# The Chemistry of Ylids. VI. Dimethylsulfonium Fluorenylide—A Synthesis of Epoxides[1]

BY A. WILLIAM JOHNSON[2] AND ROBERT B. LACOUNT

RECEIVED JULY 25, 1960

An attempt to effect a Wittig reaction between 9-dimethylsulfonium fluorenylide (IIa) and benzaldehydes to form 9-benzalfluorenes has instead led to the formation of benzalfluorene oxides (VIII) and phenyl-9-(1-methylthiomethyl)-fluorenylcarbinols (X). A pronounced solvent effect operates in this reaction. Nitrosobenzene with IIa gave N-phenylfluorenone ketoxime (XIV). The sulfur ylid IIa has been shown to be less reactive than the corresponding phosphorus (IIb,c,d) and arsenic (IIe) derivatives as was expected from its physical properties.
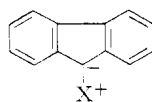
Introduction

Although the reaction between 'onium ylids (I) and carbonyl compounds to form olefins (Wittig reaction) has been known for forty years,[3] its potential has been explored and realized only within the last few years.[4] In all previous examples of its use in organic syntheses the 'onium group X has been triphenylphosphonium[5] (I, X = (C$_6$H$_5$)$_3$P).
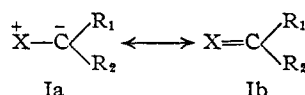
Significantly, the Wittig reaction is known to fail unless X is a group capable of stabilizing the adjacent negative charge, above and beyond coulombic interactions, in addition to any delocalization afforded by the groups R$_1$ and R$_2$. Since the bulk of this stabilization probably is derived from valence shell expansion of the heteroatom group[1a,4,5] (via resonance from Ib), any other group X capable of behaving likewise should afford an ylid capable of undergoing a normal Wittig reaction. In verification of this hypothesis we have shown recently that trialkylphosphonium ylids[1a] (IIb,c) and triphenylarsonium ylids[1b] (IIe) do so and are even more reactive than triphenylphosphonium ylids (IId) in the Wittig reaction. We now wish to report the fate of a sulfur ylid, dimethylsulfonium fluorenylide (IIa).[6] This is one of only three isolable sulfur ylids known, the other two being its 2-nitro and 2,7-dinitro derivatives.[7]

It has been shown[8] that sulfur can expand its valence shell, probably through the use of vacant low energy 3d-orbitals, and thereby afford stabilization to an adjacent negative charge (via form

IIa, X = (CH$_3$)$_2$S
IIb, X = (C$_4$H$_9$)$_3$P
IIc, X = (CH$_3$)$_3$P
IId, X = (C$_6$H$_5$)$_3$P
IIe, X = (C$_6$H$_5$)$_3$As

Ib). For example, Doering and Hoffmann[9] concluded that the heat of activation for the deuteroxide-catalyzed exchange of deuterium in trimethylsulfonium salts was lowered from that calculated on the basis of coulombic interactions by 17.2 kcal./mole. This lowering was ascribed to resonance stabilization of an ylid-type intermediate through the use of sulfur 3d-orbitals. There are numerous examples of the ability of sulfur to stabilize adjacent carbanion centers in reaction intermediates through octet expansion.[10] Ultraviolet and infrared spectroscopic studies have provided additional evidence of this phenomenon.[11] Therefore, since a sulfur group appeared to fulfil the electronic requirement for participation in a Wittig reaction, the ylid IIa was expected to react with carbonyl compounds to form olefins and dimethyl sulfoxide.

Results

The ylid IIa, m.p. 120–122°, was prepared in 82% yield according to the original procedure of Ingold and Jessop.[6a] It could be stored in vacuo or under ether for a few hours before decomposing to an orange amorphous solid. Its ultraviolet spectrum in chloroform solution was nearly identical to that of our other fluorenylides (IIb-e) except for the 368 mμ band (IIb-d λ_{max} 380–382 mμ; IIe, 390 mμ). The dipole moment of IIa was 6.2 D.,[6b] significantly lower than those of the other fluorenylides. The hydrobromide of IIa had a pK_a of 7.3 in water–dioxane.[1a] The sulfur ylid was therefore the least basic of the fluorenylides studied.
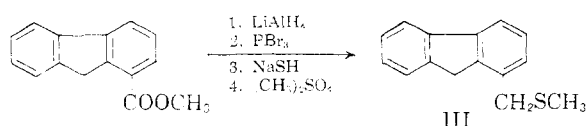
Base-catalyzed hydrolysis of IIa failed to afford fluorene as had the other fluorenylides, but its hydrobromide was readily hydrolyzed to fluorenol with warm water, a reaction that failed with the others. Extended treatment of the ylid IIa with methanolic sodium hydroxide solution gave 1-methylthiomethylfluorene (III),[12] the result of an internal anionic (Sommelet) rearrangement, together with trace amounts of other isomers. The structure of III was confirmed by a four-step synthesis from methyl fluorene - 1 - carboxylate. Traces of III were obtained from other reaction mixtures involving the use of the ylid in non-basic media.

(1) For previous papers see (a) V, A. W. Johnson and R. B. LaCount, Tetrahedron, 9, 130 (1960); (b) IV, A. W. Johnson, J. Org. Chem., 25, 183 (1960).

(2) To whom inquiries should be sent, at Department of Chemistry, University of North Dakota, Grand Forks, N. D.

(3) H. Staudinger and J. Meyer, Helv. Chim. Acta, 2, 619 (1919).

(4) (a) G. Wittig and U. Schöllkopf, Chem. Ber., 87, 1318 (1954); (b) G. Wittig and W. Haag, ibid., 88, 1654 (1955).

(5) For a review of this reaction see J. Levisalles, Bull. soc. chim. France, 1020 (1958).

(6) (a) C. K. Ingold and J. A. Jessop, J. Chem. Soc., 713 (1930); (b) G. M. Phillips, J. S. Hunter and L. E. Sutton, ibid., 146 (1945); (c) for a preliminary account of the early part of this work see A. W. Johnson and R. B. LaCount, Chemistry & Industry, 1440 (1958).

(7) E. D. Hughes and K. I. Kuriyan, J. Chem. Soc., 1609 (1935).

(8) D. P. Craig and E. A. Magnusson, ibid., 4895 (1956).

(9) W. von E. Doering and A. K. Hoffmann, THIS JOURNAL, 77, 521 (1955).

(10) G. Cilento, Chem. Revs., 60, 147 (1960).

(11) F. G. Bordwell and P. J. Boutan, THIS JOURNAL, 78, 87 (1956); S. Oae and C. C. Price, ibid., 80, 3425 (1958); A. W. Baker and G. H. Harris, ibid., 82, 1923 (1960); E. B. Knott, J. Chem. Soc., 937 (1955).

