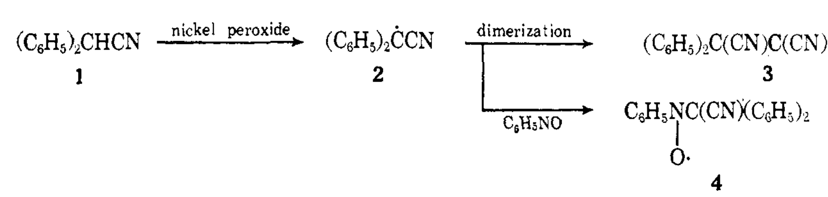

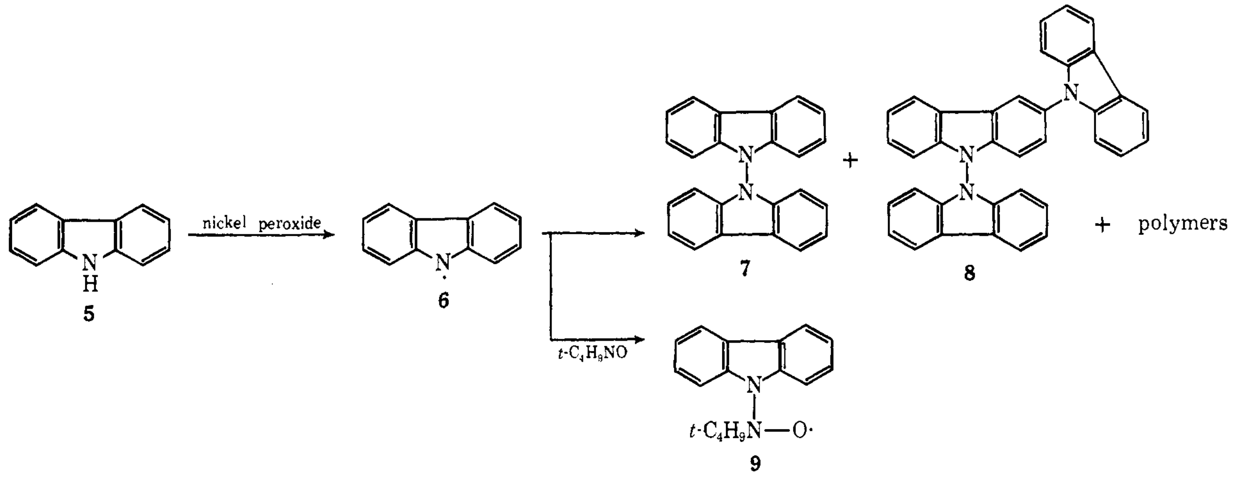

strates are collected in Table I with g values and the coupling constants. The structures of the nitroxides are reasonably deduced from their esr spectra. The nitroxides that were studied were stable and decay of their spectra was hardly noticed during the esr measurements. None of the nitroxides given in Table I was produced if a substrate, nitroso compound, or nickel peroxide was absent.[8]

The oxidation of diphenylacetonitrile (**1**) with 0.5 equiv of nickel peroxide resulted in an almost quantitative yield of tetraphenylsuccinonitrile (**3**).[1] The cyanodiphenylmethyl radical (**2**) is considered as an intermediate in this reaction, while the detection of nitroxide **4** in the presence of nitrosobenzene indicates that **2** is trapped by nitrosobenzene.

The oxidation of carbazole (**5**) with nickel peroxide in the presence of 2-methyl-2-nitrosopropane in the absence of light afforded an esr spectrum (Figure 1a) consisting of a triplet of triplets having equal intensity which was attributed to nitroxide **9**. Since the oxidation products of **5** with nickel peroxide are N,N′-dicarbazolyl (**7**) and 3-(N-carbazolyl)-N,N′-dicarbazolyl (**8**) along with some polymers,[9] detection of nitroxide **9** gives proof of the existence of the N-carbazolyl radical (**6**) in the course of the reaction.

The esr spectrum (Figure 1b) of nitroxide **10** obtained in the oxidation of acetonylacetone shows a hyperfine splitting (2.42 G) by one β proton with respect to the nitrogen atom. This observation implies that the hydrogen abstraction is not from the methyl group of acetonylacetone but from the methylene group.

