and a flow rate of 50 ml of helium per minute satisfactorily separated all components of most alkylation mixtures. In the cases of poor separation, a 2-m Ucon 50 column was an excellent substitute. A second sample was subjected to acid hydrolysis. The peak that disappeared was *O*-alkyl product, that which increased, starting ketone, and that which remained constant, *C*-alkyl material. A chromatographic analysis on the original reaction mixture before quenching showed that equal partitioning of O and C product had occurred during extraction. Glpc products from the alkylation of sodiobutyrophenone by isobutyl chloride were trapped in liquid nitrogen, dissolved separately in carbon tetrachloride, and rechromatographed. No degradation of products or isomerization of enol ether could be detected.

Cesiobutyrophenone.—To 1.8 g (8.0×10^{-3} mol) of cesium graphite (Callery Chemical Co.) and a few crystals of triphenylmethane in the reaction flask was added 100 ml of dry dimethyl sulfoxide. Immediate evolution of heat and precipitation of carbon occurred. The clear, red solution from which the carbon had settled upon standing was treated with 1.0 ml (6.6×10^{-3} mol) of butyrophenone and 5.0 ml (4.13×10^{-2} mol) of *n*-amyl chloride. After stirring for 3 hr the solution was filtered and analyzed as described above.

The Action of Sulfuric Acid on Ethyl 3,3-Diphenyl-3-hydroxypropanoate

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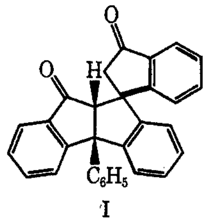
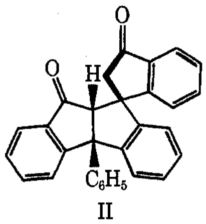
The reaction of sulfuric acid with ethyl 3,3-diphenyl-3-hydroxypropanoate gave *cis*- and *trans*-spiro[indan-1-one-3,10'-[4b,9a]dihydro-4b-phenylindeno[1,2-*a*]inden-9-one]. The structures were based on spectral data and chemical reactions. Pyrolysis of the monobromo derivatives gave benz[*a*]indeno[1,2-*c*]fluorene-9,14-dione and 7b,12-dihydro-7b-phenyldibenz[*cd,f*]indeno[2,1-*a*]azulene-12,14-dione. The former compound was also obtained by treating the trans isomer with aluminum chloride in nitrobenzene and was synthesized from benzo[*c*]fluorene.

The unusual dimerization observed in attempts to prepare 2-phenylindenone[3] suggested a study of the structures of the products obtained by the action of sulfuric acid on ethyl 3,3-diphenyl-3-hydroxypropanoate. These products have been formulated as dimers of 3-phenylindenone involving cyclobutane rings.[4-6]

In agreement with these investigations, the action of sulfuric acid on ethyl 3,3-diphenyl-3-hydroxypropanoate gave isomeric ketones melting at 255–259° (I) and 224–226° (II). The nmr spectra of these two compounds were not in agreement with the truxone structures postulated.[4,5] Isomer I gave a singlet at δ 3.88 (1 H), half of an AB quartet at δ 3.84 (J = 19 cps) (1 H), and the other half at δ 2.58 (J = 19 cps) (1 H). Isomer II showed a singlet at δ 3.51 (1 H) and a singlet at δ 3.08 (2 H). These spectra, together with the ir and mass spectral data, are better accommodated by formulation of these compounds as *trans*- and *cis*-spiro[indan-1-one-3,10'-[4b,9a]dihydro-4b-phenylindeno[1,2-*a*]inden-9-one] (I, II).[7]



I

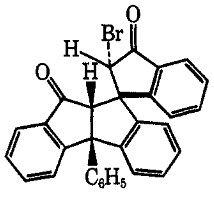


II

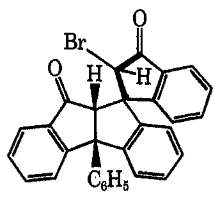
In II the methylene hydrogens are in a similar magnetic environment and appear, fortuitously, as a singlet. The environments of these two protons in isomer I are different since one of the methylene hydrogens is deshielded by the carbonyl grouping and an AB quartet is therefore observed.

Further evidence for these structures is derived from chemical behavior of the two isomeric diketones and the spectra of the products formed. In agreement with the spiran structure, isomer I was stable to chloranil and dichlorodicyanoquinone in refluxing benzene. Treatment with palladium on carbon in boiling cymene and at 250–260° effected no dehydrogenation.

The trans isomer I when treated with bromine in acetic acid gave a monobromo derivative which showed nmr spectral properties consistent with structure III.



III



IV

The 2 hydrogen appeared at δ 6.10 ppm and the 9a hydrogen (δ 3.83 ppm) showed very little change from its value in the parent compound I. The large downfield shift observed for the 2 hydrogen suggests that deshielding occurs both by the carbonyl group and the bromine atom. The structure III shown would result from the expected attack of the bromine on the less hindered side of the methylene carbon.

Cis isomer II formed a monobromo (IV) and a *gem*-dibromo compound. The nmr spectrum for IV indicates that the 2-bromo substituent must be on the same side as the 9a hydrogen since the relative shifts for the 9a hydrogen resulting from the consecutive introduction of bromine atoms is larger for the first bromine atom (0.70 ppm) than for the second (0.24 ppm). The reason for the preferential attack by the bromine may be steric.

Dehydrohalogenation of the monobromo products could only be accomplished by pyrolysis and led to the rearranged products, benz[*a*]indeno[1,2-*c*]fluorene-9,-

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[1] To whom inquiries should be addressed.

[2] Abstracted in part from the Ph.D. Thesis of N. A. R., May 1970.

[3] S. Wawzonek, G. R. Hansen, and Z. R. Zigman, *Chem. Commun.*, 6 (1969).

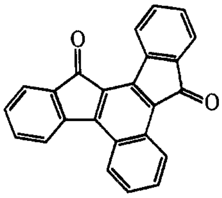
[4] F. DeFazi, *Gazz. Chim. Ital.*, **49**, 253 (1919).

[5] R. Stoermer and G. Foerster, *Chem. Ber.*, **52**, 1255 (1919).

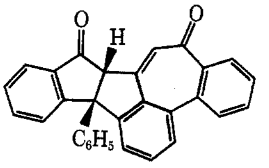
[6] B. W. Rockett and C. H. Hauser, *J. Org. Chem.*, **29**, 1394 (1964).

[7] Cis and trans refer to the relationship of the hydrogen at C-9a, and the methylene group at spiro C-10.

