[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY]

Methylene Derivatives as Intermediates in Polar Reactions. IX. The Concerted Mechanism for α-Eliminations of Haloforms[1]

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The kinetics of the alkaline hydrolysis of bromodifluoromethane and chlorodifluoromethane have been studied in aqueous solution at 0° and 20 or 25°. The reactivities are much greater than would be expected for the S_N2 mechanism. For this reason and the fact that the S_N2 mechanism has already been disproved for the basic methanolysis of chlorodifluoromethane, it is believed that the hydrolysis of these two haloforms, like that of others studied previously, involves the formation of an intermediate dihalomethylene. However, the two haloforms now studied hydrolyze faster than they would be expected (from extrapolation of data on other haloforms) to form carbanions. For this reason and the facts that α-fluorine (compared to other halogens) appears to stabilize dihalomethylenes and to destabilize trihalomethyl anions, the basic hydrolysis of bromodifluoromethane and chlorodifluoromethane is thought to be initiated by a *concerted* α-elimination, in contrast to the two-step process involving an intermediate carbanion that occurs with the haloforms studied previously. This mechanism is supported by the observation that the basic hydrolysis of deuterobromodifluoromethane, unlike that of all of the other deuterohaloforms that have been studied, is not accompanied by deuterium exchange.

Introduction

It has been found that the reaction of chlorodifluoromethane with sodium methoxide in methanol,[2] like the basic hydrolysis of chloroform[3] and other haloforms,[4] involves the intermediate formation of a dihalomethylene. With non-fluorine containing haloforms such as chloroform and bromoform, the intermediate trihalomethyl anions in the scheme

$$CHX_3 + OH^- \rightleftarrows CX_3^- + H_2O$$
$$CX_3^- \longrightarrow CX_2 + X^-$$

decompose to dihalomethylene only 0.1–0.001% of the times that they are formed in alkaline aqueous solution.[5] Thus the reaction involves a rapid reversible formation of carbanions followed by a rate-controlling decomposition of the carbanions. With haloforms such as dichlorofluoromethane,[6] bromochlorofluoromethane[5] and dibromofluoromethane[7] that contain one fluorine atom, the carbanion decomposition is still rate-controlling, but it now occurs 8–40% of the times that the carbanion is formed. It therefore seemed that with haloforms containing two fluorine atoms the carbanion formation might become the rate-controlling step of the reaction, with decomposition occurring essentially every time that the carbanion is formed. Thus, although the monofluoro compounds were more reactive than their unfluorinated analogs, the difluorinated compounds were expected to show a decrease in reactivity due to the effect of α-fluorine (relative to other halogens) of decreasing rates of carbanion formation. We decided to test this possibility.

Results and Discussion

The High Reactivity of $CHBrF_2$ and $CHClF_2$.—The halogen atoms of haloforms facilitate carbanion formation in the order I ~ Br > Cl > F, the magnitude of the change in rate produced by a given change in halogen atoms decreasing rather smoothly with the increasing reactivity of the haloform.[5] Hence when log k^{CHX_2Y} is plotted against log k^{CHX_2Z} for the three types of cases for which data are available, smooth curves are obtained. This is illustrated in Fig. 1 in which the eleven circular symbols that fall on the three curves were plotted from data on the seven haloforms, $CHCl_2F$, $CHBrClF$, $CHCl_3$, $CHBr_2F$, $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$.[8] The three of these circles that are solid, for example, have for their abscissas, log k's for $CHCl_2F$, $CHBrClF$ and $CHBr_2F$ and for their ordinates, values for $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$, in the same order.

The square symbols in Fig. 1, obtained by extrapolation[9] of the curves, may be used to calculate "predicted rate constants" for carbanion formation for bromodichloromethane and chlorodifluoromethane. These predicted rate constants should be maxima for the hydrolysis rate constants if the hydrolysis involves the intermediate formation of trihalomethyl anions. On determining the hydrolysis rate constants for bromodifluoromethane and chlorodifluoromethane, as listed in Table I, we were therefore surprised to find values at least forty times[9] as large as would be expected for carbanion formation.

TABLE I

KINETIC DATA FOR BASIC HYDROLYSIS IN AQUEOUS SOLUTION

Haloform	10^4k (l./mole sec.) 0.0°	10^4k (l./mole sec.) 20.1°	$\Delta H\ddagger$, kcal./mole	$\Delta S\ddagger$, e.u.
$CHBrF_2$	20.8 ± 0.8	374 ± 10	22.3 ± 0.7	11.1 ± 2.5
$CDBrF_2$	10.3 ± .5			
$CHClF_2$	0.17 ± .01	8.0 ± 0.5[a]	24.4 ± .8	9.0 ± 3

[a] At 25°.

