

to 3-cyanopropene. This was done by reducing the corresponding iodide (70 g., 0.164 mole) in 300 ml. of water with 350 g. of 2% sodium amalgam.²⁷ After several hours of agitation the solid disappeared. The aqueous layer was separated and treated with benzene for 24 hr. in a continuous liquid-liquid extractor. The benzene layer was dried and distilled through a 10-in. spiral wire column yielding 3.05 g. (24%) of 3-methoxybutyronitrile, b.p. 172°, n_D^{25} 1.4084 (reported,²⁸ b.p. 169–170°, n_D^{20} 1.4094). These physical constants do not distinguish it from 4-methoxybutyronitrile; reported,²⁹ b.p. 173°, n_D^{20} 1.4087. The n.m.r. spectrum was completely unambiguous, how-

ever, consisting of a doublet at τ , 8.74 ($\text{CH}_3\text{—}\overset{|}{\text{C}}\text{H—}$), a doublet at τ , 7.53 ($\text{—}\overset{|}{\text{C}}\text{H—CH}_2\text{—CN}$), an intense singlet at τ , 6.63 ($\text{CH}_3\text{—}\overset{|}{\text{O}}\text{—}$), and a low lying multiplet around τ , 6.5 ($\text{CH}_3\text{—}\overset{|}{\text{C}}\text{H—CH}_2\text{—}$). The relative intensities and the coupling constants were also appropriate to the suggested structure. The spectrum of 4-methoxybutyronitrile should include no doublets and two triplets in addi-

(27) L. Fieser, "Experiments in Organic Chemistry," D. C. Heath Co., Boston, Mass., 1955, p. 370.

(28) P. Bruylants, *Bull. soc. chim. Belges*, **31**, 175 (1922).

(29) A. Karvonen, *Ann. acad. sci. Fennicae*, **20**, No. 14 (1923).

tion to a low lying multiplet at the high field end of the spectrum.³⁰

2-Hydroxybutylmercuric iodide was prepared by the method of Hofmann and Sand³¹ and purified by crystallization from mixtures of toluene with low-boiling petroleum ether. It had m.p. 42°.

Anal. Calcd. for $\text{C}_4\text{H}_9\text{HgIO}$: C, 11.99; H, 2.26. Found: C, 12.11; H, 2.42.

2-Hydroxy-3-methoxypropylmercuric iodide was prepared by the method described for 1,2-dimethoxypropylmercuric iodide. It was a solid and was purified by crystallizing first from a mixture of ethyl acetate with petroleum ether and then twice from diethyl ether, m.p. 40–41°.

Anal. Calcd. for $\text{C}_4\text{H}_9\text{HgIO}_2$: C, 11.53; H, 2.18. Found: C, 11.04; H, 2.27.

3-Phenyl-2-methoxypropylmercuric iodide, m.p. 58° (reported,³² 58.6°) and 2-hydroxyethylmercuric iodide, m.p. 145° dec., (reported,²³ 147°) were previously known compounds.

(30) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, Chap. 6.

(31) K. A. Hofmann and J. Sand, *Ber.*, **33**, 1354 (1900).

(32) T. A. Geissman and R. M. Horowitz, *J. Am. Chem. Soc.*, **73**, 5759 (1951).

(33) K. A. Hofmann and J. Sand, *Ber.*, **33**, 1641 (1900).

The Application of Simple Equations for Calculating Bond Dissociation Energies to Thermal Degradation of Fluorocarbons

L. A. ERREDE

Contribution No. 232 from the Central Research Laboratories of the Minnesota Mining and Manufacturing Company, St. Paul 19, Minnesota

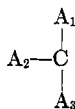
Received May 15, 1962

Bond dissociation energies of fluorocarbon compounds were calculated by means of simple equations that relate the strength of the bond in question with the molecular structure. The bond dissociation energies determined experimentally for relatively simple fluorocarbons agree within 2 kcal. with the corresponding calculated values. These equations can be used to explain the relative thermal stability of more complicated fluorocarbon compounds and to help anticipate the nature of the pyrolyzate produced assuming initial rupture to occur at the weakest bond. The pyrolysis of cyclobutanes are considered for the purpose of illustration. The thermal degradation of poly(tetrafluoroethylene) is also discussed and it is suggested that the "unzipping" process might occur *via* elimination of CF_2 fragments that subsequently couple to give C_2F_4 rather than *via* depolymerization of $\text{CF}_2\text{=CF}_2$ units directly.