14-dione (V) and a compound which may be 7b,12-dihydro-7b-phenyldibenz[*cd,f*]indeno[2,1-*a*]azulene-12,-14-dione (VI). The structure of V is based on a comparison with an authentic sample synthesized from benzo[*c*]fluorene. The formulation for VI is solely based on ir and nmr spectra; VI showed bands at 5.84 and 6.03 μ for the carbonyl groups and aromatic bands corresponding to three, four, and five adjacent aromatic hydrogens. The nmr spectrum showed a one-proton singlet at δ 3.31 in addition to the 17 aromatic protons.

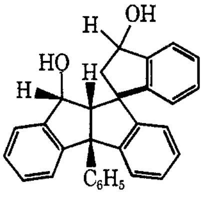


V

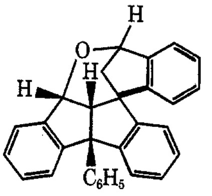


VI

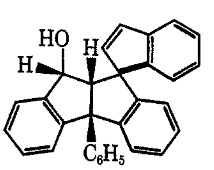
Reduction of the trans isomer I with aluminum isopropoxide gave two isomeric diols VII and a pyran VIII. The structures of the diols VII and the pyran were consistent with the spectral data. The assignment of a cis structure to the 9a,9 hydrogens in VII is based on the coupling constant of 6.5 cps observed for these two atoms. This value is only slightly less than that (7.5 cps) observed for the same hydrogens in the pyran VIII. The latter, for steric reasons, must be cis.



VIIa,b



VIII



IX

The higher melting diol VIIa (223–228°), upon heating above its melting point, gave the pyran VIII and an unsaturated alcohol, *trans*-spiro[(3*H*)-indene-3,10′-(9′*H*)-4b,9a-dihydro-9-hydroxy-4b-phenylindeno[1,2-*a*]indene] (IX). This latter formulation is based on the nmr spectrum. This diol VIIa is probably also the precursor of the pyran VIII isolated in the work-up of the aluminum isopropoxide reduction product.

The formation of the pyran VIII by acid catalysis and thermolysis of the diol VIIa suggests that the 1-hydroxyl group is trans to the 9-hydroxyindan system. Such a formulation is based on the report of the formation of 1,4-epoxycyclohexane from *trans*-1,4-cyclohexanediol in the presence of aluminum oxide.[8]

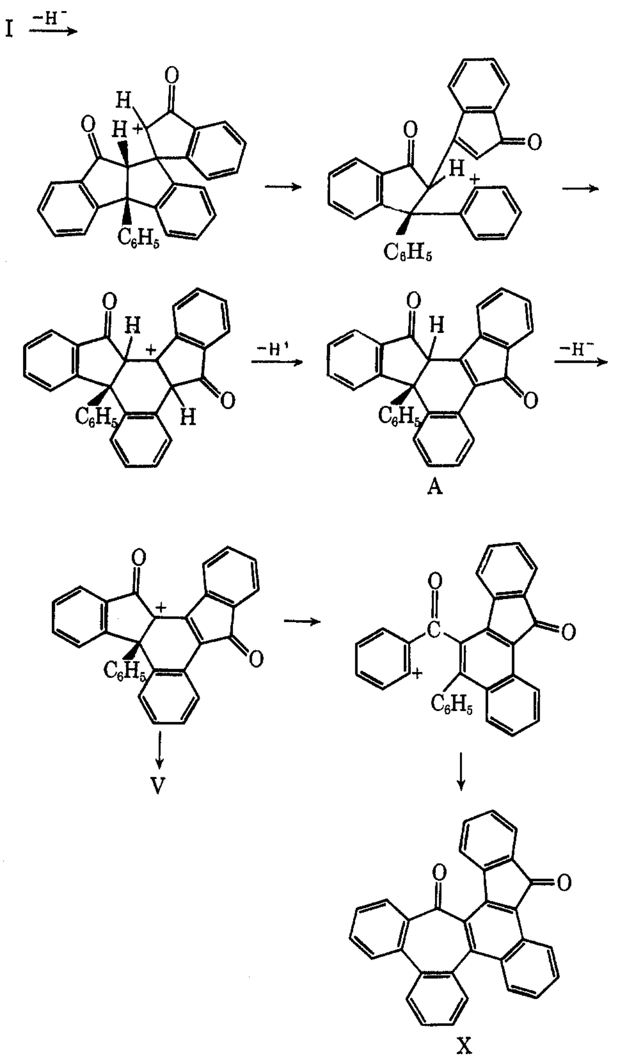
The lower melting diol VIIb in the same pyrolysis gave a mixture of products, which according to tlc analysis, consisted of six products; one of these was apparently the pyran. This mixture was not investigated further. This behavior would be consistent with a cis configuration for the 1-hydroxyl group.

Reduction of the trans isomer I by the Wolff–Kishner method gave *trans*-spiro[indan-3,10′(9′*H*)-4b,9a-dihydro-4b-phenylindeno[1,2-*a*]indan];[4] nmr studies involving decoupling of the benzylic hydrogens substantiated this formulation.

The trans isomer I could be rearranged by treatment with aluminum chloride in refluxing nitrobenzene to V and a compound which may be dibenz[*d,f*]cycloheptene-[2,3:6′,5′]benz[*c*]fluorene-5,18-dione (X). The structure of X was based solely on spectral data.

A solution of isomer I in nitrobenzene when boiled under reflux without added aluminum chloride gave only V. The cis isomer II gave only X when treated with aluminum chloride in nitrobenzene. These products could arise by the steps shown in Scheme I.

Scheme I



The apparent hydride abstraction invoked in the first step may proceed through one-electron transfers in nitrobenzene or by a direct hydride transfer to aluminum chloride in its complex with the ketone I. Such a transfer has been considered as a possibility in the isomerization of labeled 1-chloropropane.[9] The resulting carbonium ion would rearrange and lose a proton to form intermediate A. This intermediate could lose benzene by a similar mechanism and form V or could rearrange to a carbonium ion that would form X.