Since the reaction appears to be too fast to involve carbanion formation, we considered the possi-

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[1] This work was supported in part by the Office of Ordnance Research, U. S. Army.

[2] J. Hine and J. J. Porter, THIS JOURNAL, **79**, 5493 (1957).

[3] J. Hine, *ibid.*, **72**, 2438 (1950); J. Hine and A. M. Dowell, Jr., *ibid.*, **76**, 2688 (1954).

[4] J. Hine, A. M. Dowell, Jr., and J. E. Singley, Jr., *ibid.*, **78**, 479 (1956).

[5] (a) J. Hine, N. W. Burske, M. Hine and P. B. Langford, *ibid.*, **79**, 1406 (1957); (b) S. J. Ehrenson, Ph.D. Thesis, Georgia Institute of Technology, Atlanta, Georgia, 1957.

[6] J. Hine and N. W. Burske, THIS JOURNAL, **78**, 3337 (1956).

[7] Unpublished work from this Laboratory.

[8] To obtain values of k^{CHX_3} from the observed k^{CDX_3} values[5] for the five haloforms for which kinetic isotope effects were not determined directly, a value of 1.75 was chosen for k^{CHX_3}/k^{CDX_3} by averaging the values for dichlorofluoromethane (1.76) and bromochlorofluoromethane (1.74). The preliminary value[5] of k^{CDBr_2F} was replaced by a final value[7] (2.07×10^{-2} l. mole^{-1} sec.$^{-1}$).

[9] The extrapolation was done conservatively by tending to straighten the extrapolated portion of the curves. If the original curvatures were maintained, the deviations of predicted carbanion formation rate constants from observed hydrolysis rate constants would be much larger than forty-fold, especially for chlorodifluoromethane.

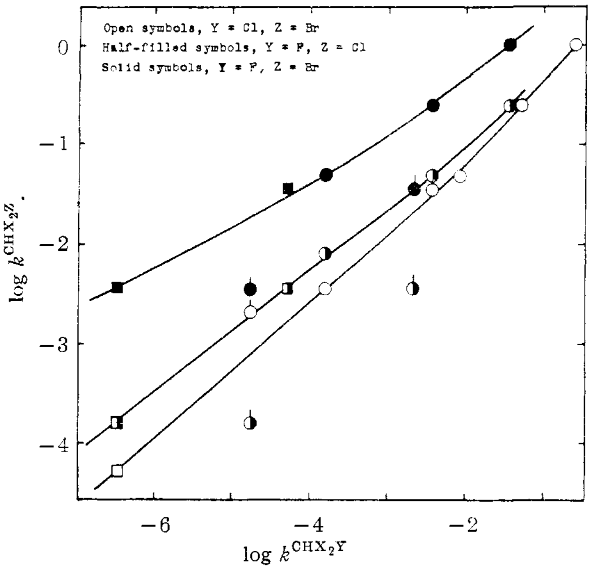

Fig. 1.—Effect of the change of one halogen atom on reactivity in the carbanion formation of haloforms. Symbols of the types, ●, ◐ and ○ were plotted from data on $CHClF_2$ and/or $CHBrF_2$. The square symbols are for values obtained by extrapolation.

bility that it might be occurring by the S_N2 mechanism. However, the data of Moelwyn-Hughes on the reactions of methyl chloride and methyl bromide with sodium hydroxide in aqueous solution[10] show that our difluoro derivatives of these compounds are 100 and 500 times as reactive at 25°. In view of the fact that α-fluorine has been shown to decrease S_N2 reactivity (compared to α-hydrogen),[11] it seems very improbable that the haloforms are reacting by the S_N2 mechanism. Further evidence may be found in the fact that the S_N2 mechanism has been disproved for the reaction of chlorodifluoromethane with sodium methoxide in methanol.[2] The fact that methyl bromide and iodide react faster with methanolic sodium methoxide[11] than with aqueous sodium hydroxide[10] while the five haloforms that have been studied react 7–100 times as fast in aqueous solution as in methanol (probably partly because methoxide ion is a weaker base than hydroxide ion)[12] suggests that the dihalomethylene mechanism is more favored in water than in methanol.

