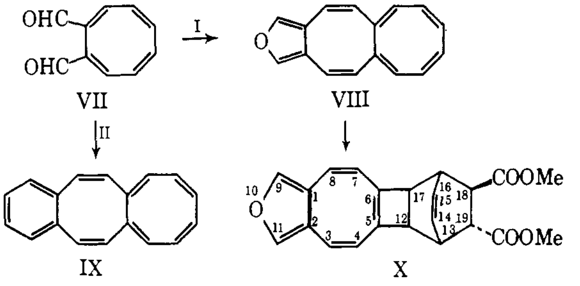
octa[*c*]furan (VI).[6] As expected, the positions of the olefinic nmr bands in V were similar to those reported for VI,[6] but the ultraviolet spectrum of V was considerably more complex.

Wittig reaction of I and cyclooctatetraene-1,2-dicarboxaldehyde (VII)[7,8] with lithium ethoxide in dimethylformamide at 90° led to 15% [3,4-*c*]furooctalene (VIII), a pale yellow liquid; mass spectrum, molecular ion at *m/e* 220.089; $\lambda_{\max}^{\mathrm{EtOH}}$ 237 mμ (ϵ 22,300), with absorption beyond 350 mμ. The nmr spectrum exhibited a 2 H singlet at τ 2.70 (furan ring protons), a 4 H singlet at 3.74 (central eight-membered ring protons), and a 6 H multiplet at 4.13–4.36 (terminal eight-membered ring protons). The compound was unstable, being rapidly oxidized in air (appearance of infrared carbonyl bands at 1708 and 1695 cm^{-1}). A dilute ethanolic solution underwent a comparatively fast reaction in diffuse daylight, with the appearance of ultraviolet maxima at 205, 255, 264, and 275 mμ; these are characteristic of a 5,6-disubstituted cycloocta[*c*]furan (see substances V and X), indicating that this system was being formed. The ultraviolet and nmr spectral properties of VIII were similar to those of benzo[*c*]octalene (IX), previously obtained in 1–2% yield by the Wittig reaction of II and VII.[7]



The terminal eight-membered ring in VIII appears to be the most reactive in Diels–Alder reactions. Thus, treatment of VIII with excess dimethyl fumarate in boiling cyclohexane for 12 hr led to 65% of the monoadduct X, an orange glass; mass spectrum, molecular ion at *m/e* 364; $\lambda_{\max}^{\mathrm{EtOH}}$ 204 mμ (ϵ 18,200), 247 sh (13,300), 256 (19,400), 266 (22,800), 276 (16,600), and 315 sh (2200). Structure X follows unequivocally from the nmr spectrum, which showed a 2 H singlet at τ 3.14 (H^9, H^{11}), a 2 H multiplet at 3.80–4.13 (H^{14}, H^{15}), a 4 H quartet centered at 4.82 (H^3, H^4, H^7, H^8), singlets (3 H each) at 6.29 and 6.35 (H^{Me}), a 4 H broad band at 7.0 (H^{12}, H^{17}, H^{18}, H^{19}), and a 2 H multiplet at 7.50–7.71 (H^{13}, H^{16}). As expected, the ultraviolet spectrum of the adduct X was similar to that of V, in agreement with the fact that both are 5,6-disubstituted derivatives of cycloocta[*c*]furan (VI).

The reported data of IV and VIII indicate that neither substance is aromatic, and that the eight-membered rings are not planar. The properties of VIII parallel those of the related benzo analog IX[7] and are in agreement with the predictions made for octalene itself.[9]

Acknowledgment. We are indebted to the Royal Society (London) for generous financial support.

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[6] E. Le Goff and R. B. LaCount, *Tetrahedron Letters*, 2787 (1965).

[7] R. Breslow, W. Horspool, H. Sugiyama, and W. Vitale, *J. Am. Chem. Soc.*, **88**, 3677 (1966).

[8] F. Sondheimer, I. C. Calder, J. A. Elix, Y. Gaoni, P. J. Garratt, K. Grohmann, G. Di Maio, J. Mayer, M. V. Sargent, and R. Wolovsky, International Symposium on Aromaticity, Sheffield, July 6–8, 1966; Special Publication No. 21, The Chemical Society, London, 1967, p 75.