None of the reactions involved in this mechanism is without analogy. The use of nitrobenzene as a dehydrogenating agent is well known with nitrogen compounds.[10] Aluminum chloride converts β,β-di(*p*-chlorophenyl)propiophenone in benzene to β,β-diphenylpro-

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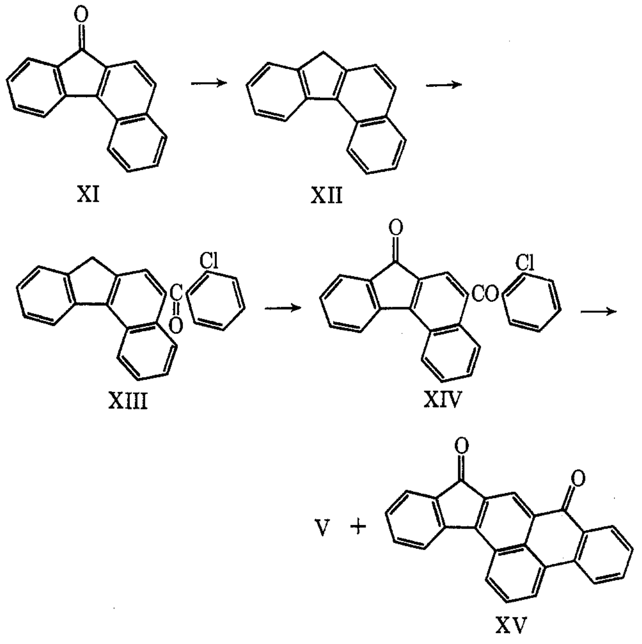
(8) H. Pines and W. O. Haag, *J. Amer. Chem. Soc.*, **83**, 2847 (1961).

(9) C. C. Lee and D. J. Woodcock, *ibid.*, **92**, 5992 (1970).

(10) R. B. Herbert, F. G. Holliman, and J. D. Kynnersley, *Tetrahedron Lett.*, 1907 (1968).

piophenone[11] probably by similar steps to those postulated.

An authentic sample of benz[*a*]indeno[1,2-*c*]fluorene-9,14-dione (V) was prepared from benzo[*c*]fluorenone (XI)[12] by the following series of reactions.



Treatment of benzo[*c*]fluorene (XII) with aluminum chloride and *o*-chlorobenzoyl chloride gave 5-(*o*-chlorobenzoyl)benzo[*c*]fluorene (XIII) in a 53% yield. Structure assignment was based on its ir and nmr spectra. Compound XIII had absorption bands at 6.09 μ for a diaryl ketone group and at 11.70 μ for one isolated aromatic hydrogen atom in the infrared spectrum.

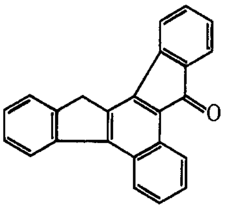
The nmr spectrum had a quartet corresponding to the 4 proton at δ 8.90. The deshielding observed is large and comparable to that reported (δ 9.02) for the 8 hydrogen in 1-(4-methoxynaphthyl)methyl ketone.[13] Two quartets were observed for the 1 and 11 hydrogens at δ 8.66 and 8.25 in agreement with the values of δ 8.61 and 8.25 found for benzo[*c*]fluorene. The assignment of the quartet at δ 8.66 to the 1 hydrogen was based on similar coupling constants to those for the quartet for the 4 hydrogen. The 6 hydrogen and 7-methylene group appeared as singlets at δ 7.59 and 3.70, respectively, and the remaining nine aromatic protons appeared as a multiplet at δ 7.40.

Two other products were isolated in this reaction and on the basis of spectral data are 9-(*o*-chlorobenzoyl)benzo[*c*]fluorene and 5,9-di(*o*-chlorobenzoyl)benzo[*c*]fluorene. The formulation of the first compound is based on the nmr spectrum; the 11 hydrogen at δ 8.15 appeared as a doublet in contrast to the quartet found for the same hydrogen in 5-(*o*-chlorobenzoyl) [*c*]fluorene (XIII). Such a behavior would result if the coupling by the 9 hydrogen were absent.

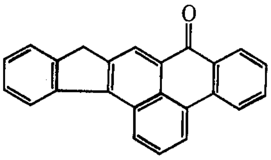
The second sample according to mass spectral analysis and nmr was impure 5,9-di(*o*-chlorobenzoyl)benzo[*c*]fluorene. The latter gave a ratio of 15.6 aromatic hydrogens to two aliphatic ones, a multiplet corresponding to two hydrogens at δ 8.67, and a doublet at δ 8.30 for one hydrogen. This sample was difficult to purify and was not studied further.

The structure of XIII was confirmed by subsequent chemical reactions. Oxidation of XIII with dichromate gave 5-(*o*-chlorobenzoyl)benzo[*c*]fluorenone (XIV), which cyclized upon treatment with sodium hydroxide in aqueous quinoline at elevated temperature to give V and benz[*de*]indeno[2,1-*b*]anthracene-8,10-dione (XV).

Cyclization of XIII directly with sodium hydroxide in aqueous quinoline gave 14-hydrobenzo[*a*]indeno[1,2-*c*]fluoren-9-one (XVI) and 10-hydrobenz[*de*]indeno[2,1-*b*]anthracen-8-one (XVII). The amount of XVI obtained was, however, insufficient for oxidization to V. Compound XVII, although difficult to obtain pure, gave XV when treated with potassium dichromate.

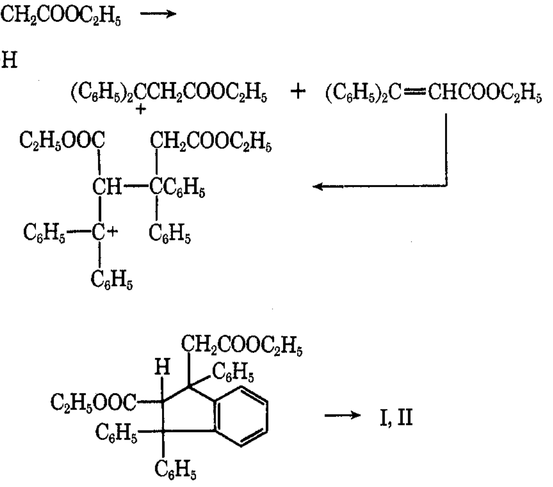


XVI



XVII

The formation of the spiro compounds I and II in the reaction of sulfuric acid with ethyl 3,3-diphenyl-3-hydroxypropanoate can be explained by the following sequence of reactions.



Dehydration of the hydroxy ester to ethyl 3,3-diphenyl-2-propenoate followed by an acid-catalyzed dimerization could lead to an intermediate capable of undergoing three cyclizations to form the spiro compounds I and II. 3-Phenylindenone, if it is formed as an intermediate in this reaction, might be expected to dimerize in the same manner.