(12) L. A. Pinck and G. E. Hilbert, THIS JOURNAL, 68, 751 (1946).

CHART I

a, $R = C_6H_4NO_2(p)$;
b, $R = C_6H_4NO_2(m)$;
c, $R = C_6H_4NO_2(o)$;
d, $R = C_6H_4CN(p)$;
e, $R = C_6H_3(Cl)_2(o,p)$;
f, $R = CH_3$

a IIa followed pathway 2 and 3; IIb-e followed pathway 1 only.

Chromatography of IIa on neutral or slightly basic alumina afforded difluorenylidene and fluorenone in 43 and 37% yields, respectively. Pyrolysis of the ylid gave no identifiable products, only the omnipresent orange amorphous solid. However, Hughes and Kuriyan[7] reported the formation of 2,2'-dinitrodifluorenylidene upon pyrolysis of 9-dimethylsulfonium (2-nitro)-fluorenylide. These transformations likely occurred by decomposition of the ylids to methyl sulfide and the "methylene" derivative IV, the latter then dimerizing to difluorenylidene or reacting with oxygen to form fluorenone.[13] Franzen[14] has recently postulated the analogous decomposition of 9-trimethylammonium fluorenylide into IV followed by its subsequent reaction with other amines. The coupling
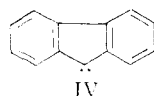
of carbenes with nucleophiles to form ylids, the reverse of the above decomposition, has been reported recently.[15]

Treatment of the ylid IIa with an equimolar quantity of p-nitrobenzaldehyde (Va) in refluxing methylene chloride solution followed by chromatography afforded difluorenylidene (2%), 1-methylthiomethylfluorene (III) (2%), traces of fluorenone, a compound A (40%) and a compound B (25%). The same reaction in ethereal solution gave 3% of A and 83% of B together with 4% of fluorenone and traces of difluorenylidene and III.

Compound A, $C_{20}H_{13}NO_3$, showed infrared absorption at 1520 and 1350 cm.$^{-1}$, characteristic of a nitro group, and at 850 cm.$^{-1}$, indicative of an epoxide function. The ultraviolet spectrum was characteristic of a 9-oxygenated fluorene. Chromic acid oxidation gave fluorenone and p-nitrobenzoic acid while pyrolysis with triphenylphosphine and hydroquinone, a procedure known to convert epoxide into olefins,[4b] gave a low yield of p-nitrobenzalfluorene (VIIa). The correctness of the suggested structure for A, p-nitrobenzalfluorene oxide (VIIIa), was confirmed by comparison with an authentic sample prepared from 9-bromofluorene and p-nitrobenzaldehyde.[16]

Compound B, $C_{22}H_{19}NO_3S$, showed infrared absorption characteristic of an alcohol (3450 cm.$^{-1}$) and a nitro group (1510 and 1345 cm.$^{-1}$) and ultraviolet absorption characteristic of an alkyl-substituted fluorene. The alcohol was shown to be primary or secondary by successful formation of a benzoate derivative. Oxidation of B with hydrogen peroxide gave a sulfone, $C_{22}H_{19}NO_5S$,

(13) W. B. DeMore, H. O. Pritchard and N. Davidson, THIS JOURNAL, **81**, 5874 (1959).
(14) V. Franzen, Chem. Ber., **93**, 557 (1960).
(15) A. J. Speziale, G. J. Marco and K. W. Ratts, THIS JOURNAL, **82**, 1260 (1960); D. Seyferth, S. O. Grim and T. O. Read, ibid., **82**, 1510 (1960).
(16) E. Bergmann and J. Hervey, Chem. Ber., **62**, 893 (1929).
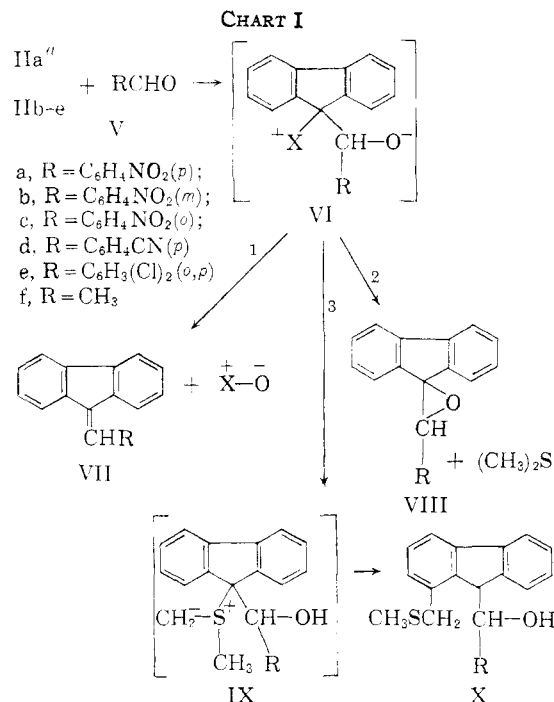
indicating the sulfur to be present as a thioether. Since B contained all of the atoms originally present in both starting materials, its structure was suspected of being derived from an initial addition of the ylid to the carbonyl group followed by an intramolecular rearrangement. Structure Xa was chosen as a working hypothesis and its correctness was demonstrated by the following transformations. Dehydration of B with phosphorus oxychloride in pyridine gave an olefin, $C_{22}H_{17}NO_2S$, whose ultraviolet spectrum was identical in shape but shifted 3–4 mμ from that of p-nitrobenzalfluorene (VIIa). Oxidation of B with chromic acid
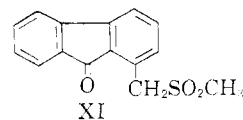
gave p-nitrobenzoic acid and fluorenone-1-dimethylsulfone (XI), identical to a sample prepared by oxidation of III. The compound B was therefore p-nitrophenyl-9-(1-methylthiomethyl)-fluorenylcarbinol (Xa).

In an effort to explore the scope of this reaction and to ascertain the reactivity of the ylid IIa, the latter was treated with several other carbonyl compounds in methylene chloride and ethereal solutions affording an alcohol X and epoxide VIII in each case. The reaction failed with cyclohexanone, benzaldehyde, o- and p-chlorobenzaldehyde affording, as the only isolable substances, the orange amorphous solid and several per cent. of difluorenylidene. Successful reactions were obtained with o-, m- and p-nitrobenzaldehydes, p-cyanobenzaldehyde and 2,4-dichlorobenzaldehyde. Reaction with acetaldehyde afforded only the oily alcohol Xf. In many cases the major products

were accompanied by and easily separated (by chromatography) from traces of fluorenone, difluorenylidene and III, all three substances being transformation products of unreacted ylid. The yields of the major products are shown in Table I.