The stable radical detected by esr during the decomposition of N-nitrosoacetanilide in benzene was presumed to be the phenyldiazotate radical by Binsch and Rüchardt,[10] but later Chalfont and Perkins[11] proposed that it had a nitroxide structure (**11**), and this view was strongly supported by Forrester.[12] The same esr spectrum as reported by Binsch and Rüchardt was obtained in the oxidation of acetanilide with nickel peroxide in the presence of nitrosobenzene. This result confirms the proposal of Chalfont and Perkins. The hyperfine splitting constant of the β nitrogen is obvious from the spectrum (Figure 1c) recorded when 3,5-dideuterionitrosobenzene was used as a radical trap instead of nitrosobenzene. The results obtained from the oxidation of phenols, alkylbenzenes, and other amines with nickel peroxide by means of this spin-trapping technique will be reported later.

Acknowledgment. The authors wish to thank Dr. K. Nishikida and Mr. S. Sakata for their assistances in obtaining the esr spectra.

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(8) A very weak phenylnitroxide esr spectrum, in most cases, was observed in mixing the substrate and nitrosobenzene at room temperature. It is supposed that nitrosobenzene abstracted a hydrogen from the substrate to form phenylnitroxide.

(9) J. Sugita, *Nippon Kagaku Zasshi*, 88, 659 (1967).

(10) See Table I, footnote *e*.

(11) G. R. Chalfont and M. J. Perkins, *J. Amer. Chem. Soc.*, 89, 3054 (1967).

(12) A. R. Forrester, *Chem. Ind.* (London), 1483 (1968).

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The Synthesis and Solvolysis of *endo*-Bicyclo[3.2.1]-oct-6-en-8-yl Tosylate

Sir:

Although the unusual reactivity ($k_{\mathrm{I}}/k_{\mathrm{II}} = 10^{11}$) of the *anti*-7-norbornenyl system was first reported more than 10 years ago,[1] interest in it and related systems still remains high.[2,3] However, most of the recent interest has been centered on the actual structure of the nonclassical 7-norbornenyl ion. Only one report has been made concerning the geometry necessary for participation of the double bond with the developing cationic center in the cyclopentene ring. Bartlett and Rice

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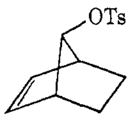
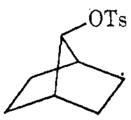
(1) (a) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Amer. Chem. Soc.*, 77, 4183 (1955); (b) S. Winstein and M. Shatavsky, *ibid.*, 78, 592 (1956).

(2) (a) P. G. Gassman and A. F. Fentiman, Jr., *ibid.*, 91, 1545 (1969); (b) J. J. Tufariello and R. J. Lorence, *ibid.*, 91, 1546 (1969); (c) J. Lhomme, A. Diaz, and S. Winstein, *ibid.*, 91, 1548 (1969); (d) P. G. Gassman and D. S. Patton, *ibid.*, 91, 2160 (1969).

(3) Y. Hata and H. Tanida, *ibid.*, 91, 1170 (1969).



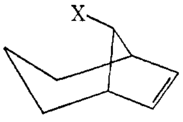
I



II

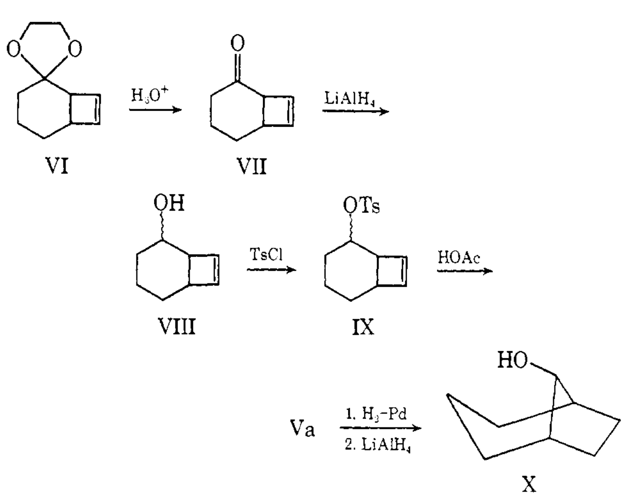
found that 4-bromocyclopentene (III) undergoes solvolysis more slowly than its saturated analog IV.[4] They concluded that the cyclopentene ring must be puckered for anchimeric assistance by the double bond as in the 7-norbornenyl system. There is no cyclopentene system which has been reported which has geometry intermediate between cyclopentene itself and the extreme puckering in norbornene.