[9] N. L. Allinger and C. Gilardeau, *Tetrahedron*, **23**, 1569 (1967).

[10] Imperial Chemical Industries Fellow.

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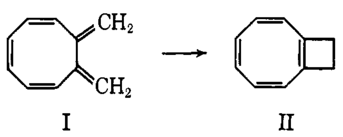
Received July 6, 1967

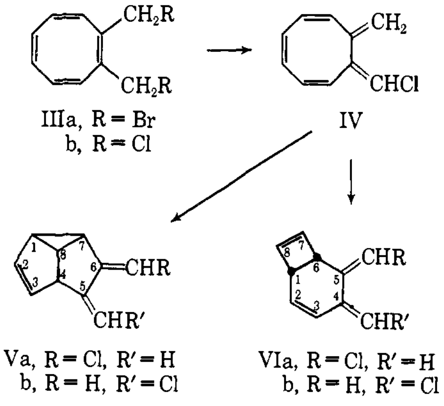
The Photorearrangement of 7-Methylene-8-chloromethylenecycloocta-1,3,5-triene[1]

Sir:

We have reported recently[2] that the irradiation of 7,8-dimethylenecycloocta-1,3,5-triene (I)[3,4] leads to bicyclo[6.2.0]deca-1,3,5,7-tetraene (II), the exocyclic double bonds being more photolabile than the endocyclic polyene system. We have now found that substitution of one of the methylene groups in I by a chloromethylene group deactivates the exocyclic diene and causes the endocyclic double bonds to be the more reactive.



The liquid chloro compound IV[5] was obtained in 88% yield from 1,2-bisbromomethylcyclooctatetraene (IIIa)[3] by treatment with lithium chloride in dimethylformamide followed by dehydrochlorination of the resulting dichloride IIIb with potassium *t*-butoxide in ether. Irradiation of IV in ether or methanol with a Hanovia medium-pressure mercury vapor lamp (2 amps, 125 w) for 2 hr at room temperature gave *ca.* 10% of 5- (or 6-) methylene-6- (or -5-) chloromethylenetricyclo[5.1.0.0^{4,8}]oct-2-ene (Va or Vb) and *ca.* 3% of 4- (or 5-) methylene-5- (or -4-) chloromethylenebicyclo[4.2.0]octa-2,7-diene (VIa or VIb). The partial structural assignments V and VI[6] follow unequivocally from the



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[1] Unsaturated Eight-membered Ring Compounds. V. For part IV, see J. A. Elix, M. V. Sargent, and F. Sondheimer, *J. Am. Chem. Soc.*, **89**, 5080 (1967).

[2] J. A. Elix, M. V. Sargent, and F. Sondheimer, *ibid.*, **89**, 180 (1967).

[3] J. A. Elix, M. V. Sargent, and F. Sondheimer, *Chem. Commun.*, 508 (1966).

[4] F. A. L. Anet and B. Gregorovich, *Tetrahedron Letters*, 5961 (1966).

[5] This substance was a mixture of stereoisomers, as evidenced by the nmr spectrum.

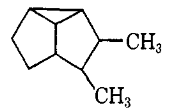
[6] The *cis* ring fusion in VI is assumed by analogy with the corresponding compound XV derived from cycloocta-1,3,5-triene (XIII) (see below).

spectroscopic properties and chemical reactions, but in neither case was it possible to determine which of the two exocyclic carbon atoms was bonded to chlorine.

