

REACTIONS OF CYCLONONATETRAENYL DIANION WITH ELECTROPHILES:
GEOMETRY AND CONFORMATION OF 1,3,6-CYCLONONATRIENES

Thomas S. Cantrell* and Andrew C. Allen#

Chemistry Department, American University, Washington, D.C. 20016
National Institutes of Health, NIADDK, Bethesda, Md., 20205

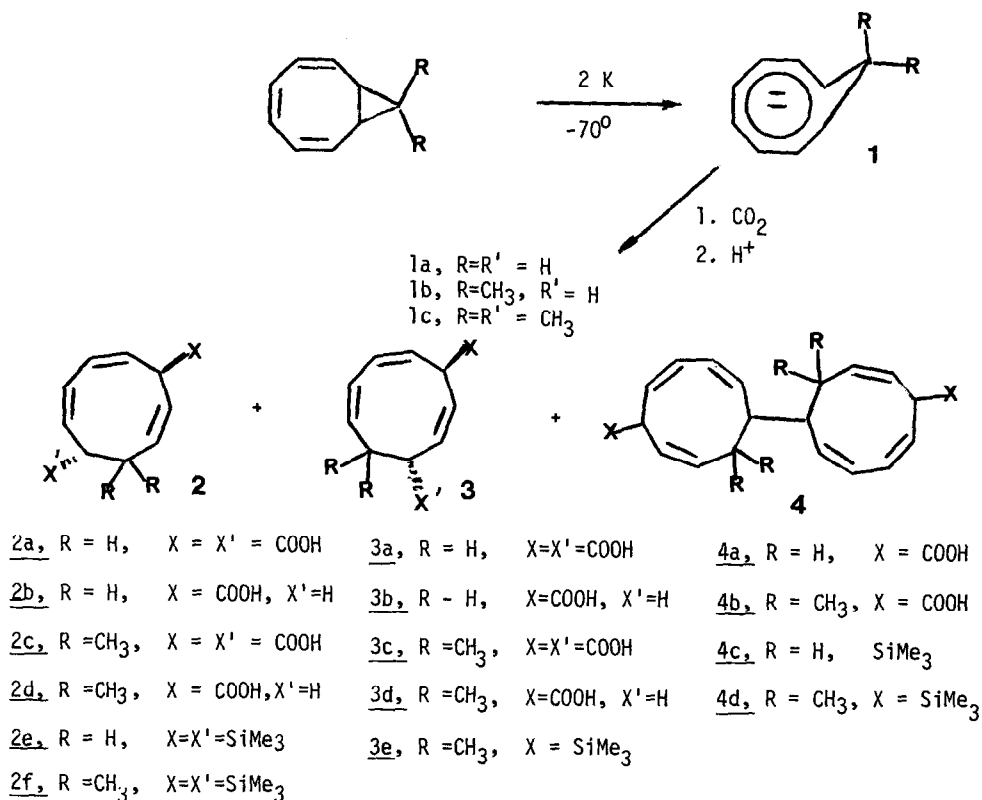
ABSTRACT: Carbonation of the parent cyclononatetraene dianion gives a mixture of (a) the minor products, 1,3,6-cyclononatriene-5,9- and 5,8-dicarboxylic acids, and (b) the major product, bis(5-carboxy-1,3,6-cyclononatrien-9-yl). In contrast, the 9,9-dimethyl dianion affords almost entirely a mixture of the two monocyclic diacids. Similar results are obtained on trimethylsilylation. Conformations of the products are discussed.

Almost 15 years ago it was reported that the monohomocyclooctatetraene dianion¹ (1a; cyclononatetraenyl dianion is, we think, a better term) underwent reaction with tetrachloromethane to give products containing two cyclopropane rings, viz., *syn* and *anti* isomers of tricyclo[7.1.0.0.^{2,4}]deca-2,5-diene.² Subsequently, other groups reported that protonation and methylation of solutions of 1a generated in liquid ammonia produced 5-methyl- and 5,9-dimethyl-1,3,6-cyclononatrienes.^{3,4} We have confirmed these results.

In our laboratory we have recently found that solutions of 1a obtained by reaction of bicyclo[6.1.0]nonatriene with potassium metal in dimethoxyethane at -70° afford, on carbonation, (a) *trans*-1,3,6-cyclononatriene-5,9-dicarboxylic acid (2a) and the corresponding 5,8-dicarboxylic acid (3a, 14% total); (b) 1,3,6-cyclononatriene-5-carboxylic acid (2d, 26%); and (c) bis(5-carboxy-1,3,6-cyclononatrien-9-yl) (4a, 41%). The structures of these products, handled for convenience as the corresponding methyl esters, were established by analysis of their 220 and 500 MHz ¹H NMR spectra, utilizing the results of extensive decoupling and NOE experiments, from the ¹³C NMR spectra, (including SFORD spectra), and by comparison of their hydrogenation products with authentic cyclononane derivatives.^{4,5,6}

