TABLE I

PENICILLIN SULFOXIDES

Sulfoxide	Formula	Yield, %	M.p., °C. dec.	Isolation method	Calcd.		Found	
					% C	% H	% C	% H
Phenoxymethylpenicillin	$C_{16}H_{18}N_2O_6S$	76	178–180[a]	a	52.45	4.95	52.66	5.18
(5-Methyl-3-phenyl-4-isoxazolyl)-penicillin (sodium salt hemihydrate)	$(C_{19}H_{18}NaN_3O_6S)_2 \cdot H_2O$	36	165–167	b	50.89	4.27	51.03	4.59
D-(−)-α-N-Carbobenzyloxyaminobenzylpenicillin hemihydrate	$(C_{24}H_{25}N_3O_7S)_2 \cdot H_2O$	52	133–135	a	56.70	5.16	56.25	5.32
D-(−)-α-Aminobenzylpenicillin dihydrate	$C_{16}H_{19}N_3O_5S \cdot 2H_2O$	25	210–212	c	47.88	5.78	48.15	5.78
6-Phthalimidopenicillanic acid hemihydrate	$(C_{16}H_{14}N_2O_6S)_2 \cdot H_2O$	35	160–162	a	51.75	4.07	51.37	4.22
6-Aminopenicillanic acid sesquihydrate	$(C_8H_{12}N_2O_4S)_2 \cdot 3H_2O$	8	248–250	c	37.06	5.83	37.10	5.57
6-N-Carbobenzyloxyaminopenicillanic acid (potassium salt monohydrate)	$C_{16}H_{17}KN_2O_6S \cdot H_2O$	46	138.5–140	b	45.48	4.53	45.70	4.28
6-Triphenylmethylaminopenicillanic acid (potassium salt hemihydrate)	$(C_{27}H_{25}KN_2O_4S)_2 \cdot H_2O$	88	213–215	b	62.16	5.03	62.29	5.06

[a] Lit.[1] m.p. 167–168° dec.; for the hemihydrate, lit.[2] m.p. 159° dec.

vibration occurred at 1020–1035 cm.$^{-1}$, and the characteristic displacement of the β-lactam carbonyl absorption band to shorter wave length[1,2] was also observed. In the sulfoxides reported here, this displacement varied from 10 to 30 cm.$^{-1}$ relative to the corresponding band in the unoxidized precursors.

Experimental Section[4]

The data on the sulfoxides prepared in this work are recorded in Table I.

General Procedure for the Preparation of Penicillin Sulfoxides.—A solution of the penicillin salt or free acid (0.10 mole) in the minimum volume of water at pH 7.5–8.0 was added to a solution of 23.5 g. (0.11 mole) of sodium metaperiodate in 750 ml. of water. The pH of the mixture was adjusted to 6.5–7.0 and maintained at this value while the solution was stirred at room temperature for 2.5 hr. The pH was then lowered to 2–2.5 by addition of 40% phosphoric acid and the product was isolated in one of the following three ways. (a) The precipitated sulfoxide was collected, thoroughly washed with cold water, dried by suction, and recrystallized from an acetone–water mixture. (b) The gummy solid which separated was extracted into ethyl acetate, and the washed and dried extract was treated with 1 molar equiv. of a 50% solution of either potassium or sodium 2-ethylhexanoate in 1-butanol. The alkali metal salt thus obtained was collected and was recrystallized from a 1-butanol–water mixture. (c) The acidic aqueous solution was extracted with a solution of 600 ml. of methyl isobutyl ketone containing 33.3 g. (0.075 mole) of dioctyl sodium sulfosuccinate (Aerosol OT). The organic phase was dried briefly over magnesium sulfate and then was treated dropwise with triethylamine to pH 5.0. The amorphous product which precipitated was collected and dried *in vacuo*.

