view of facile O → N rearrangement, the oils may contain small amounts of *N*-alkylphosphazanes.

The $TiCl_4$-catalyzed reaction of octachlorocyclotetraphosphazene and epichlorohydrin was attempted by adding $TiCl_4$ slowly to a mixture of the other reactants at 85°, followed by heating and work-up similar to that described above.

Octakis(2-chloroethoxy)cyclotetraphosphazene, 3, by reaction 1.[3] A 2-l., 3-neck round-bottom flask containing 700 ml of anhydrous pyridine and 87 g (1.5 equiv) of **2** was cooled to 15°, and 121 g (1.5 equiv) of 2-chloroethanol was added dropwise over 1 hr. After the mixture was stirred at room temperature for 20 hr, solvent was removed under vacuum below 50°. The residue was then poured into 600 g of ice–water, and the oil layer taken up with chloroform. The chloroform extract was washed with 5% HCl, 5% Na_2CO_3, and water, dried ($MgSO_4$), and concentrated on a rotary evaporator. The residual oil was concentrated further at room temperature and 0.1 Torr for 16 hr. The product was a viscous yellow oil, weight 145.2 g, 95% of theoretical yield, characterized by ir spectrum (see following paragraph on supplementary material).

Acknowledgments. The author is grateful to personnel of the Analytical Services Division, Firestone Central Research Laboratories, for technical assistance, and to The Firestone Tire and Rubber Company for permission to publish this work.

Supplementary Material Available. Nmr spectrum of compound **3** and ir spectra of **3** prepared by reactions 1 and 2 will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-74-3357.

Registry No.—**2**, 2950-45-0; **3**, 52539-64-7; $(C_2H_5)_4N^+Br^-$, 71-91-0; $(C_4H_9)_4N^+Cl^-$, 1112-67-0; LiCl, 7447-41-8; LiBr, 7550-35-8; $LiClO_4$, 7791-03-9; CsF, 13400-13-0; ethylene oxide, 75-21-8; epichlorohydrin, 106-89-8; hexachlorocyclotriphosphazene, 940-71-6.

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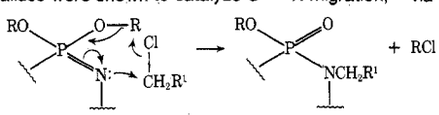
(11) Alkyl halides were shown to catalyze O → N migration,[10] *via*



(12) Melting points were determined in capillary tubes and are uncorrected. Chlorine analysis was by Schöniger flask combustion and Volhard titration. Carbon, hydrogen analyses performed by Galbraith Laboratories, Inc.
(13) C, H, and N microanalyses using an F&M Model 185 analyzer gave varying high results for **3**. *Anal.* (typical). Calcd: C, 23.5; H, 3.9; N, 6.9. Found: C, 25.5; H, 4.1; N, 7.4. Such results are presumably due to premature loss of HCl during analysis.

Reactions of Cyclopropanols with Halogenating Agents and Other Electrophiles

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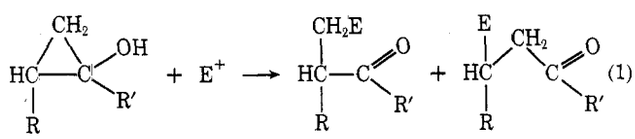
Received March 27, 1974

A study has been made of the reactions of *cis*- and *trans*-2-phenyl-1-methylcyclopropanol and their methyl ethers, *cis*- and *trans*-2-methyl-1-phenylcyclopropanol, and *cis*- and *trans*-1,2-diphenylcyclopropanol with various electrophiles, including mercuric acetate, acid, and various sources of positive halogen. The direction of ring opening is found not to depend upon the stereochemistry of the starting material. The free-radical opening of optically active *trans*-2-phenyl-1-methylcyclopropanol by $FeCl_3$ is shown to give racemic chloro ketone. The results are compared with those from related systems.

For some time we have been interested in the mechanism and stereochemistry by which cyclopropanols and their derivatives react with electrophiles.[1] In previous studies we have reported that *trans*-2-phenyl-1-methylcyclopropanol undergoes electrophilic ring opening with retention of configuration when treated with D^+ [2] and that the various cis–trans isomers of 2,3-dimethyl-1-phenylcyclopropanol ring open with inversion of configuration upon reaction with mercuric acetate[3] or various brominating agents.[4] In the course of these and other studies[1] we have also had occasion to measure the effect of a ring substituent on the direction of ring opening upon attack by an electrophilic reagent (eq 1). In the work reported in this paper we have attempted to make a more systematic study of cyclopropanol ring openings as a function of the nature and stereochemistry of the substituents R and R′, particularly as they apply to halogenation, but also for protonation and mercuration.