TABLE I

REACTION OF YLID IIa WITH ALDEHYDES

Aldehyde (R group)	Methylene chloride solvent		Ether solvent	
	Epoxide, VIII, %	Alcohol, X, %	Epoxide, VIII, %	Alcohol, X, %
p-Nitrophenyl (Va)	40	25	3	83
m-Nitrophenyl (Vb)	36	32	2	78
o-Nitrophenyl (Vc)	30	35	3	34
p-Cyanophenyl (Vd)	33	29	2	64
2,4-Dichlorophenyl (Ve)	30	33	3	26
Methyl (Vf)	0	45	..	..

The epoxides (VIII a,b,d,e) were identical to authentic samples prepared by base-catalyzed condensation of 9-bromofluorene with the appropriate benzaldehyde. o-Nitrobenzalfluorene oxide (VIIIc) was prepared from fluorenone and o-nitrobenzyl bromide after the above method failed. The structure of the alcohols Xb-e were proved by chromic acid oxidation to fluorenone-1-dimethyl sulfone (XI) and the appropriate substituted benzoic acid as was described for the p-nitro case.

Upon recrystallization from absolute ethanol 2,4-dichlorobenzalfluorene oxide (VIIIe) afforded the ring-opened hydroxy ether XII. That the cleavage occurred in the indicated direction was shown by dehydration of XII to ω-ethoxy-ω-(2,4-dichlorophenyl)-dibenzofulvene.

XII
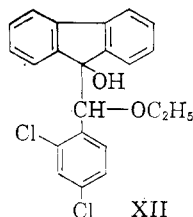
Reaction of the sulfur ylid IIa with nitrosobenzene afforded a 96% yield of the nitrone XIV, identical to a sample prepared from 9-(1-pyridinium) fluorenylide and nitrosobenzene.[17] The ultraviolet spectrum and failure to oxidize iodide ion eliminated the isomeric oxazirane structure XV from consideration.[18]

XIII   XV
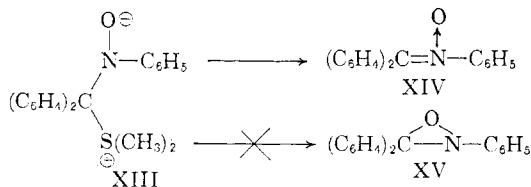
In view of the radical change in the ratio of epoxide to alcohol formed in the reaction between the ylid IIa and benzaldehydes in methylene chlo-

(17) F. Kröhnke, Chem. Ber., **83**, 253 (1950).

(18) (a) W. D. Emmons, THIS JOURNAL, **79**, 5739 (1957); (b) J. S. Splitter and M. Calvin, J. Org. Chem., **23**, 651 (1958).

ride and ether solutions, the reaction with p-nitrobenzaldehyde was examined in a series of solvents in an attempt to characterize the solvent effect (see Table II).

TABLE II

SOLVENT EFFECT IN THE REACTION OF IIa WITH p-NITRO-BENZALDEHYDE

Solvent	Dielectric constant[a]	Yields, %		Ratio A/E
		Epoxide	Alcohol	
Carbon tetrachloride	2.24	26	48	1.85
Benzene	2.28	21	48	2.28
Toluene	2.38	13	31	2.38
Diethylamine	3.60	0	69	∞
Ethyl ether	4.32	3	83	27.7
Chloroform	4.78	53	35	0.66
Tetrahydrofuran	8.20	3	67	22.4
Methylene chloride	9.08	40	25	0.63
Ethanol	24.30	53	4	0.074
Acetonitrile	37.45	0	25	∞
Methyl sulfoxide	...	0	48	∞

[a] A. A. Maryott and E. R. Smith, "Table of Dielectric Constants of Pure Liquids," Natl. Bur. Standards Circ. 514(1951); F. Buckley and A. A. Maryott, "Tables of Dielectric Dispersion Data for Pure Liquids and Dilute Solutions," ibid., 589 (1958).

In the case of acetonitrile as solvent, a 10% yield of p-nitrobenzalfluorene (VIIa) and a 4% yield of p-nitrobenzal-(1-methylthiomethyl)-fluorene were isolated in addition to the 25% yield of alcohol Xa. With methyl sulfoxide as solvent a 7% yield of p-nitrobenzal-(1-methylthiomethyl)-fluorene was isolated along with 48% of alcohol Xa.

Discussion

From a study of the pK_a's of the fluorenylide hydrobromides[1a] we had previously shown the sulfur ylid IIa to be the least basic. Consequently, the tetracovalent form (e.g., Ib), the result of octet expansion with its accompanying resonance stabilization, probably makes a greater contribution to the structure of the resonance hybrid of IIa than in the case of the other ylids. Since the first step in both the Wittig reaction and the reaction of sulfur ylids with carbonyl compounds involves the attack of an anionic center (e.g., form Ia, which in the case of the ylid IIa is a less dominant form than it is with the fluorenylides IIb-e) on a carbonyl carbon,[19] IIa was expected to be the least reactive of the fluorenylides. This expectation has been verified by our present results. The ylid reacted only with those benzaldehydes carrying powerful electron-withdrawing groups (e.g., nitro, cyano) which would result in highly polarized carbonyl groups, very susceptible to anionic addition to form the intermediates VI. For example, IIa failed to react with benzaldehyde, whereas the other four fluorenylides reacted in near quantitative yield.

Reaction between the sulfur ylid IIa and benzaldehydes did not afford benzalfluorenes (VII) as had the phosphorus and arsenic ylids.[1] To do

(19) We have previously shown this to be the case for the Wittig reaction (ref. 1a). The mechanistic considerations which follow justify this assumption for the sulfur ylid reaction. The similarity in the reactivity of the ylids IIa-e toward protons and carbonyl groups provides further justification. In the sulfur case the first step may or may not be the slow step as it was in the Wittig reaction.

so would have necessitated the attack of an oxyanion (VI) on the tertiary sulfur atom to form, in a transitory sense at least, the four-membered intermediate XVI. Completion of the oxygen

(CH₃)₂S͵ ͵CHR
         O
        XVI
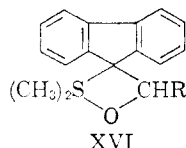
transfer and elimination of dimethyl sulfoxide would have afforded the olefin VII (pathway 1). Instead, the oxyanion displaced the sulfonium group from the C-9 position to form an epoxide (VIII) and evolve methyl sulfide (pathway 2). There is adequate analogy for such a displacement. A somewhat similar displacement has been reported[20] in the reaction between phosphonium ylids and dibenzofulvenes forming spirocyclopropanes and triphenylphosphine.