This fact combined with our interest in the determination of the actual geometries necessary for anchimeric assistance by the π system of the carbon–carbon double bond led us to the synthesis and solvolytic study of *endo*-bicyclo[3.2.1]oct-6-en-8-yl tosylate (Vc). We thought that bicyclo[3.2.1]octene should contain a cyclopentene ring which would have a degree of puckering intermediate between 7-norbornene and cyclopentene.



Va, X = OAc
b, X = OH
c, X = OTs

Acid hydrolysis of the ketal of bicyclo[4.2.0]oct-7-en-2-one (VI)[5] gave the ketone VII, bp 78–81° (16 mm).[6] Reduction of the ketone with lithium aluminum hydride afforded a mixture of the (80% *endo*-, 20% *exo*-) bicyclo[4.2.0]oct-7-en-2-ols (VIII).[7,8] Buffered acetolysis of the crude tosylates (IX) of the alcohols (VIII) gave a mixture of three acetates with the major component as 80% of the mixture.[9] However, unbuffered acetolysis gave a single acetate which was identical with the major component of the buffered acetolysis of IX. It was identified as the desired *endo*-bicyclo[3.2.1]oct-6-en-8-yl acetate (Va). Its nmr spectrum had absorption at τ 4.13 (t, 2, CH=CH), 5.25 (t, 1, CHOAc), 7.48 (m, 2, bridgehead), 7.94 (s, 3, CH_3), and 8.20–9.08 (m, 6, (CH_2)$_3$). The *endo* configuration of Va was established by its reduction with hydrogen over palladium followed by lithium aluminum hydride to give a saturated alcohol, mp 198–199°. *endo*-Bicyclo[3.2.1]octan-8-ol (X) has a reported melting point of 200.2–201°.[10] Furthermore, its ir spectrum was identical with that reported for X.[11] Reduction of Va with lithium aluminum hydride gave *endo*-bicyclo-[3.2.1]oct-6-en-8-ol (Vb), mp 169.5–171°. The tosylate of Vb was prepared, mp 68.5–70°.



The rate constants of the acetolysis of Vc were determined at two temperatures (see Table I). Examination of the product mixture of the acetolysis of Vc indicated that there was only one product formed, the parent acetate Va.

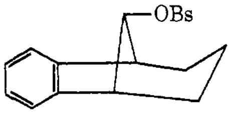
Table I. Rates of Buffered Acetolysis of *endo*-Bicyclo[3.2.1]oct-6-en-8-yl Tosylate

Temp, °C	Rate, sec^{-1}
60.1	$(7.86 \pm 0.01) \times 10^{-5}$
74.6	$(3.69 \pm 0.04) \times 10^{-4}$
25	1.0×10^{-6} [a]
$\Delta H^{\ddagger}$ = 23.9 kcal/mol	$\Delta S^{\ddagger}$ = −5.8 eu

[a] Extrapolated value.

The observation that in the acetolysis of Vc the stereochemistry of C-8 is completely preserved indicates that as in the case of I the double bond at C_6–C_7 participates in the solvolysis of Vc. The kinetic data also support anchimeric assistance ($k_{\mathrm{Vc}}/k_{\mathrm{X\text{-}OTs}} = 1.9 \times 10^5$) and presumably the formation of an intermediate nonclassical ion. It is interesting to note that while the acetolysis of Vc gives only the parent acetate as a product, *endo*-bicyclo[3.2.1]octan-8-yl tosylate (X-OTs) gives a complex mixture of six products.[10]

The results of a kinetic study of the acetolysis of 6,7,8,9-tetradehydro-5,9-methano-5H-benzocycloheptenexo-10-yl arenesulfonate (XI) have recently been reported.[3] Although XI gives essentially only parent acetate as an acetolysis product, its rate is essentially identical with that of X-OTs (allowing for corrections due to the brosylate as the leaving group). This observation along with our results ($K_{\mathrm{Vc}}/k_{\mathrm{X\text{-}OTs}} = 1.9 \times 10^5$) suggests that the double bond of Vc is more effective at participation than is the benzene ring of XI.