D-(−)-α-Aminobenzylpenicillin Sulfoxide.—D-(−)-α-N-Carbobenzyloxyaminobenzylpenicillin sulfoxide (2 g.) was dissolved in 100 ml. of 1% sodium bicarbonate solution. This solution was shaken in an atmosphere of hydrogen under an initial pressure of 45 p.s.i.g. for 2 hr. in the presence of 2 g. of 30% palladium on diatomaceous earth catalyst. The mixture was acidified to pH 2 with 6 *N* hydrochloric acid and filtered through diatomaceous earth (Dicalite). The pH of the filtrate was adjusted to 4.65, and the clear solution was concentrated under reduced pressure at 33° to a volume of 20 ml. On cooling, the sulfoxide of D-(−)-α-aminobenzylpenicillin separated and was collected and dried *in vacuo* over phosphorus pentoxide. The infrared and n.m.r. spectra of this product were identical with those obtained from the sample formed by direct oxidation of D-(−)-α-aminobenzylpenicillin.

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[4] Melting points were determined either on a Kofler hot stage, a Fisher-Johns apparatus, or in open capillaries, and are all corrected. We thank Mr. R. M. Downing and Mrs. C. Kalinowski for the microanalyses, and Messrs. D. Whitehead and A. Vulcano for infrared and n.m.r. spectral measurements.

1,2-Diphenyl-3-nitrocyclopropene or 2,3-Diphenyl-2-cyclopropenyl Nitrite[1]

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In our endeavors to synthesize potential diazocyclopropene precursors, we had occasion to attempt to nitrosate N,N-dimethyl-N′-(2,3-diphenyl-2-cyclopropenyl)urea (I). The successful method employing a modification of the technique developed by White[3] and his group in which the urea was treated with dinitrogen tetroxide at low temperature (−55°) has already been reported.[4]

However, in the earlier stages of this research, we attempted to nitrosate this material in another method developed by White[3] which employs sodium nitrite in a mixture of acetic acid and acetic anhydride. Under these conditions and using a rather large excess of the sodium nitrite, a new white compound was formed in 67% yield which gave the correct analysis for a nitro or a nitrite derivative of 1,2-diphenylcyclopropene. Since the nitro derivative would be quite interesting for a variety of reasons including its potential as a cyclopropenyl carbanion precursor, its an-

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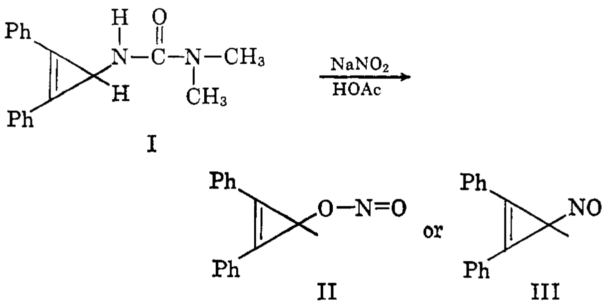
[1] Taken from a thesis submitted by John W. Kobzina in partial fulfillment of the requirements for the degree of Master of Science at the University of Florida.

[2] Alfred P. Sloan Fellow.

[3] *Cf.* E. H. White, *J. Am. Chem. Soc.*, **77**, 6008 (1955). For more recent developments in nitrosation procedures, see E. H. White and F. W. Bachelor, *Tetrahedron Letters*, 77 (1965), and references cited therein.

[4] W. M. Jones and J. M. Denham, *J. Am. Chem. Soc.*, **86**, 944 (1964).



I

II III

ticipated tendency to exist in the *aci* form, and its potential as a Michael condensation addend, we undertook to elucidate the structure of this new material. The purpose of this note is to report both the data that we have collected that relates to the structure of this compound and more convenient synthetic methods for its preparation (see Experimental Section).

As pointed out above, the unknown gave an elemental analysis in agreement with a 1,2-diphenylcyclopropene substituted with a nitro or a nitrite group. Furthermore, the mass spectrum showed that it was not a dimer (see below). The ultraviolet spectrum showed maxima (acetonitrile) at 310 mμ (ε 19,890), 295 (31,000), 282 (25,400), 227 (19,000), and 218 (21,200) which left little doubt about the diphenylcyclopropene ring having remained intact.[5] This was further confirmed by the ultraviolet spectrum in acetonitrile in the presence of fluoroboric acid which showed the typical spectrum of the 1,2-diphenylcyclopropenyl cation,[5b,6a] with maxima at 302 mμ (ε 34,600), 292 (32,600) and 245 (11,100). There was, therefore, little doubt but that the compound had either structure II or III.