The other product (X) may be accounted for by intramolecular proton transfer in VI to form a new intermediate ylid (IX, pathway 3). This transformation should be quite facile since the sulfonium group is an excellent proton-labilizing group[10] and the oxyanion is a sufficiently strong base. The intermediate IX is then converted into the observed alcohol X by a Sommelet rearrangement analogous to that occurring with the ylid itself[12] (see above).

Since the reactivity of the sulfur ylid IIa is essentially that predictable on the basis of its physical properties and, furthermore, a reasonable mechanism (Chart I) accounts for the products VIII and X, it is likely that the first step in the reaction of IIa with carbonyls is the same as that in the Wittig reaction between phosphorus ylids and carbonyls.[1a] The two mechanisms apparently diverge in the second step. Two explanations are apparent. In spite of the greater ability of sulfur over phosphorus to stabilize an adjacent negative charge by valence shell expansion,[9] sulfur is apparently less able to form a formally bonded intermediate of higher covalency, at least to the extent required in the Wittig reaction. Thus, the oxyanion VI failed to attack the tervalent sulfur to form the required intermediate XVI. There exists an additional example of this phenomenon in the early work of Ingold and co-workers[21] wherein they found that phosphonium salts, when treated with sodium hydroxide, afforded a phosphine oxide and a hydrocarbon via direct attack of hydroxide on the phosphorus atom to form a pentacovalent intermediate. This mechanism has recently been supported by VanderWerf, et al.[22] On the other hand, sulfonium salts under the same conditions gave either an alcohol or olefin together with a thioether. In each instance, the hydroxide did not attack the sulfur atom but rather an adjacent carbon or once-removed hydrogen. Thus, tervalent sulfur is not attacked by an anionic

reagent as is tetravalent phosphorus and arsenic. Bond energy differences between phosphine oxides and sulfoxides are probably the fundamental reasons behind the change in mechanism in going from sulfur to phosphorus ylids and their respective reaction with carbonyl compounds.

The greater electron-withdrawing power of the dimethylsulfonium group over a trisubstituted phosphonium group would be expected to facilitate the displacement of the former from the C-9 carbon of fluorene. We have shown, for example, that dimethylfluorenylsulfonium bromide is hydrolyzed to fluorenol in aqueous solution whereas triphenyl- or trimethylfluorenylphosphonium bromide are inert under those conditions; hence, epoxide formation is favored in the sulfur case.

The solvent effect portrayed in Table II is of some interest. There is no correlation between dielectric constant or boiling point and the ratio of epoxide to alcohol produced. It can be seen, however, that in solvents of a basic nature alcohol is favored while in slightly acidic solvents epoxide formation is favored, though to a lesser degree. In neutral solvents the ratio of alcohol to epoxide is near 2:1. The exact nature of this solvent effect is unknown. It is possible that basic media facilitate the proton exchange from VI to IX thereby favoring alcohol formation. The unexpected isolation of the p-nitrobenzalfluorenes using acetonitrile and methyl sulfoxide solvents is being investigated further to clarify their mode of formation.

Reaction between the ylid IIa and nitrosobenzene gave the thermodynamically more stable product. The intermediate XIII could conceivably collapse to an oxazirane (XV) by oxyanion displacement of the sulfonium group as in the epoxide synthesis. Instead, the free electron pair on nitrogen is apparently the displacing agent, affording the nitrone XIV. Significantly, oxaziranes are thermally isomerized[18a] to the more stable valence tautomeric nitrones whereas the reverse isomerization is effected by photochemical excitation.[18b]

Henry and Wittig recently reported the formation of diphenylacetaldehyde (XVII) rather than the expected 1,1-diphenylethylene from the reaction of benzophenone with triphenylarsonium- or triphenylstibonium methylide.[23] They proposed that XVII arose by rearrangement of an intermediate (unisolable) 1,1-diphenylethylene oxide (XVIII), formed analogous to VIII. Cope,

                        O
                       ⁄ \
(C₆H₅)₂CHCHO   (C₆H₅)₂C—CH₂
      XVII   XVIII
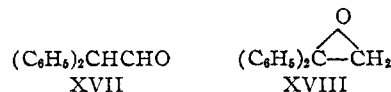
et al.,[24] have shown that XVIII will not rearrange to XVII under basic conditions (as are present in the above reaction) but will do so under mineral or Lewis acid conditions. Triphenylarsine is the only major constituent present under the conditions of Henry and Wittig which appears to have even a remote chance of catalyzing the rearrangement of XVIII to XVII. Since in our experiments with arsenic ylids IIe[1b] we obtained the normal

(20) R. Mechoulam and F. Sondheimer, This Journal, 80, 4386 (1958).

(21) C. K. Ingold, et al., J. Chem. Soc., 531, 533 (1933).

(22) C. A. VanderWerf, W. E. McEwen and M. Zanger, This Journal, 81, 3806 (1959).

(23) M. C. Henry and G. Wittig, ibid., 82, 563 (1960).

(24) A. C. Cope, P. A. Trumbull and E. R. Trumbull, ibid., 80, 2844 (1958).

olefin products rather than any carbonyl compounds, we wished to examine the discrepancy between their results and ours. Since we now had available epoxides related to products from a Wittig reaction, we checked their stability to triphenylarsine under Wittig's conditions. As expected, VIIIa was recovered unchanged in 94% yield after refluxing for several hours in a chloroform solution containing an equimolar quantity of triphenylarsine. It is conceivable that XVIII was actually produced in their reaction but rearranged in the course of working up the reaction (hydrolysis with 6 N hydrochloric acid). If such is not the case, it is obvious that the necessary oxygen transfer from carbon 1 to carbon 2 in the precursor of XVIII must have occurred *before* loss of the triphenylarsine group.

It is expected that most, if not all, sulfur ylids will react as did dimethylsulfonium fluorenylide, the major product being an epoxide. Use of hydrocarbon groups other than fluorenyl should eliminate formation of the alcohol X and should provide much more reactive ylids, thereby widening the scope and usefulness of the reaction. The full scope of this reaction and the preparation of other sulfur ylids is being investigated.

Acknowledgment.—We thank Dr. L. A. Pinck for a generous sample of XI.

Experimental[25]

9-Dimethylsulfonium Fluorenylide (IIa).—Dimethyl-9-fluorenylsulfonium bromide, m.p. 131–132°, was prepared in 99% yield according to Ingold's procedure.[6a] To 8.8 g. of this salt in 200 ml. of water was added 10% sodium hydroxide solution until precipitation was complete. The pale yellow solid was filtered then washed successively with water, 95% ethanol, absolute ethanol and ether. Drying *in vacuo* over P_2O_5 yielded 7.2 g. (82%) of ylid IIa, m.p. 120–122°; $\lambda_{max}^{CHCl_3}$ 251 mμ (log ϵ 4.6), 259 (4.8), 282 (3.7), 331 (3.2) and 368 (3.3) (lit. m.p. 70–75°,[6a] 126–127°[6b]).