XI

It is concluded, in light of the rate ratios of the unsaturated to saturated compounds of the three systems discussed (see Table II), that the degree of puckering in the cyclopentene ring and hence the distance between the π system of the carbon–carbon double bond and devel-

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[4] P. D. Bartlett and M. R. Rice, *J. Org. Chem.*, 28, 3351 (1963).

[5] H. O. House and T. H. Cronin, *ibid.*, 30, 1061 (1965).

[6] C. G. Scouten, F. E. Barton, Jr., J. R. Burgess, P. R. Story, and J. F. Garst, *Chem. Commun.*, 78 (1969).

[7] A. C. Cope, S. Moon, C. H. Park, and G. L. Woo, *J. Amer. Chem. Soc.*, 84, 4865 (1962).

[8] A small portion of the alcoholic mixture was converted to the acetates and analyzed by glpc.[7]

[9] The nmr spectrum of a mixture of the two minor acetates suggested that they were the epimeric bicyclo[3.3.0]oct-3-en-2-yl acetates.

[10] C. S. Foote and R. B. Woodward, *Tetrahedron*, 20, 687 (1964).

[11] A. C. Cope, J. M. Grisar, and P. E. Peterson, *J. Amer. Chem. Soc.*, 82, 4299 (1960).

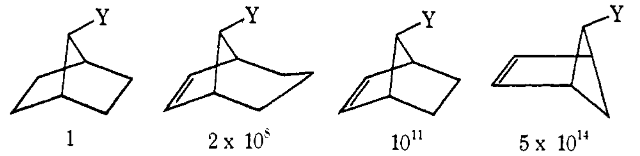
Table II. Rate Ratios (Unsaturated/Saturated) of Related Cyclopentene Systems

Compounds	$k_{\mathrm{unsat}}/k_{\mathrm{sat}}$	Ref
I, II	10^{11}	1
Vc, X-OTs	1.9×10^5	This work and ref 10
III, IV	0.25	4

oping positive charge are extremely crucial in the overall effect of anchimeric assistance of the carbon–carbon double bond in the cyclopentenyl system.[12]

Acknowledgment. This work was supported in part by a grant from the Petroleum Research Fund, administered by the American Chemical Society.

[12] The recent report of the solvolysis of a derivative of the *exo*-bicyclo[2.1.1]hex-2-en-5-yl system (S. Masamune, S. Takada, N. Nakatsuka, R. Vukov, and E. N. Cain, *J. Amer. Chem. Soc.*, **91**, 4322 (1969)) allows a comparison of the relative rates of the three related cyclopentenyl systems with the norbornyl system at 25°.



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Oxidative Additions and Catalysis of Olefin Hydrogenation by Tris(triphenylphosphine)nitrosylrhodium

Sir:

Organotransition metal chemistry is conveniently organized into patterns of analogous reactions such as oxidative additions whereby d^n complexes add two-electron oxidants forming d^{n-2} products.[1] At least a few examples of oxidative additions are known for each even d^n configuration, but d^8 [2] and more recently d^{10} complexes[3] have been the most thoroughly studied.

The present work stems from our interest in expanding the scope of d^{10} oxidative additions to neutral complexes of elements to the left of the nickel triad by exploring reactions of nitrosyls. This project led us to consider another question which ultimately may be more significant.