The Concerted Mechanism.—Of the fifteen haloforms for which basic hydrolysis rates have been studied, the five most reactive all contain a fluorine atom to stabilize the intermediate dihalomethylene (and either a bromine or iodine atom to be lost as an anion in the rate-controlling step of the reaction).[4,5] The hydrolysis rate data thus seem to show that fluorine atoms stabilize dihalomethylenes (or at least the transition states leading to them) much better than other halogen atoms and, in fact, this hypothesis is supported by the results of quantitative correlation of the relative hydrolysis rates of haloforms.[5b] Since fluorine atoms (relative to other halogen atoms) retard carbanion formation while speeding dihalomethylene formation from haloforms, the replacement of other halogens by fluorine tremendously increases the tendency of trihalomethyl anions to decompose to dihalomethylenes.

From the fact that the hydrolyses of chloro- and bromodifluoromethane are so much faster than would even be expected for carbanion formation, we infer that the carbanion is not a real reaction intermediate in these cases. Apparently two fluorine atoms have added so greatly to the tendency of the carbanion to decompose to dihalomethylene that it decomposes as it forms. As the removal of the haloform hydrogen begins, the negative charge thus placed on carbon causes the synchronized cleavage of the carbon–chlorine (or bromine) bond.

$$HO^- + HCF_2Cl \longrightarrow \overset{-\delta}{HO}\text{--}H\text{--}\overset{-\delta}{CF_2}\text{--}\overset{-\delta}{Cl} \longrightarrow HOH + CF_2 + Cl^-$$

Each of the two processes helps the other. The greater the negative charge on carbon the more easily is the halide ion lost. The greater the extent to which the halide ion is lost, the more acidic is the hydrogen atom being removed by base. Thus it is possible to go directly to what is probably the most stable of the dihalomethylenes and by-pass what would be a relatively unstable trihalomethyl anion.

The Hydrolysis of Deuterobromodifluoromethane.—Our hypothesis that there is thus both a concerted and stepwise mechanism for α-eliminations is reminiscent of the similar duality of mechanisms for β-eliminations.[13] A method for testing for the carbanion mechanism for β-elimination as in other cases for which carbanion intermediates have been postulated is to see whether reaction of the starting material is accompanied by its deuterium exchange. We have applied this test to our reaction by studying deuterobromodifluoromethane. We prepared this compound by the action of mercuric fluoride on 94 ± 1% deuterobromoform and assumed that its deuterium content was the same. If its hydrolysis proceeds by a concerted mechanism to yield difluoromethylene and if the difluoromethylene is not reverted to haloform, then, unlike the other nine deuterohaloforms that have been studied,[5–7] deuterated bromodifluoromethane may *increase* in deuterium content as it hydrolyzes, since the protium compound would be expected to react faster due to a kinetic isotope effect.[14] The rate-controlling steps for the two isotopically different species will be

$$CDBrF_2 + OH^- \xrightarrow{k_1} HOD + CF_2 + Br^-$$

$$CHBrF_2 + OH^- \xrightarrow{k_2} HOH + CF_2 + Br^-$$

The two kinetic equations

$$\frac{dD}{dt} = k_1D \text{ and } \frac{dH}{dt} = k_2H$$

where $D = [CDBrF_2]_t$ and $H = [CHBrF_2]_t$ may be combined to give

$$\frac{dH}{dD} = \frac{k_2}{k_1}\frac{H}{D}$$

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[10] E. A. Moelwyn-Hughes, *Proc. Roy. Soc.* (*London*), **A196**, 540 (1949).

[11] J. Hine, C. H. Thomas and S. J. Ehrenson, THIS JOURNAL, **77**, 3886 (1955); J. Hine, S. J. Ehrenson and W. H. Brader, Jr., *ibid.*, **78**, 2282 (1956).

[12] J. Hine and M. Hine, *ibid.*, **74**, 5266 (1952).

[13] J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, sec. 7-1a.

[14] K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

which, upon separation of variables, integration and evaluation of the integration constant gives

$$\log \frac{H_0}{H} = \frac{k_2}{k_1} \log \frac{D_0}{D} \qquad (1)$$

The value of the kinetic isotope effect k_2/k_1 was determined directly (2.02 ± 0.14) by determining the rate constant for the hydrolysis of the deuterohaloform (Table I). The fact that this rate constant did not climb significantly during the kinetic run showed that the hydrolysis reaction was not accompanied by any large amount of deuterium exchange. In addition we extracted the unreacted haloform from two reaction solutions and found that its deuterium content actually had increased, from 94% to 96.5 ± 1% after 31 ± 2% reaction and to 99.5 ± 0.5% after 92 ± 2% reaction. Since the values that may be calculated from eq. 1 are 95.5 and 99.4%, respectively, the amount of haloform that exchanged hydrogen with the solvent was negligible.