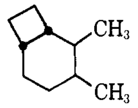
Substance V was an unstable pale yellow liquid; mass spectrum, molecular ions at *m/e* 166.036 and 164.039; λ_{max}^{EtOH} 264 mμ (ϵ 5900); $\nu_{max}^{CCl_4}$ 880 (s) cm^{-1} (*exo*-methylene). The nmr spectrum (CCl_4, 100 Mcps) showed a 1 H singlet at τ 3.72 (*exo*-methine proton), two quartets (1 H each) at 4.44 and 4.63 (H^2, H^3; $J_{2,3}$ = 5 cps, $J_{2,1} = J_{3,4}$ = 1 cps), two singlets (1 H each) at 5.28 and 5.50 (*exo*-methylene protons), a 1 H quartet at 6.44 (H^4; $J_{4,8}$ = 6 cps, $J_{4,3}$ = 1 cps), a 1 H quartet at 7.33 (H^8; $J_{8,1} = J_{8,4} = J_{8,7}$ = 6 cps) overlapping with a 1 H triplet at 7.50 (H^7; $J_{7,1} = J_{7,8}$ = 6 cps), and a 1 H sextet at 7.71 (H^1; $J_{1,7} = J_{1,8}$ = 6 cps, $J_{1,2}$ = 1 cps).

Substance VI also was an unstable pale yellow liquid; mass spectrum, molecular ions at *m/e* 166.036 and 164.039; λ_{max}^{EtOH} 262 mμ (ϵ 9600); $\nu_{max}^{CCl_4}$ 1560 (m) cm^{-1} (cyclobutene), 900 (s) and 890 (s) (*exo*-methylene). The nmr spectrum (CCl_4, 60 Mcps) showed two narrow bands (total, 1 H) at τ 3.37 and 3.55 (*exo*-methine proton),[7] a 4 H multiplet at 3.75–4.10 (olefinic ring protons), two narrow bands (1 H each) at 4.86 and 5.11 (*exo*-methylene protons), and a 2 H multiplet at 6.24–6.51 (bridgehead protons).

Structures V and VI were confirmed by catalytic hydrogenation. Reduction of V in methanol over palladium–calcium carbonate led to 2,3-dimethyltricyclo-$[5.1.0.0^{4,8}]$octane (VII) as a colorless liquid, virtually homogeneous by glpc; mass spectrum, molecular ion at *m/e* 136. A minor product of this reaction showed a molecular ion at *m/e* 138; this substance was the major product when the reduction of V was carried out in acetic acid over platinum and presumably resulted from cleavage of the cyclopropane ring. Similar hydrogenation of VI in methanol over palladium–calcium carbonate gave 2,3-dimethylbicyclo[4.2.0]octane (VIII) as a colorless liquid, homogeneous by glpc; mass spectrum, molecular ion at *m/e* 138.

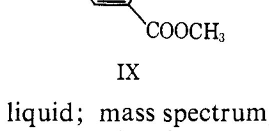


VII

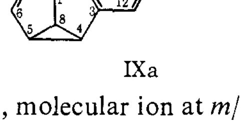


VIII

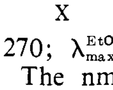
The exocyclic double bonds of V and VI constitute diene systems which undergo reaction with dimethyl acetylenedicarboxylate to give benzenoid products by concomitant dehydrochlorination. Thus, treatment of V with this ester in boiling cyclohexane for 48 hr gave 90% dimethyl 2,3-benzotricyclo$[5.1.0.0^{4,8}]$octa-2,5-diene-10,11-dicarboxylate (IX), a benzo derivative of "semibullvalene" (X).[8] Substance IX was a colorless liquid; mass spectrum, molecular ion at *m/e* 270; λ_{max}^{EtOH} 218 mμ (ϵ 26,800) and *ca.* 268 sh (7000). The nmr spectrum (CCl_4, 100 Mcps) uniquely defined structure IX, showing two singlets (1 H each) at τ 2.41 and 2.64 (H^9, H^{12}), a 1 H quartet at 4.40 (H^6; $J_{6,5}$ = 5.5 cps, $J_{6,7}$ = 2.5 cps), a 1 H quartet at 4.79 (H^5; $J_{5,6}$ = 5.5 cps, $J_{5,4}$ = 2.5 cps), a 1 H quartet at 6.08 (H^4; $J_{4,8}$ = 6.5 cps, $J_{4,5}$ = 2.5 cps), a 6 H singlet at 6.18 (H^{Me}), a 1 H quartet at 6.68 (H^8; $J_{8,1} = J_{8,4} = J_{8,7}$ = 6.5 cps), a 1 H triplet at 6.91 (H^1; $J_{1,7} = J_{1,8}$ = 6.5 cps), and a 1 H sextet at 7.19 (H^7; $J_{7,1} = J_{7,8}$ = 6.5 cps, $J_{7,6}$ = 2.5 cps). The nmr spectrum of IX (toluene-d_8) at 100° was essentially unchanged, no interconversion with IXa being detectable.[9]