The nitrosyl ligand usually acts as NO$^+$ bonding linearly and forming analogs to carbonyl compounds one triad to the right.[4] However, the bonding and geometries of other nitrosyl complexes are controversial. Recent X-ray diffraction studies have revealed examples where the M–N–O angle approaches 120°[5] and the ligand may be considered as NO$^-$, whereas other complexes exhibit intermediate angles.[6] It seems likely that the two extreme forms may not represent deep energy minima, but that a wide range of angles may be accessible, perhaps giving rise to fluxional behavior. Inasmuch as the limiting forms, NO$^+$ and NO$^-$, are usually found in complexes whose coordination geometries reflect the implied oxidation state of the central metal, a conformational deformation of the other ligands about the metal might be expected to accompany any wide amplitude bending of the NO group. The most important result of such a deformation would be the creation of a vacant coordination site at the central metal reflecting the implied increase in its oxidation state. Inasmuch as coordinative unsaturation is a key feature of many homogeneous metal catalysts, a thermally accessible or chemically induced conformational change of this type could confer on a nitrosyl complex catalytic activity not found with its carbonyl cognate.

This hypothesis remains speculative, but in those few cases in which the reactions of nitrosyl complexes have been compared with carbonyl analogs, striking differences are found. Examples include mechanisms of ligand replacement reactions[7] and catalysis of diene dimerization.[8] Catalysis of olefin hydrogenation by the rhodium nitrosyl **1a** described below can be added to this list.

The rhodium and iridium nitrosyls, **1a** and **1b**, were prepared by bubbling NO through a boiling THF solution of the appropriate trichloride in the presence of excess Ph_3P and granulated zinc, affording yields of 98 and 40%.[9]

$$\mathrm{MX_3\cdot 3H_2O + 3L \xrightarrow[\text{THF, }65^\circ]{\text{Zn, NO}} M(NO)L_3}$$

$$\mathrm{L = Ph_3P} \qquad \begin{array}{l}\mathbf{1a}, \mathrm{M = Rh}\\ \mathbf{b}, \mathrm{M = Ir}\end{array}$$

Both nitrosyls undergo a series of oxidative addition reactions with reagents such as halogens, mercuric halides, hydrogen halides, alkyl halides, and acyl halides. Roper[10] has recently reported reactions of the iridium complex **1b**, but certain of his results are different from those for the rhodium complex **1a** described herein.

Treatment of **1a** with I_2 or HgI_2 afforded the five-coordinate diiodide **2**

$$\mathrm{Rh(NO)L_3 + I_2 \longrightarrow \underset{\mathbf{2}}{Rh(NO)I_2L_2} + L}$$

elemental mercury being formed in the latter case. The NO band shifts from 1610 to 1630 cm^{-1} during the reactions (Table I) in contrast to Roper's[10] result with the iridium complex where the product has a lower (1560 cm^{-1}) NO band. A phosphine ligand is ejected during these reactions.

Benzoyl chloride adds to **1a** forming a five-coordinate benzoyl adduct **3a**,

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[1] J. P. Collman, *Accounts Chem. Res.*, 1, 136 (1968).

[2] J. P. Collman and W. R. Roper, *Advan. Organometal. Chem.*, **7**, 54 (1968).

[3] (a) R. Ugo, *Coord. Chem. Rev.*, 3, 319 (1968); (b) J. P. Birk, J. Halpern, and A. L. Pickard, *Inorg. Chem.*, 7, 2672 (1968); *J. Am. Chem. Soc.*, 90, 4491 (1968).

[4] (a) W. P. Griffith, *Advan. Organometal. Chem.*, 7, 211 (1968); (b) B. F. G. Johnson and J. A. McCleverty, *Progr. Inorg. Chem.*, 7, 277 (1966).

[5] D. J. Hodgson, N. C. Payne, J. A. McGinnety, R. G. Pearson, and J. A. Ibers, *J. Am. Chem. Soc.*, **90**, 4486 (1968).

[6] A. T. McPhail and G. A. Sim, *J. Chem. Soc., A*, 1858 (1968), and references therein.

[7] D. E. Morris and F. Basolo, *J. Am. Chem. Soc.*, **90**, 2531 (1968), and references therein.

[8] J. P. Candlin and W. H. James, *J. Chem. Soc., C*, 1856 (1968).

[9] The rhodium complex was also prepared by the earlier method: W. Hieber and K. Heinecke, *Z. Anorg. Allgem. Chem.*, **316**, 321 (1962).

[10] C. A. Reed and W. R. Roper, *Chem. Commun.*, 155 (1969).