene suggests photochemical allowedness; in agreement with theory, photoexcitation of **1** with 2537-Å radiation resulted in rapid formation of the above-mentioned retrograde products.

Admixture of equimolar amounts of **1** and N-phenylmaleimide in benzene solution at room temperature resulted in the gradual deposition of colorless crystals of (4 + 2)π adduct **7** (94%), mp 277–279°.[6] The stereochemistry of this cycloaddition product has been assigned in accordance with the observed vicinal proton coupling constant and established precedence.



7

In light of these limited observations, it would appear that orbital overlap of ten π electrons in the unusual fashion enforced by the inflexibility of pentaene **1** results in little or no enhancement of thermodynamic stabilization. Nevertheless, the ready availability of hydrocarbon **1** now makes possible the opportunity to examine the effect of such an arrangement of π-atomic orbitals on chemical reactivity, a point on which we hope to report further at a later date.

(11) National Institutes of Health Predoctoral Fellow, 1966–1968.

Leo A. Paquette, J. Christopher Philips[11]
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

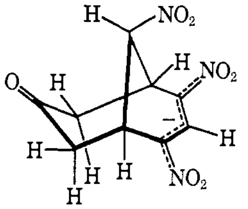
Received April 22, 1969

Condensation of Acetone with *sym*-Trinitrobenzene. Structure of the Bicyclic Product

Sir:

Attempts to clarify the complex reaction of acetone with *sym*-trinitrobenzene and diethylamine have been made by a number of workers.[1–5] N,N-Diethyl-*p*-nitroaniline and 2-acetonyl-1,3-dinitropropane have been identified as products.[1] In addition, an unknown red compound has been isolated from the reaction mixture.[1,3] This material has an intense absorption at 510 mμ and is similar to the red product isolated by Abe[4] from a mixture of *sym*-trinitrobenzene, acetone, and aqueous ammonia. On the basis of an elemental analysis of the red product prepared using diethylamine, Osugi and Muneo[3] proposed a structure containing acetone, *sym*-trinitrobenzene, and amine in a molar ratio of 1:1:2. The elemental analysis reported by Foster and Fyfe[1] is not consistent with this stoichiometry or with a 1:1:1 adduct. A crystalline sample was not obtained, however.

We have isolated the red compound by Foster and Fyfe's method and after recrystallization from chloroform obtained red crystals, mp 171–172°, $\lambda_{max}^{100\%\ EtOH}$ mμ (ε): 510 (30,300). The elemental analysis and nmr spectrum (acetone-d_6), Figure 1, are consistent with **1**. A 1:1:1 adduct ($C_{13}H_{20}N_4O_6$) requires C, 45.35; H, 5.85; N, 16.27. Found: C, 45.40; H, 5.78, N, 16.25. The proton on the dinitropropenide portion of **1** appears as a singlet at δ 8.52 (1 H). The N-H protons appear as a broad singlet at δ 6.84 (2 H). The bridge H-CNO_2 proton appears as a triplet centered at δ 5.72, J = 3 cps (1 H). The appearance of this proton 1.3 ppm downfield from the absorption observed for a dilute solution of nitromethane in acetone (δ 4.4) and 1.0 ppm downfield from the methine proton of 2-nitropropane leads us to believe that the nitro group on the one-carbon bridge is directed toward the anionic portion of the molecule. If it were not, the bridge proton would occupy a position directly above the delocalized system, a region of high shielding, and would be expected to appear at higher fields than in normal aliphatic nitro compounds. In addition, if the bridge proton is directed toward the carbonyl function it would lie in a deshielding region (assuming conformational mobility of the keto bridge). The coupling constant of 3 cps is consistent with a dihedral angle of 50° between the bridging and bridgehead protons,[6] a value in accord with models of **1**, and the coupling observed in related bicyclic systems.[7] The two bridgehead protons appear



, $H_2\overset{+}{N}(CH_2CH_3)_2$

1

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(1) R. Foster and C. A. Fyfe, *Tetrahedron*, **22**, 1831 (1962).
(2) Penkett, Thesis, University of Leeds, 1963.
(3) J. Osugi and Muneo, *Rev. Phys. Chem. Japan*, 37, 43 (1967).
(4) T. Abe, *Bull. Chem. Soc. Japan*, 32, 997 (1959).
(5) C. R. Allen, A. J. Brook, and E. F. Caldin, *J. Chem. Soc.*, 2171 (1961).
(6) H. Conroy, *Advan. Org. Chem.*, **2**, 265 (1960).