Anal. Calcd. for $C_{15}H_{14}S$: C, 79.62; H, 6.23; S, 14.15. Found: C, 78.61; H, 6.57; S, 14.45.

The ylid hydrobromide had a pK_a of 7.3 in 31.7% water-dioxane.[1a] Boiling 0.25 g. of the hydrobromide in 20 ml. of water for 3 hours gave a precipitate of colorless needles (68%), m.p. 151.5–152.0°, identical to authentic fluorenol.

Chromatography of 0.34 g. of ylid IIa on 40 g. of alumina gave 0.10 g. (43%) of difluorenylidene, m.p. 193–195°, and 0.10 g. of fluorenone, m.p. 80–82°, both identical to authentic samples.

1-Methylthiomethylfluorene (III). A. From the Ylid IIa.—To a solution of 2 g. of sodium hydroxide in 20 ml. of methanol was added 0.55 g. of IIa and the mixture was heated under reflux for 4 hours. Water was added and the resultant precipitate was dried. Recrystallization from ethanol gave 0.45 g. (82%) of III as tan microcrystals, m.p. 73–75° (lit.[12] m.p. 77°).

Anal. Calcd. for $C_{15}H_{14}S$: C, 79.62; H, 6.23; S, 14.15. Found: C, 79.92; H, 6.38; S, 14.32.

Oxidation of III (0.11 g.) with 1.4 g. of sodium dichromate in acetic acid followed by quenching with water gave 0.07 g. (53%) of fluorenone-1-dimethyl sulfone (XI) which crystallized from ethanol as fine yellow needles, m.p. 191–192°, identical to an authentic sample.[12]

Anal. Calcd. for $C_{15}H_{12}SO_3$: C, 66.18; H, 4.44; S, 11.78. Found: C, 66.34; H, 4.64; S, 11.63.

B. From Methyl Fluorene-1-carboxylate.—Oxidation of 75 g. of fluoranthene with chromic acid[26] gave 48.5 g.

---

(25) Melting points are uncorrected. Analyses by Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y. All chromatograms used Merck alumina, No. 71707, as adsorbent. All comparisons with authentic samples were made by admixture melting point and infrared spectral determinations.

(61%) of fluorenone-1-carboxylic acid, m.p. 186–188° (lit.,[26] 191–193°). Reduction of 31 g. of this keto acid with hydrogen over 10% palladium-carbon in ethanol gave 22.9 g. (79%) of fluorene-1-carboxylic acid, m.p. 241–243° (lit.[26] m.p. 245°). Esterification of 8.0 g. of this acid by heating under reflux with methanol and sulfuric acid gave 7.9 g. (93%) of methyl fluorene-1-carboxylate which crystallized from ethanol as colorless needles, m.p. 84–85°, λ_{max} 1710 cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_{12}O_2$: C, 80.37; H, 5.38. Found: C, 80.50; H, 5.50.

Addition of 7.2 g. (0.032 mole) of methyl ester to a solution of 0.87 g. (0.023 mole) of lithium aluminum hydride in ether followed by gentle warming for 2 hours then decomposition of the alcoholate gave 5.6 g. (88%) of 1-hydroxymethylfluorene which crystallized from benzene as colorless needles, m.p. 145.5–146.5°, λ_{max} 3300 cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_{12}O$: C, 85.69; H, 6.16. Found: C, 85.91; H, 6.42.

To a stirred solution of 2.7 g. of phosphorus tribromide in 10 ml. of tetrahydrofuran was added 4.5 g. of the alcohol in 60 ml. of tetrahydrofuran at −5°. After 2 hours the temperature was raised to 20° and the solution stirred overnight. The solution was poured into water, the precipitate (5.3 g., 92%) collected and recrystallized from ethanol to afford 1-bromomethylfluorene as colorless needles, m.p. 100.5–102.0°.

Anal. Calcd. for $C_{14}H_{11}Br$: C, 64.88; H, 4.28; Br, 30.83. Found: C, 64.86; H, 3.99; Br, 30.97.

To a solution of 0.56 g. of sodium in 75 ml. of ethanol through which hydrogen sulfide had been passed was added 3.26 g. of the bromide. After warming for 2 hours and pouring into water 2.26 g. (85%) of crude 1-thiomethylfluorene was recovered. A sample crystallized from benzene as colorless plates, m.p. 173–175°.

Anal. Calcd. for $C_{14}H_{12}S$: C, 79.21; H, 5.70; S, 15.10. Found: C, 79.44; H, 5.65; S, 14.99.

A solution of 1.6 g. of crude thiol was dissolved in 10 ml. of 10% aqueous sodium hydroxide and 1.1 g. of methyl sulfate was added. After 1 hour of warming the solution was cooled and extracted with ether to afford 1.17 g. (69%) of crude III which was crystallized from ethanol as colorless microcrystals, m.p. 73–75°, identical to that formed in A above.

Reaction of the Ylid IIa with Aldehydes.—The following general procedure was used in all reactions. Equimolar quantities (5–10 mmoles) of the aldehyde and ylid IIa were added to 40 ml. of methylene chloride forming a dark red-brown solution. On warming, the color lightened to a clear orange. The solution was heated under reflux for 3 hours then the solvent was removed *in vacuo*. The semisolid residue was then chromatographed on alumina. The order of elution of the various products was: difluorenylidene and III, 25–50% benzene–hexane; fluorenone, 50–75% benzene–hexane; epoxide–benzene; alcohol–chloroform. All reactions were repeated in ether solution.

A. *p*-Nitrobenzaldehyde.—The aldehyde (1.34 g.) and the ylid (2.0 g.) were allowed to react in methylene chloride as above to afford 0.02 g. (2%) of difluorenylidene, m.p. 193–195°; 0.03 g. (2%) of III, m.p. 73–75°; traces of fluorenone; 1.10 g. (40%) of *p*-nitrobenzalfluorene oxide (VIIIa), which crystallized from hexane–ethanol as tan plates, m.p. 152–154°, identical to an authentic sample (*Anal.* Calcd. for $C_{20}H_{13}NO_3$: C, 76.19; H, 4.16; N, 4.44. Found: C, 76.42; H, 4.38; N, 4.37.); and 0.83 g. (25%) of *p*-nitrophenyl-9-(1-methylthiomethyl)-fluorenylcarbinol (Xa) which crystallized from benzene–ethanol as fine colorless needles, m.p. 194–195°.

