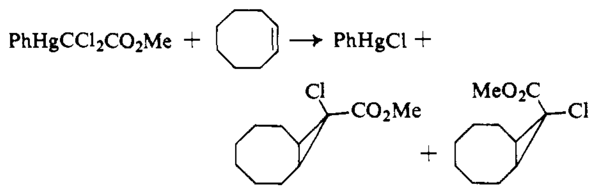
(2)

drous sodium iodide in 1,2-dimethoxyethane (DME)[4] in the presence of cyclohexene, presumably because of complicating side reactions of the $\mathrm{MeO_2CCl_2^-}$ intermediate with C=O groups in the starting material and in any cyclopropane product that might have been produced.

Organomercury systems which serve well in the transfer of $\mathrm{CF_3CCl}$ also have been prepared (eq 3). Thermolysis

$$\mathrm{PhHgCl + Me_3COK + CF_3CXYH \xrightarrow[-10\ to\ 0^\circ]{THF} PhHgCXYCF_3 + Me_3COH + KCl} \quad (3)$$

X = Y = Cl, 75% yield, mp 146–148.5°
X = Cl; Y = Br, 86% yield, mp 141–143°

of $\mathrm{PhHgCCl_2CF_3}$ in the presence of cyclooctene (threefold excess) in chlorobenzene at 160° in a bomb tube did not proceed in high conversion during 6.5 days; phenylmercuric chloride was formed in only 25% yield. Glpc analysis of the trap-to-trap distilled filtrate indicated the formation of the *anti* and *syn* isomers of 9-chloro-9-trifluoromethylbicyclo[6.1.0]nonane in a total yield of 11%. Since phenyl(bromodichloromethyl)mercury decomposes so much more readily under comparable conditions than phenyl(trichloromethyl)mercury and hence is a much more effective $\mathrm{CCl_2}$ precursor,[5] the mercurial $\mathrm{PhHgCClBrCF_3}$ was prepared. As expected, it was much less stable and was almost completely decomposed (giving PhHgBr in 82% yield) on being heated in cyclooctene solution at reflux for 5.5 days. The 9-chloro-9-trifluoromethylbicyclo[6.1.0]nonane isomer to be eluted first upon glpc analysis using a DC-200 silicone oil column ($n^{25}\mathrm{D}$ 1.4371) was formed in 64% yield; the other isomer, $n^{25}\mathrm{D}$ 1.4439, was produced in 10% yield. In addition, a third product, present in 5% yield, was identified as 9-bromo-9-trifluoromethylbicyclo[6.1.0]nonane, $n^{25}\mathrm{D}$ 1.4571. Since the starting halocarbon used in the preparation of phenyl(1-bromo-1-chloro-2,2,2-trifluoroethyl)mercury, $\mathrm{CF_3CClBrH}$ ("Fluothane," a product of the Ayerst Laboratories), was 99.9% pure by glpc (*i.e.*, free of $\mathrm{CF_3CBr_2H}$), the formation of the $\mathrm{CF_3CBr}$–cyclooctene adduct in 5% yield possibly represents a minor side reaction in which $\mathrm{CF_3CBr}$ and phenylmercuric chloride are produced. Such lack of specificity is not too surprising in view of the higher reaction temperature used. A similar lack of specificity was observed in the reaction of this mercurial with triethylsilane (eq 4).

$$\mathrm{PhHgCClBrCF_3 + Et_3SiH \xrightarrow[reflux]{PhCl} \underset{(51\%)}{Et_3SiCHClCF_3} + \underset{(4\%)}{Et_3SiCHBrCF_3}} \quad (4)$$

Sodium iodide in DME was found to displace the $\mathrm{CF_3CCl_2^-}$ anion from mercury. However, the anion decomposed with β elimination of fluoride ion, forming 1,1-dichloro-2,2-difluoroethylene, rather than *via* α elimination of chloride ion to give $\mathrm{CF_3CCl}$ (eq 5), in agreement with the previous work by Hine.[6] This experiment thus

$$\mathrm{PhHgCCl_2CF_3 + Na^+I^- \xrightarrow{DME} PhHgI + Na^+CCl_2CF_3^- \rightarrow NaF + CCl_2{=}CF_2} \quad (5)$$

provides further proof that *thermal* carbene extrusion from phenyl(polyhalomethyl)mercury compounds does not proceed by way of polyhalomethyl anion intermediates.