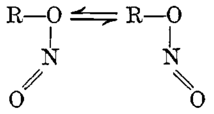
However, to distinguish conclusively between these two structures has not proved a simple task. In the first place, we did not feel that the classical tests to distinguish between nitroalkanes and nitrites would be of very much use since the inordinate stability of the cyclopropenyl cation[6b] could quite conceivably promote ionization of the NO_2^- from the nitro compound and this, in turn, would obviate the usefulness of the normal tests for alkyl nitrites.[7] Chemically, the compound did behave like a nitrite (see below).

Examination of the spectra of this material proved interesting although somewhat frustrating.

The infrared spectrum showed two very strong absorptions at 1545 and 1360 cm.$^{-1}$. These peaks are typical of nitro compounds.[8] The infrared was devoid of absorption between 1680 and 1610 cm.$^{-1}$, the area in which a nitrite is supposed to show a doublet.[8] Thus, the infrared suggests the nitrocyclopropene structure.

Examination of the 360–400-mμ region of the ultraviolet spectrum also suggested the nitrocyclopropene structure. Thus, whereas nitroalkanes are normally devoid of absorption in this region, alkyl nitrites have been found to show low-intensity absorption ($n \rightarrow \pi^*$, ε 100) in this region.[9] In the compound under question, there was virtually no absorption in this region. At 370 mμ, the extinction coefficient of an obvious tail to the diphenylcyclopropene absorption was less than 10. Thus, this region of the ultraviolet also suggests the nitrocyclopropene structure.

The n.m.r. spectrum also supported the nitrocyclopropene structure. Aside from the typical phenyl resonances, the n.m.r. spectrum showed a single peak at τ 4.72. With the exception of primary aliphatic nitrites (α-hydrogen, τ 5.22[10,11]), the α-hydrogen of alkyl nitrites generally appears well below τ 4.72. For example, the α-hydrogen of isopropyl nitrite[10] appears at τ 4.54, and that of benzyl nitrite[12] at τ 4.50. Furthermore, from data on other cyclopropenes, the diphenylcyclopropene ring generally causes an appreciable downfield shift of the methylene hydrogen.[13] The α-hydrogen of the cyclopropenyl nitrite would therefore be predicted to appear well below the observed τ 4.72. On the other hand, the α-hydrogen of nitroalkanes generally appears well above τ 4.72. For example, the α-hydrogen resonance of 2-nitropropane has been reported at τ 5.33[14] (and 5.48[15]), and that of 3-nitropropene at τ 5.13.[16] A further downfield shift by the diphenylcyclopropene ring could well lead to the observed τ 4.72. Furthermore, it is well known[12] that the spectrum of the hydrogen α to a nitrite is temperature dependent. This results from retardation of the *cis–trans* interconversion of the two isomeric nitrite structures IV and V. The temperature dependence of the n.m.r. spectrum of the unknown was therefore investigated. There was no detectable splitting of the τ 4.72 peak (in acetone) at temperatures as low as −90°. Nitrites usually show broadening around −50° and splitting is complete at −90°. Thus, again, the evidence suggests the nitrocyclopropene structure.



IV V

However, on the other side of the argument, the mass spectrum supports the nitrite structure. The peaks of primary interest were those that appeared at mass 237 (parent peak, very small[17]), 207 (corresponding to

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[5] *E.g.*, see (a) R. Breslow, R. Winter, and M. Battiste, *J. Org. Chem.*, **24**, 415 (1959); (b) R. Breslow, J. Lockhart, and H. W. Chang, *J. Am. Chem. Soc.*, **83**, 2375 (1961).