Simple but reliable equations for calculating bond dissociation energies of hydrocarbon compounds were deduced empirically as described in preceding publications.^{1,2} The bond dissociation energy (D) is given in terms of the characteristic binding coefficients (ϵ) of the two groups comprising the bond in question. Thus for the bond $\text{R}_1\text{—R}_2$

$$D = 71\epsilon_1\epsilon_2 \quad (1)$$

It was also shown that the ϵ of the group



is given by

$$\epsilon = 0.43 + 0.162(\epsilon_1 + \epsilon_2 + \epsilon_3) \quad (2)$$

provided that the groups (or atoms) A_1 , A_2 , A_3 do not have a center of unsaturation α to one of the central carbon atoms. The ϵ_g of radicals such as $\cdot\text{CH}_2\text{C}_6\text{H}_5$, $\cdot\text{CH}(\text{C}_6\text{H}_5)_2$, and $\cdot\text{CH}_2\text{CH=CH}_2$ cannot be calculated by equation 2, but rather must be determined experimentally.^{1,2} Once the ϵ value is determined for one member of a homologous series such as $\text{CR}_1\text{R}_2\text{A}_1$ (or $\text{CR}_1\text{A}_1\text{A}_2$) where A is a group with a center of unsaturation α to the central carbon atom, the ϵ value for all other members of that series can be calculated by means of equation 2.

Only a relatively few key experimental bond dissociation energies of this sort are available from thermal degradation studies. However, the ap-

(1) L. A. Errede, *J. Phys. Chem.*, **64**, 1031 (1960).

(2) (a) L. A. Errede, *ibid.*, **65**, 2262 (1961); (b) equation 8 of this publication should read: $\log k_2/k_1 = 4.00(\epsilon_1 + \epsilon_2) - 2.85 - 6.44 \epsilon_g$.

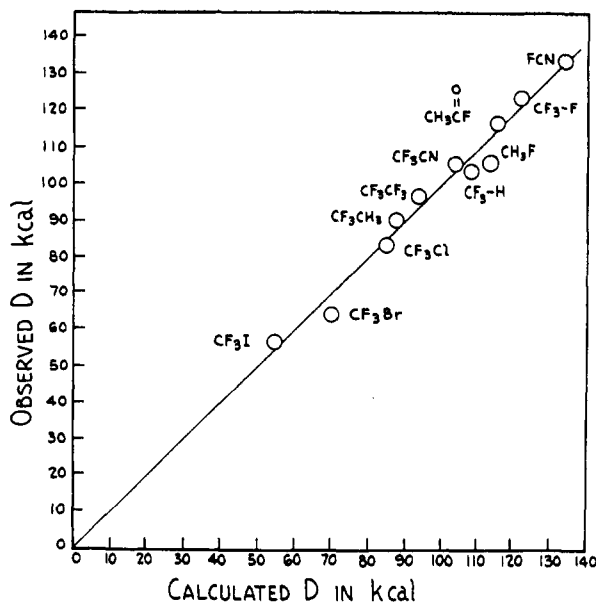


Fig. 1.—Comparison of calculated and observed bond dissociation energies for fluorocarbon compounds.

proximate bond dissociation energy of bonds such as $X-CR_2A$ where A is CO_2R , $-COR$, and $-CN$ can be calculated² by equation 3 using kinetic data obtained in studies involving addition of $CH_3\cdot$ to olefinic molecules.³

$$\epsilon_x = \frac{4.00(\epsilon_1 + \epsilon_2) - 2.85 - \log(k_2/k_1)}{6.44} \quad (3)$$

The term k_2/k_1 is Szwarc's methyl affinity value (k_2 is the rate constant for addition of a methyl radical to the olefin and k_1 is the rate constant for abstraction of a hydrogen atom from isoöctane), ϵ_1 and ϵ_2 are the ϵ values of the substituents (H or CH_3) attached to the carbon atom site where addition of the methyl radical to the olefin occurs.