Relation to Other α-Eliminations.—Such α-eliminations with rearrangement as the formation of diphenylacetylene from 2,2-diphenylvinyl halides and base have been known for some time.[15] As Hauser has pointed out[16] these reactions may be concerted or may proceed by as many as three steps. In view of Bothner-By's evidence for some isomerization of the intermediate anion[17] it seems probable that this reaction involves at least two steps. A somewhat similar α-elimination, the Hofmann reaction of amides, is clearly stepwise.[16] In no previously reported α-elimination does there appear to be any strong evidence for a concerted mechanism. The dehydrohalogenation of *n*-octyl chloride by potassium amide, a reaction that has been reported to proceed partly by an α-elimination mechanism, has been shown to be unaccompanied by deuterium exchange of the starting halide.[18] However, this sort of evidence, like our observed non-exchange of deuterobromodifluoromethane, can be explained reasonably by the assumption that there is a true intermediate carbanion but that it practically invariably loses a halide ion to complete the α-elimination instead of coördinating with a proton to revert to starting material. We feel that this is much weaker evidence for a concerted mechanism than our observation that the loss of halide ion appears to add driving force to the proton removal. The change of mechanism from stepwise to concerted in such a related series as the haloforms suggests that it may occur in other series too.

The reactivity of CHF_2SF_5 toward alkali in contrast to the inertness of CF_3SF_5 suggests the occurrence of an α-elimination to give the difluoromethylene intermediate.[19] The fact that fluoroform is unreactive suggests that the SF_5 group is more easily displaced with its bonding electron pair than is fluorine.

When it is considered that the halide ion being displaced is certainly being solvated and that anion solvations is an acidic type of function,[20] our concerted mechanism is seen to be quite similar to the mechanism suggested by Horiuti, Tanabe and Tanaka[21] for the hydrolysis of chloroform, a reaction for which we have proposed a stepwise mechanism.

Experimental

Reagents.—Bromodifluoromethane (du Pont) was used directly from the cylinder without further purification. Its infrared spectrum showed it to contain less than 1% dibromofluoromethane and less than 1% fluoroform. The chlorodifluoromethane used has been described previously.[2]

Deuterobromodifluoromethane.—Deuterobromodifluoromethane was prepared from bromoform by deuteration followed by reaction with mercuric fluoride. About 7.5 g. of anhydrous sodium carbonate was dissolved in 100 g. of 99.5+% deuterium oxide, and 20 ml. of this solution was shaken with 100 ml. of freshly distilled bromoform for 4 hr. The bromoform layer was then shaken with a fresh 20 ml. of Na_2CO_3–D_2O solution for 17 hr. after which infrared measurements[6] showed it to be 84% deuterated. An additional 6 hr. of shaking with a third fresh portion of the heavy water and 16 hr. with a fourth batch yielded 95 ml. of 94 ± 1% deuterobromoform. The deuterobromoform was added gradually with stirring over a period of 1 hr. to 213 g. of mercuric fluoride, and then the reaction flask was heated until the unreacted bromoform distilled. While most of the product was deuterodibromofluoromethane, collected in the ice-cooled receiver, about 10 ml. of liquid was found in the Dry Ice trap. When the trap was allowed to warm the material distilling between pot temperatures of −15 and 18° was collected (about 3 ml.). This material was allowed to vaporize through a fritted glass tube into about 800 ml. of oxygen-free water at 0° until the distilling flask reached 0°. Extraction of a portion of the 800 ml. of aqueous solution with carbon disulfide and infrared measurements showed absorption maxima (in order of decreasing intensity) at 9.32, 8.76, 10.07, 9.00, 10.30, 11.29, 15.08, 10.48, 14.16, 10.64, 13.53 and 11.02 μ. Separate measurements on $CHBrF_2$, $CHBr_2F$ and $CDBr_2F$ showed the 9.00 and 14.16 μ maxima very probably to be due to $CHBrF_2$ and the 11.29 and 15.08 μ maxima due to $CDBr_2F$. We have assumed that the bromodifluoromethane prepared was 94 ± 1% deuterated just as the bromoform from which it was made. Infrared measurements showed that 1.5 ± 0.5 mole % of $CDBr_2F$ was also present. The addition of 0.15 ml. of 0.04877 *N* sodium hydroxide solution to 20 ml. of the aqueous $CDBrF_2$ solution containing phenolphthalein gave a strong pink color. This showed that there was present no more than 0.5% of materials that are acidic or that liberate acids very easily (compounds such as HF, $COBr_2$, COF_2, COBrF, etc.).

