The present study was restricted to reactions performed on quantities of *ca.* 1–2 mg as it was not possible to take the safety precautions advised by Smith[5] for dealing with unknown compounds containing xenon in larger amounts. This precluded solvent extractions, ordinary ir and nmr studies, as well as elemental analysis, with mass spectrometry being the most suitable analytic tool available. Mass spectra were carried out on an Atlas single-focusing CH_4 spectrometer at 70 V at an ion source of $\sim 80°$ using high amplification. Experiments were performed on dry materials at room temperature and the XeF_2 was transferred under nitrogen. The final products were not kept free of air or moisture before insertion into the mass spectrometer within 2 hr of preparation.

The addition of a few crystals of XeF_2 to *ca.* 1 ml of trifluoroacetic acid–anhydride mixture resulted in a violently exothermic reaction in which all the liquid was driven off leaving a whitish solid which exploded gently when being transferred. The other two reactions were carried out in the solid state by merely adding the XeF_2 to several milligrams of the salt, and the product was analyzed without being separated from the salt. The reaction products in all three cases showed characteristic Xe^+ (and Xe^{2+}) peaks in the mass spectrum, and no peaks appeared at m/e corresponding to XeF^+ and XeF_2^+ which occur along with Xe^+ in ratios of *ca.* 6:4:3 in the starting material XeF_2 itself.[6] A large CF_3^+ peak and a large CH_3CO^+ peak were observed in the low mass regions of the two respective salt–product mixtures, all of which peaks disappeared after the materials were allowed to stand for several days.

It is expected that the products are indeed $Xe(OCOCF_3)_2$ and $Xe(OCOCH_3)_2$ as any other likely reaction would have evolved Xe, although this interpretation remains to be confirmed. The solid and $Xe(OCOCF_3)_2$ differs from the product of Iskraut, *et al.*,[4] in color, mass spectrum, and stability; the occurrence of peaks corresponding to XeF^+ and XeF_2^+ in these authors' mass spectrum seems to indicate the presence of either XeF_2 or $XeF_2(OCOCF_3)_2$ as impurities, and the latter might even be the reaction product obtained given also the peaks at $XeCO_2F^+$ and $XeCOF^+$. It is also possible to interpret the Xe^+ in the mass spectrum of their acetates to indicate that they have obtained stable $Xe(OCOCH_3)_2$ in addition to the other decomposition products of $Xe(OCOCH_3)_4$.

It seem reasonable to suppose that other organic esters as well as the inorganic esters $Xe(ONO_2)_2$ and $Xe(OSO_2)_2$ could be prepared, and in view of the increased stability of related cyclic systems[1b,3] we would expect that compounds such as xenon di- and trisuccinate and the dilactone of di(*o*-phenylcarboxylic acid)xenon dioxide would possess unusual stability.

We believe that the ease with which these simple substitution reactions appear to take place on divalent xenon (as well as on trivalent iodine, etc.[1,3]) serves as evidence for the potentially important role of xenon and other hypervalent atoms in organic chemistry.[7]

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(5) R. B. Smith in "Noble Gas Compounds," H. H. Hyman, Ed. University of Chicago Press, Chicago, Ill., 1963, p 126.

(6) M. H. Studies and E. N. Sloth, in ref 5, p 47.

(7) Initial attempts to prepare both PhXeF and xenonium fluorenyl ylide, in collaboration with J. Klein, by treating XeF_2 with appropriate lithium organics, did not succeed. It is expected, however, that appropriate conditions can be found under which these products can be obtained.

(8) Address all correspondence to Belfer Graduate School of Science, Yeshiva University, New York, N. Y. 10033.

Jeremy I. Musher[8]
Hebrew University, Jerusalem, Israel
and Belfer Graduate School of Science, Yeshiva University
New York, New York 10033

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4,5:6,7-Dibenzoxonin and 4,5:6,7-Dibenzothionin

Sir:

The preparation of unsaturated monocyclic systems having ten π electrons has been the object of a considerable body of research,[1] and it has become apparent that any gain in delocalization energy resulting from the adoption of a planar, aromatic conformation is seriously offset by the consequent nonbonded interactions and bond angle strain.[2] Such skeletal strain may be relieved by distortion from planarity, by valence tautomerism, or by a combination of these effects. The contrast between the cyclononatetraenyl anion, which exists as the monocyclic aromatic system **2a**,[3] and cyclooctatetraene epoxide, which exists as the nonplanar, bicyclic system **1b**,[5] illustrates the competition between aromaticity and skeletal strain that is found in the ten π electron monocyclic systems.[6] However, suitable benzannelation of the monocyclic systems **2b,c**[7] should suppress the electronic rearrangement to the bicyclic form as this involves disruption of the benzenoid system, and such benzannelated derivatives might, therefore, be aromatic.[8]