[6] (a) D. G. Farnum and M. Burr, *ibid.*, **82**, 2651 (1960). (b) J. D. Roberts, A. Streitwieser, and C. M. Regan, *ibid.*, **74**, 4579 (1952); R. Breslow, *ibid.*, **79**, 5318 (1957).

[7] *Cf.* N. D. Cheronis and J. B. Entrikin, "Identification of Organic Compounds," Interscience Publishers, Inc., New York, N. Y., 1963, p. 143; F. Feigl, "Spot Tests in Organic Analysis," Elsevier Publishing Co., New York, N. Y., 1960, p. 178; N. D. Cheronis and T. S. Ma, "Organic Functional Group Analysis," Interscience Publishers, Inc., New York, N. Y., 1964, p. 181.

[8] C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press Inc., New York, N. Y., 1963, pp. 271–274.

[9] A. Altshuller, I. Cohen, and C. M. Schwab, *J. Phys. Chem.*, **62**, 621 (1958); J. W. Sidman, *Chem. Rev.*, **58**, 689 (1958).

[10] R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1962; W. D. Phillips, C. E. Looney, and C. P. Spaeth, *J. Mol. Spectry.*, **1**, 35 (1957).

[11] "Varian High Resolution Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962, Spectrum No. 374.

[12] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., 1959, New York, N. Y., pp. 371–374.

[13] Unpublished results from these laboratories.

[14] Reference 12, Spectrum No. 41.

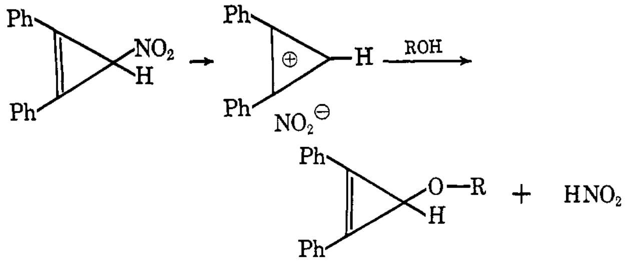
[15] R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1900, p. 84.

[16] Y. V. Baskov, T. Urganski, M. Witanowski, and L. Stefaniak, *Tetrahedron*, **20**, 1519 (1964).

[17] Reference 15, p. 16.

loss of NO from the molecule), 191 (base peak corresponding to the diphenylcyclopropenyl cation), 46 (NO_2 ion), and 30 (NO ion). It has been reported that the ratio of the mass 30 to 46 peaks is diagnostic of alkyl nitrites and nitro compounds. Thus, it has been found that for a set of four nitro compounds[18] this ratio averaged 8.1 (ranging from 4.4 to 27), whereas the same ratio for the corresponding nitrites[19] averaged 148 (ranging from 70 to 250). In our compound, this ratio was found to be 104, thus supporting the nitrite structure. The peak at mass 207 (1.32 times as intense as the mass 30 peak) is also suggestive of the nitrite structure since it is hard to visualize a simple way the nitro compound could lose a mass 30 fragment. However, examination of the literature showed that other nitroalkanes[18] do show this same behavior (usually to a lesser extent), and so this evidence cannot be taken as definitive.

A variety of efforts was made to gain insight into the structure of the unknown by chemical means. Basically, the classical tests[7] to distinguish between nitroalkanes and alkyl nitrites depend on preferential nitrosating ability of the alkyl nitrite. The ability of the unknown to act as a nitrosating agent was clearly demonstrated simply by dissolving it in alcohol. Thus, in methanol, within 35 min. it had completely lost its nitrogen function. Furthermore, when this same reaction was run in isoamyl alcohol, it was found that the product, in addition to cyclopropenyl ethers, was isoamyl nitrite. This facile ester exchange could ordinarily be interpreted as very strong evidence for the nitrite structure.[20] However, it must be recognized that rapid ionization of a nitrocyclopropene followed by ether formation would give rise to a mole of nitrous acid which could also effect the formation of the isoamyl nitrite. In fact, the ease of ionization of the nitrogen-containing group in the unknown was rather dramatically demonstrated by our finding that addition of 1 drop of 50% fluoroboric acid to a sample of the unknown in acetonitrile in a 1-cm. ultraviolet cell caused complete ionization and conversion to the diphenylcyclopropenyl cation in less than 15 sec.