Anal. Calcd. for $C_{22}H_{19}NO_3S$: C, 69.98; H, 5.07; S, 8.49; N, 3.71. Found: C, 70.27; H, 5.52; S, 7.33; N, 3.78.

To a solution of 0.56 g. of VIIIa in 15 ml. of acetic acid was added a solution of 2.0 g. of chromic acid in 2 ml. of water and 1 ml. of acetic acid and the solution was heated under reflux for 2 hours. It was then poured into water, basified and extracted with ether to afford 0.08 g. (25%) of fluorenone which crystallized from hexane as yellow

---

(26) L. F. Fieser and A. M. Seligman, THIS JOURNAL, 57, 2175 (1935).

needles, m.p. 81–82°, identical to an authentic sample. Acidification of the aqueous portion and ether extraction gave 0.24 g. (81%) of *p*-nitrobenzoic acid which crystallized from water as colorless microcrystals, m.p. 230–233°, identical to an authentic sample.

Pyrolysis of 0.25 g. of VIIIa with 0.21 g. of triphenylphosphine and a trace of hydroquinone for 10 minutes at 180° followed by chromatography gave 0.02 g. (7%) of *p*-nitrobenzalfluorene, m.p. 160–162°, identical to an authentic sample.

The carbinol Xa with benzoyl chloride in pyridine gave a benzoate which crystallized from ethanol as tan prisms, m.p. 192–192.5°, λ_{max} 1717 cm.$^{-1}$.

Anal. Calcd. for $C_{29}H_{23}NO_4S$: C, 72.51; H, 4.83; S, 6.67; N, 2.92. Found: C, 72.89; H, 5.23; S, 7.14; N, 3.32.

Heating under reflux a solution of 0.25 g. of Xa with 1 ml. of 30% hydrogen peroxide in 15 ml. of acetic acid for 2 hours followed by removal of the acetic acid and crystallization of the residue from a small amount of acetic acid gave *p*-nitrophenyl-9-(1-fluorenyldimethyl sulfone)-carbinol as fine colorless needles, m.p. 260–262°, λ_{max} 1295 and 1126 cm.$^{-1}$.

Anal. Calcd. for $C_{22}H_{19}NO_5S$: C, 64.52; H, 4.68; S, 7.83; N, 3.42. Found: C, 64.47; H, 5.77; S, 8.36; N, 3.68.

To 0.30 g. of Xa in 3 ml. of pyridine was added 0.25 g. of phosphorus oxychloride at ice temperature. The solution was warmed on a steam-bath for 2 hours then poured into ice-water forming a yellow precipitate (0.19 g., 65%) of *p*-nitrobenzal-(1-methylthiomethyl)-fluorene which crystallized from acetone as yellow microcrystals, m.p. 169–170°; λ_{max} 227, 262 and 352 mμ.

Anal. Calcd. for $C_{22}H_{17}NO_2S$: C, 73.50; H, 4.77; S, 8.92; N, 3.90. Found: C, 73.73; H, 4.99; S, 9.06; N, 4.18.

A solution of 0.75 g. of Xa was oxidized with chromic acid and worked up as for VIIIa above to afford 0.34 g. (100%) of *p*-nitrobenzoic acid, m.p. 229–231°, and 0.15 g. (28%) of fluorenone-1-dimethyl sulfone (XI), m.p. 197–198°, both identical to authentic samples.

Reaction of IIa and *p*-nitrobenzaldehyde in ethereal solution gave traces of difluorenylidene and III, 4% fluorenone, 3% of VIIIa and 83% of Xa. Reaction of IIa with *p*-nitrobenzaldehyde in acetonitrile solution gave 5% difluorenylidene, 25% of Xa, 10% of *p*-nitrobenzalfluorene, m.p. 167–168°, and 4% of *p*-nitrobenzal-(1-methylthiomethyl)-fluorene, m.p. 168–170°. Reaction of IIa with *p*-nitrobenzaldehyde in methyl sulfoxide gave a trace of difluorenylidene, 2% of III, 48% of Xa and 7% of *p*-nitrobenzal-(1-methylthiomethyl)-fluorene.

B. *m*-Nitrobenzaldehyde.—Reaction of 0.6 g. of ylid IIa with 0.4 g. of *m*-nitrobenzaldehyde in methylene chloride solution gave a trace of difluorenylidene; 0.3 g. (36%) of *m*-nitrobenzalfluorene oxide (VIIIb) which crystallized from ethanol as colorless microcrystals, m.p. 150–151°, identical to an authentic sample (*Anal.* Calcd. for $C_{20}H_{13}NO_3$: C, 76.19; H, 4.16; N, 4.44. Found: C, 76.64; H, 4.47; N, 4.65); and 0.32 g. (30%) of *m*-nitrophenyl-9-(1-methylthiomethyl)-fluorenylcarbinol (Xb) which crystallized from ethanol as colorless microcrystals m.p. 144.5–145.0°.

Anal. Calcd. for $C_{22}H_{19}NO_3S$: C, 69.98; H, 5.07; S, 8.49; N, 3.71. Found: C, 70.02; H, 5.02; S, 8.52; N, 3.90.

Oxidation of 0.5 g. of the carbinol Xb with chromic acid as described above afforded 0.13 g. (35%) of fluorenone-1-dimethyl sulfone, m.p. 200–201°, and 0.05 g. (13%) of fluorenone-1-carboxylic acid, m.p. 189–191°, both identical to authentic samples, and 0.15 g. (65%) of *m*-nitrobenzoic acid, which crystallized from benzene as a pale yellow powder, m.p. 141.5–143.0° (lit.[27] m.p. 140–141°).

Reaction of IIa and *m*-nitrobenzaldehyde in ethereal solution gave traces of difluorenylidene and III, 2% of fluorenone, 2% of VIIIb and 78% of Xb.

C. *o*-Nitrobenzaldehyde.—Reaction of 1.5 g. of ylid IIa with 1.0 g. of *o*-nitrobenzaldehyde in methylene chloride solution gave a trace of difluorenylidene; 0.04 g. (3%) of III, m.p. 76–77°; 0.59 g. (30%) of *o*-nitrobenzalfluorene oxide (VIIIc) which crystallized from ethanol–benzene as colorless

needles, m.p. 183–184°, identical to an authentic sample (*Anal.* Calcd. for $C_{20}H_{13}NO_3$: C, 76.19; H, 4.16; N, 4.44. Found: C, 76.24; H, 4.33; N, 4.47.); and 0.88 g. (35%) of *o*-nitrophenyl-9-(1-methylthiomethyl)-fluorenylcarbinol (Xc) which crystallized from ethanol–hexane as pale yellow prisms, m.p. 137–138°.