Experimental Section[14]

***cis*-Spiro[indan-1-one-3,10′-[4b,9a]dihydro-4b-phenylindeno[1,2-*a*]inden-9-one] (II) and *trans*-Spiro[indan-1-one-3,10′-[4b,9a]dihydro-4b-phenylindeno[1,2-*a*]inden-9-one] (I).**—To 40.0 g of ethyl 3,3-diphenyl-3-hydroxypropanoate[15] was added 160 ml of concentrated sulfuric acid. Initial addition of acid to the ester

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[11] J. T. Eaton, D. B. Black, and R. C. Fuson, *J. Amer. Chem. Soc.*, **56**, 687 (1934).

[12] A. Schaarschmidt, *Ber.*, **49**, 1444 (1916).

[13] G. O. Dudek, *Spectrochim. Acta*, **19**, 691 (1963).

[14] Melting points are corrected. Nmr spectra were determined using Varian A-60 and HA-100 spectrophotometers. Mass spectra were obtained on a Hitachi RMUGE mass spectrometer.

[15] H. Rupe and E. Busolt, *Chem. Ber.*, **40**, 4539 (1907).

gave a yellow color which quickly turned to a deep emerald green. After standing at room temperature for 24 hr with occasional stirring, the dark, syrupy solution was slowly poured into 2.5 l. of ice and water with vigorous stirring, and the resulting white precipitate was filtered and taken up in hot absolute ethanol. The insoluble material A was filtered and the filtrate on cooling gave 10.36 g of white crystals, mp 210–245°. Upon further concentration of the filtrate, a second crop (3.11 g) was obtained, melting at 220–226°, and a third crop (2.02 g), melting at 203–211°. The first crop upon recrystallization from absolute ethanol gave 5.44 g of *trans*-spiro[indan-1-one-3,10′-[4b,9a]dihydro-4b-phenylindeno[1,2-*a*]inden-9-one] (I), mp 255–257° (lit.[4] 252–253°). Further concentration of this solution gave a mixture of the two isomers.

The insoluble product A upon recrystallization from absolute ethanol gave an additional 6.22 g of the trans isomer I: mp 255–257°; ir (Nujol) 5.85 (C═O), 5.98 (C═O), 14.20 μ (phenyl); nmr ($CDCl_3$) δ 7.51 (m, 17 aromatic H), 3.88 (s, CHCO), 3.84 (d, 1 H, J = 19 cps, CH_2CO), 2.58 (d, 1 H, J = 19 cps, CH_2CO); mass spectrum (70 eV) m/e (parent peak) 412.

Anal. Calcd for $C_{30}H_{20}O_2$ (412.44): C, 87.35; H, 4.88. Found: C, 87.41; H, 4.97.

A mixture of the two isomers (6 g, mp 202–212°) was chromatographed on a column containing 400 g of silica gel with benzene as the solvent. The trans isomer I (1.42 g) eluted first and was followed by 1.30 g of a mixture of the two isomers melting at 190–205°. *cis*-Spiro[indan-1-one-3,10′-[4b,9a]dihydro-4b-phenylindeno[1,2-*a*]inden-9-one] (II) (4.38 g) was eluted last. An analytical sample was obtained by recrystallization from ethyl acetate: mp 223.5–225° (lit.[4] 224°); ir (Nujol) 5.82 (C═O), 14.30 μ (phenyl); nmr ($CDCl_3$) δ 7.23 (m, 17 aromatic H), 3.51 (s, CHCO), 3.09 (s, 2 H, CH_2CO); mass spectrum (70 eV) m/e (parent peak) 412.

Anal. Calcd for $C_{30}H_{20}O_2$ (412.44): C, 87.35; H, 4.88. Found: C, 87.72; H, 4.83.

The total yield of products isolated was 23.39 g (76.7%).

***trans*-Spiro[2-bromoindan-1-one-3,10′-[4b,9a]dihydro-4b-phenylindeno[1,2-*a*]inden-9-one] (III).**—The trans isomer I (5.0 g) dissolved in glacial acetic acid (1 l.) was treated dropwise with a solution of bromine (2.1 g) in 60 ml of glacial acetic acid over a period of 4 hr. Removal of the solvent at reduced pressure was followed by two additions of toluene and removal of this solvent. The resulting white solid was taken up in 75 ml of hot benzene and the white crystals obtained on cooling were recrystallized from ethyl acetate: yield 2.9 g; mp 250–252° dec; ir (Nujol) 5.73 (C═O), 5.83 (C═O), 14.25 μ (phenyl); nmr ($CDCl_3$) δ 7.42 (m, 17 aromatic H), 6.10 (s, C(Br)HCO), 3.83 (s, CHCO).

Anal. Calcd for $C_{30}H_{19}BrO_2$: C, 73.35; H, 3.90. Found: C, 73.54; H, 3.99.

A second crop of III was obtained by concentrating the filtrate and adding petroleum ether (bp 60–68°), yield 2.1 g, mp 247.5–249°. The combined yield was 5.0 g.

***cis*-Spiro[2-bromoindan-1-one-3,10′-[4b,9a]dihydro-4b-phenylindeno[1,2-*a*]inden-9-one] (IV).**—The cis isomer II (2.00 g) in glacial acetic acid (1 l.) was treated dropwise with 1.70 g of bromine. The resulting solution was allowed to stand overnight and the solvent was removed at reduced pressure. The solid obtained upon recrystallization from benzene melted at 229–230° dec: yield 1.64 g; ir (Nujol) 5.73 (C═O), 5.82 (C═O), 14.28 μ (phenyl); nmr ($CDCl_3$) δ 7.38 (m, 17 aromatic H), 5.28 (s, CH(Br)CO), 4.21 (s, CHCO).

Anal. Calcd for $C_{30}H_{19}BrO_2$: C, 73.35; H, 3.90. Found: C, 73.55; H, 3.74.

***cis*-Spiro[2,2-dibromoindan-1-one-3,10′-[4b,9a]dihydro-4b-phenylindeno[1,2-*a*]inden-9-one].**—Bromine (4.64 g) in 50 ml of chloroform was added dropwise to a stirred solution of 5.36 g of II in 200 ml of chloroform. After 12 hr 2.06 g of pyridine was added to the reaction mixture, followed by 0.46 g of bromine. The reaction mixture, after being allowed to stand for another 12 hr, was washed with water and the solvent was removed. The resulting solid when recrystallized from benzene melted at 269–270° dec: yield 5.27 g; ir (Nujol) 5.73 (C═O), 5.81 (C═O), 14.32 μ (phenyl); nmr ($CDCl_3$) δ 7.47 (m, 15 aromatic H), 6.30 (m, 2 aromatic H), 4.45 (s, CHCO).

Anal. Calcd for $C_{30}H_{18}Br_2O_2$: C, 63.18; H, 3.18. Found: C, 63.23; H, 3.10.