In attempts to obviate the problem of ionization, attempts were made to reduce either the nitrogen function or the cyclopropene double bond. All attempts failed. Invariably, the odor of ammonia was detected and the products contained no nitrogen. The only characterized product was 1,2-diphenylpropane. This behavior is again suggestive of a nitrite structure but, again, is not conclusive. Attempts to use the unknown as an active hydrogen compound in a Michael condensation also failed; the attempts led only to tars and nitrogen-free products.

Finally, it should be pointed out that the method of synthesis also points to the nitrite structure. Thus, it is well known[21] that nucleophilic substitutions involving NO_2^- as the attacking group give varying mixtures of nitro and nitrite products depending on whether the reaction goes by an SN1 or SN2 mechanism, the SN1 favoring the nitrite, and, certainly, reaction of 1,2-diphenylcyclopropenyl perchlorate with nitrite must be classified as an SN1 process.

Thus, in summary, there is still not conclusive evidence to distinguish between these two possible structures, and whatever the structure, certain of its properties must be considered anomalous.

The infrared, ultraviolet, and n.m.r. spectra strongly support the nitro structure, whereas the mass spectrum and the chemical reactions support the nitrite. However, it must be remembered that the mass spectral conclusions are based on very meager data and the chemical data can also be explained in terms of an easily ionized nitro compound.

Experimental Section

Experimental analyses were performed by the Galbraith Analytical Laboratories, Knoxville, Tenn. Infrared spectra were recorded on a Beckman IR10 infrared spectrophotometer. Ultraviolet spectra were recorded on a Cary 14 recording spectrophotometer. N.m.r. spectra were run in deuteriochloroform and acetone (for the low-temperature work) with tetramethylsilane as internal reference, using a Varian DP-60 instrument. The mass spectrum was determined on a Bendix Model 14 Time-of-Flight mass spectrometer.

1,2-Diphenyl-3-nitrocyclopropene or 2,3-Diphenyl-2-cyclopropenyl Nitrite.—1,2-Diphenylcyclopropenyl perchlorate was prepared by the method of Farnum.[6] To 15 ml. of 70% perchloric acid cooled in an ice bath was slowly added 125 ml. of acetic anhydride. To this cold mixture was then added 11.3 g. of 1,2-diphenylcyclopropene-3-carboxylic acid which had been prepared by the method of Breslow, Winter, and Battiste.[5] The mixture was stirred in the ice bath for 90 min. at which time the cyclopropenyl perchlorate was precipitated from solution with ether. Filtration gave 8.45 g. (75%) of crude perchlorate salt. This crude material was then dissolved in a cold (ice bath) mixture of 45 ml. of acetic anhydride and 150 ml. of acetic acid. To the vigorously stirred mixture was then added 2.48 g. (1 equiv.) of sodium nitrite. After stirring in the ice bath for 1 hr., a second equivalent of sodium nitrite was added. The mixture was stirred for 1 hr. more at which time ice–water was added to precipitate the product. Filtration gave a quantitative yield of nearly colorless product, m.p. 114–115° dec. One crystallization from chloroform–petroleum ether (b.p. 20–40°) gave pure product, m.p. 119° dec.

Anal. Calcd. for $C_{15}H_{11}NO_2$: C, 75.94; H, 4.67; N, 5.90. Found: C, 75.87; H, 4.87; N, 5.73.

The same material was formed in 67% yield and quantitatively by treating N,N-dimethyl-N′-(2,3-diphenyl-2-cyclopropenyl)-urea and bis(2,3-diphenyl-2-cyclopropenyl) ether with sodium nitrite in acetic acid–acetic anhydride under essentially the same conditions as are given above. It was also formed in 45% yield by treating the perchlorate with sodium nitrite in dimethylformamide at 0°.