Hydrolysis Kinetics.—The kinetics of the alkaline hydrolysis were studied by techniques of which the following run with bromodifluoromethane at 0° is an example. About 500 ml. of an aqueous solution of bromodifluoromethane was prepared by bubbling the gas into a 500 ml. flask full of oxygen-free water and surrounded by a water-ice slurry. Eleven 40-ml. pipets full of this solution were removed in as rapid succession as possible. Further precautions to minimize loss of the haloform from the aqueous solution include the use of cold pipets and of nitrogen pressure to fill the pipets. The third and ninth samples were emptied into 100-ml. flasks containing 20 ml. of 0.1467 *N* carbonate-free sodium hydroxide solution and allowed to stand at 0° for 2 hr. They were then allowed to warm to room temperature (25°) during an hour and finally heated to 45° for 30 minutes to ensure complete hydrolysis of the haloform. Titration of the unreacted base with 0.06360 *N* perchloric acid showed that the haloform in sample 3 had been 0.02294 *N* and that in sample 9, 0.01917 *N*. The normality of a haloform solution toward base is equal to 3 + *f* times its molarity. Expression of our usual rate equation[3,4] in the form

$$k = \frac{2.303}{t(b - [3 + f]a)} \log \frac{(3 + f)a(b - [3 + f]x)}{b/([3 + f]a - [3 + f]x)}$$

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[15] P. Fritsch, *Ann.*, **279**, 319 (1894); see Bothner-By[17] for other references.

[16] C. R. Hauser, THIS JOURNAL, **62**, 933 (1940).

[17] A. A. Bothner-By, *ibid.*, **77**, 3293 (1955).

[18] D. G. Hill, W. A. Judge, P. S. Skell, S. W. Kantor and C. R. Hauser, *ibid.*, **74**, 5599 (1952).

[19] G. A. Silvey and G. H. Cady, *ibid.*, **72**, 3624 (1950).

[20] Ref. 13, pp. 44, 47.

[21] J. Horiuti, K. Tanabe and K. Tanaka, *J. Research Inst. Catalysis*, Hokkaido Univ., III, No. 3, 119, 147 (1955). We do not comment any further on this work since we hope first to resolve our differences by collaborative experiments.

where $a = [\mathrm{CHX_3}]_0$, $b = [\mathrm{OH^-}]_0$, $x = \Delta[\mathrm{CHX_3}]_t$, t = time (in seconds), and f = fraction of haloform that gives formate, shows that we need not know f nor a provided that we know the normality of haloform, $(3 + f)a$, and the change in hydroxide ion concentration, $(3 + f)x$. Each of the other nine 40-ml. samples of aqueous haloform solution was put in a 50-ml. volumetric flask at 0°. The haloform normalities of these solutions were calculated from the values found for the third and ninth samples with the assumption of a constant change in concentration between each two consecutive samples. The alternate assumption that the change is proportional to the concentration gives calculated normalities that never differ from those used by more than 0.8%. At recorded times, 10 ml. of 0.1470 N sodium hydroxide solution at 0° was pipetted by a cold pipet into each of the nine 50-ml. volumetric flasks. The reactions were stopped at recorded times by pouring the contents of the volumetric flasks into 25 ml. of cold 0.06200 N perchloric acid. Samples 1 and 2 were stopped within 30 seconds to serve as "zero points." The excess acid was titrated to the brom cresol purple end-point with 0.04877 N carbonate-free sodium hydroxide solution. The data obtained are given in Table II.

TABLE II

HYDROLYSIS OF $\mathrm{CHBrF_2}$ IN AQUEOUS SOLUTION AT 0°[a]

Sample no.	Time[b] (sec.)	Δ Titer, ml. 0.04877 N NaOH	10^3k (l./mole sec.)
4	690	0.69	1.924
5	1,235	1.21	2.005
6	2,125	1.88	1.918
7	3,060	2.48	1.885
8	6,110	4.50	1.985
10	8,080	5.58	2.167
11	11,035	6.55	2.095
		Av.	1.997 ± 0.079

[a] $[\mathrm{NaOH}]_0 = 0.02930$. [b] From the time the zero points (1 and 2) were taken.

