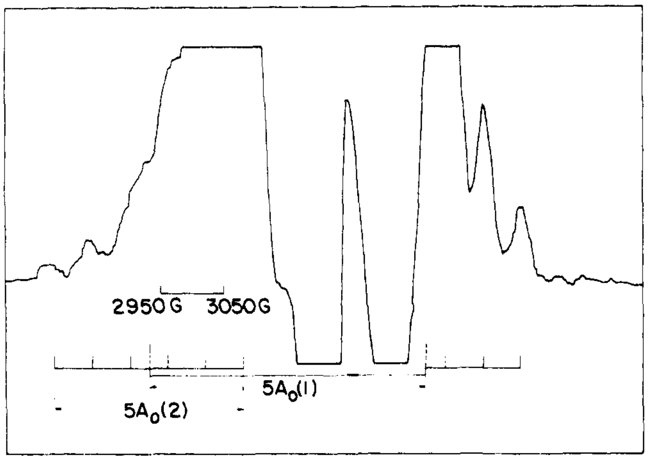

Figure 2. Second derivative X-band ESR spectrum of a frozen solution of Co(bzacen)py-$^{17}O_2$ (~40 atom %) complex in CH_2Cl_2 at −100°.

script, the work of Hoffman, Szymanski, and Basolo[7] became available to us. These workers have carefully repeated parts of Tovrog and Drago's ESR and NMR experiments and conclude that "the observations are artefacts caused by the presence of O_2".

The asymmetry of the O_2^- group in frozen solution is not inconsistent with the equivalence of the oxygen atoms in solution. As we suggested earlier, it seems probable that the O_2^- group is jumping between two equivalent bent conformations in solution, and that this motion is frozen in the solid. In single crystals, the O–O group is known, from X-ray studies, to be bent.[8] In this connection it is of significance that Collman et al.[9] have explained the temperature dependence of the line width of the O_2 stretching frequency in an Fe(II) porphyrin dioxygen complex as due to a rapid thermal equilibrium between several rotomeric states. "Lowering the temperature apparently brings about an increase in the population of the most stable conformer". In our case we postulate two energetically equivalent conformations in solution. In the solid state, the degeneracy is split by the local environment of each molecule in the rigid lattice.

In conclusion we feel that, at least for Co(bzacen), the description of bound oxygen in terms of an O_2^- structure is unambiguously proved, by our own and other workers results, and that such a structure occurs in most if not all cobalt(II) adducts of dioxygen.

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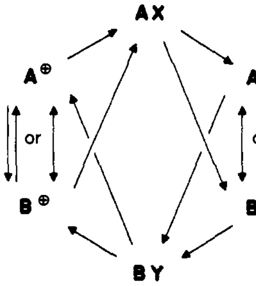
Reversible Charge Control. The Barbaralyl-Bicyclo[3.2.2]nonatrienyl Example

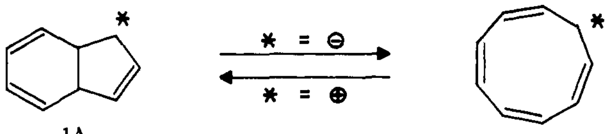
Sir:

Rational synthetic methodology has long recognized the technique of deliberately shifting thermodynamic control from the ultimate product to a chemical intermediate. For example, "contrathermodynamic" alkene isomerizations are achieved through the greater thermodynamic stability of the primary alkalboranes.[1] Alkylaromatic isomerizations can be made highly selective through the greater thermodynamic stability of the tertiary carbonium ion.[2]

It has apparently not been recognized that cyclic conjugated and homoconjugated topologies allow extending this strategy to the *reversible charge control* of a desired carbon skeleton.[3] In detail, such control would (a) select anionic conditions to transform a derivative of one structural isomer, more stable as the cation (AX in Scheme I), into a derivative of the second (BY), more stable as the anion. Then (b) it would select cationic conditions to achieve the reverse transformation. **1A** $\rightleftharpoons$ **1B** provides a (still incompletely realized)[4] pericyclic example.