IX

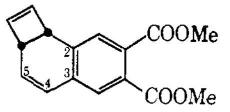


IXa

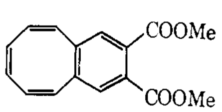


X

Treatment of VI with dimethyl acetylenedicarboxylate under similar conditions yielded 50% of a pale yellow liquid, consisting of a *ca.* 1:1 mixture of dimethyl 2,3-benzobicyclo[4.2.0]octa-2,4,7-triene-10,11-dicarboxylate (XI) and dimethyl benzocyclooctatetraene-10,11-dicarboxylate (XII).[10] Substance XII presumably arose by valence tautomerism of XI, and heating the mixture in tetrachloroethylene at 120° for 72 hr indeed resulted in complete conversion to XII, identified by comparison with an authentic sample.[3] Hence, the 2,3-benzobicyclo[4.2.0]octa-2,4,7-triene system present in XI exhibits thermal stability intermediate between that of bicyclo[4.2.0]octa-2,4,7-triene[11] and 2,3:4,5-dibenzo-[4.2.0]octa-2,4,7-triene.[12]



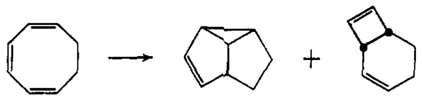
XI



XII

We have reported previously[2] that the irradiation of 7-methylene-8-bromomethylenecycloocta-1,3,5-triene (IV, Br instead of Cl) gives rise to II. It has now been found that this reaction in addition yields *ca.* 3% of 5- (or 6-) methylene-6- (or -5-) bromomethylenetricyclo-$[5.1.0.0^{4,8}]$oct-2-ene (V, Br instead of Cl); mass spectrum, molecular ions at *m/e* 210 and 208; nmr spectrum (CCl_4, 100 Mcps) similar to that of V, showing a 1 H singlet at τ 3.55, two quartets (1 H each) at 4.36 and 4.66, two singlets (1 H each) at 5.22 and 5.42, a 1 H quartet at 6.33, and a 3 H multiplet at 7.24–7.80.

The above-described irradiation results parallel those obtained with cycloocta-1,3,5-triene (XIII). Irradiation of the latter substance has been shown to lead to tricyclo$[5.1.0.0^{4,8}]$oct-2-ene (XIV) and bicyclo-[4.2.0]octa-2,7-diene (XV), as well as cycloocta-1,5-diene and octa-1,3,5,7-tetraene.[13,14]



XIII XIV XV

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[7] The integrated ratio of the bands was *ca.* 1:4, indicating the presence of a *ca.* 1:4 mixture of two isomers (probably stereoisomers).

[8] H. E. Zimmerman and G. L. Grunewald, *J. Am. Chem. Soc.*, **88**, 183 (1966).

[9] The degenerate Cope rearrangement which occurs with semibullvalence (X)[8] is precluded in IX, due to the fused benzene ring.

[10] This conclusion is based on the nmr spectrum of the mixture (CCl_4, 100 Mcps), which showed the bands of authentic XII,[3] as well as the following bands due to XI: two singlets at τ 2.55 and 2.63 (benzenoid protons), a multiplet at 3.82–4.16 (olefinic protons), a singlet at 6.11 (methyl protons), and a multiplet at 6.20 (bridgehead protons). The structural assignment was supported by the presence of a maximum at 290 mμ in the ultraviolet spectrum.

[11] E. Vogel, H. Keefer, and W. Roth, *Angew. Chem.*, **76**, 432 (1964).

[12] E. Vogel, W. Frass, and J. Wolpers, *ibid.*, **75**, 979 (1963).