The dibromo compound was also obtained by treating IV with bromine and pyridine in glacial acetic acid or with bromine in chloroform.

Pyrolysis of *trans*-Spiro[2-bromoindan-1-one-3,10′-[4b,9a]dihydro-4b-phenylindeno[1,2-*a*]inden-9-one].—The bromo compound III (1.00 g) was heated at 270–280° for 1 hr under nitrogen. The products from two such reactions were chromatographed on 200 g of alumina with 50% petroluem ether (bp 60–68°) –benzene as the starting solvent. The first component eluted was recrystallized twice from benzene and once from ethyl acetate and gave 0.01 g (0.73%) of orange crystals of benz[*a*]indeno[1,2-*c*]fluorene-9,14-dione (V), mp 244–246.5°. Purification by sublimation under reduced pressure gave a sample melting at 246–247.5°: ir (KBr) 5.84 (C═O), 5.88 μ (C═O); nmr (HA-100) ($CDCl_3$) δ 8.93 (pseudo d[16], 13 H, J = 7 cps), 8.20 (pseudo d, 10 or 1 H, J = 7 cps), 7.88 (pseudo d, 10 or 1 H, J = 8 cps), 7.40 (pseudo A_2B_2 system, 8 aromatic H); mass spectrum (70 eV) m/e (parent peak) 332.

Anal. Calcd for $C_{24}H_{12}O_2$ (332): C, 86.73; H, 3.64. Found: C, 86.61; H, 3.63.

The second component when recrystallized twice from benzene gave 0.05 g (3.65%) of red crystals, mp 313.5–316°. This solid when recrystallized once from ethyl acetate gave orange needles of 7b,12a-dihydro-7b-phenyldibenz[*cd*,*f*]indeno[2,1-*a*]azulene-12,14-dione (VI) melting at 313–315.5°: ir (KBr) 5.82, 5.85 (C═O), 6.03 (C═O), 12.80 (three adjacent aromatic hydrogens), 14.18 μ (phenyl); nmr ($CDCl_3$) (HA-100) δ 8.49 (apparent t, 1 aromatic H), 7.99 (d, J = 8 cps, 1 aromatic H), 7.69 (d, J = 7 cps, 1 aromatic H), 7.10 (m, 14 aromatic H), 3.32 (s, CHCO).

Anal. Calcd for $C_{30}H_{18}O_2$: C, 87.43; H, 4.52. Found: C, 87.18; H, 3.95.

The remaining material was difficult to purify and was not studied further.

Pyrolysis of *cis*-Spiro[2-bromoindan-1-one-3,10′-[4b,9a]dihydro-4b-phenylindeno[1,2-*a*]inden-9-one].—Pyrolysis of the cis compound IV at 265° gave a similar mixture of compounds from which V and VI were isolated by chromatography in similar yields to those obtained from the trans compound III.

Meerwein–Ponndorf–Verley Reduction of *trans*-Spiro[indan-1-one-3,10′-[4b,9a]dihydro-4b-phenylindeno[1,2-*a*]inden-9-one].—A mixture of the trans isomer I (20.00 g) and 49 g of aluminum isopropoxide in 2.5 l. of anhydrous isopropyl alcohol was refluxed for 6 days with a very slow distillation of the isopropyl alcohol. Isopropyl alcohol was added to the reaction flask to keep the volume between 1.5 and 2 l. during this time. At the end of this period the volume was decreased to approximately 1 l. at reduced pressure, and 400 ml of 21.5% aqueous hydrochloric acid was added to the cooled solution. The resulting solid was filtered and the filtrate extracted with benzene. The solid and benzene extracts were combined and heated in order to effect solution of the solid. More benzene and ether were added and the solid A which remained was filtered. The filtrate was washed with dilute hydrochloric acid. The solvent was removed at reduced pressure and the residue taken up in 3.5 l. of absolute methanol. Concentration of the solution to 1.5 l. caused crystallization of 1,9′-oxido-*trans*-spiro[indan-3,10′(9′*H*)-4b,9a-dihydro-4b-phenylindeno[1,2-*a*]indene] (VIII): yield 1.89 g; mp 239–241.5°; ir (Nujol) 9.00, 9.14, 9.28 (ether), 14.31 μ (phenyl); nmr ($CDCl_3$) δ 7.25 (m, 17 aromatic H), 5.48 (d, J = 7.5 cps, OCHCH, half of an AB quartet), 3.45 (d, J = 7.5 cps, OCHCH, half of an AB quartet), 5.10 (q, $OCHCH_2$, X quartet of an ABX system), 2.11 (o, CH_2, AB octet of an ABX system); mass spectrum (70 eV) parent m/e peak 398.

Anal. Calcd for $C_{30}H_{22}O$ (398.30): C, 90.65; H, 5.58. Found: C, 90.87; H, 5.62.

The solid A was taken up in 4 l. of hot absolute methanol and on cooling gave *trans*-spiro[1-hydroxyindan-3,10′(9′*H*)-4b,9a-dihydro-9-hydroxy-4b-phenylindeno[1,2-*a*)indene] (VIIa): yield 4.07 g; mp 223–228° dec; ir (Nujol) 3.05 (broad, OH), 8.94, 9.07 (CO), 14.29 μ (phenyl); nmr (pyridine-d_5) δ 7.36 and 6.73 (m, 17 aromatic H), 5.87 (d, J = 6.5 cps, CHOHCH, half of an AB quartet), 4.19 (d, J = 6.5 cps, CHOHCH, half of an AB quartet), 5.52 (q, $CHOHCH_2$, X quartet), 3.19 (q, CHOHCH(H), B quartet), 2.05 (q, CHOHCH(H), A quartet), 5.01 (broad absorption, 1.4 H, OH), the last peak disappearing on treatment with D_2O; mass spectrum (70 eV) m/e (parent peak) 398.

Anal. Cald for $C_{30}H_{24}O_2$ (416.32): C, 86.48; H, 5.81. Found: C, 86.67; H, 5.70.