The ϵ_x of a monovalent atom X , where X is H, F, Cl, Br, and I, is equal approximately to the square root of the atom's electronegativity (E) divided by its respective C—X bond length (r).

$$\epsilon_x = \sqrt{E}/r \quad (4)$$

Some ϵ values, determined from reported bond dissociation energy data⁴⁻⁷ of hydrocarbon compounds are given in Table I. Thus, the energy required to dissociate a given bond in a molecule can be calculated in terms of the molecular structure by means of equations 1 through 4. The calculated values agree within 2 kcal. with 80% of the cor-

(3) M. Szwarc and J. H. Binks, "Theoretical Organic Chemistry," The Kekule Meeting, London, 1958; Butterworth's Scientific Publications, London, 1959.

(4) M. Szwarc, *Chem. Rev.*, **47**, 75 (1950).

(5) A. H. Sehon and M. Szwarc, *Ann. Rev. Phys. Chem.*, **8**, 439 (1957).

(6) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd ed., Butterworth's Scientific Publications, London, 1958.

(7) N. N. Semenov, "Some Problems in Chemical Kinetics and Reactivity," Princeton University Press, Princeton, New Jersey (1958).

TABLE I

ϵ VALUES FOR CALCULATING BOND DISSOCIATION ENERGIES DEDUCED FROM EXPERIMENTAL DATA

Group	ϵ	Group	ϵ	Group	ϵ
H—	1.32	CH_3 —	1.08	CF_3 —	1.15
F—	1.49	CH_2CH_2 —	1.05	CCl_3 —	0.94
Cl—	1.04	$CH_3CH_2CH_2$ —	1.03	CBr_3 —	.85
Br—	0.86	$CH_3CH_2CH_2CH_2$ —	1.03	CH_2Cl —	1.04
I—	.68	$(CH_2)_2CH$ —	1.01	CH_2Br —	1.00
		$(CH_2)_2C$ —	0.95	$CHCl_2$ —	0.97
				$CHBr_2$ —	.92

Calculated ϵ -Values Using Equation 2

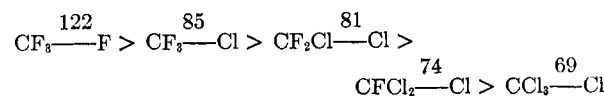
Group	ϵ	Group	ϵ
CF_3CF_2 —	1.10	CF_2H —	1.12
$CF_3CF_2CF_2$ —	1.09	CFH_2 —	1.10
$CF_3CF_2CF_2CF_2$ —	1.09	CF_2Cl —	1.10
$(CF_3)_3CCF_2$ —	1.07	$CFCl_2$ —	1.01
$(CF_2)_2CF$ —	1.04	CF_2Br —	1.05
$(CF_3)_2C$ —	0.99	$CFBr_2$ —	0.95

responding experimental data.¹ The calculated values agree within 8 kcal. with most of the other 20%. A few reported data deviate considerably (> 10 kcal.), but these data are questioned by the researchers themselves or by those who have compiled extensive reviews in this field.⁴⁻⁷

If applicable to fluorocarbon compounds, these equations could be particularly useful, since relatively few bond dissociation energies of this class of compounds have thus far been reported.⁴⁻⁷ It is necessary, however, to have some criteria for evaluating the validity of these equations when applied to fluorocarbon compounds. The extent to which the relatively few reported experimental values agree with the corresponding calculated data can be seen in Fig. 1. Although this agreement is good, the examples shown are those of relatively simple compounds and one still wonders whether or not the equations are valid for the more complicated structures.

It is possible to check this extrapolation in a qualitative way by comparing the results obtained in pyrolytic studies using fluorocarbon compounds with those anticipated on the basis of the calculated bond dissociation energies. The rate-determining step for homogeneous decomposition is rupture of the weakest bond in the molecule; hence, the relative thermal stability of molecules should parallel the corresponding order of calculated bond dissociation energies, if equations 1 and 2 are valid for the more complicated fluorocarbon structures.

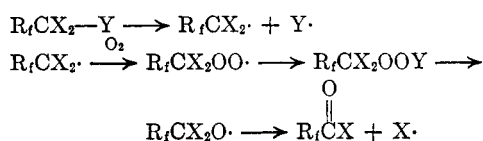
Trenwith and Watson⁸ studied the thermal decomposition of chlorofluoromethanes over aluminum oxide using a gas flow system. Their data show that the relative thermal stability of these compounds decreases in the order



(8) A. B. Trenwith and R. H. Watson, *J. Chem. Soc.*, 2368 (1957).

