Accepting that in such a system the yields of C_2H_5D and CD_3H are equivalent to the yields of the CH_3^+ and CH_4^+ ions, respectively,[15] we can derive a value of 0.85 for the ratio CH_4^+/CH_3^+, independent of pressure from 1 to 5 torr. Considering the differences in experimental techniques, this value is in fair agreement with the value of 1.1 obtained by Dibeler, *et al.*,[11] and to the values of 0.67 and 0.95 measured for the CH_4^+/CH_3^+ ratio in methane ionized by collision with excited metastable (2 $^1S_0$ and 2 $^3S_1$) helium atoms (20.6 and 19.8 eV, respectively) in the study of Herce, *et al.*[13] In the latter study, and in the present one, the methane ion/methyl ion ratio did not change when CD_4 was substituted for CH_4.

The total ion pair yield of CH_4^+ plus CH_3^+, derived from product yields and saturation current measurements, was 0.86. As will be discussed later,[7] possibly 5–10% of the $[CH_4^+]^*$ ions undergo process 3 to form CH_2^+.

We also examined the rare gas sensitized photolysis of methane, in which methane ions with varying amounts of excess energy can be formed by charge transfer from different rare gas ions. As anticipated,[16] at constant intensity and at pressures where all quanta are absorbed, the saturation current values measured for pure xenon, krypton, and argon were identical. In contrast, a current of only about 3% of that value was seen when neon (IP = 21.56 eV) was introduced into the vessel.

In experiments where the rare gas/methane ratio was about 10, and the total pressure 15 torr, methane ions are formed mainly by charge transfer

$$A + h\nu\,(21.2\ \text{eV}) \longrightarrow A^+ + e \qquad (9)$$

$$A^+ + CH_4 \longrightarrow [CH_4^+]^* + A \qquad (10)$$

The CH_4^+/CH_3^+ ratios, determined by the interceptor technique described above, are given in Table I for the krypton- and argon-sensitized photolyses. The results agree reasonably well with those of von Koch,[17] measured in a tandem mass spectrometer at a pressure of approximately 10^{-5} torr.

Table I. Rare Gas Sensitized Photolysis of Methane

	Kr^+ 14.00–14.66 eV	Ar^+ 15.76–15.93 eV
CH_4^+/CH_3^+	1.25 1.60[a]	<0.07 0.01[a]

[a] Data of H. von Koch, *Arkiv Fysik*, **28**, 529 (1965).

In all the rare gas sensitized photolyses, the ion pair yields which could be attributed to the hydrocarbon ions were close to unity, indicating that charge-transfer process 10 is efficient.

A more detailed account of the far-ultraviolet photolysis of CH_4 and other hydrocarbons carried out with an enclosed neon resonance lamp, as well as the helium resonance lamp, is forthcoming. The ionization quantum yields of a variety of organic and inorganic compounds will also be reported shortly.[18]

Acknowledgment. The authors are greatly indebted to S. G. Lias, who collaborated on certain aspects of this work.

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[16] J. A. R. Samson, *J. Opt. Soc. Am.*, **54**, 6 (1964).

[17] H. von Koch, *Arkiv Fysik*, **28**, 529 (1965); see also: F. H. Field, H. N. Head, and J. L. Franklin, *J. Am. Chem. Soc.*, **84**, 1118 1962); G. G. Meisels, W. H. Hamill, and R. R. Williams, Jr., *J. Phys. Chem.*, **61**, 1456 (1957).

[18] NOTE ADDED IN PROOF. After this communication had been submitted for publication, a study of the photolysis of methane at 584 Å (C. A. Jensen and W. F. Libby, *J. Chem. Phys.*, **49**, 2831 (1968)) appeared. The latter study emphasizes the formation of polymer product. Also, the lamp used in that investigation was of a different design.

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Organic Esters of Xenon

Sir:

Upon adding a few crystals of XeF_2 to excess trifluoroacetic acid, solid silver trifluoroacetate, and solid sodium acetate, we have obtained products whose mass spectra show the presence of nonvolatile xenon and fail to show the presence of xenon fluorides. We interpret these results as indirect evidence in favor of the formation of xenon ditrifluoroacetate and xenon diacetate according to the simple scheme

$$XeF_2 + 2RCOOH \longrightarrow Xe(OCOR)_2 + 2HF \qquad R = CF_3$$

and

$$XeF_2 + 2RCOOM \longrightarrow Xe(OCOR)_2 + 2MF \qquad R = CF_3, CH_3$$

although such an interpretation must, in the absence of further information, be considered speculative. As a study of the hypothesized xenon esters and the many xenon compounds related to them would require a serious experimental program which we are not prepared to undertake at present, we have decided to report these results, preliminary and incomplete though they be.

The possibility of synthesizing organic compounds containing xenon using rather typical procedures of organic chemistry has been discussed by the author[1] and independently by Hellwinkel[2] as part of discussions of higher valence compounds of elements in groups V–VIII of the periodic table. The experiments described here were undertaken in order to illustrate the theoretical contention[1] that xenon should have a chemistry similar to that of iodine, which, in turn has a chemistry similar to that of selenium, tellurium, phosphorus, and arsenic.[3] In the only previous study on organic xenon compounds, and which seems not to have been followed up elsewhere in the literature, Iskraut, Taubenest, and Schumacher[4] have prepared what are perhaps $Xe(OCOCF_3)_4$ and $Xe(OCOCH_3)_4$.

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[1] (a) J. I. Musher, "The Chemistry of Hypervalent Molecules," *Angew. Chem.*, in press; *Science*, **141**, 736 (1963). For related syntheses, see (b) W. C. Agosta, *Tetrahedron Letters*, 2681 (1965), and (c) H. K. Livingston, J. W. Sullivan, and J. I. Musher, *J. Polymer Sci.*, **C22**, 195 (1968). Xenon diacetate is discussed along with other related compounds in (d) J. I. Musher, "Higher Valences, Geometrical Isomers and New Molecules," 1964, (privately circulated); (e) "Higher Valence Inorganic Cyclic Diesters," 1965, unpublished.

[2] D. Hellwinkel, lecture on the 70th birthday of G. Wittig, 1968, unpublished.

[3] See, *e.g.*, D. Hellwinkel and G. Fahrbach, *Chem. Ber.*, **101**, 574 (1968), and previous articles cited therein.

[4] A. Iskraut, R. Taubenest, and E. Schumacher, *Chimia*, **18**, 188 (1964).

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.

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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.