The present results, as well as earlier studies,[7,8] suggest that further research on the organomercury route to functional carbenes will be fruitful and that much new and useful carbene chemistry can be developed *via* this organometallic approach. We are actively pursuing further studies in this area.

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(9) National Science Foundation Trainee, 1966–1967; National Science Foundation Graduate Fellow, 1967–1969.

(10) Lewis Paul Chapin Fellow in Chemistry, 1968–1969.

Dietmar Seyferth, David C. Mueller,[9] Robert L. Lambert, Jr.[10]
Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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Reaction of Xenon Difluoride with Benzene[1]

Sir:

A variety of methods for selectively halogenating aromatic compounds are currently available. For fluorination, however, the picture is less satisfactory. The direct fluorination of benzene with fluorine gas[2] or cobaltic fluoride[3] yields only a mixture of nonaromatic fluorocarbons and tar. Ellis and Musgrave[4] have found that the primary process in the reaction of benzene and $\mathrm{ClF_3C}$ in $\mathrm{CCl_4}$ in the presence of $\mathrm{CoF_2}$ is one of substitution to give fluorobenzene and chlorobenzene in 26.6 and 58.5% yields, respectively. Addition compounds, biphenyls, and tar were also found. Fluorination of substituted benzenes by this method gave products consistent with an electrophilic mechanism.[5] $\mathrm{CF_3OF}$ has been found to react with salicylic acid to give, presumably by electrophilic substitution, 3- and 5-fluorosalicylic acids.[6]

We wish to report that xenon difluoride reacts with

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(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) N. Fukuhara and L. A. Bigelow, *J. Am. Chem. Soc.*, **60**, 427 (1938).

(3) A. K. Barbour, H. D. MacKenzie, M. Stacey, and J. C. Tatlow, *J. Appl. Chem.*, **4**, 347 (1954).

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(6) D. H. R. Barton, A. K. Ganguly, R. H. Hesse, S. N. Loo, and M. M. Pechet, *Chem. Commun.*, **806** (1968).

excess benzene in CCl_4 in the presence of small amounts of HF to yield fluorobenzene in 68% yield (based on benzene consumed).

Spectrograde CCl_4 (14.737 g) was distilled over sodium sulfate *in vacuo* into a Kel-F tube containing 7.23×10^{-3} mol of XeF_2 whose ir spectrum indicated a trace of HF. Zone-refined benzene (2.66×10^{-2} mol) was distilled over Na_2SO_4 into the mixture, which was frozen in liquid nitrogen. The solution was warmed to 25° and approximately 30% of the XeF_2 dissolved. After 25 min the colorless solution turned yellow and then very dark green; the XeF_2 crystals dissolved and xenon gas was evolved. After 53 min, gas evolution had ceased and reaction appeared to be complete. A vacuum was applied to the reaction mixture and all volatile material was collected in a U tube at −78° to give 16.754 g of distilled material, leaving 0.294 g of black tar. Hydrogen fluoride was formed, as evidenced by etching of the U tube. The infrared spectrum of the distillate, when compared with literature data, a synthetic mixture of a few per cent benzene and fluorobenzene in CCl_4, and their individually measured spectra strongly suggested the presence of fluorobenzene. The distillate was then chromatographed on a 13-ft column of diethylene glycol succinate on 30–60 mesh Chromosorb R. Using both thermal conductivity and flame ionization detectors, only three peaks were found, corresponding in retention time to CCl_4, benzene, and fluorobenzene. From a calibration curve it was found that the distillate contained 1.35%[7] fluorobenzene and 10.65% benzene. Retention times obtained from chromatograms of all possible polyfluorobenzenes and several polyfluorocyclohexanes indicated their absence in the distillate.