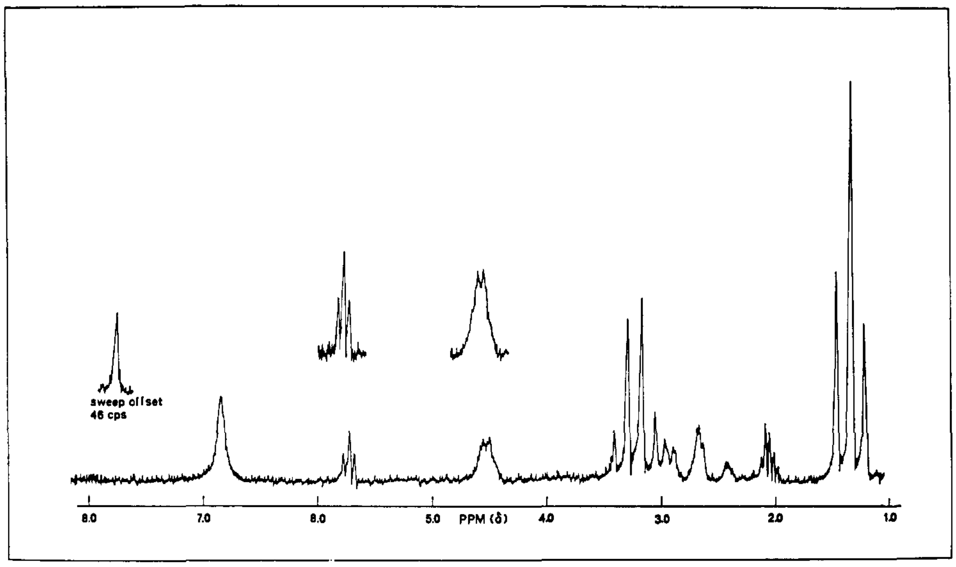


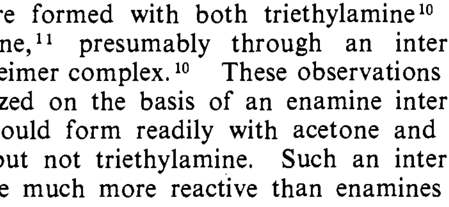
Figure 1. Nmr spectrum of 1 in acetone-d_6.

as a poorly resolved doublet centered at δ 4.53 (2 H). Irradiation of this broad absorption collapses the triplet at δ 5.72 to a singlet. The quartet from diethylammonium cation is centered at δ 3.28 (4 H). A complex pattern is observed from δ 3.0 to 2.3 resulting from protons α to the carbonyl (4 H). Irradiation of the peak at δ 2.68 collapses the broad doublet at δ 4.53 to what appears as a poorly resolved quartet but leaves the triplet at δ 5.72 unchanged. The complex absorption at δ 2.07 results from partially protonated acetone-d_6 solvent. Foster and Fyfe also observed contamination with acetone in the nmr spectrum.[1] We have found that if the spectrum is run immediately after dissolution of 1 in acetone-d_6, the amount of contamination is no greater than in pure solvent. Upon standing, however, the absorption at δ 6.84 (N–H) disappears and the absorption for protonated solvent intensifies. In addition, the singlet at δ 8.52 (dinitropropenide proton) appears broadened in about 3 hr. These observations are indicative of exchange of diethylammonium and dinitropropenide protons with solvent.

The infrared spectrum of 1 shows an absorption at 1710 cm^{-1} (C=O), 1550 cm^{-1} (NO_2), and a broad peak at 1425–1520 cm^{-1} (NO_2^-). The NO_2 absorption in Meisenheimer salts appears at about 1500 cm^{-1}.[8] In these systems a full negative charge is distributed among three nitro groups, lowering the asymmetric N–O stretching frequency from 1550 cm^{-1}. In **1** a full negative charge is distributed between two nitro groups, lowering the absorption frequency even further.

The visible absorption spectrum of **1** in ethanol shows the previously reported maximum at 510 mμ. This absorption is characteristic of the dinitropropenide portion of the molecule and has been observed in other systems containing this function.[9,10] We have successfully prepared structures analogous to **1** in which one of the nitro groups on the delocalized anionic portion of the molecule is replaced by a cyano group.[11] The visible absorption is shifted to 376 mμ, and the compound appears bright yellow instead of red. The nmr spectrum of the cyanodinitro adduct is very similar to that of **1** except that the propenide proton appears at much higher field (δ 7.5).