Production of the 9,9-dimethylcyclononatetraenyl dianion (1c) as above and subsequent carbonation gave, in stark contrast to the above findings, almost entirely the monocyclic products *trans*-8,8-dimethyl-1,3,6-cyclononatriene-5,9-dicarboxylic acid (2c, 55%) and the corresponding 9,9-dimethyl-5,8-dicarboxylic acid 3c (18%), with only a trace amount of the *bis* product 4c. In neither case was any product detected which was a bicyclo[6.1.0]nonatriene derivative, as was reported for reaction of 1a with CCl₄.² This remarkable difference in behavior, also shown in the reactions of 1a and 1c with trimethylsilyl chloride (*vide infra*) must be a manifestation of a

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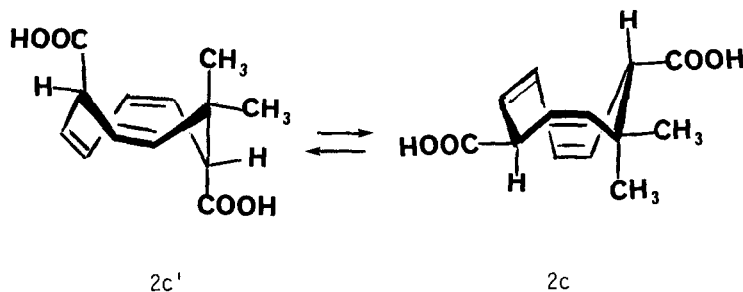


considerable difference in the stability, and hence reactivity, of 1a and 1c. Paquette and co-workers have observed the reactivity of solutions of 1a, b, and c in liquid ammonia to be in the order 1a > 1b > 1c.⁴ They have attributed this stability/reactivity to a conformational effect, the methyls forcing C_1 and C_9 of 1c into closer proximity, thus increasing the overlap of the orbitals on those carbons, with a consequent increase in the homoaromatic stability and decrease in reactivity (here to traces of oxygen to produce the radical anion which couples to afford the precursor to the bis products of type 4). We are continuing our studies on the behavior of other derivatives of 1 in order to further delineate the structure-reactivity relationships in such dianions, and also in order to increase our understanding of the nature of homoaromatic character and the factors governing stability and reactivity in such systems.^{7,10}

While a considerable number of cyclononene derivatives have been reported, most of these are of uncertain geometry, and there are only a few known cyclononatrienes.⁸ Extensive decoupling and NOEDS experiments on the dimethyl ester of 2c and on the dimethyl ester of the bis compound 4c allowed a complete structural analysis, yielding the shift assignments and couplings shown in Table I for 2c. Among the key features are the 3-bond couplings for hydrogens on doubly bonded carbons, i.e., $J_{1,2}$, $J_{3,4}$, and $J_{6,7}$ for 2c and 4a.⁹ The values of 10.0-10.8 for 2c and 4a are indicative of a cis relationship between those hydrogens in each case, and consequently we assign the geometry of all three double bonds in the cyclononatrienes obtained in this work as cis (Z). While inspection of Dreiding and Fieser models indicates that a tublike conformation might be

Table I

δ , ppm	
H ₁	6.013
H ₂	6.205
H ₃	6.03
H ₄	5.651
H ₅	4.076
H ₆	5.61
H ₇	
C ₈ -CH ₃	1.216
C ₈ -CH ₃	1.165
H ₉	3.030
O-CH ₃	3.62
	3.65



couplings, Hz			
J _{1,9}	10.3	J _{3,4}	10.3
J _{1,2}	10.8	J _{4,5}	10.0
J _{1,3}	0.5	J _{5,6}	7.4
J _{2,3}	2.64	J _{5,7}	1.5
J _{2,4}	1.5	J _{6,7}	---
J _{2,9}	0.5		

least hindered and most flexible, variable temperature NMR measurements by Paquette, et al., indicate the preferred conformation of the cyclononatrienes studied by them to be a crown-like shape.^{4b} Indeed, NOEDS experiments on our compound 2c in which the methyl signal at higher field is irradiated, result in increases in the intensities of the vinyl hydrogen signals on C-5 and C-1. Accordingly, we conclude the preferred conformation of 2c is the crown-like structure shown above, possibly in mobile equilibrium with the inverted crown labelled 2c'. The assignment of the stereochemistry of the carboxyl groups as trans to each other was made initially by inspection of Dreiding models; in the cis isomer one carboxyl would be in a highly congested environment. This was later confirmed by comparison of the hydrogenation product of 2a with authentic cis and trans-cyclononane-1,5-dicarboxylic acids.⁵

The reactions of 1a and 1c with trimethylsilyl chloride were also studied. The results paralleled those for the carbonations. Thus 1a afforded mainly bis product 4c,⁹ (58%) with a minor amount of the monocyclic compound which appears to possess structure 2e. On the other hand the 9,9-dimethyl dianion 1c yields only the monocyclic bis (trimethyl) derivative 2f (60%). The greater preference for formation of monocyclic product in the silylation reaction is due not only to the greater stability and lower reactivity toward oxygen of the dimethyl dianion as previously mentioned, but also to the severe crowding which would exist in a bis (cyclononatrienyl) product bearing trimethylsilyl groups. In none of the reactions studied did we observe any cyclopropane-type products of the type reported by Ogliaruso.² Our investigations in this area are continuing.