The calculated B.D.E., in kcal., for the weakest bond in chlorofluorocarbon molecules are shown directly above the bonds in question and the anticipated qualitative relationship of decreasing B.D.E. and decreasing thermal stability is readily noted.

Haszeldine,^{9,10} *et al.*, studied the oxidation of saturated fluorocarbons having the general formula $CF_3(CF_2)_nCX_2YZ$, where X, Y, and Z are H, F, Cl, Br, and I. They postulated that the reaction is initiated by rupture of the weakest bond in the molecule. Bond rupture was caused photochemically or thermally. They postulated further that rupture was followed by a series of reactions leading to the corresponding acyl halide essentially as indicated below:



Actually, the exact mechanism that ensues after initial bond rupture need not concern us here. The important point for this discussion is that the rate controlling step is rupture of the weakest bond in the molecule. Hence, the relative ease of oxidation for a series of compounds should again parallel the relative decreasing order of the corresponding calculated bond dissociation energies.

The relative ease of oxidation of fluorocarbon compounds studied semiquantitatively by Haszeldine is shown in Table II. The ease of oxidation increases as one goes from bottom to top and from left to right as indicated by the arrows. The calculated bond dissociation energy is given directly over the weakest bond in the molecule. It is noted that the ease of thermal oxidation increases directly

TABLE II
CORRELATION OF BOND DISSOCIATION ENERGY AND EASE OF OXIDATION

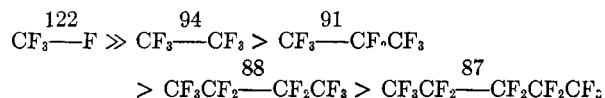
56	53	49
CF_3-I	$CF_3CF_2CF_2-I$	$CF_3CF_2CFCl-I$
64		
CF_2Br-Br		
67		
CF_2Cl-Br		
70	67	63
CF_3-Br	$CF_3CF_2CF_2-Br$	$CF_3CF_2CFCl-Br$
85	81	76
CF_3-Cl	$CF_3CF_2CF_2-Cl$	$CF_3CF_2CFCl-Cl$
108	103	
CF_3-H	$CF_3CF_2CF_2-H$	

The relative ease of oxidation reported qualitatively by Haszeldine^{9,10} increases in the direction of the arrows. The bond dissociation energy, calculated by means of equations 1 and 2, for the weakest bond in the molecule is shown directly above the bond in question. It is noted that the relative ease of oxidation, parallels the relative bond dissociation energy for the weakest bond in the molecule.

(9) W. C. Francis and R. N. Haszeldine, *J. Chem. Soc.*, 2151 (1955).
(10) R. N. Haszeldine and F. Nyman, *ibid.*, 387, 420 (1959).

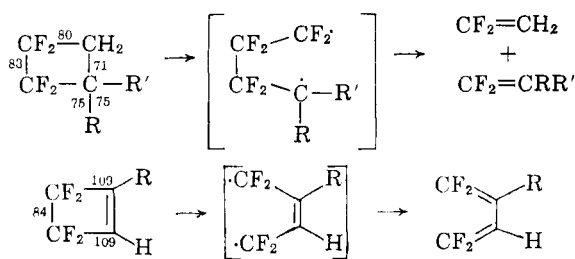
as the ease of thermal rupture of the molecule's weakest bond as calculated by means of equations 1 and 2.

Cady, *et al.*,^{11,12} studied the decomposition of linear saturated fluorocarbons in a closed system containing a platinum wire heated to about 1200°. They reported that the thermal stability decreases in the following order:



The B.D.E. calculated for the weakest bonds in the molecules are given in kcal; directly above the bond in question. Again it is noted that this order of thermal stability parallels the order of calculated bond dissociation energies for the weakest bonds.