Heats and entropies of activation were calculated from the absolute rate equation[22]

$$k = \frac{\mathbf{k}T}{h} e^{-\Delta H^{\ddagger}/RT} e^{\Delta S^{\ddagger}/R}$$

Hydrolysis of Deuterobromodifluoromethane.—The kinetics of the hydrolysis of deuterobromodifluoromethane were studied by techniques like those described for the protium compound in the previous section. The "uncorrected" rate constant of (1.09 ± 0.03) × 10^{-3} l./mole. sec. obtained was corrected to (1.03 ± 0.05) × 10^{-3} by allowing for the presence of the more reactive protium compound and deuterodibromofluoromethane. The isotopic analyses were carried out by extracting the aqueous reaction solution with carbon disulfide and running the infrared spectrum of the extract. The per cent. protium compound present was calculated by comparison of the 7.88 and 9.01 μ bands of $\mathrm{CHBrF_2}$ with the 8.76 and 9.32 μ bands of $\mathrm{CDBrF_2}$ in this extract and also in an extract of the starting material and assuming that the starting material was 94% deuterated. Any error in the assumption would result in a proportional error in the same direction in our analyses and would therefore have little effect on our conclusion that hydrolysis is unaccompanied by deuterium exchange.

Acknowledgments.—We wish to acknowledge our indebtedness to the "Kinetic" Chemical Division of E. I. du Pont de Nemours and Company for a sample of bromodifluoromethane.

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[22] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 14.

ATLANTA, GEORGIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STANFORD UNIVERSITY]

The Synthesis of 4-Isopropyl-1-methylbicyclo[3,1,0]-3-hexenon-2[1] an Isomer of Umbellulone

BY HOWARD E. SMITH[2] AND RICHARD H. EASTMAN

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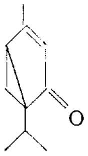
The structure of umbellulone (I) has been confirmed by the unambiguous synthesis of an isomer, 4-isopropyl-1-methylbicyclo[3,1,0]-3-hexenon-2 (II), which contains the same chromophoric system and has an ultraviolet absorption spectrum practically identical with the anomalous absorption spectrum reported for umbellulone.

In conjunction with the current interest in the spectroscopic and chemical properties of the cyclopropane ring[3] and in view of the characteristic ultraviolet absorption spectrum[4] of umbellulone[5] (I)[6] (Fig. 1), described by Gillam and West[4] as anomalous in that it differs from that of any known α,β-unsaturated ketone, the unambiguous synthesis of an isomer, 4-isopropyl-1-methylbicyclo[3,1,0]-3-hexenon-2 (II), of umbellulone was undertaken. Since this isomer contains the same chromophoric system as umbellulone and has an ultraviolet absorption spectrum practically identical with that of umbellulone (compare in Fig. 1), the absorption spectra must be associated with the unique conjugated system present in both substances. The particular isomer was chosen for synthesis rather than umbellulone, since it not only confirms the structure of umbellulone but it is also a convenient intermediate for a projected total synthesis of the ses-



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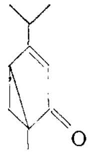
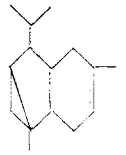
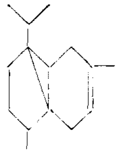


II



III



IV

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[1] This material is taken from the dissertation of Howard E. Smith offered in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Stanford University. Preliminary reports of this synthesis were presented before the 125th Meeting of the American Chemical Society, Dallas, Texas, March, 1956, and published in *J. Org. Chem.*, **21**, 830 (1956).

[2] Eli Lilly and Co. Fellow 1953–1955.

[3] (a) R. H. Eastman and A. Oken, THIS JOURNAL, **75**, 1029 (1952); (b) R. H. Eastman, *ibid.*, **76**, 4115 (1954); (c) R. H. Eastman and J. C. Selover, *ibid.*, **76**, 4118 (1954); (d) R. H. Eastman and S. K. Freeman, *ibid.*, **77**, 6642 (1955); (e) R. J. Mohrbacher and N. Cromwell, *ibid.*, **79**, 401 (1957), and earlier papers.

[4] A. E. Gillam and T. F. West, *J. Chem. Soc.*, 95 (1945).

[5] F. B. Power and F. H. Lees, *ibid.*, 629 (1904).

[6] F W. Semmler, *Ber.*, **40**, 5017 (1907).