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References and Notes

1. For recent review on homoaromaticity, see R. F. Childs, *Accts. Chem. Res.*, **1984**, 347-353 (17).
2. M. Ogliaruso, *J. Amer. Chem. Soc.*, **1970**, 7490-7492 (92).
3. (a) W. H. Okamura, T. I. Ito, and P. M. Kellett, *Chem. Commun.*, **1971**, 1317-1318.
(b) T. I. Ito, F. C. Baldwin, and W. H. Okamura, *Chem. Commun.*, **1971**, 1440-1441.
4. (a) L. A. Paquette and S. V. Ley, *J. Amer. Chem. Soc.*, **1974**, 6670-6679 (96).
(b) L. A. Paquette, S. V. Ley, S. G. Traynor, J. T. Martin, and J. M. Geckle, *J. Amer. Chem. Soc.*, **1976**, 8162-8172 (98).
5. Authentic cyclononane-1,5-dicarboxylic acids were prepared by the method of R. Sands, *J. Org. Chem.*, **1969**, 2794-2795 (34) and **1964**, 2488-2489 (29).
6. Spectral data on compounds other than 2c and 4a will be reported in our subsequent full paper; data on 4a and 4c is given in footnote 9 below.
7. Complete experimental details on the present work and on our ongoing experiments in this area will be subsequently reported in our full paper.
8. (a) *cis*-2-cyclononenone, R. Noyori and M. Kato, *Bull. Chem. Soc. Japan*, **1974**, 1460-1466 (47);
(b) *trans*-2-cyclononenone, M. Regitz and J. Ruter, *Chem. Ber.*, **1969**, 3877-3890 (102).
9. (a) 4a: mp 141-142° IR(KBr): 1732 cm⁻¹; ¹H NMR (500 MHz) δ 5.97 (2H, d, J=10.3), 5.90 (2H, d, J=10.3), 5.85 (2H, 2d, J=J'=10.1), 5.69 (2H, 2d, J=J'=10.1), 5.58 (2H, 2d, J=J'=10.3), 5.34 (2H, 2d, br, J=J'=10.1), 4.02 (2H, 2d, J=J'=10.3), 3.68 (6H, s, OCH₃), 2.01 (4H, 2d, J=8.0, J'=2.5), and 1.82 (2H, 2d, J=8.0, J'=2.5); ¹³C NMR: 173.4, 137.4, 131.0, 127.1, 126.3, 125.6, 123.9, 52.1, 48.0, 45.5, and 30.6 ppm; Mass spectrum: (E.I., 70 ev); M/e 354 (P, 4), 295 (11), 294 (17), 235 (13), 177 (25), 143 (22), 117 (80), and 91 (100).
(b) 2c: mp 56°, X=X'=COOCH₃; IR: 1730 cm⁻¹; ¹H NMR data in the Table; UV (CH₃OH) 228 nm (E=2500); M/e 264 (P, 10), 232 (43), 204 (35), 173 (68), and 145 (100).
(c) Silyl compound 4c: mp 150°; ¹H NMR: (220 MHz): δ 5.92 (2H, 2d, J=J'~10), 5.86 (4H, ddd, J~10), 5.46 (4H, ddd, J=J'=10.3), 5.30 (2H, 2d, J~10), 2.72 (2H, 2d, J=J'=10.3), 1.98 (6H, M), and -0.03 (18H, s); M/e (CI) 384 (P, 22) and 192 (100).
(d) 2f: mp ca. 5°; ¹H NMR: (220 MHz): δ 5.38 (2H, ddd, J=10.0, J'=2.2), 5.22 (2H, s), 5.05 (2H, dd, J=10.3, J'=10.0), 3.50 (2H, ddd, br), 1.65 (3H, s), 1.15 (3H, s), 0.02 (9H, s) and -0.01 (9H, s); M/e 294 (P, 100), 220 (75).
10. We have observed that bubbling oxygen through the solutions of 1a at -70° before carbonation suppresses almost completely the formation of the monocyclic products 2a, 2d, and 3a, with a consequent increase in the yield of *bis* product 4a, supporting our suggestion that 4a arises via oxidation of 1a during the carbonation.

* The data given refer to the dimethyl ester of 4a.