Communications

See Editorial, *J. Org. Chem.*, **37**, No. 19, 4A (1972).

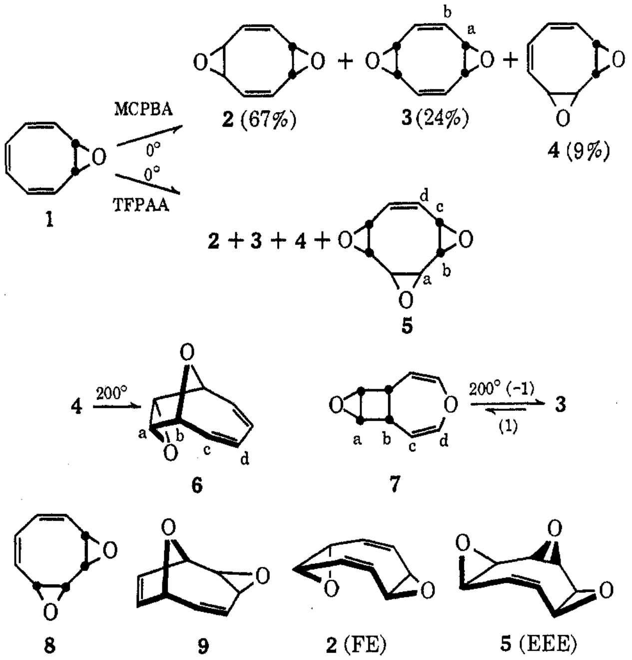
Dioxa and Trioxa Derivatives of C_8H_8

Summary: Peracid oxidation of cyclooctatetraene oxide yields dioxiranes **2**, **3**, and **4** and trioxirane **5**, while thermal treatment of **3** and **4** affords isomers **7** and **6**, respectively.

Sir: In an extension of our work with the heteronins[1] and their bicyclic tautomers[2-4] we have synthesized compounds containing additional heteroatoms within the basic C_8H_8 constituent and we now report on one trioxa and five dioxa members of the family.[5]

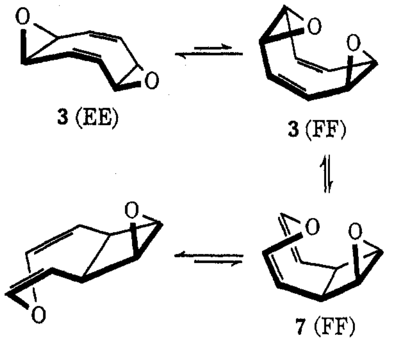
Treatment of cyclooctatetraene oxide (**1**)[6] with *m*-chloroperbenzoic acid produces, in 75% yield, a three-component mixture consisting of[7] ~67% **2** [mp 40.5–41°; nmr (60 MHz, $CDCl_3$) τ 3.93 (2 H, d, J = 11 Hz), 4.42 (2 H, br d, J = 11 Hz), 6.19 (2 H, d, J = 2 Hz), 6.40 (2 H, s); uv $\lambda_{max}^{C_6H_{14}}$ 198 nm (ϵ ~4300); *m/e* 136 (P^+, 42%)], 24% **3** [mp 165.5–166.5°; nmr (60 MHz, $CDCl_3$) τ 4.20 (4 H, s), 6.33 (4 H, s); uv $\lambda_{max}^{C_6H_{14}}$ 196 nm (ϵ ~2100); *m/e* 136 (P^+, 6.3%)], and 9% **4** [mp 41–42°; nmr (60 MHz, $CDCl_3$) τ 3.93 (2 H, d, J = 11 Hz), 4.25 (2 H, d, J = 11 Hz), 6.36 (2 H, d, J = 4 Hz), 6.83 (2 H, d, J = 4 Hz); $\lambda_{max}^{C_6H_{14}}$ 222 nm (ϵ 2500); *m/e* 136 (P^+, 35%)]. Exposure of **1** to trifluoroperacetic acid instead of *m*-chloroperbenzoic acid yields in 70% yield a mixture[7] of **2** (30%), **3** (50%), **4** (5%), and the trioxa homolog, **5** [15%, mp 145–146°; nmr (60 MHz, $CDCl_3$) τ 4.02 (2 H, s), 6.43 (2 H, d, J = 3.5 Hz), 6.63 (2 H, d, J = 3.5 Hz), 6.90 (2 H, s); uv $\lambda_{max}^{C_6H_{14}}$ 200 nm (ϵ ~1100); *m/e* 152 (P^+, 1.3%)] (Scheme I).

Scheme I



The structural and stereochemical details of **2** follow from its nmr spectrum which implicates the presence of two magnetically distinct nonadjacent oxirane functions within a rigid frame,[8] *e.g.*, **2** (FE).[9] By contrast, the nmr spectrum of **3** requires a structure with only two magnetically distinct sets of protons. In addition, the absence of coupling between "olefinic" and "oxirane" protons in **3** is consistent with its existence in the diextended form **3** (EE) (Scheme II), in which the H_a–H_b dihedral angle is measured (from Dreiding molecular models) to be ~90° as opposed to the sterically more demanding difolded arrangement **3** (FF) where H_a–H_b is estimated at ~40°.[10] The formulation of **4** as a 1,3-dioxirane also follows from the nmr spectrum which is best accommodated by the presence of two symmetrically disposed, vicinally positioned oxirane groups. The trans disposition of the groups in **4** is also indicated by the nmr characteristics of this substance[11] and is further confirmed by its conversion to **5** on oxidation and to **6** on thermolysis (*vide infra*).