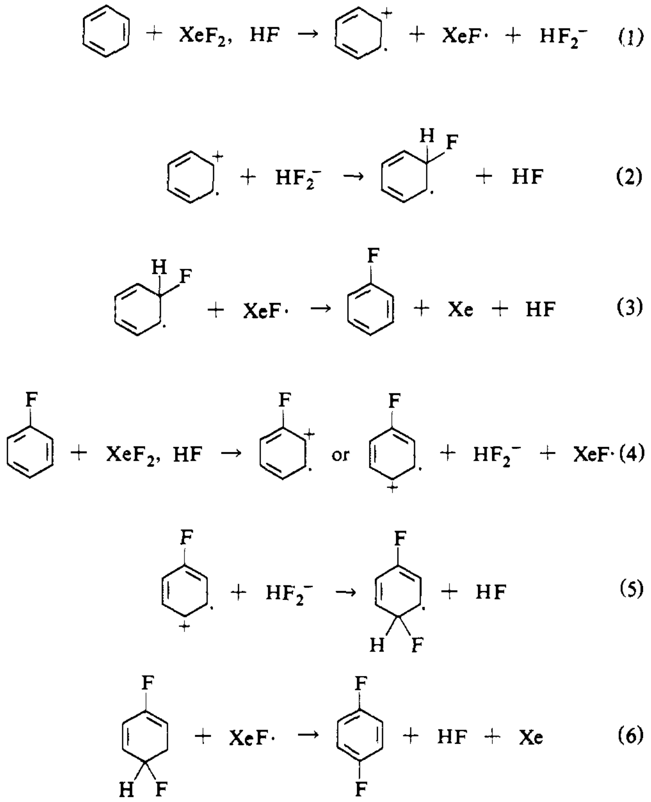
The residue from the distillate was allowed to stand at room temperature for 10 days, after which 34 mg of needles, mp 72–73°,[8] sublimed from the tarry residue. The infrared spectrum of the needles indicated the presence of 2- and 4-fluorobiphenyls. The mass spectrum of the needles confirmed the presence of monofluorobiphenyl and also indicated the presence of biphenyl, difluorobiphenyl, and trifluorobiphenyl.

No separate solvent is required for reaction. When 4.1×10^{-2} mol of benzene was allowed to react with 1.26×10^{-2} mol of XeF_2 for 2.5 hr, the distillate was composed of 88.72% benzene, 10.28% fluorobenzene, 0.7% *p*-difluorobenzene, and 0.3% *o*-difluorobenzene. The above-mentioned dimers were found in the 0.027 g of needles which sublimed from the 0.640 g of tar. The infrared spectrum and mass spectral analysis indicated the same products as in the reaction in CCl_4. Hydrogen fluoride (1.85×10^{-3} mol) was determined by condensing the vapor phase into 1.000 *M* NaOH and back titrating with 1.000 *M* HCl.

The reaction is strongly catalyzed by HF, as indicated by the following observations. XeF_2 was distilled from anhydrous NaF and then held in an evacuated system at −78° for 12 hr. The residual pressure was 4×10^{-5} mm, and no HF bands were observed in the infrared spectrum. When 1.429×10^{-2} mol of this material was used for reaction with 4.939×10^{-2} mol of benzene in 16.403 g of CCl_4, reaction had not commenced even after 2.5 hr (compare observations above). However, when 1.428×10^{-3} mol of HF was condensed into the reaction mixture, frozen in liquid nitrogen, a green layer developed immediately at the interface. As the reaction warmed to room temperature, xenon gas was liberated. The importance of HF was confirmed by opening the Kel-F tube to an evacuated ballast volume and removing HF. The reaction stopped and proceeded again after condensing the HF back into the Kel-F tube, as evidenced by the renewed release of Xe gas.

Electron spin resonance studies of the reaction are currently in progress. Preliminary results indicate radicals are present, but optimum conditions for identification have not yet been found.