On the basis of these results it is believed that equations 1 through 4 can be used with confidence for calculating the approximate bond dissociation energies in fluorocarbon molecules; hence one has a useful tool for predicting what the initial radical fragments will be when a fluorocarbon is subjected to thermal rupture in the absence of catalytic surfaces. If one understands the secondary reactions (and the complicating variables associated therewith) that follow the initial thermal bond rupture, one may guess the approximate composition of the final pyrolyzate. This is, the case, however, in only a few well known simple thermal reactions, as, for example, the pyrolysis of fluorocyclobutanes.¹³⁻²¹ In these reactions, initial C—C bond rupture occurs at the weakest bond in the molecule to afford a 1,4-diradical which as Criegee has shown²² undergoes scission at the 2,3-position thus yielding the corresponding unsaturated compounds as indicated below:



Numerous examples of this type are known and the products obtained appear to be consistent with this

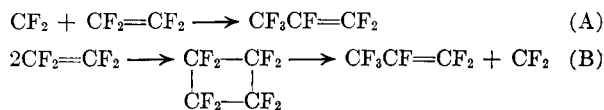
- (11) R. C. Steundenberg and G. H. Cady, *J. Am. Chem. Soc.*, **73**, 4165 (1952).
(12) G. C. Rogers and G. H. Cady, *ibid.*, **73**, 3523 (1951).
(13) D. D. Coffman and R. D. Cramer, U. S. Patent 2,461,523 (1949).
(14) A. N. Sachanen, U. S. Patent 2,582,283 (1952).
(15) B. Atkinson and V. A. Trenwith, *J. Chem. Soc.*, 2082 (1953).
(16) C. B. Miller and J. D. Chaffee, U. S. Patent 2,674,631 (1954).
(17) D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 1881 (1955).
(18) J. L. Anderson, U. S. Patents 2,733,089; 2,733,278; 2,743,303 (1956).
(19) W. T. Miller, U. S. Patent 2,733,277 (1956).
(20) B. Atkinson and V. A. Atkinson, *J. Chem. Soc.*, 2086 (1957).
(21) J. J. Drysdale, U. S. Patent 2,861,095 (1958).
(22) R. Criegee, *Ber.*, **68**, 665 (1935).

TABLE III
 PYROLYSIS OF FLUOROCARBONS^a

Fluorocarbon	Carrier gas	Starting material	Products isolated ^b					Total	Rel.
			C	CF ₃ X	CF ₃ CF ₂ X	CF ₃ CF ₂ -CF ₂ X	CF ₃ (CF ₂) _n X ₂		
CF ₃ CF ₃	Cl ₂	4		58				62	35
CF ₃ CF ₃	Br ₂	77		23				100	35
CF ₃ CF ₂ CF ₃	H ₂	49	7	15	8		2	81	36
CF ₃ CF ₂ CF ₂ CF ₂ CF ₃	Cl ₂	22		5	5	.. ^c	16 ^c	58	35

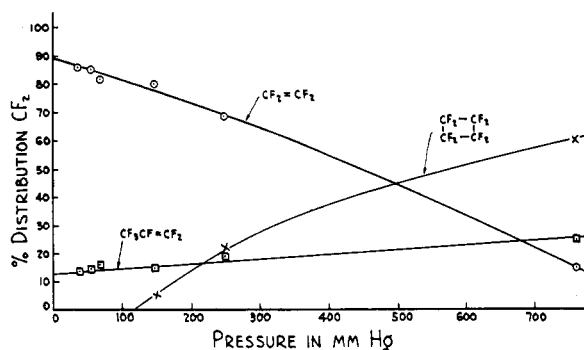
^a Simons, *et al.*,^{35,36} passed a stream of fluorocarbon and carrier gas mixture at atm. pressure through a quartz tube where pyrolysis occurred at 800–900° for an average residence time of six to thirty seconds. ^b Reported^{35,36} as percentage CF₂ isolated as the product indicated. ^c Product also contained unknown amount of CF₃CF₂CF₂Cl.

Lewis and Naylor³³ pyrolyzed tetrafluoroethylene in an evacuated continuous feed system in such a way that the decomposition products escaped quickly from the pyrolysis chamber and were collected down stream in a cold trap. These workers then correlated the composition of the pyrolyzate obtained at 600° as a function of the pressure. When their data are recalculated in terms of CF₂ distribution and then plotted as a function of pressure as shown in Fig. 3, it is noted that: (1) the percentage CF₂ isolated as CF₂=CF₂ decreases steadily with pressure, (2) the percentage CF₂ isolated as cyclic-C₄F₈ increases from 0% at about 100 mm. to 60% at about 760 mm., and finally (3) the percentage of CF₂ isolated as C₃F₆ only increases from about 10% at 0 mm. to about 25% at 760 mm. Atkinson³⁴ has shown kinetically that C₃F₆ is formed *via*: (A) a reaction of CF₂ with C₂F₄ or (B) thermal decomposition of cyclo-C₄F₈ produced *via* dimerization of two C₂F₄ units.



