of NO_2 gives it first consideration. If it is NO_2 and if it is the N in NO_2 that bonds to the abstracted H, then there is a resemblance between chlorinations *via* $R_2NH\cdot^+$ and oxidations *via* NO_2. In both cases, a highly electron withdrawing group is attached to a nitrogen radical.

The reactions were stirred with a mechanical stirrer. Excess NO_2 was vented through a water trap. Two phases were present initially at 90°, but the mixture became homogeneous as the reaction progressed.

The monoacids and diacids were isolated by cooling to 25°, diluting to 10% HNO_3, saturating with Na_2SO_4, extracting with ether, and removing the ether. After weighing, the acids were analyzed by conversion to their methyl esters with CH_2N_2 and gas chromatography of the esters. Both EGSS-X and SE-30 0.25-in. columns[10] were used because the retention time of methyl hexadecanoate was close to that of dimethyl octanedioate on the EGSS-X column and close to that of dimethyl tridecanedioate on the SE-30 column. Retention times and response curves were determined using authentic samples of the methyl esters of the C_3, C_5–C_8, C_{10}, C_{12}, C_{14}, and C_{16} monoacids and C_6–C_{10}, C_{12}, C_{14}, and C_{16} diacids.

Preliminary studies on the C_8, C_{10}, C_{12}, and C_{14} monoacids confirm the principles established with hexadecanoic acid. There have been numerous studies of HNO_3 oxidations of alcohols and ketones to diacids and a few studies on HNO_3 oxidation of crude hydrocarbon fractions to small diacids. The two subjects have been reviewed,[11] but neither are directly germane to this report.

Acknowledgment. This work was supported by a grant from the National Science Foundation. This support is gratefully acknowledged.

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(10) Columns supplied by Applied Science Laboratories, State College, Pa., 16801.

(11) E. H. Pryde and J. C. Cowan in "Condensation Monomers," J. K. Stille, Ed., Wiley, New York, N. Y., Chapter 1.

(12) National Science Foundation Fellow.

N. C. Deno,* Craig Pierson,[12] Selim Seyhan
Department of Chemistry, The Pennsylvania State University
University Park, Pennsylvania 16802

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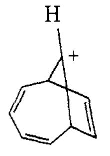
Rearrangement Reactions of Bicyclo[4.2.1]nona-2,4,7-trien-9-yl Cations[1]

Sir:

The bicyclo[4.2.1]nona-2,4,7-trien-9-yl cation (**1**) and its derivatives are of interest with respect to their properties,[1,2] the processes by which they isomerize,[1,2a–d] and their possible homoaromaticity[2e] and bicycloaromaticity.[2e–g] We should now like to describe further the behavior of bicyclo[4.2.1]nona-2,4,7-trien-9-yl cations and clarify their paths of rearrangement.[2d]



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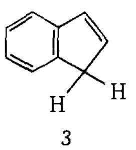
syn-Bicyclo[4.2.1]nona-2,4,7-trien-9-yl *p*-toluenesulfonate[3] (**2**) and di-*syn*-bicyclo[4.2.1]nona-2,4,7-trien-9-yl sulfite have each been reported to give indene (**3**) when heated;[2d] decomposition of **2** in the presence of lithium aluminum hydride yields *cis*-8,9-dihydroindene (**4**).[2d] The **3** and **4** apparently arise from the *cis*-8,9-dihydro-1-indenyl cation (**5**) generated.[4] Of



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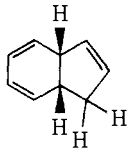

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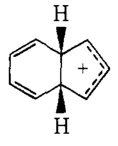

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the overall routes by which **1** (=**1a**) might isomerize to **5** (=**9** and **10**a or **14**a), two of the most prominent possibilities involve bishomotropylium ion processes resulting from (1) interaction of the diene bridge (eq 1) with the cationic center (C-9) and the monoene bridge and migration of C-2 or C-5 to C-9 to yield cation **8**a *via* **7**a[2d,5] and (2) bridging of C-7 and C-8 of the monoene unit (eq 1) with the cationic site (C-9) and with C-2 and C-5 of the diene system to give **13**a[5] *via* reorganization of **12**a. Mechanisms analogous to that of eq 1 are apparently involved in conversion of *syn*-9-hydroxy-9-phenylbicyclo[4.2.1]nona-2,4,7-triene (**15**) by thionyl chloride and pyridine, *via* **1**a, to *exo*-1-chloro-9-phenyl-*cis*-8,9-dihydroindene[2b,6] and in isomerization of bicyclo[4.2.1]nona-2,4,7-trien-9-one (**16**) to 1-indanone by boron trifluoride[2d] in ethyl ether or *p*-toluenesulfonic acid[1] in benzene.