Reduction of the Unknown.—A sample of the unknown was treated with hydrogen at 20° and atmospheric pressure in ethyl acetate using 100 mg. of palladium black as the catalyst. After 5 hr. of reaction, there had been an uptake of 313 cc. of hydrogen. The reaction mixture had a strong odor of ammonia. The product of the reaction, after distillation onto a cold finger at 10 mm. in a bath at 100°, was a clear liquid which showed the same refractive index (1.5563) and infrared spectrum as authentic diphenylpropane.[22] Interruption of the reduction before com-

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[18] J. Collin, *Bull. Soc. Roy. Sci. Liege*, **23**, 194 (1954).

[19] L. D'Or and J. Collin, *ibid.*, **22**, 285 (1953).

[20] P. Tarte, *J. Chem. Phys.*, **23**, 979 (1955).

[21] *Cf.* E. S. Gould, Mechanism and Structure in Organic Chemistry, Holt, Rinehart, and Winston, Inc., New York, N. Y., 1959, p. 297.

[22] *Proc. Acad. Sci. USSR, Chem. Sect.*, **130**, 322 (1960); National Advisory Committee Aeronautics, Technical Note No. 2557, 1951.

plete reaction showed only the diphenylpropane and starting material.

Reaction of the Unknown with Alcohols.—A solution of 23.9 mg. of the unknown in 2.0 ml. of absolute, reagent grade methanol was maintained at room temperature, and the reaction was monitored by thin layer chromatography using silica gel plates. The plates were developed with 50:50 ether–petroleum ether. The first sample was taken after 1 min. Appreciable bis(2,3-diphenylcyclopropenyl) ether had already formed at that time. After 35 min. there was no detectable trace of the starting material left. The thin layer showed only one spot corresponding to the bis ether. The identity of the product was confirmed by removing the solvent and comparing the residue with the known material.

When the unknown was dissolved in isoamyl alcohol instead of methanol, it was possible to follow production of the other anticipated reaction product, the alkyl nitrite. Isoamyl nitrite was indeed observed by g.l.p.c. and, although the yield was not determined precisely, it appeared to be nearly quantitative.

Acknowledgment.—J. W. K. wishes to thank the Ford Foundation for financial support during a portion of the time when this research was underway. The authors wish also to thank Dr. W. S. Brey, Jr., for conducting the n.m.r. investigations.

Preparation of 1,1-Dihalo-2-methylpropenes

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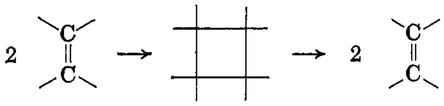
The high reactivity of many olefinic compounds somewhat restricts potential reactions at their functional groups. If such reactions have to be carried out, it is necessary to eliminate the olefinic double bond temporarily. A convenient route for this purpose is reported in this note.

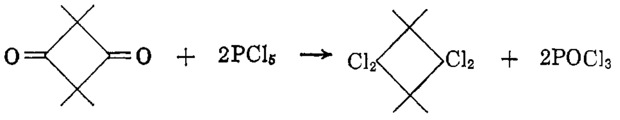
It is well known that under proper conditions many ethylene derivatives can be dimerized, forming cyclobutane derivatives.[2–3] At higher temperatures this reaction can be reversed.[4–7]



Reactions at the functional groups can be carried out with the cyclobutane derivatives and following this the reaction product may be cleaved.

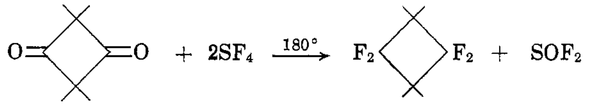
This route is especially suited for ethylenes which form symmetrical cyclobutanes by head-to-tail dimerization. The feasibility of this route has been shown by the conversion of dimethylketene into dimethyldihaloethylene.