Anal. Calcd. for $C_{22}H_{19}NO_3S$: C, 69.98; N, 5.07; S, 8.49; N, 3.71. Found: C, 70.19; H, 4.74; S, 8.56; N, 3.87.

Oxidation of 0.75 g. of the carbinol Xc with chromic acid as described above afforded 0.22 g. (41%) of fluorenone-1-dimethyl sulfone, m.p. 197–199°, identical to an authentic sample, and 0.45 g. (54%) of *o*-nitrobenzoic acid which crystallized from water as pale yellow needles, m.p. 148.0–148.5° (lit.[27] m.p. 148°).

Reaction of IIa and *o*-nitrobenzaldehyde in ethereal solution gave a trace of III, 3% of VIIIc and 34% of Xc.

D. *p*-Cyanobenzaldehyde.—Reaction of IIa (1.5 g.) with 0.87 g. of *p*-cyanobenzaldehyde in methylene chloride solution gave 0.03 g. (3%) of difluorenylidene, m.p. 193–195°; 0.65 g. (33%) of *p*-cyanobenzalfluorene oxide (VIIId) which crystallized from ethanol as colorless needles, m.p. 152–152.5°, identical with an authentic sample (*Anal.* Calcd. for $C_{21}H_{13}NO$: C, 85.41; H, 4.44; N, 4.74. Found: C, 85.17; H, 4.53; N, 4.97); and 0.32 g. (29%) of *p*-cyanophenyl-9-(1-methylthiomethyl)-fluorenylcarbinol (Xd) which crystallized from benzene as colorless needles, m.p. 202–203°.

Anal. Calcd. for $C_{23}H_{19}NOS$: C, 77.25; H, 5.36; N, 3.92; S, 8.97. Found: C, 77.16; H, 5.37; N, 4.30; S, 8.94.

Oxidation of 0.75 g. of the carbinol Xd with chromic acid gave 0.17 g. (31%) of fluorenone-1-dimethyl sulfone, m.p. 197.5–198.5°, identical to an authentic sample, and 0.31 g. (77%) of *p*-cyanobenzoic acid which crystallized from water as colorless plates, m.p. 210–212° (lit.[28] m.p. 219°).

Reaction of IIa and *p*-cyanobenzaldehyde in ethereal solution gave a trace of III, 2% of difluorenylidene, 2% of VIIId and 64% of Xd.

E. 2,4-Dichlorobenzaldehyde.—Reaction of IIa (1.5 g.) with 1.16 g. of 2,4-dichlorobenzaldehyde in methylene chloride solution gave 0.67 g. (30%) of 2,4-dichlorobenzalfluorene oxide (VIIIe) which crystallized from ethanol–benzene, propanol or acetone as colorless prisms, m.p. 188.5–190°, identical with an authentic sample (*Anal.* Calcd. for $C_{20}H_{12}Cl_2O$: C, 70.81; H, 3.57; Cl, 20.90. Found: C, 71.05; H, 3.47; Cl, 20.70); and 0.86 g. (33%) of oily 2,4-dichlorophenyl-9-(1-methylthiomethyl)-fluorenylcarbinol (Xe), λ_{max} 3440 cm.$^{-1}$ (the yield was estimated from benzoate formation and the dehydration reaction). A benzoate crystallized from ethanol as tan microcrystals, m.p. 146–147°.

Anal. Calcd. for $C_{29}H_{22}Cl_2O_2S$: C, 68.92; H, 4.39; S, 6.34; Cl, 14.03. Found: C, 69.19; H, 4.66; S, 6.06; Cl, 13.56.

Recrystallization of the epoxide VIIIe from absolute ethanol gave 9-(2,4-dichlorophenylethoxy)-methyl-9-hydroxyfluorene (XII) as colorless clusters, m.p. 135.5–136.5°, λ_{max} 3420 cm.$^{-1}$.

Anal. Calcd. for $C_{22}H_{18}Cl_2O_2$: C, 68.57; H, 4.71; Cl, 18.41. Found: C, 68.80; H, 4.77; Cl, 18.34.

Dehydration of 0.25 g. of XII with 0.15 ml. of phosphorus oxychloride in pyridine gave 0.18 g. (76%) of ω-ethoxy-ω-(2,4-dichlorophenyl)-dibenzofulvene which crystallized from ethanol as colorless needles, m.p. 170–171°; λ_{max} 258 mμ (log ϵ 4.8), 293 (4.1), 303 (4.1) 336 (2.9) and 353 (2.9).

Anal. Calcd. for $C_{22}H_{16}Cl_2O$: C, 71.93; H, 4.39; Cl, 19.31. Found: C, 72.22; H, 4.48; Cl 19.11.

Dehydration of 1.0 g. of alcohol Xe with 0.5 ml. of phosphorus oxychloride in pyridine gave 2,4-dichlorobenzal-(1-methylthiomethyl)-fluorene (59%) which crystallized from ethanol as pale yellow needles, m.p. 121–122°; λ_{max} 229 mμ (log ϵ 3.7), 253 (3.5), 262 (3.6) and 315 (3.1).

Anal. Calcd. for $C_{22}H_{16}Cl_2S$: C, 68.91; H, 4.21; Cl, 18.50; S, 8.36. Found: C, 69.11; H, 4.36; Cl, 18.47; S, 8.60.

Oxidation of 0.44 g. of the alcohol Xe with chromic acid gave 0.08 g. (27%) of fluorenone-1-dimethyl sulfone, m.p. 197–199°, identical to an authentic sample, and 0.22 g.

(27) L. W. Bass and T. B. Johnson, This Journal, **46**, 460 (1924).

(28) P. Kattwinkel and R. Wolffenstein, *Chem. Ber.*, **34**, 2423 (1901).

(52%) of 2,4-dichlorobenzoic acid which crystallized from benzene as colorless microcrystals, m.p. 158–159° (lit.[29] m.p. 161–162°).

Reaction of IIa with 2,4-dichlorobenzaldehyde in ethereal solution gave 3% of VIIIe and 26% of Xe.

F. Acetaldehyde.—Reaction of 1.5 g. of ylid IIa with 0.9 g. of acetaldehyde in methylene chloride (sealed tube) gave an oily alcohol Xf (45%), λ_{max} 3390 cm.$^{-1}$. It formed a benzoate which crystallized from ethanol as colorless prisms, m.p. 141.5–143.5°.

Anal. Calcd. for $C_{24}H_{22}O_2S$: C, 76.97; H, 5.92; S, 8.56. Found: C, 76.99; H, 5.95; S, 8.27.

