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FLUXIONAL ISOMERISM IN THE BICYCLO[4.2.2]DECA-2,4,7,9-TETRAENE SERIES

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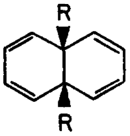
A flurry of activity in this field has recently produced proof that fluxional isomerism exists in bicyclo[4.2.2]deca-2,4,7,9-tetraene ("prebullvalene") and its derivatives.[1-4] We have irradiated a number of [4.4.3]propella-2,4,7,9-tetraene derivatives and have reported the isolation of the primary photo products in two of these. These were thermally isomerized to the corresponding "prebullvalene" derivatives[5] but our more recent results require that we correct two structures previously formulated[5] as 3c and 3e, to 4c and 4e, respectively. This arose from faulty interpretation of spectroscopic data, partly due to the use of a 60 MHz instrument. The 100 MHz spectra of the compounds concerned leave no doubt as to the correctness of 4c and 4e[6] (see the Table).



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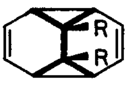

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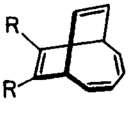

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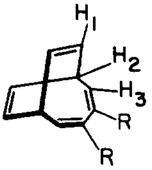

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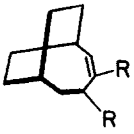

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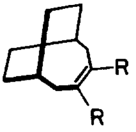

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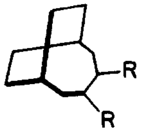


7

R,R = a -CO-O-CO- ; b -CO-NH-CO- ; c -CO-NMe-CO- ; d -CO-O-CH_2- ; e -CH_2-O-CH_2-

The structure analogously formulated tentatively as 3a[7] has also been corrected to 4a, unfortunately without stating explicitly that a correction was being made.[4] The formulation of 3a was first questioned on chemical grounds by Bloomfield and McConaghy.[3] (Cf. Ref.4, footnote 7). Information kindly supplied by Dr. Bloomfield led us to reinvestigate our published[5] structures 3c and 3e.[8]

We thus reduced 4a-4c and obtained as the major products mixtures of hexahydro-derivatives, 5 and 6, having the same skeletal structure as 4, as shown in the accompanying summary. A minor amount of octahydro-derivative 7 occasionally accompanied 5 and 6. The summary also shows that the various reduction products were interrelated chemically. The product ratio in reduction of "prebullvalene" derivatives is temperature dependent and it is clear that both 1,2- and 1,4- reduction occurs with respect to the conjugated diene in the substrate. Octahydro-derivatives are presumably obtained by further reduction of products of type 5.

Summary of Reductions of "Prebullvalene" derivatives and Interrelation of Reduction Products

$$\begin{tikzcd}
4a \arrow[r, "\text{Pt/EtOAc}", "\text{room temp.}"'] & \begin{array}{l}5a\ (1\ \text{part})\\ \text{m.p. } 103^\circ\end{array} \arrow[d, "NH_4OH", "\Delta"'] & + & \begin{array}{l}6a\ (9\ \text{parts})\\ \text{m.p. } 143^\circ\end{array} \arrow[d, "NH_4OH", "\Delta"'] & + & \begin{array}{l}7a(\text{minor})\ (\text{cf. Refs.3,4}).\\ \text{m.p. } 106^\circ\end{array} \\
4b \arrow[r, "\text{Pt/EtOAc}", "\text{room temp.}"'] & \begin{array}{l}5b\ (1\ \text{part})\\ \text{m.p. } 186^\circ\end{array} \arrow[d, "CH_2N_2"] & + & \begin{array}{l}6b\ (4\ \text{parts})\\ \text{m.p. } 175^\circ\end{array} \arrow[d, "CH_2N_2"] & & \\
4c \arrow[r, "\text{Pt/EtOAc}", "\text{room temp.}"'] & \begin{array}{l}5c\ (4\ \text{parts})\\ \text{m.p. } 91^\circ\end{array} & + & \begin{array}{l}6c\ (1\ \text{part})\\ \text{m.p. } 88\text{-}89^\circ\end{array} & + & 7c\ (\text{minor; unisolated}) \\
4c \arrow[r, "\text{Pt/EtOAc}", "0^\circ"'] & 5c\ (1\ \text{part}) & + & 6c\ (1\ \text{part}) & &
\end{tikzcd}$$

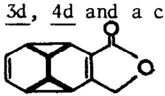
One vinylic proton may be observed in the NMR spectra of compounds of type 5, accompanied by 2 allylic protons and spin decoupling demonstrated the connection between these. Compounds of type 6, however, exhibited the expected four allylic protons.