It is now reported that 9-deuterio-*syn*-bicyclo[4.2.1]nona-2,4,7-trien-9-yl *p*-toluenesulfonate (mp 83–85°, lit[2d] mp 83–85°), prepared by reduction of **16** with sodium borodeuteride in deuterium oxide–methanol-*O-d* and reaction of the 9-deuterio-*syn*-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene (mp 51–52.5°, lit.[2d] mp 51–52.5°) with *p*-toluenesulfonyl chloride in pyridine, is converted at 74° in dimethyl sulfoxide to 2-deuterioindene (**14c**, eq 2, >74% yield). The indene isolated contains one atom of deuterium per molecule and its nmr spectrum, τ 2.71 (m, 4 H, aromatic H), 3.18 (m, 1 H, H at C-1), and 6.66 (m, 2 H, H at C-3), is identical with that of **14c** obtained by reducing 2-indanone (**18**) with sodium borodeuteride in deuterium oxide–methanol-*O-d*, reaction of 2-deuterio-2-indanol with *p*-toluenesulfonyl chloride–pyridine, and elimination of 2-deuterio-2-indanyl *p*-toluenesulfonate with potassium *tert*-butoxide in dimethyl sulfoxide. Conversion of **17** to **14c** thus occurs by a sequence as in eq 2 and

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(1) This research is abstracted primarily from the Ph.D. Dissertation of D. C. Sanders, The Ohio State University, Columbus, Ohio, 1972; *Diss. Abstr. B*, **33**, 3561 (1973).

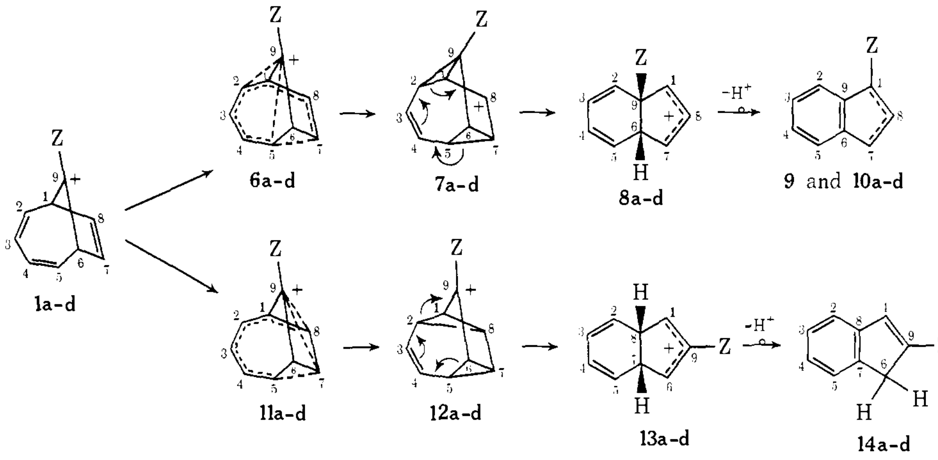
(2) (a) T. S. Cantrell and H. Shechter, *J. Amer. Chem. Soc.*, **89**, 5868 (1967); (b) A. S. Kende and T. L. Bogard, *Tetrahedron Lett.*, 3383 (1967); (c) R. E. Leone and P. von Schleyer, *Angew. Chem., Int. Ed. Engl.*, **9**, 860 (1970); (d) T. A. Antkowiak, D. C. Sanders, G. B. Trimitsis, J. B. Press, and H. Shechter, *J. Amer. Chem. Soc.*, **94**, 5366 (1972); (e) J. B. Grutzner and S. Winstein, *ibid.*, **94**, 2200 (1973); (f) M. J. Goldstein, *ibid.*, **89**, 6359 (1967); (g) M. J. Goldstein and R. Hoffmann, *ibid.*, **93**, 6193 (1971).

(3) In naming bicyclo[4.2.1]nona-2,4,7-trienes, the substituent at C-9 cis to the diene bridge is designated as syn.

(4) Cation **5** may give **3** by elimination and sigmatropic rearrangement or/and by rearrangement and elimination.

(5) It is to be emphasized that when Z = H (eq 1 and 2), **7a** and **12a** are identical chemically when equivalently delocalized.

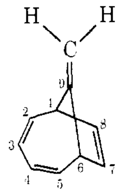
(6) Reference 2b has also found that *exo*-1-hydroxy-9-phenyl-*cis*-8,9-dihydroindene is converted by *p*-toluenesulfonic acid, possibly *via* **8b** (eq 1), to 1- and 3-phenylindenes (**9b** and **10b**).



a, Z = H b; Z = C_6H_5, c; Z = D d; Z = CH_3

implies that there is specific transannular monoene–diene interaction[7] in **1c** as in **12c** leading to **13c**.