Scheme II



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[1] A. G. Anastassiou, *Accounts Chem. Res.*, **5**, 281 (1972).

[2] A. G. Anastassiou and R. P. Cellura, *J. Org. Chem.*, **37**, 3126 (1972).

[3] A. G. Anastassiou, R. L. Elliott, and A. Lichtenfeld, *Tetrahedron Lett.*, 4569 (1972), and references cited therein.

[4] A. G. Anastassiou and B. Chao, *Chem. Commun.*, 979 (1971); *ibid.*, 277 (1972).

[5] All new substances yielded correct combustion analyses.

[6] W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Justus Liebigs Ann. Chem.*, **560**, 93 (1948); A. C. Cope and B. D. Tiffany, *J. Amer. Chem. Soc.*, **73**, 4158 (1951).

[7] Experimental details will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JOC-73-2421. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

[8] Meaningfully, the nmr resonances of **2** remain temperature invariant on cooling to −85° but undergo the expected coalescence or heating. The observed coalescence temperature, T_c (diphenyl ether) ~135°, corresponds to a $\Delta G^{\ddagger}$ term of ~20.5 kcal/mol for the ring inversion process which alters the effective shape of the molecule from static C_s to dynamic C_{2h}.

[9] The notations F and E stand for folded and extended, respectively, and are employed as a conformational label of each C_8H_8O unit present in the molecule.

[10] The nmr spectrum of **3** remains invariant in the temperature range of −60° to 161°. This finding might be interpreted in one of two ways: (i) **3** is conformationally rigid and (ii) **3** (EE) is the predominant component in a rapidly interconverting system of **3** (EE) and **3** (FF). In light of the nmr demonstration that **2** is conformationally rigid, we strongly favor the first interpretation, *i.e.*, that **3** is rigidly held as shown in **3** (EE).

[11] Inspection of Dreiding molecular models reveals that of the two stereoisomers **4** and **8** only the former possesses such static symmetry (C_2) and dihedral angles as are consistent with the nmr characteristics of the 1,3-dioxirane.

The nmr spectrum of **5** requires that the molecule possess C_s symmetry and, further, that it exist in the sterically favorable conformation shown in **5** (EEE), where both dihedral angles, H_a–H_b and H_c–H_b, are estimated at ~90°.[12]

Prolonged exposure of **4** at 198°, in benzene, leads cleanly and irreversibly ($k = 1.36 \pm 0.15 \times 10^{-5}$ sec^{-1}; $\Delta G^{\ddagger} = 38.5$ kcal/mol)[13] to **6** [mp 97–97.5°; nmr (60 MHz, C_6D_6) τ 3.8–4.5 (4 H, $H_d + H_c$), 5.82 (2, H dd, H_b, $J_{bc} = 4.5$ Hz, $J_{ba} = 2$ Hz), 6.52 (2 H, d, H_a, $J_{ab} = 2$ Hz); uv $\lambda_{\max}^{C_6H_{14}}$ 237 nm (sh, ϵ 680), 245 (sh, 950), 253 (1200), 262 (1240), 272 (720); m/e 136 (P^+, 59%)] by what appears to be an unprecedented $[1,5]_s$ thermal shift of an oxa bridge. The assignment of an anti dioxa structure to **6** follows from the magnitude of J_{ab} (2 Hz)[14] and confirms the trans disposition of the oxirane groups in **4**.

In sharp contrast to the **4** → **6** conversion thermolysis of **3** at 202°, in benzene, produces an equilibrium mixture consisting (nmr) of ~60% **3** and 40% **7** [mp 33–34°; nmr (60 MHz, $CDCl_3$) τ 3.72 (2 H, d, H_d, $J_{dc} = 8$ Hz), 5.50 (2 H, dd, H_c, $J_{cd} = 8$ Hz, $J_{cb} = 2.5$ Hz), 6.60 (2 H, s, H_a), 7.25 (2 H, br s, H_b); uv $\lambda_{\max}^{C_6H_{14}}$ 206 nm (ϵ ~3700), 218 (3400); m/e 136 (P^+, 33%)] and materializing with $k_1 = 5.0 \times 10^{-5}$ sec^{-1}, $\Delta G^{\ddagger} = 37.6$ kcal/mol, and $k_{-1} = 7.87 \pm 0.23 \times 10^{-5}$ sec^{-1}, $\Delta G^{\ddagger} = 37.2$ kcal/mol. With regard to mechanism, we note that the obvious requirement of coiled forms **3** (FF) and **7** (FF) for bond relocation (Scheme II) coupled with the undoubted natural tendency of these substances to favor sterically less demanding conformations, *e.g.*, **3** (EE), introduces at this stage some uncertainty as to whether the measured activation reflects the EE to FF ring inversion,[10] the productive **3** (FF) $\rightleftarrows$ **7** (FF) "Cope" process, or possibly a combination of both.