The results thus far are consistent with, and strongly suggestive of, the mechanism given by eq 1–6.



Similar mechanisms may be written to account for the formation of biphenyl and fluorinated biphenyls. The conspicuous absence of 3-fluorobiphenyl agrees with the suggested mechanism. In eq 4 one would expect *ortho–para* orientation by fluorine toward further electrophilic attack, which is, in fact, found.

The above scheme essentially agrees with Bartlett's[9,10] observations of HF catalysis in the reactions of XeF_2 and his prediction that reaction may take place by ionization to XeF^+ or similar species followed by electron transfer to give XeF · and, under our conditions, to give the radical cation of benzene.

It is interesting to note that when benzene is dissolved in concentrated sulfuric acid containing potassium persulfate a green solution develops which displays a poorly resolved seven-line esr spectrum. However, it was not definitely concluded that this species was the radical cation of benzene, since the splitting between lines was less than

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[7] All per cents are understood to be w/w unless otherwise specified.

[8] Biphenyl, mp 70°; 2-fluorobiphenyl, mp 71–72°; 3-fluorobiphenyl, mp 26–27°; 4-fluorobiphenyl, 74.2–74.5°.

[9] N. Bartlett and F. O. Sladky, *Chem. Commun.*, 1046 (1968).

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expected.[11] Further elucidation of the mechanism of oxidative fluorination and determination of its scope with respect to both aromatic and alphatic compounds are currently in progress.

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M. J. Shaw, H. H. Hyman
Chemistry Division, Argonne National Laboratory
Argonne, Illinois 60439

R. Filler
Department of Chemistry, Illinois Institute of Technology
Chicago, Illinois 60600

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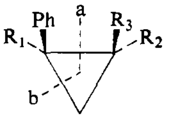
Steric and Electronic Factors in the Reductive Cleavage of Methyl-Substituted Phenylcyclopropanes and Spiro[2.4]hepta-4,6-dienes

Sir:

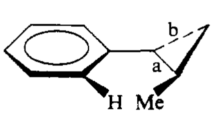
An interesting aspect of the general problem of cyclopropane conjugation,[1] *viz.*, the reductive cleavage of conjugated cyclopropane rings with alkali metals in liquid ammonia, has received an increasing amount of attention. Several authors have concluded that in various cyclopropyl ketones the bond which is cleaved is the one which best overlaps with an adjacent carbonyl[2] (or phenyl)[2c,d] orbital. The question of the importance of electronic or "inductive"[3] (as opposed to steric) effects has received somewhat less attention.[2d,4] Recently, however, it was reported that the cleavage of 1-methyl-2,2-diphenylcyclopropane (**1a**) by pathway a is favored over pathway b (to give 1,1-diphenylbutane (**2**) and 1,1-diphenyl-2-methylpropane (**3**), respectively) by a factor of 5.0–5.7.[5] It was stated that this result might be expected on the basis of the fact that a methyl group would be predicted to stabilize a radical-anion activated complex for pathway a relative to that for pathway b. However, only one canonical form of the activated complex was considered; in addition, steric effects in the activated complexes would be difficult to evaluate without data from simpler model compounds.[5]

We have employed methyl groups as probes of charge distribution in the activated complexes of several simple conjugated cyclopropyl systems. The reductive cleavages of *trans*- and *cis*-1-methyl-2-phenylcyclopropanes[6] by lithium in liquid ammonia at *ca.* -33° *have been found to be highly regioselective*[7] *reactions.*[8] The *trans* isomer **1b** is cleaved primarily *via* pathway b ($k_b/k_a = 360 \pm 20$) whereas the *cis* isomer **1c** is cleaved somewhat more slowly *in the opposite direction* ($k_a/k_b =$ *ca.* 70). In addition, the cleavage of 1,1-dimethyl-2-phenylcyclopropane[9] was shown to have $k_a/k_b = 2.3 \pm 0.1$. In each case the products were analogous to **2** and **3**.[10]