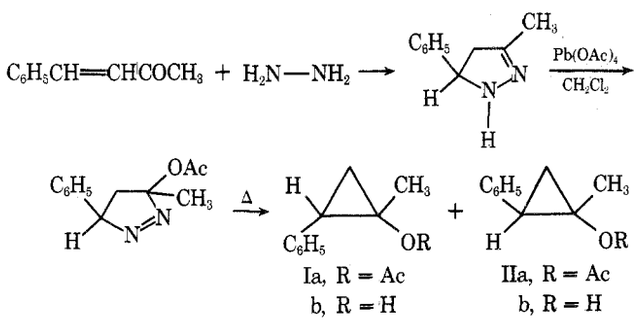
(1)

Results

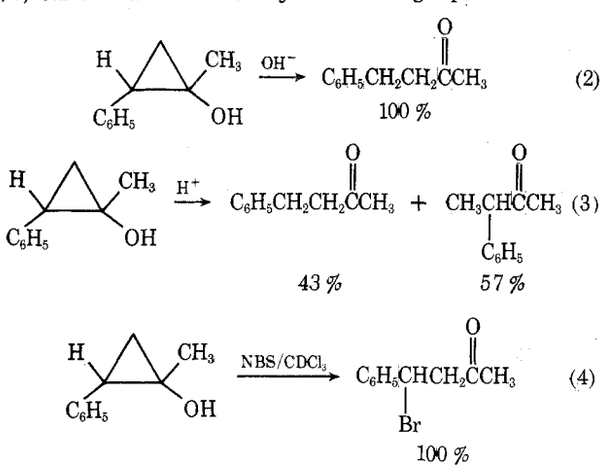
***cis*-2-Phenyl-1-methylcyclopropanol (Ib).** The first system chosen for study in this investigation was *cis*-2-phenylcyclopropanol (Ib) since we had previously determined the product composition on ring opening of the trans isomer.[2] We were interested in determining if simple cis–trans isomerization would have any effect on the direc-

tion of opening. Unfortunately the method we had used for the preparation of the trans isomer[2] was not applicable to the cis isomer, and we had to prepare and separate a cis–trans mixture of cyclopropyl acetates (Ia and IIa) prepared by a modification of Freeman's method[5] (Scheme I). The isomers were difficult to separate, but we were finally able to obtain small quantities of pure Ia by careful column chromatography. The pure crystalline cis alcohol, Ib, was obtained from Ia by reaction with methyllithium and work-up under carefully controlled pH conditions. Once pure, it, like the trans isomer, was indefinitely stable when stored in a polyethylene bottle in the cold. Its spectral properties were in full accord with its assigned structure.

Scheme I



Base-catalyzed cleavage of Ib (eq 2) at 85–90° in 50:50 (v/v) 0.2 *N* NaOH–dioxane yielded a single product which

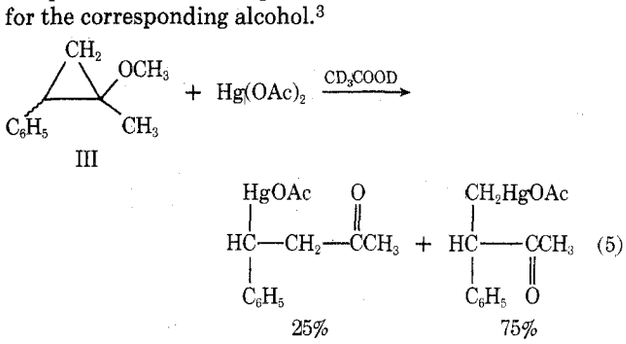


was identified as 4-phenyl-2-butanone by comparison of its nmr spectrum and gpc retention time with those of an authentic sample. Acid-catalyzed cleavage of Ib (eq 3) was carried out under conditions similar to those reported earlier[2] for the trans isomer by heating at 90–95° in 50:50 (v/v) 2 *N* HCl–dioxane. Ring opening occurred in >97% yield to give 4-phenyl-2-butanone (43%) and 3-phenyl-2-butanone (57%) in essentially the same ratio as that found for the trans isomer (40%:60%).[2] Finally, Ib was treated with *N*-bromosuccinimide in $CDCl_3$ in the dark. Reaction occurred immediately. The nmr spectrum of the product was consistent with the formation of 4-bromo-4-phenyl-2-butanone as the sole product (eq 4), just as was found previously to be the case for the trans isomer (IIb).[4] Thus the change in stereochemistry at C-2 has no effect on the direction of ring opening.