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(1) T. J. Katz, *J. Amer. Chem. Soc.*, **82**, 3784, 3785 (1960); M. Avram, G. Mateescu, and C. D. Nenitzescu, *Ann.*, **636**, 174 (1960); M. Avram, C. D. Nenitzescu, and E. Marica, *Chem. Ber.*, **90**, 1857 (1957); R. C. Cookson, J. Hudec, and J. Marsden, *Chem. Ind.* (London), 21 (1961); E. Vogel, W. Meckel, and W. Grimme, *Angew. Chem. Intern. Ed. Engl.*, **3**, 643 (1964); E. E. van Tamelen and B. Pappas, *J. Amer. Chem. Soc.*, **85**, 3296 (1963); E. E. van Tamelen and T. L. Burkoth, *ibid.*, **89**, 151 (1967); S. Masamune, C. G. Chin, K. Hojo, and R. T. Seidner, *ibid.*, **89**, 4804 (1967); G. Schröder and T. Martini, *Angew. Chem. Intern. Ed. Engl.*, **6**, 806 (1967); K. Grohmann and F. Sondheimer, *J. Amer. Chem. Soc.*, **89**, 7119 (1967); R. H. Mitchell and F. Sondheimer, *ibid.*, **90**, 530 (1968); A. P. Bindra, J. A. Elix, and M. V. Sargent, *Tetrahedron Letters*, 4335 (1968); P. J. Mulligan and F. Sondheimer, *J. Amer. Chem. Soc.*, **89**, 7118 (1967).

(2) In the ten π electron series only the cyclooctatetraenyl dianion[1] and the cyclononatetraenyl anion[3] have been well characterized. However, the three aromatic 1,6-methano-bridged species, the bicyclo-[4.3.1]decatetraenyl anion, 1,6-methano[10]annulene, and the bicyclo-[5.4.1]dodecapentaenyl cation, have all been synthesized.[4]

(3) T. J. Katz and P. J. Garratt, *J. Amer. Chem. Soc.*, **85**, 2852 (1963); **86**, 5194 (1964); E. A. La Lancette and R. E. Benson, *ibid.*, **85**, 2853 (1963); **87**, 1941 (1965).

(4) E. Vogel, Special Publication No. 21, The Chemical Society, London, 1967, p 143.

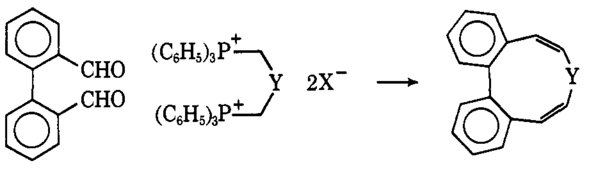
(5) A. C. Cope, P. T. Moore, and W. R. Moore, *J. Amer. Chem. Soc.*, **80**, 5505 (1958).

(6) A recent report on the photoirradiation of **1b** suggests that the photoproducts arise *via* excited all-*cis*-oxonin **2b**: J. M. Holovka, P. D. Gardner, C. B. Strow, M. L. Hill, and T. V. Van Auken, *J. Amer. Chem. Soc.*, **90**, 5041 (1968).

(7) By analogy with the difference in properties between furan and thiophene, it is possible that thionin (**2c**), which is unknown, may itself be an aromatic system.

1a, X = CH$^-$
b, X = O
c, X = S

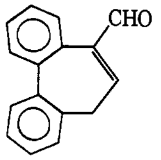
2a, X = CH$^-$
b, X = O
c, X = S



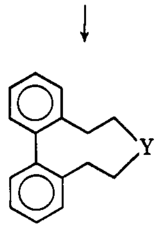
3

4a, Y = O; X = Br
b, Y = S; X = Cl

5a, Y = O
b, Y = S



7



6a, Y = O
b, Y = S

We now report the synthesis of the first known derivatives of the oxonin and thionin systems, 4,5:6,7-dibenzoxonin (**5a**) and 4,5:6,7-dibenzothionin (**5b**). A Wittig reaction between **3** (1.05 g, 5.0 mmol) and **4a** (3.72 g, 5.0 mmol)[9] with lithium methoxide (0.38 g, 10.0 mmol) in DMF at 80° for 3 hr gave, after rapid chromatography on silica gel followed by sublimation, a 6% yield of 4,5:6,7-dibenzoxonin (**5a**), 65 mg, mp 99°. The spectral properties [mass spectrum *m/e* 220.088 (calcd 220.089); ir (CCl_4) 1663, 1650 (enol ether double bonds), 1070 cm^{-1} (ether); uv (EtOH) 217 (18,630), 250 (sh) (6285), 293 nm (ϵ 400)] are in accord with the assigned structure.[10] The nmr spectrum, a multiplet at τ 2.2–3.0 (8 H) and an AB double doublet at τ 3.95 (J_{AB} = 7.0 Hz, 2 H) and 4.70 (J_{BA} = 7.0 Hz, 2 H), supports the all-*cis* configuration. Catalytic hydrogenation (Pt, methanol) of **5a** gave 4,5:6,7-dibenzoxonan (**6a**), mp 82–83°, in 80% yield. The mass spectrum (*m/e* 224) showed that four atoms of hydrogen had been added, and the ir and nmr spectra [τ 2.6–3.0 (8 H), 6.0–6.6 (4 H), 7.3–7.7 (4 H)] were in agreement with structure **6a**.