It is noted in Fig. 3 that C₃F₆ is isolated as a component of the pyrolyzate obtained below 100 mm. pressure even though cyclo-C₄F₈ is not. Hence, reaction scheme B can be eliminated entirely below 100 mm. It is conceivable, however, that the radical chain fragment might cleave at the γ -(C—C) bond to afford a 1–3 diradical which could rearrange to CF₃CF=CF₂. This probability, however, is very small. Hence, it appears that C₃F₆ may be formed *via* route A thus indicating the transient existence of CF₂ fragments.

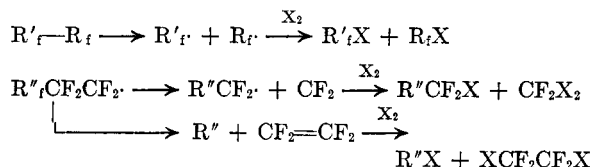
In another series of experiments Simons, *et al.*,^{35,36} studied the thermal decomposition at 800–900° of low molecular weight linear fluorocarbon in a gas flow system using hydrogen, chlorine, or bromine as the carrier gas. Under these conditions the free radical fragments produced by thermal rupture of a fluorocarbon C—C bond react immediately with the carrier gas to afford a more stable



DATA TAKEN FROM E. E. LEWIS U.S. PAT. 2,406,153; J. AM. CHEM. SOC. 69 1966 (1947)

Fig. 3.—Pyrolysis of poly-(tetrafluoroethylene) at 600°.

moiety thereby minimizing the “unzipping” reaction during the short residence time (6–30 sec.) in the pyrolysis zone.



Their results are summarized in Table III. The products isolated by them account for 60–100% of the CF₂ units metered to the pyrolysis system. It is noted that neither CF₂=CF₂ nor any end product that could be attributed to this compound, as a reactive intermediate was isolated, although a considerable amount of CF₂X₂ was isolated when the pyrolyzed linear fluorocarbon contained more than two carbon atoms. Simons, *et al.*,^{35,36} caution that CF₂X₂ could have formed as a result of RfCF₂—CF₂X bond rupture, and hence the isolation of CF₂X₂ does not of necessity prove unzipping *via* CF₂ elimination. The respective bond dissociation energies calculated by means of the equations given in the introduction indicate that the α -(C—C) bond is not particularly weak even when the terminal atom is Cl as indicated by the calculated bond dissociation energies shown below:



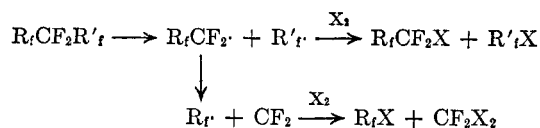
Hence, one would expect to obtain some Cl(CF₂)_n-Cl, when *n* is 2 or 3 *via* subsequent random C—C rupture of the monochlorofluorocarbon.

(33) E. E. Lewis and M. A. Naylor, *J. Am. Chem. Soc.*, **69**, 1968 (1947).

(34) B. Atkinson and V. A. Atkinson, *J. Chem. Soc.*, 2086 (1957).

(35) T. J. Brice, W. H. Pearlson, and J. H. Simons, *J. Am. Chem. Soc.*, **71**, 2499 (1949).

(36) W. R. James, W. H. Pearlson, and J. H. Simons, *ibid.*, **72**, 1761 (1950).



Since only CF_2X_2 and no other disubstituted fluorocarbon was obtained, it must be concluded that CF_2X_2 was formed most probably *via* CF_2 elimination from the fluorocarbon radical fragment followed by reaction with the carrier gas.

On the basis of these results it is believed that "unzipping" of a fluorocarbon chain may very probably occur *via* CF_2 elimination rather than *via*

$CF_2=CF_2$ elimination. The work of Simons, *et al.*, however, must be repeated using the improved methods of analysis such as gas chromatography and nuclear magnetic resonance before one can conclude with considerable certainty that this is indeed the true mode of decomposition.

