

drous sodium iodide in 1,2-dimethoxyethane  $(DME)^4$  in the presence of cyclohexene, presumably because of complicating side reactions of the MeO<sub>2</sub>CCl<sub>2</sub><sup>-</sup> 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  $CF_3CCl$  also have been prepared (eq 3). Thermolysis

PhHgCl + Me<sub>3</sub>COK + CF<sub>3</sub>CXYH 
$$\xrightarrow{\text{THF}}_{-10 \text{ to } 0^{\circ}}$$
  
PhHgCXYCF<sub>3</sub> + Me<sub>3</sub>COH + KCl (3)  
X = Y = Cl, 75% yield, mp 146–148.5°  
X = Cl; Y = Br, 86% yield, mp 141–143°

of PhHgCCl<sub>2</sub>CF<sub>3</sub> 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-9trifluoromethylbicyclo[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 CCl<sub>2</sub> precursor,<sup>5</sup> the mercurial PhHgCClBrCF<sub>3</sub> 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  $(n^{25}D)$ 1.4371) was formed in 64% yield; the other isomer,  $n^{25}$ 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,  $n^{25}$ D 1.4571. Since the starting halocarbon used in the preparation of phenyl(1-bromo-1-chloro-2,2,2-trifluoroethyl)mercury, CF<sub>3</sub>CClBrH ("Fluothane," a product of the Ayerst Laboratories), was 99.9% pure by glpc (i.e., free of CF<sub>3</sub>CBr<sub>2</sub>H), the formation of the CF<sub>3</sub>CBr-cyclooctene adduct in 5% yield possibly represents a minor side reaction in which  $CF_3CBr$  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).

PhHgCClBrCF<sub>3</sub> + Et<sub>3</sub>SiH 
$$\xrightarrow{PhCl}_{reflux}$$
  
Et<sub>3</sub>SiCHClCF<sub>3</sub> + Et<sub>3</sub>SiCHBrCF<sub>3</sub> (4)  
(51%) (4%)

Sodium iodide in DME was found to displace the CF<sub>3</sub>-

CCl<sub>2</sub><sup>-</sup> anion from mercury. However, the anion decomposed with  $\beta$  elimination of fluoride ion, forming 1,1-dichloro-2,2-difluoroethylene, rather than via  $\alpha$  elimination of chloride ion to give  $CF_3CCl$  (eq 5), in agreement with the previous work by Hine.<sup>6</sup> This experiment thus

PhHgCCl<sub>2</sub>CF<sub>3</sub> + Na<sup>+</sup>I<sup>-</sup> 
$$\xrightarrow{\text{DME}}$$
 PhHgI + Na<sup>+</sup>CCl<sub>2</sub>CF<sub>3</sub><sup>-</sup> →  
NaF + CCl<sub>2</sub>=CF<sub>2</sub> (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,<sup>7,8</sup> 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.

Acknowledgments. The authors are grateful to the Air Force Office of Scientific Research ((SRC)-OAR) for generous support of this work through U.S. Air Force Grant No. AFOSR-68-1350 and to the Ayerst Laboratories, Inc., Rouses Point, N. Y., for a gift of 1,1,1-trifluoro-2-chloro-2-bromoethane.

(6) J. Hine, R. Wiesboeck, and O. B. Ramsay, ibid., 83, 1222 (1961).

(7) D. Seyferth and E. M. Hanson, ibid., 90, 2438 (1968).

(8) D. C. Mueller and D. Seyferth, ibid., in press.

(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,<sup>9</sup> Robert L. Lambert, Jr.<sup>10</sup> Department of Chemistry, Massachusetts Institute of Technology Cambridge, Massachusetts 02139 Received December 20, 1968

## Reaction of Xenon Difluoride with Benzene<sup>1</sup>

## 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<sup>2</sup> or cobaltic fluoride<sup>3</sup> yields only a mixture of nonaromatic fluorocarbons and tar. Ellis and Musgrave<sup>4</sup> have found that the primary process in the reaction of benzene and  $ClF_3C$  in  $CCl_4$  in the presence of  $CoF_2$  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.<sup>5</sup> CF<sub>3</sub>OF 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

(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,
- (4) J. F. Ellis and W. K. R. Musgrave, J. Chem. Soc., 3608 (1950).
  (5) J. F. Ellis and W. K. R. Musgrave, *ibid.*, 1036 (1953).
  (6) D. H. R. Barton, A. K. Ganguly, R. H. Hesse, S. N. Loo, and M. M. Bachet, Chem. Commun. 96 (1968).
- M. M. Pechet, Chem. Commun., 806 (1968).

<sup>(4)</sup> D. Seyferth, M. E. Gordon, J. Y.-P. Mui, and J. M. Burlitch, J. Am. Chem. Soc., 89, 959 (1967). (5) D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D.

Simmons, Jr., A. J.-H. Treiber, and S. R. Dowd, ibid., 87, 4259 (1965).