2-Phenyl-1-methylcyclopropanol Methyl Ether (III). To determine if the direction of ring opening would change if the free hydroxyl group were masked, the methyl ether was prepared. This was accomplished in 76% yield when a 1:3 mixture of *cis*- and *trans*-2-phenyl-1-methylcyclopropanol in ether was treated with diazomethane and aluminum chloride.[6] This method proved much superior to several others tried, including alkylation with methyl iodide, trimethyloxonium tetrafluoroborate, or diazomethane and boron trifluoride.

These cyclopropanol methyl ethers (III) are significantly less reactive toward cleavage with acid than the corresponding alcohols. However, upon heating at 95–105° in 60:40 dioxane–sulfuric acid (8.3 *N*), ring opening is complete within 26 hr. The products are 62% 3-phenyl-2-butanone and 38% 4-phenyl-2-butanone, a mixture which is not significantly different from that found for the corresponding alcohols. The reaction was monitored by gpc from the beginning, and at no time were there more than three components present, the starting ether mixture (III) and the two ketonic products. Moreover the ratio of ketones did not change during the course of the reaction. It thus seems very unlikely that any rearrangement of products or incursion of alternate methods of ring opening (for instance carbon–oxygen cleavage followed by rearrangement to an allylic cation) could be occurring.

Reaction of the ether mixture (III) with an equivalent of mercuric acetate was carried out in acetic acid-d_4 and the results monitored by nmr spectroscopy. The reaction was complete within less than 10 min at room temperature and the product mixture (eq 5) was identical with that found for the corresponding alcohol.[3]



In contrast to the results for protonation and mercuration, where ring opening occurred identically for the ether and the alcohol, although somewhat more slowly on the former, the cyclopropanol methyl ethers (III) could not be induced to react with *tert*-butyl hypochlorite even after several days. Yet the alcohols react immediately, almost explosively, even at ice-bath temperatures. The ether mixture does react slowly with *N*-bromosuccinimide, as compared to an almost instantaneous reaction of the alcohols, but a complex mixture of reaction products is obtained and the products anticipated for simple brominative ring opening could not be detected. These results are in accord with previous observations that cyclopropanols are almost unique in their ability to react readily with halogenating agents.[4]

Stereochemistry of Halogenation of *trans*-2-Phenyl-1-methylcyclopropanol (IV). We have previously shown that 2,3-dimethyl-1-phenylcyclopropanols and their acetates brominate stereospecifically with inversion of configuration, while the alcohols react with chlorinating agents in a nonstereospecific manner and the acetates do not react at all.[4] To account for the lack of stereospecificity upon chlorination, we proposed an oxidative attack on the OH bond leading to ring opening *via* a radical mechanism since cyclopropanols are known to be easily oxidized. Indeed the threo:erythro product ratio obtained upon chlorination is the same as that obtained by ferric chloride oxidation[4] (eq 6), a process which has been shown to occur by way of radical intermediates.[7] One reasonable explanation for our results with the 2-phenyl compounds might be that the phenyl group greatly accelerates this oxidative pathway so that the reaction occurs exclusively on the O–H bond. To test

EXPERIMENTAL SECTION

All boiling and melting points are uncorrected. Melting points were taken on a Fischer-Johns melting point apparatus. Glc analyses were performed on an Aerograph Model 202 or an F&M scientific Corporation Model 700 gas chromatograph. The columns used are listed as follows and are referred to by letter with the temperature used specified for each individual analysis: A 10' x 3/8" aluminum column containing 5% SE-30 on 60:80 Chromosorb W; B 5' x 1/4" stainless steel column containing 20% Carbowax 20M on 60:80 Chromosorb W; C 5' x 1/4" stainless steel column containing 15% Apiezon L on 60:80 Chromosorb W; D 5' x 1/4" stainless steel column containing 10% Apiezon L on 60:80 Chromosorb W.