Scheme I



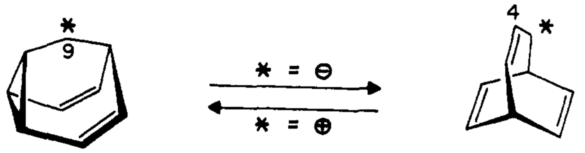


1A

1B

Two further experimental criteria protect this strategy from mechanistic and theoretical distraction: (c) AX must retain its structural integrity under cationic conditions and (d) BY must do the same under anionic ones. No experimental system that we know has yet satisfied all four criteria.

Previous studies of the 9-barbaralyl (**2A**) $\rightleftharpoons$ 4-bicyclo[3.2.2]nonatrienyl (**2B**) transformations did, however, satisfy three. (b) Aqueous acetone hydrolysis of 4-bicyclo[3.2.2]nonatrienyl *p*-nitrobenzoate[5a] or 3,5-dinitrobenzoate[5b] provides 9-barbaralol as the exclusive alcohol product. (c) 9-Barbaralyl tosylate also provides no other alcohol under similar conditions.[5c] (d) Potassium *tert*-butoxide catalyzed hydrogen exchange of bicyclo[3.2.2]nonatriene proceeds without rearrangement.[5a,d] So too does Na/K transformation of 4-methoxybicyclo[3.2.2]nonatriene to the anion followed by methanol[5a] or *tert*-butyl alcohol[5d] protonation.



2A

2B

We here complete the last formal requirement by reporting the first unambiguous synthesis of 9-halobarbaraianes and their anionic transformation to bicyclo[3.2.2]nonatriene and to two of its alkylated derivatives.

9-Bromobarbaralane[6] was obtained from the corresponding alcohol,[7] triphenylphosphine, and carbon tetrabromide[8] in 79% yield. 9-Chlorobarbaralane[9] was obtained both by the analogous use of carbon tetrachloride (61%) as well as by thionyl chloride treatment of bicyclo[3.2.2]nonatrien-4-ol (87%).

Most explicitly, Na-K-LiBr treatment of 9-chlorobarbaralene in 1,2-dimethoxyethane-d_{10} at −20° generated the deep green color and unmistakable ^{1}H NMR spectrum of lithium bicyclo[3.2.2]nonatrienide.[5a,10] Although contamination by (as much as 20%) bicyclo[3.2.2]nonatriene could not entirely be avoided, no more than 2% barbaralane[11a] was ever present. As expected, alcohol protonation of these anionic solutions provided only bicyclo[3.2.2]nonatriene (101% from methanol, 68% from *tert*-butyl alcohol, each contaminated by less than 1.3% barbaralane[11b]). Qualitatively similar results were also obtained: (a) in tetrahydrofuran solution, (b) employing the bromide rather than the chloride, or (c) with the chloride in tetrahydrofuran containing triethylamine.

4-Methylbicyclo[3.2.2]nonatriene[12] appeared also to be the exclusive methyl iodide alkylation product of such anionic solutions. The significantly more sluggish reaction of 9-chlorobarbaralane with *n*-butyllithium in refluxing ether[13] provided 75% of a 1:1 mixture of bicyclo[3.2.2]nonatriene and its 4-*n*-butyl derivative[14] after aqueous protonation.

The sense of reversible charge control (i.e., $\mathbf{2A} \underset{+}{\overset{-}{\rightleftharpoons}} \mathbf{2B}$) is of course consistent with qualitative theoretical descriptions of the bicyclo[3.2.2]nonatrienyl anion (bicycloaromatic) and cation (antibicycloaromatic).[3] The more quantitative treatments required by the 9-barbaralyl ions enhance this bias. The cation ($\mathbf{2A}^+$) is highly stabilized; the anion would need to possess a half-filled degenerate HOMO—at least in the idealized D_{3h} geometry.[15,16]

The extent to which such control is realized, however, is subject to experimental detail in a way that is theoretically less obvious. For example, protonation of the bicyclo[3.2.2]nonatrienyl anion by HCl (rather than by ROH) generates barbaralane (2-9%)[11b] in addition to bicyclo[3.2.2]nonatriene (71-79%)[11b] under kinetically controlled conditions.[18] Whatever its ultimate mechanistic rationale,[20] this experiment recalls (and was suggested by) the corresponding collapse of isomeric purity from solvolytically generated nonbornenyl and nonbornadienyl cations.[21] There, increased yields of tricyclic product are achieved when alcohols and carboxylic acids are replaced by the more nucleophilic borohydride and methoxide anions.