[13] W. R. Roth and B. Peltzer, *ibid.*, **76**, 378 (1964); J. Zirner and S. Winstein, *Proc. Chem. Soc.*, 235 (1964); O. L. Chapman, G. W.

Acknowledgment. We are indebted to the Royal Society (London) for generous financial support.

Borden, R. W. King, and B. Winkler, *J. Am. Chem. Soc.*, **86**, 2660 (1964).

(14) For the mechanism of the reaction leading to cyclopropane derivatives, see J. Meinwald and P. H. Mazzocchi, *ibid.*, **89**, 1755 (1967).

(15) Imperial Chemical Industries Fellow.

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Received July 6, 1967

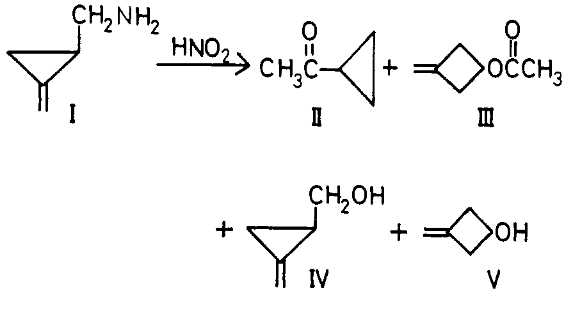
Deamination of Methylenecyclopropylcarbinylamine

Sir:

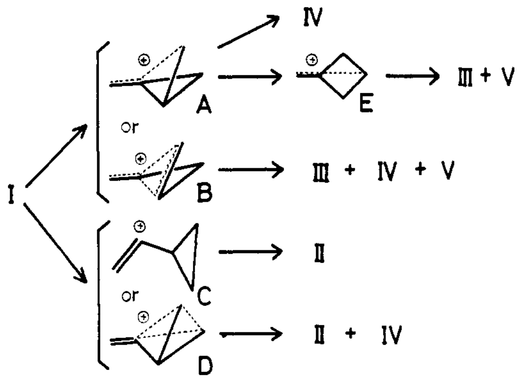
The current interest on reactions involving vinyl cation intermediates[1] prompts us to report the deamination of methylenecyclopropylcarbinylamine (I), which suggests that a vinyl cation is formed by cleavage of a carbon–carbon bond.

Amine I was prepared by the ammonolysis of ethyl methylenecyclopropanecarboxylate[2] followed by the lithium aluminum hydride reduction of the resulting amide. Its infrared spectrum shows bands at 3360 and 3295 cm^{-1} for the amino group, 3065, 1745, and 886 cm^{-1} for the terminal methylene group, and 3040 and 1019 cm^{-1} for the cyclopropane group. Its nmr spectrum exhibits a multiplet centered at τ 4.90 (2 H, terminal methylene), a doublet at 7.52 (2 H, methylene group adjacent to the amino group), and a broad multiplet at 8.30–9.46 with a sharp singlet at 9.09 (5 H, ring protons and amino group). The phenyl isothiocyanate adduct melted at 70–71°.

The treatment of I with sodium nitrite in 20% aqueous acetic acid gave acetylcyclopropane (II), 3-methylenecyclobutyl acetate (III), methylenecyclopropylcarbinol (IV), and 3-methylenecyclobutanol (V) with a vpc peak area ratio of 2.3:1.0:1.6:16.4, along with three other minor components.[3] Compound II was identified by comparison of its mass and infrared spectra and vpc retention time with those of an authentic sample,[4] and the carbinol V was identified by comparison of its infrared and nmr spectra with the reported value.[5] The infrared spectrum of the acetate III exhibits bands at 3080, 1740, 1240, 1070, 1032, and 882 cm,$^{-1}$ showing the presence of an ester group and a terminal methylene group. Its nmr spectrum is very similar to that of V except that the peak of the hydroxyl proton is replaced by a sharp singlet of an acetoxy group at τ 8.15. The acetylation of V gave III, and the lithium aluminum hydride reduction of III gave V. The nmr and infrared spectra and vpc retention time of IV are the same as those of an authentic sample of IV prepared by the lithium aluminum hydride reduction of ethyl methylenecyclopropanecarboxylate.[2]