The results for the conformationally mobile methylphenylcyclopropanes clearly demonstrate the importance of both electronic and steric factors. The high regioselectivity observed in the cleavage of the *trans* isomer **1b** (in which there is no steric bias for either pathway) shows that a methyl group exerts a large destabilizing "inductive" effect (relative to hydrogen). This is consistent with a description of the activated complex in which there is substantial negative charge on the cyclopropyl β-carbon of the bond undergoing cleavage. In the case of the *cis* isomer **1c** the conformation of maximum overlap for cleavage of bond b (**4**) possesses a substantial steric interaction between the methyl group and the *ortho* hydrogen on the phenyl ring. Therefore, cleavage of bond a is greatly favored in spite of the destabilizing effect of the methyl group. The nearly equal rates of cleavage of bonds a and b in 1,1-dimethyl-2-phenylcyclopropane (**1d**) represent a balancing of electronic and steric factors. On the basis of our results it can be stated that the cleavage of **1a** by pathway a is *hindered* (rather than accelerated)[5] by the "inductive" effect of the methyl group and that a steric effect similar to that discussed for **1c** is the dominant factor.



1a, R₁ = Ph;
R₂ = H; R₃ = Me
b, R₁ = R₃ = H;
R₂ = Me
c, R₁ = R₂ = H;
R₃ = Me
d, R₁ = H;
R₂ = R₃ = Me



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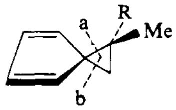

5a, R = H
b, R = Me

The destabilizing effect of a methyl group appears to be reasonably general, as is shown by the results for the cleavage of 1-methylspiro[2.4]hepta-4,6-diene[11,12] (**5a**) by sodium in liquid ammonia at *ca.* -33°. This cleavage is instantaneous and exothermic; 1- and 2-*n*-propyl- and 1-

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(1) For leading references see (a) M. Yu Lukina, *Russ. Chem. Rev.*, **31**, 419 (1962); (b) S. W. Staley, *J. Am. Chem. Soc.*, **89**, 1532 (1967); (c) P. von R. Schleyer and G. W. Van Dine, *ibid.*, **88**, 2321 (1966); (d) T. Tsuji, I. Moritani, and S. Nishida, *Bull. Chem. Soc. Japan*, **40**, 2338 (1967); (e) S. Sarel, J. Yovell, and M. Sarel-Imber, *Angew. Chem. Intern. Ed. Engl.*, **7**, 577 (1968).

(2) (a) T. Norin, *Acta Chem. Scand.*, **19**, 1289 (1965); (b) W. G. Dauben and E. J. Deviny, *J. Org. Chem.*, **31**, 3794 (1966); (c) H. E. Zimmerman, K. G. Hancock, and G. C. Licke, *J. Am. Chem. Soc.*, **90**, 4892 (1968); (d) R. Fraisse-Jullien and C. Frejaville, *Bull. Soc. Chim. France*, 4449 (1968); (e) A. J. Bellamy and G. H. Whitham, *Tetrahedron*, **24**, 247 (1968).

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(4) There is qualitative evidence which suggests that both steric and electronic factors are of importance: (a) H. E. Zimmerman, R. D. Rieke, and J. R. Scheffer, *ibid.*, **89**, 2033 (1967); (b) see also H. O. House and C. J. Blankley, *J. Org. Chem.*, **33**, 47 (1968).

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(9) G. L. Closs and R. A. Moss, *J. Am. Chem. Soc.*, 86, 4042 (1964).

(10) The material balances in this work were essentially unity (by the internal standard method).

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(12) The reductive cleavage of spiro[2.4]hepta-4,6-diene has been reported: K. Alder, H.-J. Ache, and F. H. Flock, *Chem. Ber.*, **93**, 1888 (1960). See also G. Schröder, *ibid.*, **97**, 3140 (1964), and W. Huckel, S. Gupte, and M. Wartini, *ibid.*, **99**, 1388 (1966), for related reductions.