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(6) *M/e* 196, 198; ^{1}H NMR τ (CDCl$_3$) 4.14 (t, J = 7.5 Hz) and 4.36 (t, J = 7.5 Hz) (2.14), 5.73 (t, J = 7.5 Hz) and 5.95 (t, J = 2.5 Hz) (4.81), 7.24 (dt, J = 2.5, 7.5 Hz) (2.04) ppm. Anal. Calcd: C, 54.85; H, 4.60; Br, 40.55. Found: C, 54.72: H, 4.79; Br, 40.78.

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(9) (a) Mp 18.5°; *m/e* 152, 154; ^{1}H NMR τ(CDCl$_3$) 4.15 (t, J = 7.5 Hz) and 4.42 (t, J = 7.5 Hz) (1.99), 5.88 (t, J = 7.5 Hz) and 6.05 (t, J = 3.0 Hz) (5.00), 7.35 (dt, J = 3.0, 7.5 Hz) (1.99); Anal. Calcd: C, 70.83; H, 5.94; Cl, 23.23. Found: C, 70.77; H, 6.13; Cl, 23.20. (b) This structure had hitherto incorrectly been assigned to a material of somewhat different melting point (106°) and spectroscopic properties.[7] Professor Doering's gracious concurrence in this reevaluation is gratefully acknowledged.

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(11) (a) By ^{1}H NMR integration at τ 5.7–6.7 ppm. (b) By GC, using cumene as a calibrated internal standard.

(12) In 60% yield; *m/e* 132; ^{1}H NMR τ(CCl$_4$) 3.35–4.4 (m) (5), 5.15–5.5 (m) (1), 7.10 (m) (2), 7.9 (m) (1), and 9.00 (d, J = 7 Hz) (3) ppm.

(13) Neither the bromide nor the chloride react with methyl- or *n*-butyllithium at a preparatively convenient rate at ambient temperatures.

(14) *M/e* 174; ^{1}H NMR τ (CCl$_4$) 3.3–4.4 (m) (5), 3.25 (dt) (1), 7.0 (m) (2), 8.07 (m) (3), 8.68 (d, J = 4 Hz) (6), and 9.08 (t, J = 7 Hz) (3).

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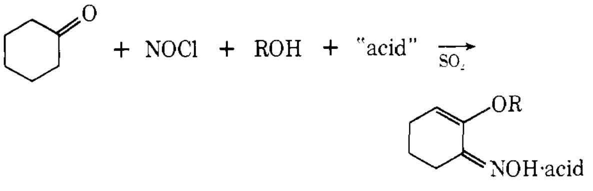
Nitrosation in Organic Chemistry. Nitrosolysis, a Novel Carbon–Carbon Bond Cleavage Effected through Nitrosation. Nitrosolysis of Ketones

Sir:

While cyclopentanone, cyclohexanone, and cycloheptanone undergo nitrosation to give the corresponding α,α'-dioximino ketones,[1,2] larger ring cyclic ketones[3] and aliphatic open chain ketones[1] give mononitrosation products.

We would like to report a new nitrosation technique for mononitrosation of cyclohexanone which led to the development of the nitrosolysis reaction—a novel single-step carbon–carbon bond cleavage of various ketones effected through nitrosation. Reaction of cyclohexanone with nitrosyl chloride in liquid sulfur dioxide in the presence of an alcohol and 1 equiv of a suitable acid (eq 1) provides an entry



(1)