The impure solids and filtrates obtained from the previous recrystallization attempts were combined (wet 10–11 g) and

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[16] Pseudo d means that the doublets are split again with small coupling constants.

chromatographed on 1 kg of silica gel. The initial solvent was 80% benzene–hexane and was gradually changed to 15% ether–benzene. The diol VIIa isolated previously came off first and amounted to 3.00 g, total yield 7.07 g (35.0%). The solvent was changed to ether and 3.94 (19.5%) of crude *trans*-spiro[1-hydroxyindan-3,10′(9′*H*)-4b,9a-dihydro-9-hydroxy-4b-phenylindeno[1,2-*a*]indene] (VIIb) was isolated. Recrystallization from benzene gave white crystals melting at 221–224° dec: ir (Nujol) 2.74 (shoulder), 2.88 (OH), 9.05 (CO), 14.33 μ (phenyl); nmr (acetone-d_6) δ 7.25 (m, 17 aromatic H), 5.57 (unresolved t, $\mathbf{C}HOHCH_2$ (ABX)), 5.20 (d unresolved, $J = 6.5$ cps, CHOHCH (AB)), 3.38 (d, $J = 6.5$ cps, CHOHCH), 4.60 (q, HO on C-1 or C-9), 3.13 (q, $CHOHC\mathbf{H}_2$, B quartet of ABX), 2.95 (s, shoulder, HO on C-1 or C-9), 2.27 (q, $CHOHC\mathbf{H}_2$, A quartet of an ABX system) (addition of D_2O caused the absorptions at δ 4.60 and 2.95 to disappear and those at 5.57 and 5.20 to become well defined); mass spectrum (70 eV) *m/e* (parent peak) 398.

Anal. Calcd for $C_{30}H_{24}O_2$ (416.32): C, 86.48; H, 5.81. Found: C, 86.62; H, 5.59.

Pyrolysis of *trans*-Spiro[1-hydroxyindan-3,10′(9′*H*)-4b,9a-dihydro-4b-phenylindeno[1,2-*a*]indene].—The diol VIIa (1.50 g) was heated at 235° for 0.5 hr and the reaction mixture was taken up in benzene. This solution was chromatographed on silica gel (120 g) with 75% petroleum ether (bp 60–70°) –benzene as the starting solvent. The first product isolated was 1,9′-oxido-*trans*-spiro[indan-3,10′(9′*H*)-4b,9a-dihydro-4b-phenylindeno[1,2-*a*]indene] (VIII) and after recrystallizing from petroleum ether (bp 80–100°) gave 0.25 g of white crystals of the pyran VIII, mp 241–245°.

The second component isolated was *trans*-spiro[(3*H*)-indene-3,10′(9′*H*)-4b,9a-dihydro-9-hydroxy-4b-phenylindeno[1,2-*a*]indene (IX). Recrystallization from petroleum ether (bp 80–100°) gave IX: mp 204–206° dec; yield 0.73 g; ir (Nujol) 2.76 (OH), 9.07 (CO), 14.26 μ (phenyl); nmr ($CDCl_3$) δ 7.20, 6.28 (m, 17 aromatic H), 6.63 (d, $J = 5.5$ cps, $ArC\mathbf{H}{=}CH$, AB doublet), 5.60 (d, $J = 5.5$ cps, $ArCH{=}C\mathbf{H}$, AB doublet), 5.31 (q, CHOHCH), 4.25 (d, $J = 7$ cps, $CHOHC\mathbf{H}$), 2.37 (d, $J = 11.5$ cps, OH). Upon deuteration, the height of the doublet at 2.37 decreased by half and the quartet at 5.31 collapsed to a doublet ($J = 7$ cps, 1 H).

Anal. Calcd for $C_{30}H_{22}O$: C, 90.45; H, 5.58. Found: C, 90.36; H, 5.45.

Wolff–Kishner Reduction of *trans*-Spiro[indan-1-one-3,10′-[4b,9a]dihydro-4b-phenylindeno[1,2-*a*]inden-9-one] (I).—The trans isomer I (1.00 g) was treated with 0.86 g of potassium hydroxide and 1.06 g of 85% hydrazine hydrate in 100 ml of ethylene glycol at 180° for 3 hr and at 195° for 10 hr. The reaction mixture was poured into water and extracted with ether. The dried ether extract was chromatographed on 100 g of silica gel with petroleum ether (bp 60–68°) as the solvent and gave white *trans*-spiro[indan-3,10′(9′*H*)-4b,9a-dihydro-4b-phenylindeno[1,2-*a*]indan] which was recrystallized from ethyl acetate: yield 0.25 g; mp 204–204.50° (lit.[5] 201–202°); ir (Nujol) 14.36 μ (phenyl; nmr (HA-100) ($CDCl_3$) δ 7.02 (m, 17 aromatic H), 3.41 (q, $C\mathbf{H}CH_2Ar$, quartet of an ABC system), 2.99 (m, $CHC\mathbf{H}_2Ar$ and $CH_2C\mathbf{H}_2Ar$, the combined AB portion of an ABC system and the BB′ portion of an AA′BB′ system integrating for 4 protons), 2.16 (apparant A′ sextet ($C\mathbf{H}(H)CHAr$) of an AA′BB′ system), 1.67 (apparent A sextet ($CH(\mathbf{H})CH_2Ar$)). Decoupling experiments in which the peak at 2.99 ppm was saturated caused the A quartet of the ABC system to collapse to a singlet and the AA′ part of the AA′BB′ system to collapse to an AB quartet with $J = 13$ cps.

Action of Aluminum Chloride on *trans*-Spiro[indan-1-one-3,10′-[4b,9a]dihydro-4b-phenylindeno[1,2-*a*]inden-9-one].—A mixture of the trans isomer I (2.00 g) and 1.41 g of aluminum chloride in 125 ml of nitrobenzene was refluxed for 5 days under nitrogen. The nitrobenzene was removed at reduced pressures and the residue was chromatographed on 200 g of alumina with 50% petroleum ether (bp 60–68°) –benzene as the starting solvent. Two products were isolated. The first was benz[*a*]indeno[1,2-*c*]fluorene-9,14-dione (V) (0.16 g). The second product was dibenz[*d*,*f*]cycloheptene[2,3:6′,5′]benzo[*c*]fluorene-5,18-dione (X) (0.145 g) which after recrystallization from benzene gave orange needles melting at 272–274°: ir (KBr) 5.88 ($C{=}O$), 6.03 μ ($C{=}O$); nmr (HA-100) ($CDCl_3$) δ 9.35 (pseudo d, $J = 8$ cps, 1 aromatic H), 8.51 (pseudo d, $J = 7$ cps, 1 aromatic H), 8.36 (pseudo d, $J = 8$ cps, 1 aromatic H), 5.64 (pseudo d, $J = 6$ cps, 1 aromatic H), 7.50 (m, 12 aromatic H); mass spectrum (70 eV) *m/e* (parent peak) 408.

Anal. Calcd for $C_{30}H_{16}O_2$ (408): C, 88.21; H, 3.95. Found: C, 88.14; H, 3.96.

The same reaction without the aluminum chloride gave a 16.2% yield of V.