We were able to isolate the primary photo-product 2b, obtained by irradiation of 1b[9,10] in methanol at -78°. This was thermally converted into 4b, m.p. 248-255°(dec.) with a half-life of ca. 1.5 hr. for the conversion 2b→4b in methanol at 52°. Our attempts at isolation of 2a and 2d after irradiation of 1a and 1d, respectively, in methanol at -78°, were unsuccessful although their presence could be detected ($CDCl_3$ at -42°; allylic cyclopropyl protons τ 7.63; 7.90 and 8.35, respectively) along with the products of their respective thermal isomerizations.

The 100 MHz room temperature spectrum of the analytically pure "prebullvalene"

Table of Spectral Data

Cpd.	UV(nm;logε) MeOH	IR(ν_{CO};cm^{-1})	NMR(τ)	Cpd.	UV(nm;logε) MeOH	IR(ν_{CO};cm^{-1}) $CHCl_3$	NMR;No.of Allylic H
4a	255;3.95 310(sh);3.14	1765(s) 1785(s) 1835(s) ($CHCl_3$)	2.45(doub.;$2H_3$;J=8.5c/s);4.22(mult.;$4H_1$) both collapse to singlet on decoupling;6.20-6.45(mult.;$2H_2$) collapses to doublet on decoupling ($CDCl_3$)	5a	229;3.98	1770(s) 1795(w) 1830(m)	2
4b	254;3.86 295(sh);3.14	1720(s) 1760(s) (KBr)	3.50(doub.;$2H_3$;J=9c/s);5.25(mult.;$4H_1$)both collapse to singlet on decoupling;7.32-7.70(mult.;$2H_2$)(Py-d_5)	5b	226;3.22	1675(s) 1725;1735(s) 1775(s)	2
4c	248;4.12 293(sh);3.41	1690(s) 1760(m) (KBr)	2.61(doub.;$2H_3$;J=9c/s);4.21(mult.;$4H_1$)both collapse to singlet on decoupling;6.30-6.50(mult.;$2H_2$) collapses to doublet on decoupling; 6.94(sing.;$NC\underline{H}_3$)($CDCl_3$)	5c	229;3.43	1675(s) 1705;1715(s) 1770(s)	2
4d		See Text		6a	253;3.72	1770(s) 1835(m)	4
4e	265;3.58 272;3.51 286(sh);3.34		3.90(doub.;$2H_3$;J=9c/s);4.31(mult.;$4H_1$)both collapse to singlet on decoupling;5.51(doub.;$C\underline{H}_2O$);6.70-6.90(mult.;$2H_2$)collapses to doublet on decoupling($CDCl_3$)	6b	220;3.54 227(sh);3.52	1720;1730(s) 1780(w)	4
2b	end absorption 220;3.81	1700(s) 1780(s) (KBr)	3.96-4.08(mult.;4 vinyl H)collapses to singlet on decoupling;7.74-7.85 (mult.;4 cyclopropyl H) collapses to singlet on decoupling ($CDCl_3$)	6c	225;3.37 237(sh);3.20	1710(s) 1775(w)	4

lactone, m.p. 93.5-95°, evidenced the presence of 3d, 4d and a cyclopropane derivative different from 2d, tentatively believed to be  (allylic cyclopropyl protons τ 8.18). Since the "prebullvalene" lactone is the only member of the series whose 100 MHz NMR spectrum at room temperature does not exhibit the exclusive presence of structure 4 rather than 3, it is possibly the black sheep in the family and thus could be its most interesting member. A separate communication will be submitted on this subject.[11]

All the compounds reported herein afforded satisfactory analytical and molecular weight data. The full details will be submitted for publication in the Israel Journal of Chemistry.

References and Footnotes

1) M. Jones, Jr. and B. Fairless, Tetrahedron Letters, 4881(1968).
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3) J.J. Bloomfield and J.S. McConaghy Jr., preceding paper in this issue.
4) W. Grimme, H.J. Riebel and E. Vogel, Angew.Chem., 80, 803(1968).
5) E. Babad, D. Ginsburg and M.B. Rubin, Tetrahedron Letters, 2361(1968).
6) We thank Prof. Dr. W. von Philipsborn of the University of Zürich for these spectra and for their unequivocal interpretation.
7) E. Vogel, W. Grimme, W. Meckel, H.J. Riebel and J.F.M. Oth, Angew.Chem., 78, 599(1966).
8) Letter from Dr. J.J. Bloomfield, July 12, 1968.
9) E.R. Wagner and A.D. Rudzik, J.Med.Chem., 10, 607(1967).
10) Mr. C. Amit prepared this compound in much higher yield, unpublished results from this Laboratory.
11) J. Altman, E. Babad, J.J. Bloomfield, D. Ginsburg, W. von Philipsborn and M.B. Rubin, unpublished results.