Compared to dioxides **3** and **4**, trioxirane **5** displays striking thermal stability, remaining unchanged (nmr) on heating at 255° for ~20 hr.

Despite their requirement for high thermal activation, the bond relocations of **3** and **4** proceed entirely along symmetry-allowed pathways, the failure of either substrate to rearrange to the symmetry-disallowed isomer **9** being especially notable in this connection. Orbital symmetry control must also be responsible for the resistance of these substances to thermolyze into monocyclic structures, which sharply contrasts the tendency of their $C_6H_6O_2$ and $C_6H_6O_3$ counterparts to do so readily.[15] Specifically, cross-link disrotation of **2**, **3**, **4**, and **5** to all-cis monocyclic frames is predicted to be possible in the electronically excited state but not in the ground state. Preliminary experimentation designed to test this prediction has, to date, been frustrated by the lack of effective chromophores in these substances.

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(12) The conformational rigidity of **5** is perhaps best understood in light of the fact that ring inversion would necessarily convert the arrangement shown in **5** (EEE) into the sterically less accessible FFF form.

(13) The rate of rearrangement in C_6D_6 was monitored by nmr spectroscopy.

(14) Examination of Dreiding molecular models reveals the H_a–H_b dihedral angle to be ~20° for **6** and ~80° for the alternate (exo) stereochemical arrangement. The association of $J = 2$ Hz with the 20° dihedral angle of the endo stereochemical variant (**6**) follows from a well-documented correlation of J *vs.* dihedral angle among cyclic epoxides: K. Tori, T. Komeno and T. Nakagawa, *J. Org. Chem.*, **29**, 1136 (1964); see also ref 15a.

(15) (a) H. J. Alterbach and E. Vogel, *Angew. Chem.*, **84**, 985 (1972); (b) E. Vogel, H.-J. Altenbach, and D. Cremer, *ibid.*, **84**, 983 (1972); (c) E. Vogel, H.-J. Altenbach, and C.-D. Sommerfeld, *ibid.*, **84**, 986 (1972); (d) R. Schwesinger and H. Prinzbach, *ibid.*, **84**, 990 (1972).

(16) Eastman Kodak Graduate Fellow, 1973.

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The Fast Base-Induced Reaction of α,α-Dichloromethyl Methyl Ether with Organoboranes. A New General Route from Organoboranes to the Corresponding Carbon Structures

Summary: The base-induced reaction of α,α-dichloromethyl ether with a representative series of organoboranes provides a new convenient low temperature route to tertiary carbinols in high yield.

Sir: The reaction of organoboranes with α,α-dichloromethyl methyl ether (DCME) induced by lithium triethylcarboxide provides a convenient route to the corresponding tertiary carbinols in excellent yield (eq 1). The initial transfer reaction is very rapid, being complete within 15 min at 25 or 0°, and the boron intermediates are oxidized readily to the corresponding carbinols. Consequently, this reaction provides a valuable means of converting organoboranes into the corresponding carbon structures under relatively mild conditions of time and temperature.

$$R_3B + CHCl_2OCH_3 + LiOCEt_3 \xrightarrow[25^\circ]{\text{THF}} \xrightarrow{\text{NaOH, } H_2O_2} R_3COH \quad (1)$$

This procedure (eq 2) provides a simple alternative

$$(n\text{-Bu})_3B + CHCl_2OCH_3 + LiOCEt_3 \xrightarrow[15\ min]{\text{THF, } 25^\circ} [\ ] \xrightarrow{[O]} \underset{94\%}{(n\text{-Bu})_3COH} \quad (2)$$

to the reaction of organoboranes with carbon monoxide[1-3] (eq 3) or with sodium cyanide and trifluoroacetic anhydride[4] (eq 4) as synthetic routes for the replacement of boron in organoboranes by carbon.

$$(n\text{-Bu})_3B + CO \xrightarrow[8\ \text{hr}]{\text{diglyme, } 125^\circ} [\ ] \xrightarrow{[O]} \underset{90\%}{(n\text{-Bu})_3COH} \quad (3)$$

$$[(n\text{-Bu})_3BCN]^-Na^+ \xrightarrow[-78^\circ,\ \text{then } 45^\circ \text{ for } 12\ \text{hr}]{(CF_3CO)_2O} [\ ] \xrightarrow{[O]} \underset{73\%}{(n\text{-Bu})_3COH} \quad (4)$$

Treatment of a representative series of organoboranes, many of which are readily prepared by the hydroboration of

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(1) M. E. Hillman, *J. Amer. Chem. Soc.*, **84**, 4715 (1962).

(2) H. C. Brown and M. W. Rathke, *J. Amer. Chem. Soc.*, **89**, 2737 (1967).

(3) For a review of the carbonylation reaction of organoboranes with pertinent literature references, see H. C. Brown, *Accounts Chem. Res.*, **2**, 65 (1969).

(4) A. Pelter, M. G. Hutchings, and K. Smith, *Chem. Commun.*, 1048 (1971).