The cis isomer II (2.00 g) when refluxed with aluminum chloride (1.41 g) in nitrobenzene (125 ml) for 2.5 days under nitrogen gave 0.13 g of X as the only identifiable product.

Benzo[*c*]fluorene (XII).—Benzo[*c*]fluorenone (XI) (100 g) was heated with potassium hydroxide (83.0 g) and 85% hydrazine (100 ml) in ethylene glycol (1 l.) at 120–140° for 1.5 hr. The resulting mixture was distilled until the temperature reached 190° and kept at this point for 4.5 hr. During the distillation nitrogen was introduced at the top of the flask to reduce foaming. The resulting solid was filtered and the filtrate was treated with 187 ml of 6 *N* hydrochloric acid. The resulting precipitate was combined with the first solid isolated and chromatographed on silica gel (1 kg) using petroleum ether (bp 60–68°) as the solvent. Benzo[*c*]fluorene was eluted first and melted at 124–125° (lit.[17] 124.5°): yield 56.0 g; ir (Nujol) 12.44 (two adjacent aromatic hydrogens); nmr ($CDCl_3$) δ 8.61 (d, $J = 8$ cps, 1 aromatic H), 8.25 (d, $J = 7$ cps, 1 aromatic H), 7.50 (m, 8 aromatic H), 3.78 (s, CH_2).

Condensation of Benzo[*c*]fluorene (XII) with *o*-Chlorobenzoyl Chloride.—A solution of benzo[*c*]fluorene (XII) (50.00 g) and *o*-chlorobenzoyl chloride (42.00 g) in 300 ml of carbon disulfide was treated with 46.2 g of alumunum chloride during the course of 2.5 hr. The red reaction mixture was stirred at room temperature for an additional 3 hr and finally heated at 35–40° for 0.5 hr. The resulting product was treated with 1.5 l. of crushed ice and the red aqueous layer was extracted with 500 ml of benzene whereupon the red coloration disappeared. The combined organic extracts were dried over anhydrous calcium chloride and the solvent was removed at reduced pressure. The residue was chromatographed on 1.5 kg of silica gel with 30% benzene–petroleum ether (bp 60–68°) as the first solvent. Benzo[*c*]fluorene (XII) (0.76 g) was eluted first. The second component isolated was 5-(*o*-chlorobenzoyl)benzo[*c*]fluorene (XIII). Recrystallization from benzene gave yellow needles: mp 150–151°; yield 44.00 g; ir (Nujol) 6.09 ($C{=}O$), 11.70 μ (one aromatic hydrogen); nmr ($CDCl_3$) (HA-100) δ 8.90 (q, J 3 cps, 1 aromatic H), 8.66 (q, $J = 3$ cps, 1 aromatic H), 8.25 (pseudo d, $J = 7$ cps, 1 aromatic H), 7.59 (s, 1 aromatic H α to CO group), 7.40 (m, 9 aromatic H), 3.70 (s, CH_2).

Anal. Calcd for $C_{24}H_{15}OCl$: C, 81.24; H, 4.26. Found: C, 80.99; H, 4.23.

The third product from the column was 9-(*o*-chlorobenzoyl)-benzo[*c*]fluorene, which when recrystallized from benzene gave light yellow granular crystals (8.99 g): mp 176–177.5°; ir (Nujol) 6.06 μ ($C{=}O$); nmr (HA-100) ($CDCl_3$) δ 8.45 (pseudo d, $J = 8$ cps, 1 aromatic H), 8.15 (d, $J = 8$ cps, 1 aromatic H), 7.51 (m, 11 aromatic H), 3.72 (s, CH_2).

Anal. Calcd for $C_{24}H_{15}OCl$: C, 81.24; H, 4.26. Found: C, 81.58; H, 4.04.

The fourth component was impure 5,9-di(*o*-chlorobenzoyl)-benzo[*c*]fluorene, which when recrystallized from a benzene–petroleum ether (bp 60–68°) mixture gave a yellow solid (16.68 g): mp 166–169°; ir (Nujol) 6.03 ($C{=}O$), 11.55 μ (one aromatic hydrogen); nmr ($CDCl_3$) δ 8.67 (m, 2 aromatic H), 8.30 (d, 1 aromatic hydrogen), 7.58 (m, 12.6 aromatic H), 3.82 (s, CH_2); mass spectrum (70 eV) *m/e* 530, 493. This sample did not give a satisfactory C and H analysis.

5-(*o*-Chlorobenzoyl)benzo[*c*]fluorenone (XIV).—A solution of 5-(*o*-chlorobenzoyl)benzo[*c*]fluorene (XIII) (5.00 g) and 6.49 g of potassium dichromate in 100 ml of glacial acetic acid was refluxed for 2.75 hr and poured into water. The golden colored solid was filtered and recrystallized from benzene: yield 3.05 g; mp 202–203°; ir (Nujol) 5.85 ($C{=}O$), 6.03 μ ($C{=}O$); nmr (HA-100) ($CDCl_3$) δ 8.62 (m, 2 aromatic H), 7.98 (pseudo d, $J = 7$ cps, 1 aromatic H), 7.39 (m, 10 aromatic H).

Anal. Calcd for $C_{24}H_{13}O_2Cl$: C, 78.16; H, 3.55. Found: C, 77.95; H, 3.71.

An additional 1.77 g of product was obtained from the filtrate from the first recrystallization. The total yield was 4.82 g.

Cyclization of 5-*o*-(Chlorobenzoyl)benzo[*c*]fluorenone (XIV).—XIV (1 g) was heated with sodium hydroxide (0.7 g) in a mixture of water (3.3 ml) and quinoline (3.3 ml) in a bomb at 255–265° for 8 hr. The product was dissolved in benzene and washed with

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(17) J. W. Cook, A. Dansi, C. L. Hewett, J. Iball, W. V. Mayneord, and E. Roe, *J. Chem. Soc.*, 1323 (1935).

10% hydrochloric acid and water. Two similar cyclizations were carried out with 2.0 and 2.5 g of the fluorenone XIV, and the products were combined and chromatographed on silica gel (400 g) with 80:20 benzene–petroleum ether (bp 60–68°) as the initial solvent. The first product eluted was benz[*a*]indeno[1,2-*c*]fluorene-9,14-dione (V) (0.12 g). Recrystallization from benzene gave orange needles melting at 244–247°. Further elution gave 1.54 g of V contaminated with the starting material XIV. This sample was purified by recrystallization from benzene.