The formation of III and V as the major products and the absence of 2-methylenecyclobutanol in the deamination products suggest a considerable interaction between the π electrons of the double bond and the nearby situated cationic center, such as is shown in A or B.[6] Of special interest is the formation of acetylcyclopropane,



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(1) M. Hanack and J. Haeffner, *Tetrahedron Letters*, 2191 (1964); M. Hanack, J. Haeffner, and I. Herterich, *ibid.*, 875 (1965); M. Hanack and I. Herterich, *ibid.*, 3847 (1966); M. Hanack and J. Haeffner, *Chem. Ber.*, **99**, 1077 (1966); W. D. Clossen and S. A. Roman, *Tetrahedron Letters*, 6015 (1966); M. Bertrand and M. Santelli, *Compt. Rend.*, **259**, 2251 (1964); H. R. Ward and P. D. Sherman, Jr., *J. Am. Chem. Soc.*, **89**, 1963 (1967); D. S. Noyce, M. A. Matesich, M. D. Schiavelli, and P. E. Peterson, *ibid.*, **87**, 2295 (1965); P. E. Peterson and R. J. Kamat, *ibid.*, **88**, 3152 (1966); P. E. Peterson and J. E. Duddey, *ibid.*, **88**, 4990 (1966); W. M. Jones and F. W. Miller, *ibid.*, **89**, 1960 (1967).

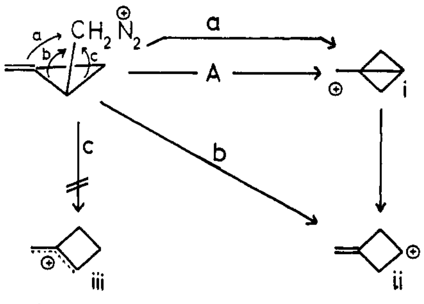
(2) J. A. Carbon, W. B. Martin, and L. R. Swett, *ibid.*, **80**, 1002 (1958); E. F. Ullman and W. J. Fanshawe, *ibid.*, **83**, 2379 (1961).

(3) These four components, II–V, constituted 87% of the total products in the peak area ratio.

(4) G. W. Cannon, R. C. Ellis, and J. R. Leal, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 597.

(5) D. E. Applequist and G. F. Fanta, *J. Am. Chem. Soc.*, **82**, 6393 (1960).

(6) A referee has suggested that structures A, B, D, and E may only be transition states rather than intermediates. The lack of kinetic data prevents us from speculating on the exact nature of the intermediates. The use of nonclassical structures in this report is primarily for simplicity of representation and does not at present have any mechanistic significance. Thus, with respect to structure E, for example, the formation of III and V may well be explained *via* classical intermediates i and ii (pathway a)[7] or even by direct ring expansion to ii (pathway b). In the last case, the absence of 2-methylenecyclobutanol (pathway c) in the reaction products may be taken as an example of a vinyl group being a good migrating group[8] and/or an example of the steric inhibition of normal allylic stabilization in the transition state from I to iii.[9]



(7) E. F. Kiefer and J. D. Roberts, *J. Am. Chem. Soc.*, **84**, 784 (1962); K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965). See, however, the unpublished results of Martin and Anderson cited in the paper of Applequist and Fanta.[5]

(8) W. Herz and G. Caple, *J. Org. Chem.*, **29**, 1691 (1964); R. S. Bly and R. T. Swindell, *ibid.*, 30, 10 (1965). We are indebted to the anonymous referee for bringing our attention to these reports.

(9) P. Nangia and S. W. Benson, *J. Am. Chem. Soc.*, **84**, 3411 (1962); W. von E. Doering and J. C. Gilbert, *Tetrahedron Suppl.*, 7, 397 (1966); M. R. Willcott and E. Goerland, *Tetrahedron Letters*, 6341 (1966); J. A. Berson and R. S. Wood, *J. Am. Chem. Soc.*, **89**, 1043 (1967).