It is intended that the decomposition of very thin films of polytetrafluoroethylene in an evacuated system be re-examined in such a way that the primary reactive fragments pass directly to a mass spectrometer or are quenched on the walls of the apparatus before secondary reactions can occur to give the usual stable end products.

Ring Size Effects in the Neophyl Rearrangement. III.¹ The Acetolysis of 1-Phenylcyclopropylcarbinyl Arenesulfonates^{2,3}

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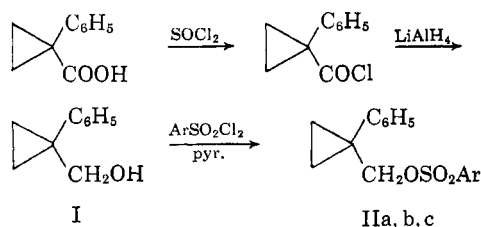
1-Phenylcyclopropylcarbinol (I) and its benzene-, *p*-bromobenzene-, and *p*-toluenesulfonate derivatives (II) were prepared. The acetolysis of these sulfonates showed first-order kinetics, with rate constants only slightly larger than that reported for cyclopropylcarbinyl benzenesulfonate itself. The sulfonates showed greatly different activation parameters, reflecting the difference in leaving groups. When the acetolysis of the *p*-toluenesulfonate ester was performed in the presence of sodium acetate, 1-phenylcyclobutyl acetate (IV) was the only product (100%). The slight relative rate acceleration found with these arenesulfonates is discussed in terms of possible ground state energy differences, while the formation of but one product, with little or no internal return, is interpreted in terms of a localized, more classical ion in these cases. Transformations within the 1-phenylcyclobutyl system are also reported.

Our interest in ring size effects in the neophyl rearrangements⁴ led to the study of the acetolysis of the neophyl-like 1-phenylcycloalkylcarbinyl arenesulfonates. The cyclopropyl member of this series of compounds⁵ showed such different behavior from the others that we thought it sensible to communicate the results on it separately.

That cyclopropylcarbinyl compounds are endowed with special reactivity in carbonium ion processes is beyond doubt. But just why and in what way this special reactivity occurs is still being discussed, notwithstanding the intensive and revealing work of Roberts and his group.⁶

While we do not wish to enter the arena with new mechanistic proposals, we do wish to note the consequences of a phenyl substituent at the 1-ring position in this system and to suggest how these consequences might be accommodated by present theory.⁷

1-Phenylcyclopropylcarbinol (I, m.p. 32.5–33°) was obtained in high yield from the corresponding acid chloride by reduction with lithium aluminum hydride. The arenesulfonate derivatives (II) were



prepared through reaction of the alcohol I with the appropriate arenesulfonyl chloride in pyridine. The benzenesulfonate (IIa, Ar = C_6H_5- , dec. 48°, 89%) and *p*-bromobenzenesulfonate (IIb, Ar = *p*- BrC_6H_4- , dec. 35°, 46%) were white crystal-

(1) Paper II, J. W. Wilt and C. A. Schneider, *J. Org. Chem.*, **26**, 4196 (1961).

(2) Taken from the Ph.D. dissertation of D. D. R., Loyola University, February, 1962. Some of this material was presented at the 140th National Meeting of the American Chemical Society, Chicago, Illinois, September 3–8, 1961, p. 10Q of the abstracts.

(3) Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(4) J. W. Wilt and Bro. H. Philip, F.S.C., *J. Org. Chem.*, **24**, 441 (1959), **25**, 891 (1960), and ref. 1 deal with ring size effects in the radical neophyl rearrangement. A study of such effects in the carbene neophyl rearrangement has been completed and will be reported soon (J. Kosturik).

(5) For the 1-phenylcyclobutyl- through 1-phenylcycloheptyl-carbinyl systems, see J. W. Wilt and D. D. Roberts, *ibid.*, **27**, 3434 (1962).

(6) For a recent study, one of many from that laboratory, see M. S. Silver, M. C. Caserio, H. E. Rice, and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 3671 (1961).

(7) R. A. Snee, K. M. Lewandowski, I. A. I. Taha, and B. R. Smith, *ibid.*, **83**, 4843 (1961), have reported the kinetic consequences of a phenyl group (*cis* and *trans*) at the 2-ring position of this system, using β -naphthalenesulfonates and trifluoroacetates.