Although the bicyclic structure **1** is obtained from the reaction of acetone, *sym*-trinitrobenzene, and diethylamine, the stable Meisenheimer salt **2** is isolated when triethylamine is used as the base.[12] With more acidic ketones (*i.e.*, acetylacetone, dibenzyl ketone) structures like **1** are formed with both triethylamine[10] and diethylamine,[11] presumably through an intermediate Meisenheimer complex.[10] These observations may be rationalized on the basis of an enamine intermediate which would form readily with acetone and diethylamine, but not triethylamine. Such an intermediate would be much more reactive than enamines formed from dibenzyl ketone or acetylacetone.



2

Enamines form rapidly and reversibly in ketonic solutions of secondary amines[13] and react readily with nitro olefins.[14] A reasonable route for the formation of **1** might, therefore, involve attack of the enamine from acetone and diethylamine on *sym*-trinitrobenzene to yield **3**, followed by intramolecular cyclization and hydrolysis to **1**.

The detailed pathways leading to **2**, N,N-diethyl-*p*-nitroaniline, and 2-acetonyl-1,3-dinitropropane are presently under investigation in our laboratory.

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(7) For example, the bridgehead protons of norbornadiene are coupled to the bridging protons by 2.5 cps.

(8) R. Foster and C. A. Fyfe, *Rev. Pure Appl. Chem.* **16**, 61 (1966).

(9) R. Foster and C. A. Fyfe, *Tetrahedron*, **21**, 3363 (1965).

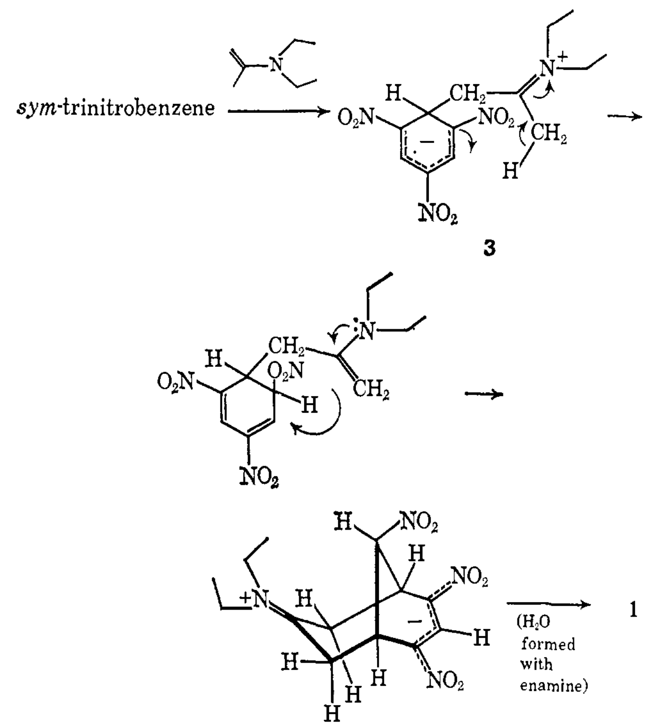
(10) R. Foster, M. I. Foreman, and M. J. Strauss, *Tetrahedron Letters*, 4949 (1961).

(11) This work will be published elsewhere.

(12) R. Foster and C. A. Fyfe, *J. Chem. Soc., B*, 53 (1966).

(13) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963).

(14) M. E. Kuehne and L. Foley, *J. Org. Chem.*, **30**, 4280 (1965).



Acknowledgments. The authors wish to thank the National Aeronautics and Space Administration and the University of Vermont for an Institutional Grant in support of this research. We also wish to thank Professor M. E. Kuehne for helpful discussion and comments.

Michael J. Strauss, Horst Schran
Department of Chemistry, The University of Vermont
Burlington, Vermont 05401
Received February 19, 1969

Direct Observation of the Rate of Planar–Tetrahedral Equilibrium of Four-Coordinate Nickel(II) by Nuclear Magnetic Resonance. Diastereoisomeric Dihalobis(dissymmetric tertiary phosphine)nickel (II) Complexes[1]

Sir:

Dynamical planar (diamagnetic) ⇄ tetrahedral (paramagnetic) interconversions in four-coordinate nickel(II) complexes are well established. Nmr studies of a variety of nickel(II) chelate complexes have been carried out. The ligands involved include salicylaldimines,[2] aminotroponimines,[3] naphthaldimines,[4] β-ketoamines,[5] and ditertiary phosphines.[6] In all previously studied cases, the planar–tetrahedral interconversion was found to be rapid on the nmr time scale such that for a given nucleus only a single resonance was observed at a frequency which represents a weighted average over diamagnetic and isotropically shifted paramagnetic environments. For such conformational equilibria, the averaged nuclear resonance shifts from their diamagnetic positions, $\Delta\nu_i^{av}$, are given by[7]