4,5:6,7-Dibenzoxonin (**5a**) behaves as an enol ether, treatment with aqueous hydrochloric acid in ethanol giving an aldehyde [mp 116–117°; uv (EtOH) 227 (24,200), 245 nm (ϵ 22,450)] which was assigned structure **7** on the basis of the mass, ir, and nmr spectral data and by analogy with the behavior of benzo[*d*]oxepin.[9]

A Wittig reaction between **3** (2.1 g, 10.0 mmol) and **4b** (6.60 g, 10.0 mmol)[11] with lithium methoxide (0.146 g, 21 mmol) in methanol under high dilution conditions at room temperature gave, after chromatography on silicic acid, a 10% yield of 4,5:6,7-dibenzothionin (**5b**) (241 mg, mp 121–122°).[12] The spectral properties [mass spectrum, *m/e* 236.065 (calcd 236.066); ir 1615, (vinyl sulfide), 1467, 1437, 1331 cm^{-1}; uv (cyclohexane) 254 nm (sh) (ϵ 5250)] are in accord with the assigned structure. The nmr spectrum, a multiplet at τ 2.6–3.1 (8 H) and an AB double doublet at τ 3.62 (J_{AB} = 10.5 Hz, 2 H) and 4.31 (J_{BA} = 10.5 Hz, 2 H), together with the absence of absorption in the *trans* double bond region of the ir spectrum, supports the all-*cis* configuration. Desulfurization of **5b** with Raney nickel gave the known 2,2′-diethylbiphenyl (71%),[13] and hydrogenation of **5b** (10% Pd–C, EtOAc) for 5 hr gave 38% of 4,5:6,7-dibenzothionan (**6b**), mp 74–75°. The mass spectrum (*m/e* 240.099) showed that four atoms of hydrogen had been added, and the nmr spectrum [τ 2.6–3.1 (8 H), 7.0–7.6 (8 H)] was consistent with **6b**.

The nmr and uv spectra of **5a** and **5b** clearly indicate that these systems are not aromatic and that they exist in buckled, nonplanar conformations. Benzannelation, although it has prevented valence tautomerism to the bicyclo[6.1.0] system, has not led to the adoption of a planar, aromatic conformation.[14] It thus appears that the gain in delocalization energy attained in the planar, all-*cis* conformation is greater for the cyclononatetraenyl anion (**2a**) than for either oxonin (**2b**), 4,5:6,7-dibenzoxonin (**5a**), or 4,5:6,7-dibenzothionin (**5b**).

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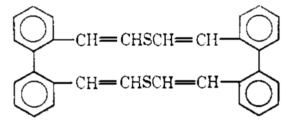
[8] Conversely, annelation depresses cyclic delocalization in the macrocyclic ring system by destabilizing contributing structures involving the disruption of the benzenoid sextet.

[9] K. Dimroth, G. Pohl, and H. Follmann, *Chem. Ber.*, **99**, 634 (1966).

[10] Satisfactory analytical or high-resolution mass spectral data have been obtained for all new compounds.

[11] K. Dimroth, H. Follman, and G. Pohl, *Chem. Ber.*, **99**, 642 (1966).

[12] A second crystalline compound was also isolated (194 mg, 8% yield, mp 125–130°) to which we assign structure i.



i

[13] (a) P. M. Everitt, D. M. Hall, and E. E. Turner, *J. Chem. Soc.*, 2286 (1956); (b) J. R. Shelton and J. F. Suida, *J. Org. Chem.*, **31**, 2028 (1966). The ir spectrum of our sample is in agreement with that reported,[13b] and the mass and nmr spectra are consistent with those expected for 2,2′-diethylbiphenyl. The uv spectrum [230 (4750), 264 (1260), 271 nm (ϵ 910), lit.[13a] *ca.* 227 (sh 6000), 263.4 (730), 271 nm (ϵ 560)] differs from that reported in absorption intensity.

[14] The increase in bond angle strain resulting from annelation may have prevented the adoption of a planar conformation, but this appears unlikely in view of the finding that *sym*-dibenzcyclooctatetraene readily forms the planar dianion.[15] However we are investigating this eventuality by a synthesis of the 1,2:3,4-dibenzocyclononatetraenyl anion.

[15] T. J. Katz, M. Yoshida, and L. C. Siew, *J. Amer. Chem. Soc.*, **87**, 4516 (1965).

A. P. Bindra, J. A. Elix
Chemistry Department, Australian National University
Canberra, ACT 2600, Australia

P. J. Garratt
Chemistry Department, University College
London, W.C.1, England

R. H. Mitchell
University Chemical Laboratories
Cambridge, England

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Rates of Decomposition of Nitro Radical Anions

Sir:

The importance of radical ions as intermediates in organic reactions is now being realized. Heretofore, most investigations have involved aromatic radical ions due to their relative stability and the theoretical