the 3 and/or 6 position, gave $m/e$ 54 in the preferential process but $m/e$ 55 in the less preferred process. The retro-Diels–Alder fragment is the most intense by a good deal in the mass spectrum of 4-vinylcyclohexene,[5] indicating that rearrangement of the molecular skeleton upon ionization is an extremely unlikely cause for the selectivity we have observed.

Numerically, the ($m/e$ 54):($m/e$ 55) ratio (corrected for isotopes) is found to be 1.49 at 81.6 ev,[6] 1.36 at 25.6 ev, 1.85 at 20.6 ev, and 1.62 at 15.6 ev. It will be noted that the selectivity is a maximum at 20.6 ev; this interesting result is accompanied by a maximum in the per cent $\Sigma_{24}$ arising from retro-Diels–Alder cleavage. Obviously, the selectivities are substantial and much greater than possible combined experimental and correction errors. Furthermore, the secondary isotope effect difference associated with only one deuterium atom must be far too small to be a major factor.

The idea that there may be selectivity in mass spectral fragmentation even though identical ions and neutral fragments are formed in two separate processes from the same molecular ion has therefore been confirmed. If the selectivity arises in quasi-equilibrium processes, there must be different activated complexes for paths 1a and 1b, both of which correspond to eventually breaking the same two bonds of the molecular ion. Several extremely interesting possibilities exist for the structures of these two activated complexes, ranging from "simple" explanations involving isomeric *molecular* ions (*e.g.*, *s-trans* and *s-cis* or cyclic and open chain), which seem unlikely for the present reaction and conditions, to "ground state" *and* (low-lying) electronically excited activated complexes or even electronic potential energy surface(s) involving two saddle points.

Investigation of such possibilities should prove to be very fruitful in understanding mass spectral fragmentation mechanisms. Study of cyclic adducts wherein no *s-cis* or *s-trans* possibility exists, as well as other experiments which suggest themselves, will further elucidate this new phenomenon.

tions and essentially none at the 4 (tertiary) position. Rearrangement during deuteration of the bromo derivative would give 3-vinylcyclohexene, which is excluded by absence of nmr absorption between $\delta$ 2 and 3 in the deuterated compound; the compound was purified by vpc three times. Therefore, the deuterium is present exclusively in the 3 and/or 6 positions; an average of ten nmr integrations indicated ~5% nondeuterated contaminant.

(4) D. Craig and R. B. Fowler, *J. Org. Chem.*, **26**, 713 (1961).

(5) For a discussion of retro-Diels–Alder fragmentations in mass spectra, see H. Budzikiewicz, J. I. Brauman, and C. Djerassi, *Tetrahedron*, **21**, 1855 (1965).

(6) The ionizing voltages reported have been very approximately corrected by adding 5.6 v to the observed value, as determined using argon as a standard.

**Eileen P. Smith, Edward R. Thornton**
*Department of Chemistry, University of Pennsylvania*
*Philadelphia, Pennsylvania 19104*

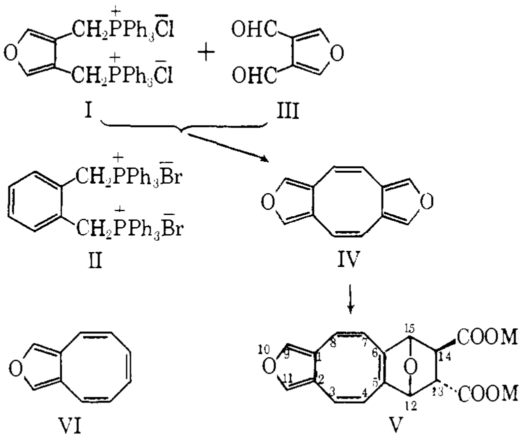
*Received June 14, 1967*

## [1,2:5,6]Di[*c*]furocyclooctatetraene and [3,4-*c*]Furooctalene[1]

*Sir:*

We report the synthesis of [1,2:5,6]di[*c*]furocyclooctatetraene (IV) and [3,4-*c*]furooctalene (VIII), tricyclic systems containing a periphery of 16 $\pi$ and 18 $\pi$ electrons, respectively.

A key intermediate in the synthesis of both IV and VIII was furan-3,4-bis(methylenetriphenylphosphonium chloride) (I) (mp >250°),[2] readily obtained in quantitative yield from 3,4-bischloromethylfuran[3] by treatment with triphenylphosphine in boiling dimethylformamide. No triphenylphosphine could be detected when I was treated with base, in marked contrast to the behavior of the corresponding benzenoid compound, *o*-xylylenebis(triphenylphosphonium bromide) (II).[4] This difference is presumably due to the low bond order of the 3,4-furan bond and may account for the finding that I gives yields superior to those of II in the Wittig reaction.