Dimethylketene can be easily dimerized to 1,1,3,3-tetramethylcyclobutanedione (I).[8] The reaction of the dione I with phosphorus pentachloride in refluxing carbon tetrachloride forms 1,1,3,3-tetrachloro-2,2,4,4-tetramethylcyclobutane (II) in almost quantitative yield.



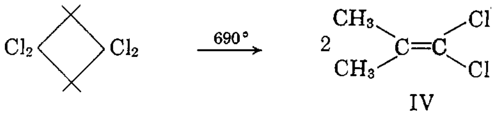
I II

More vigorous conditions have to be applied for the preparation of 1,1,3,3-tetrafluoro-2,2,4,4-tetramethylcyclobutane (III). I has to be heated with a twofold excess of sulfur tetrafluoride in the presence of hydrogen fluoride at 160° for 60 hr. None of III is isolated if the reaction is carried out without catalyst.[9]



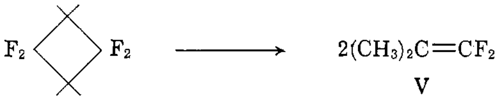
I III

The pyrolysis of II is carried out at 690° (wall temperature) and 0.1–0.5 mm. The formation of side products is reduced if the pyrolysis is run in an unpacked tube. The yield of IV is 34% at a conversion of 39%.



II IV

1,1-Difluoro-2-methylpropene (V) is isolated in 23% yield at a conversion of 33%.



III V

Experimental Section

Preparation of 1,1,3,3-Tetrachloro-2,2,4,4-tetramethylcyclobutane (II).—A mixture of 200 g. of tetramethylcyclobutanedione, 1000 g. of phosphorus pentachloride, and 2 l. of carbon tetrachloride was heated at reflux temperature for 3 hr. Carbon tetrachloride and most of the phosphorus oxychloride were distilled off. The remaining liquid was poured with stirring over crushed ice. The solid was isolated by filtration and recrystallized from a mixture of ethanol and water: yield 317 g., 89%, m.p. 234–236°.

Anal. Calcd. for $C_8H_{12}Cl_4$: C, 38.40; H, 4.80; Cl, 56.80. Found: C, 38.4; H, 4.5; Cl, 56.6.

The infrared spectrum showed major bands at 955 (breathing vibration, cyclobutane ring), 1370, and 1385 (*gem*-dimethyl) cm.$^{-1}$, besides 840, 880, 1205, and 1450 cm.$^{-1}$. The n.m.r. spectrum has a singlet at 92 c.p.s. with carbon tetrachloride as solvent and tetramethylsilane as the internal standard using a Varian A-60 n.m.r. spectrometer.

Pyrolysis of 1,1,3,3-Tetrachloro-2,2,4,4-tetramethylcyclobutane (II).—During a 2-hr. period 40 g. of II was passed through a 30-cm. long tube, which was heated at 700° at 0.1–0.5 mm. The vapors were condensed in a Dry Ice–acetone trap. Fractionation yielded 13.7 g. (34%) of dichloromethylpropene (IV), b.p. 108–110°,[10] and 24.2 g. of starting material.

The n.m.r. spectrum showed a singlet at 113 c.p.s. below TMS

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[1] Farbenfabriken Bayer A.-G., Werk Uerdingen, Wissenschaftliches Hauptlaboratorium, Krefeld, Germany.

[2] A. L. Henne and R. P. Ruth, *J. Am. Chem. Soc.*, **69**, 279 (1947).

[3] M. Prober and W. T. Miller, *ibid.*, **71**, 598 (1949).

[4] J. N. Butler and R. B. Ogawa, *ibid.*, **85**, 3346 (1963).

[5] R. W. Vreeland and D. F. Swinehart, *ibid.*, **85**, 3349 (1963).

[6] B. F. Gray and H. O. Pritchard, *J. Chem. Soc.*, 1002 (1956).

[7] J. L. Anderson, U. S. Patent 2,733,278 (1956).

[8] H. Staudinger and E. Suter, *Ber.*, **53**, 1085 (1920).

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[10] J. Faworski, *Chem. Zentr.*, 606 (1899).