Rearrangement of bicyclo[4.2.1]nona-2,4,7-trien-9-yl cations has been extended to acid catalyzed elimination of *syn*-9-hydroxy-9-methylbicyclo[4.2.1]nona-2,4,7-triene (**19**)[8] and isomerization of 9-methylenebicyclo[4.2.1]-nona-2,4,7-triene (**10**). Alcohol **19** was prepared (86% yield) from **16** and methylmagnesium bromide at 0° and subsequent acidification; **20** was obtained (77% yield) from **16** and methylenetriphenylphosphorane in dimethyl sulfoxide at 74°. Dehydration of **19** and isomerization of **20** by *p*-toluenesulfonic acid in benzene at 74° give 2-methylindene (**14d**, >80% yields); 1-methylindene (**9d**) and 3-methylindene (**10d**) were not detectable in these experiments by sensitive gas chromatographic methods. The conversions of **19** and **20** to **14d** are analogous to that of **17** to **14c** and indicate that the 9-methylbicyclo[4.2.1]nona-2,4,7-trien-9-yl cation (**1d**) rearranges by a specific bridging mechanism as in eq 2. The cationic conversion of **20** to **14d** reveals also that there is no formal initial stereochemical requirement at C-9 for entry into the rearrangement system of eq 2.[9] It is noted further that the previous exclusive conversion of **15** by *p*-toluenesulfonic acid to 2-phenylindene (**14b**)[2b] and the pyrolyses of *syn*-9-acetoxy-9-methylbicyclo-[4.2.1]nonatriene and *syn*-9-benzoyloxy-9-phenylbicyclo-[4.2.1]nonatriene at 184° in *o*-dichlorobenzene to **14d** and to **14b**, respectively,[2c] are now understandable *via* the reaction path of eq 2.



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What is not yet definitive, however, are the structural and environmental factors which allow bicyclo[4.2.1]-nona-2,4,7-trien-9-yl cationic reactions to occur *via* rearrangement processes as in eq 1. A major fact yet to be determined is whether sequences which begin as in eq 2 give products which presently appear to have been derived *via* eq 1. Based on the present information, however, it may be that bicyclo[4.2.1]nona-2,4,7-trien-9-yl cations, stabilized by electron-donor delocalizing groups at C-9 and possibly by solvent interaction at C-9 from the sterically available anti direction, do not bring out sufficient monoene–diene interaction from below as in **12**, and thus migration of C-2 or C-5 of the diene bridge to C-9 becomes the effective entry to *cis*-8,9-dihydroindenyl derivatives.

Acknowledgment. We should like to thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

David C. Sanders, Harold Shechter*
Chemistry Department, The Ohio State University
Columbus, Ohio 43210

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[7] The physical constants of all intermediates and products compare favorably with literature values. The deuterium contents (~100%) of all labeled materials were confirmed by mass spectral and nmr methods.

[8] Alcohol **19** is identical with that prepared previously from dilithium cyclooctatetraenide and acetyl chloride and hydrolysis.[2a]

[9] The importance of hybridization at C-9 and the shape of bicyclo-[4.2.1]nona-2,4,7-triene systems is also indicated by the recent observations that, based on photoelectron spectra, there is considerable interaction of the π systems in **20** but none in bicyclo[4.2.1]nona-2,4,7-triene: M. T. Reetz, R. W. Hoffmann, W. Schäfer, and A. Schweig, *Angew. Chem.*, **85**, 45 (1973).

An Extension of the Nitrosyl–Aryldiazo Analogy. The Structure of an Aryldiazo Group Coordinated to Rhodium in a Doubly Bent Fashion

Sir:

Since the first unequivocal structural evidence for a bent M–N–O linkage in transition metal chemistry was presented,[1] chemical and structural interest in these systems has expanded rapidly. A recent tabulation[2] includes eight transition metal nitrosyl complexes out of 52 in which the M–N–O angle is between 120 and 128°. The analogy between NO^+ (linear M–N–O) and RN_2^+ (R = aryl) on the one hand and between NO^- (M–N–O angle, 120°) and RN_2^- on the other is an obvious one and suggests that the aryldiazo[3] ligand has the same amphoteric nature as does nitric oxide. We wish to report the first structural

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[1] D. J. Hodgson, N. C. Payne, J. A. McGinnety, R. G. Pearson, and J. A. Ibers, *J. Amer. Chem. Soc.*, **90**, 4486 (1968); D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, **7**, 2345 (1968).

[2] B. A. Frenz and J. A. Ibers, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci., Phys. Chem.*, **11**, 33 (1972).

[3] Consistent with the nomenclature proposed for C_6H_5NNH, phenyldiazene, and with that for $C_6H_5NN^+$, phenyldiazonium ion, we adopt the names phenyldiazeno, instead of phenyldiimido, and phenyldiazo, instead of phenylazo, when these moieties are coordinated to a metal; phenyldiazo is used for both forms, RN_2^+ and RN_2^-. See E. M. Kosower, *Accounts Chem. Res.*, **4**, 193 (1971).