Wittig reaction of I and furan-3,4-dicarboxaldehyde (III)[5] with lithium ethoxide in dimethylformamide at 90° yielded 44% [1,2:5,6]di[*c*]furocyclooctatetraene (IV), colorless plates, mp 131–133° dec; mass spectrum, molecular ion at $m/e$ 184.055; $\lambda_{\max}^{\text{EtOH}}$ 239 m$\mu$ ($\epsilon$ 43,500), 246 (46,300), 296 sh (5600), 308 (6200), and 320 sh (4800). The nmr spectrum (all in $CCl_4$, 60 Mcps) showed 4 H singlets at $\tau$ 2.73 (furan ring protons) and 4.00 (eight-membered ring protons). The substance was unstable, the crystals rapidly becoming yellow and then orange on standing in air (appearance of infrared carbonyl bands at 1700 and 1670 cm$^{-1}$).

Treatment of IV with excess dimethyl fumarate in boiling benzene for 96 hr gave 77% of the monoadduct V, orange prisms, mp 110–111°; mass spectrum, molecular ion at $m/e$ 328; $\lambda_{\max}^{\text{EtOH}}$ 206 m$\mu$ ($\epsilon$ 16,200), 247 sh (15,500), 256 (19,800), 265 (19,100), 276 (11,200), and 315 (3200). The nmr spectrum confirmed structure V, showing a 2 H singlet at $\tau$ 3.03 ($H^9$, $H^{11}$), a 4 H multiplet at 3.97–4.73 ($H^3$, $H^4$, $H^7$, $H^8$), a 2 H broad singlet at 5.24 ($H^{12}$, $H^{15}$), singlets (3 H each) at 6.27 and 6.36 ($H^{Me}$), and a 2 H quartet centered at 6.68 ($H^{13}$, $H^{14}$). The adduct V is a 5,6-disubstituted derivative of cyclo-

---

(1) Unsaturated Eight-Membered Ring Compounds. IV. The following papers are considered to belong to this series: part I: J. A. Elix, M. V. Sargent, and F. Sondheimer, *Chem. Commun.*, 508 (1966); part II: *ibid.*, 509 (1966); part III: *J. Am. Chem. Soc.*, **89**, 180 (1967).

(2) Satisfactory elemental analyses or high-resolution mass spectra were obtained for all new compounds.

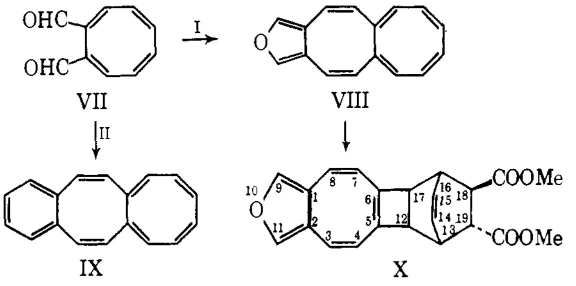
(3) K. Y. Novitskii, Y. K. Yur'ev, V. N. Zhingareva, and E. F. Egorova, *Dokl. Akad. Nauk SSSR*, **148**, 856 (1963); *Chem. Abstr.*, **59**, 3859c (1963).

(4) J. A. Elix, K. Grohmann, M. V. Sargent, and F. Sondheimer, unpublished observations; see C. E. Griffin, K. R. Martin, and B. E. Douglas, *J. Org. Chem.*, **27**, 1627 (1962); C. E. Griffin and J. A. Peters, *ibid.*, **28**, 1715 (1963).

(5) Substance III (mp 75–76°) was obtained in 12% yield from 3,4-bishydroxymethylfuran[3] by oxidation with manganese dioxide in boiling chloroform.

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 m$\mu$ ($\epsilon$ 22,300), with absorption beyond 350 m$\mu$. The nmr spectrum exhibited a 2 H singlet at $\tau$ 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 m$\mu$; 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 mono-adduct X, an orange glass; mass spectrum, molecular ion at *m*/*e* 364; $\lambda_{\max}^{\mathrm{EtOH}}$ 204 m$\mu$ ($\epsilon$ 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 $\tau$ 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 ($H^{\mathrm{Me}}$), 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.

**J. A. Elix, M. V. Sargent,[10] F. Sondheimer**
*University Chemical Laboratory*
*Cambridge, England*
*Received July 6, 1967*

---

[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).

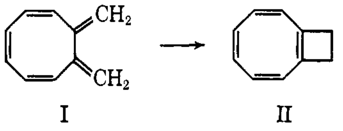
[10] Imperial Chemical Industries Fellow.

---

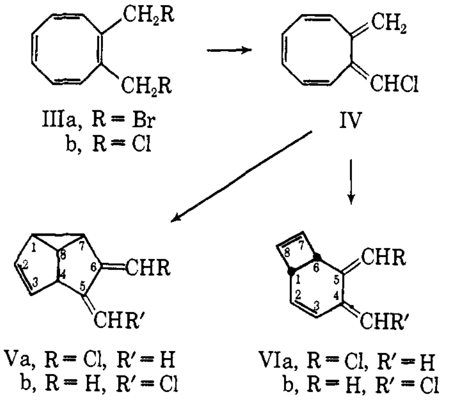
## The Photorearrangement of 7-Methylene-8-chloromethylenecycloocta-1,3,5-triene[1]

*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



---

[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).