The third component (0.3 g) isolated was recrystallized from benzene and gave benz[*de*]indeno[2,1-*b*]anthracene-8,10-dione (XV), mp 323–330°. Further purification by chromatography and recrystallization from benzene gave a sample melting at 330–331.5°: ir (KBr) 5.84 (C=O), 6.07 μ (C=O).

Anal. Calcd for $C_{24}H_{12}O_2$: C, 86.73; H, 3.64. Found: C, 86.69; H, 3.85.

Cyclization of 5-(*o*-Chlorobenzoyl)benzo[*c*]fluorene (XIII).—The fluorene XIII (1.5 g) was heated with sodium hydroxide (0.78 g) in water (3.75 ml) and quinoline (3.75 ml) in a bomb at 260° for 6 hr. The resulting product was extracted with benzene and ether and the extract was washed with hydrochloric acid. Removal of the solvent gave a solid which was chromatographed on silica gel (200 g) using 8:2 benzene–petroleum ether (bp 60–68°) as the initial solvent. The first compound eluted was 14-hydrobenz[*a*]indeno[1,2-*c*]fluoren-9-one (XVI) (0.6 g). Recrystallization from benzene gave orange needles melting at 236–237°, ir (Nujol) 5.90 μ (C=O).

Anal. Calcd for $C_{24}H_{14}O$: C, 90.54; H, 4.43. Found: C, 90.83; H, 4.68.

The second component (0.76 g) eluted from the silica gel was recrystallized from benzene and gave 10-hydrobenz[*de*]indeno[2,1-*b*]anthracen-8-one (XVII). The yellow needles melted at 214–215°. Sublimation raised the melting point by 1°; ir (Nujol) showed 6.08 μ (C=O).

This sample did not give a satisfactory C and H analysis.

Benz[*de*]indeno[2,1-*b*]anthracene-8,10-dione (XV).—A solution of the indene XVII (0.25 g) and potassium dichromate (0.42 g) in acetic acid (4 ml) was refluxed for 1.5 hr. Analysis by tlc of the product indicated that the major product was starting material. Further oxidation of the material gave a brown precipitate which was dissolved in benzene. Chromatography on silica gel (2 g) with benzene as the initial solvent gave as the second component benz[*de*]indeno[2,1-*b*]anthracene-8,10-dione (XV). Recrystallization from benzene gave orange needles (0.01 g) melting at 332–333.5°.

Registry No.—I, 27915-35-1; II, 27915-36-2; III, 27915-37-3; IV, 27915-38-4; V, 27921-55-7; VI, 27915-39-5; VIIa, 27915-40-8; VIIb, 27971-71-7; VIII, 27915-41-9; IX, 27915-42-0; X, 27971-72-8; XII, 205-12-9; XIII, 27921-57-9; XIV, 27921-58-0; XV, 27921-59-1; XVI, 27921-60-4; XVII, 27921-61-5; sulfuric acid, 7664-93-9; ethyl 3,3-diphenyl-3-hydroxypropanoate, 894-18-8; *cis*-spiro[2,2-dibromoindan-1-one-3,10′-[4b,9a]dihydro-4b-phenylindeno[1,2-*a*]inden-9-one, 27915-43-1; *trans*-spiro[indan-3,10′(9′*H*)-4b,9a-dihydro-4b-phenylindeno[1,2-*a*]indan], 27915-44-2; 9-(*o*-chlorobenzoyl)benzo[*c*]fluorene, 27921-62-6; 5,9-di-(*o*-chlorobenzoyl)benzo[*c*]fluorene, 27921-63-7.

Stable Carbonium Ions. CIV. Protonated Alicyclic Ethers and Sulfides[1]

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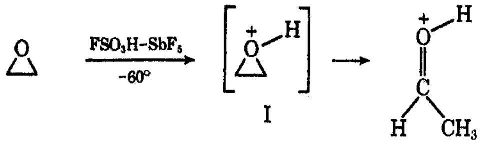
Three-, four-, five-, and six-membered protonated alicyclic ethers and sulfides have been studied in $FSO_3H–SbF_5–SO_2$ solution generally at −60° by pmr spectroscopy.[3] At low temperatures the onium ions were observed with negligible exchange rates and, with exception of the three-membered ring compounds, without ring opening followed by polymerization. Comparison of alicyclic protonated ethers and sulfides with ethylene and tetramethylene halonium ions show regular changes in the series of related onium ions.

The protonation of alkyl ethers[3a] and sulfides[3b] in superacid solutions has been investigated. We report now the observations of protonated alicyclic ethers and sulfides in the superacid systems $FSO_3H–SbF_5$ ("magic acid") and $HF–SbF_5$.

Results and Discussion

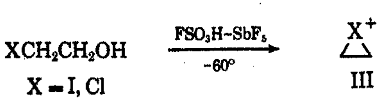
Protonated Oxiranes.—The observation of protonated oxiranes was attempted in superacid solutions, *e.g.*, $FSO_3H–SbF_5$, $HF–SbF_5$, at low temperatures. The results of the protonation of ethylene oxide (oxirane) in "magic acid" or $HF–SbF_5$ at temperatures between −10 and +95° (in SO_2ClF) are not conclusive as the reaction products cannot be easily identified owing to competing polymerization reactions. A broad nmr signal is observed at approximately δ 5.00 which by comparison with the methylene absorptions of the ethylenebromonium ion as well as protonated aziridine could be due to protonated oxirane. When samples were left standing at 0° for a few days, the spectral features of protonated acetaldehyde II were observed.



I

II

Other attempted routes to protonated oxirane also proved difficult. The reaction of 2-iodo- and 2-chloroethanol in "magic acid" yields quantitatively the corresponding ethylenehalonium ion III.[4]



III

Propylene oxide (2-methyloxirane) in "magic acid" solution at −60 to −78° yields an nmr spectrum which indicates the presence of a minor amount of protonated propionaldehyde and a species [rather broad nmr ab-

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[1] Part CIII: G. A. Olah, D. P. Kelly, and R. G. Johanson, *J. Amer. Chem. Soc.*, **92**, 4137 (1970).

[2] Taken in part from the Ph.D. dissertation of P. J. Szilagyi, Case Western Reserve University, 1969.

[3] (a) G. A. Olah and D. H. O'Brien, *J. Amer. Chem. Soc.*, **89**, 1725 (1967); (b) G. A. Olah, D. H. O'Brien, and C. U. Pittman, Jr., *ibid.*, **89**, 2996 (1967).

[4] G. A. Olah, J. M. Bollinger, and J. Brinich, *ibid.*, **90**, 2587 (1968); G. A. Olah and J. M. Bollinger, *ibid.*, **89**, 4744 (1967); **90**, 947 (1968).