Oxidation of 0.1 g. of the benzoate with chromic acid gave 0.03 g. (92%) of benzoic acid, m.p. 120–121°, identical to an authentic sample, and 0.01 g. (15%) of fluorenone-1-dimethyl sulfone.

Dehydration of 0.6 g. of the carbinol Xf with 0.4 ml. of phosphorus oxychloride in pyridine gave a low yield of an oil whose ultraviolet spectrum, λ_{max} 257 mμ, was compatible with its formulation as 9-ethylidene-1-methylthiomethyl-fluorene.

Synthesis of Benzalfluorene Oxides (VIII).—In a representative synthesis 2.5 g. (0.01 mole) of 9-bromofluorene,[30] 1.34 g. (0.01 mole) of *p*-cyanobenzaldehyde and 1.0 g. of potassium carbonate in 30 ml. of methanol were heated under reflux with stirring for 2.5 hours. Water was added, the precipitate washed thoroughly with water then the *p*-cyanobenzalfluorene oxide (VIIId) (2.0 g., 66%) crystallized from ethanol as colorless needles, m.p. 152–154°. The following were prepared in an identical manner (see above for analyses): *p*-nitrobenzalfluorene oxide (VIIIa), 50% yield, m.p. 152–154° (lit.[16] 153°); *m*-nitrobenzalfluorene oxide (VIIIb), 41%, m.p. 150–151°; 2,4-dichlorobenzalfluorene oxide (VIIIe), 57%, m.p. 187–189°; *p*-chlorobenzalfluorene oxide, 50%, m.p. 140–141°.

o-Nitrobenzalfluorene oxide could not be prepared in the above manner, the starting materials being recovered unchanged. The following method was then employed. Reduction of 10 g. of *o*-nitrobenzaldehyde in 100 ml. of methanol with 1.3 g. of sodium borohydride for 1 hour at room temperature followed by quenching with water gave 9.5 g. (94%) of *o*-nitrobenzyl alcohol which crystallized from water as colorless needles, m.p. 71.5–73° (lit.[31] m.p. m.p. 74°). To 6.0 g. of this alcohol in 90 ml. of ether was added 8.0 g. of phosphorus tribromide over 0.5 hour at −10° with stirring. The solution was then heated under reflux for 2 hours then quenched with water. Evaporation of the ether layer gave 6.5 g. (77%) of *o*-nitrobenzyl bromide which crystallized from aqueous ethanol as colorless plates, m.p. 44–46° (lit.[32] m.p. 46–47°). Condensation of 4.5 g. of fluorenone with 4.3 g. of *o*-nitrobenzyl bromide in 50 ml. of methanol containing 2.0 g. of potassium carbonate, followed by chromatography, gave 0.05 g. (10% based on unrecovered fluorenone) of *o*-nitrobenzalfluorene oxide (VIIIc) which crystallized from ethanol–benzene as colorless needles, m.p. 185–187° (lit.[16] m.p. 111°).

Reaction of the Ylid IIa with Nitrosobenzene.—A solution of 1.5 g. of ylid IIa and 0.71 g. of nitrosobenzene in 35 ml. of methylene chloride was heated under reflux for 3 hours after which the yellow precipitate (1.7 g., 94%) was filtered. Recrystallization from ethanol gave N-phenylfluorenone ketoxime (XIV) as yellow needles, m.p. 192–193°. The same reaction in ethereal solution gave XIV in 96% yield.

Anal. Calcd. for $C_{19}H_{13}NO$: C, 84.11; H, 4.83; N, 5.16. Found: C, 84.30; H, 4.84; N, 5.29.

Hydrolysis of XIV by stirring in an aqueous ethanolic solution of 6 N sulfuric acid at room temperature for 8 hours gave a quantitative yield of fluorenone, m.p. 81–82°, identical to an authentic sample. Chromatography of XIV on alumina effected hydrolysis of 50% of the sample.

N-Phenylfluorenone Ketoxime (XIV).—To 5.0 g. of 9-bromofluorene[30] in 15 ml. of benzene was added 5 ml. of pyridine. The solution was heated under reflux for 4 hours then cooled overnight affording a precipitate of 3.9 g. (62%) of 1-(9-fluorenyl)-pyridinium bromide, m.p. 194–197° (lit.[17] m.p. 199–200°). To a solution of 0.32 g. of this bromide and 0.1 g. of nitrosobenzene in 10 ml. of ethanol was added 1 ml. of 10% aqueous sodium hydroxide. Quenching with water after 2 minutes gave 0.25 g. (93%) of XIV, identical to that prepared from IIa (above).

(29) E. Roberts and E. E. Turner, *J. Chem. Soc.*, 1846 (1927).
(30) G. Wittig and G. Felletschin, *Ann.*, **555**, 133 (1944).
(31) F. Schenck, *Chem. Ber.*, **67**, 1571 (1934).
(32) J. F. Norris, M. Watt and R. Thomas, THIS JOURNAL, **38**, 1077 (1916).

The Stereochemistry of the Chromic Acid Oxidation of Tertiary Hydrogens[1]

BY KENNETH B. WIBERG AND GORDON FOSTER

The chromic acid oxidation of (+)-3-methylheptane in 91% acetic acid gave (+)-3-methyl-3-heptanol with 70–85% retention of configuration. The reaction showed a kinetic isotope effect. The mechanistic implications of these and related data are discussed.

We have recently studied the chromic acid oxidation of diphenylmethane in 91–95% acetic acid[2] and have obtained evidence that the reaction involves the formation of the benzhydryl radical in the first step. The data did not, however, permit us to determine the nature of the succeeding steps leading to benzophenone. In order to be better able to obtain information of this type, we have now investigated the oxidation of a hydrocarbon with one tertiary hydrogen. Here, based on the work of Sager and Bradley,[3] we would expect to be able to study the oxidation of the hydrocarbon to the tertiary alcohol.

The information on the oxidation of compounds of this type is meager. However, both Roček,[4] and Sager and Bradley[3] agree that the predominate reaction is the attack at the tertiary hydrogen, that the alcohol is the first isolable compound to be formed, and that further reaction involves the rate-controlling dehydration of the alcohol. The latter authors also observed a kinetic isotope effect, indicating that carbon–hydrogen bond cleavage occurred in the rate-determining step.

As in the case of the oxidation of diphenylmethane,[2] the rate-determining step may involve any one of the five reactions

(2) K. B. Wiberg and R. J. Evans, *Tetrahedron*, **8**, 313 (1960).
(3) W. F. Sager and A. Bradley, THIS JOURNAL, **78**, 1187 (1956).
(4) J. Roček, *Coll. Czech. Chem. Comm.*, **22**, 1509, 1519 (1952).