$$\frac{\Delta\nu_i^{av}}{\nu} = -\frac{a_i}{2S}\frac{\gamma_e}{\gamma_H}\frac{g\beta S(S+1)}{3kT}N_t \qquad (1)$$

$$N_t = [\exp(\Delta G^\circ/RT) + 1]^{-1}$$

Here N_t is the mole fraction of tetrahedral species, ΔG° is the standard free-energy change for the planar ⇄ tetrahedral equilibrium, and the other symbols have their usual significance. It has been estimated that the lifetime of the stereoisomers is less than 10^{-3} or 10^{-4} sec[3,8] (only averaged resonances are observed in the pmr spectra) and greater than 10^{-13} sec (separate electronic spectra observed for the planar and tetrahedral species). Planar–tetrahedral equilibria are known for monodentate tertiary phosphine complexes of the type $Ni(PR_3)_2X_2$ where X = Cl, Br, I, and PR_3 is an alkyldiaryl- or dialkylarylphosphine;[9] however, heretofore no nmr studies of these systems have been made. The present authors recently reported[10] the pmr spectra of complexes of dissymmetric tertiary phosphines of the type $Ni(PR_1R_2R_3)_2X_2$ where X = I and $PR_1R_2R_3$ is methylphenyl-*p*-anisylphosphine. The multiplicity of pmr peaks was incorrectly (*vide infra*) attributed to a separation of resonances of the active (*dd* or *ll*) and *meso* (*dl*) diastereoisomers for the complexes synthesized from racemic phosphine. The present report deals with the X = Cl and Br analogs which, unlike the iodide, undergo a dynamical planar–tetrahedral equilibrium in solution. The unique feature of the present systems is that at low temperatures the rate of planar–tetrahedral interchange has been slowed so that separate resonances are observed for the two stereoisomers. For the first time, it is possible to measure this interconversion rate by nmr techniques.

Racemic and active, $[\alpha]_D$ −6.5° (methanol), methylphenyl-*p*-anisylphosphine were synthesized by the method of Korpiun, *et al.*,[11] except that the reduction of phosphine oxide to phosphine was accomplished stereospecifically with hexachlorodisilane.[12] The complexes of both active and racemic phosphine were synthesized under nitrogen as described previously[10] except that a few milliliters of hot hexane was added to the ethanolic solutions before filtration. Satisfactory elemental analyses were obtained and the complexes were found to be monomeric in benzene at 37° by osmometry.

Thermodynamic Parameters for the Planar–Tetrahedral Equilibrium. At and above room temperature only a single averaged resonance is observed for each set of equivalent protons and eq 1 may be applied. Assignments were made by comparison with the well-established triphenylphosphine analogs[13] and are indicated in Figure 1. ΔG° values were obtained from the magnitudes of the isotropic shifts of the *meta* proton reso-

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(1) This research was supported by the National Science Foundation through Grant GP 6321.

(2) A. Chakravorty, J. P. Fennessey, and R. H. Holm, *Inorg. Chem.*, **4**, 26 (1965).

(3) D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *J. Am. Chem. Soc.*, **85**, 397 (1963).

(4) A. Chakravorty and R. H. Holm, *Inorg. Chem.*, **3**, 1010 (1964).

(5) G. W. Everett, Jr., and R. H. Holm, *Proc. Chem. Soc.*, 238 (1964); *J. Am. Chem. Soc.*, **87**, 2177 (1965).

(6) G. R. Van Hecke and W. D. Horrocks, Jr., *Inorg. Chem.* **5**, 1968 (1966).

(7) W. D. Horrocks, Jr., *J. Am. Chem. Soc.*, **87**, 3779 (1965).

(8) M. J. O'Connor, R. E. Ernst, and R. H. Holm, *ibid.*, **90**, 4561 (1968).

(9) M. C. Browning, J. R. Mellor, D. J. Morgan, S. A. J. Pratt, L. E. Sutton, and L. M. Venanzi, *J. Chem. Soc.*, 693 (1962), and references therein.

(10) L. H. Pignolet and W. D. Horrocks, Jr., *Chem. Commun.*, 1012 (1968).

(11) O. Korpiun, R. A. Lewis, J. Chickos, and K. Mislow, *J. Am. Chem. Soc.*, **90**, 4842 (1968).

(12) K. Naumann, G. Zon, and K. Mislow, *ibid.*, **91**, 2788 (1969).

(13) G. N. LaMar, W. D. Horrocks, Jr., and L. C. Allen, *J. Chem. Phys.*, **41**, 2126 (1964).