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<sub>4</sub> (14.737 g) was distilled over sodium sulfate *in vacuo* into a Kel-F tube containing  $7.23 \times 10^{-3}$ mol of XeF<sub>2</sub> whose ir spectrum indicated a trace of HF. Zone-refined benzene  $(2.66 \times 10^{-2} \text{ mol})$  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<sub>2</sub> dissolved. After 25 min the colorless solution turned yellow and then very dark green; the XeF<sub>2</sub> 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  $-78^{\circ}$  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<sub>4</sub>, 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  $72-73^{\circ}$ ,<sup>8</sup> 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  $4.1 \times 10^{-2}$  mol of benzene was allowed to react with  $1.26 \times 10^{-2}$  mol of XeF<sub>2</sub> 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<sub>4</sub>. Hydrogen fluoride ( $1.85 \times 10^{-3}$  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<sub>2</sub> was distilled from anhydrous NaF and then held in an evacuated system at  $-78^{\circ}$  for 12 hr. The residual pressure was  $4 \times 10^{-5}$  mm, and no HF bands were observed in the infrared spectrum. When  $1.429 \times 10^{-2}$  mol of this material was used for reaction with  $4.939 \times 10^{-2}$  mol of benzene in 16.403 g of CCl<sub>4</sub>, reaction had not commenced even after 2.5 hr (compare observations above). However, when  $1.428 \times$ 

(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°.

 $10^{-3}$  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.

$$\bigcirc$$
 + XeF<sub>2</sub>, HF  $\rightarrow$   $\bigcirc^+$  + XeF $\cdot$  + HF<sub>2</sub><sup>-</sup> (1)

$$\begin{array}{c} H \\ F \\ \hline \\ \end{array} + \chi_{eF} \rightarrow \begin{array}{c} F \\ F \\ \hline \\ \end{array} + \chi_{e} + HF \quad (3) \end{array}$$

$$\begin{array}{c} F \\ \hline \\ \end{array} + XeF_2, HF \rightarrow \begin{array}{c} F \\ \hline \\ \end{array} + \begin{array}{c} F \\ \\ \end{array} + HF_2^- + XeF (4) \end{array}$$

$$\underbrace{\stackrel{F}{\vdash}}_{+} + HF_2^- \rightarrow \underbrace{\stackrel{F}{\vdash}}_{H} + HF$$
(5)

$$F + XeF \rightarrow F + HF + Xe$$
(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 *orthopara* orientation by fluorine toward further electrophilic attack, which is, in fact, found.

ł

The above scheme essentially agrees with Bartlett's<sup>9,10</sup> observations of HF catalysis in the reactions of XeF<sub>2</sub> and his prediction that reaction may take place by ionization to XeF<sup>+</sup> or similar species followed by electron transfer to give XeF  $\cdot$  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

(9) N. Bartlett and F. O. Sladky, Chem. Commun., 1046 (1968).
(10) F. O. Sladky, P. A. Bulliner, and N. Bartlett, *ibid.*, 1048 (1968).

expected.<sup>11</sup> 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.

(11) J. R. Bolton and A. Carrington, Proc. Chem. Soc., 174 (1961).

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 Received November 27, 1968

## 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<sup>2</sup> (or phenyl)<sup>2c,d</sup> orbital. The question of the importance of electronic or "inductive"<sup>3</sup> (as opposed to steric) effects has received somewhat less attention.<sup>2d,4</sup> 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 radicalanion 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.<sup>5</sup>

We have employed methyl groups as probes of charge

(1) For leading references see (a) M. Yu Lukina, Russ. Chem. Rev., (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).

(3) The stability of carbanions is known to decrease in the order primary > secondary > tertiary: (a) J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1968, pp 142-146; however, the C-C bond dipole may be in the direction of the methyl group in "tetrahedral" carbanions; (b) G. S. Hammond in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, p 440; (c) N. C. Baird and M. A. Whitehead, *Theor. Chim.* Acta, 6, 167 (1966); (d) V. W. Laurie and J. S. Muenter, J. Am. Chem. Soc., 88, 2883 (1966).

(4) There is qualitative evidence which suggests that both steric and (b) There is quarket 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).
(5) H. M. Walborsky and J. B. Pierce, *ibid.*, 33, 4102 (1968); see also ref 2c and O. M. Nefedov, N. N. Novitskaya, and A. D. Petrov, Debl. (1964).

Dokl. Akad. Nauk SSSR, 152, 629 (1963), for related reactions.

distribution in the activated complexes of several simple conjugated cyclopropyl systems. The reductive cleavages of trans- and cis-1-methyl-2-phenylcyclopropanes<sup>6</sup> by lithium in liquid ammonia at  $ca. -33^\circ$  have been found to be highly regioselective<sup>7</sup> reactions.<sup>8</sup> The trans isomer **1b** is cleaved primarily via pathway b  $(k_{\rm b}/k_{\rm a} = 360 \pm 20)$ 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<sup>9</sup> was shown to have  $k_a/k_b = 2.3 \pm 0.1$ . In each case the products were analogous to 2 and 3.<sup>10</sup>

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  $\beta$ -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)<sup>5</sup> by the "inductive" effect of the methyl group and that a steric effect similar to that discussed for 1c is the dominant factor.

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<sup>11,12</sup> (5a) by sodium in liquid ammonia at  $ca. -33^{\circ}$ . This cleavage is instantaneous and exothermic; 1- and 2-n-propyl- and 1-

(6) J. P. Freeman, J. Org. Chem., 29, 1379 (1964).
(7) A. Hassner, *ibid.*, 33, 2684 (1968).
(8) The initial work on this problem was done by W. L. Maloy. Several compounds were prepared by A. Dorsky.

(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).

(11) This was prepared by an extension of the method of R. Ya. Levina, N. N. Mezentsova, and O. V. Lebedev, Zh. Obshch. Khim., 25, 1094 (1955). All new compounds have been fully characterized by spectral methods and gave satisfactory analyses. (12) The reductive cleavage of spiro[2.4]hepta-4,6-diene has been

(19) The function of the state of a photo-tribulation of the state of Huckel, S. Gupte, and M. Wartini, ibid., 99, 1388 (1966), for related reductions.