Infrared spectra were obtained on a Beckman IR-10 or a Perkin-Elmer Model 457 spectrophotometer calibrated with the 1604 cm^{-1} band of polystyrene. Solution spectra were obtained using solvent-matched sodium chloride cells of 0.05 mm or 0.10 mm thickness. Nmr spectra were obtained on Varian Associates A-60 or A-60-A spectrometers at 60 megacycles and the symbols s, d, dd, t, and m refer to singlet, doublet, doublet of doublets, triplet, and multiplet. Spin decoupling experiments were done on a Varian Associates HA-100 spectrometer at 100 megacycles. All mass spectra were obtained using a Varian M-66, Varian MAT CH-7, or Consolidated Electrodynamics Corporation Type 21-103C (modified) spectrometer.

Synthesis of 2-Phenyl-1-methylcyclopropyl Acetates (Ia and IIa).--The acetate mixture was prepared according to the following procedure patterned after that of Freeman[5] with some modifications.

Benzalacetone[15] (50 g, 0.34 mole) and 200 ml of absolute ethanol were placed in a 500-ml three-neck round-bottom flask. Hydrazine (15 g, 0.45 mole) was added to the stirred solution over a period of 5--10 min with some evolution of heat. The reaction mixture was heated at reflux for 3 hr, then cooled, and the ethanol-water removed on a rotary evaporator at 70-75° to yield 55 g (100%) of a yellow oil which had properties consistent with those expected for 3-methyl-5-phenyl-2-pyrazoline: nmr ($CDCl_3$) τ = 8.05 (s, 3, CH_3), 7.21 (m, 2, CH_2), 5.30 (t, 1, CH), 5.07 (broad s, 1, N-H), 2.71 (s, 5, C_6H_5); ir (CCl_4) 3370 (N-H) and 1630 cm^{-1} (C=N). This crude 2-pyrazoline was used in the next step without further purification.

A flame-dried two-liter three-neck round-bottom flask was charged with 216 g (0.49 mole) of lead tetraacetate and 600 ml of dry CH_2Cl_2 while nitrogen was passed through the flask. The pyrazoline (55 g) in 200 ml of dry CH_2Cl_2 was added to the well-stirred slurry over a period of 1--5 hr, maintaining the temperature at 10-20°. The mixture was then heated at reflux for 1 hr, stirred for 6.5 hr at room temperature and 400 ml of water was added to the reaction mixture. After the aqueous layer was extracted with 250 ml of CH_2Cl_2, the combined CH_2Cl_2 extracts were extracted repeatedly with saturated $NaHCO_3$ solution and water over a period of at least 1 hr or until the solution remained neutral after standing for a period of 30 min. After drying ($MgSO_4$), the solvent was removed on a rotary evaporator to yield 74.8 g of a brown oil which had properties consistent with those expected for the 3-acetoxypyrazoline: nmr ($CDCl_3$) τ = 8.22 (s, CH_3), 7.94 (s, acetate CH_3), 8.37, 7.45 (m, CH_2), 4.03 (dd, CH), 2.65 (m, C_6H_5), ir (CCl_4) 1755 (C=O), 1567 cm^{-1} (cis azo).

The brown oil was heated in a distillation apparatus. At 130-140° a vigorous evolution of nitrogen occurred. After the initial reaction had subsided, heating at 170-190° for 20 min resulted in no further evolution of nitrogen. The brown oil was distilled and a fraction (bp 80-83°/0.5 mm; lit. bp 70°/0.35 mm[5]) was the expected acetates (27.15 g or 42%, cis:trans ~ 1:3).

Separation of cis- and trans-2-Phenyl-1-methylcyclopropyl Acetates (Ia and IIa).--A sample of the acetate mixture (10.5 g) was separated on a 38 mm x 90 cm silica gel column (260 g Baker powder) eluting with Skellysolve B-benzene mixtures. After combining appropriate fractions 6 g of the trans acetate (IIa), 3.6 g of a mixture of acetates, and 0.3 g of the cis acetate (Ia) was obtained. cis-Enriched acetate mixtures from several of the above chromatographies were combined to yield 7 g of the acetates (61% cis, 39% trans). Separation of this mixture on a large silica gel column (38 mm x 90 cm ~250 g of Baker powdered silica gel) with Skellysolve B-benzene mixtures as eluents yielded 1.4 g of the trans acetate (IIa), 2.10 g of a mixture of acetates, and 2.3 g of the cis acetate (Ia). Spectral data supported the assignment of the cis and trans acetates: trans acetate (IIa): nmr ($CDCl_3$) τ = 8.82 (m, 5, CH_3 and cyclopropane CH_2), 8.02 (s, 3, acetate CH_3), 7.68 (dd, 1, cyclopropane CH), 2.77 (s, 5, C_6H_5); ir ($CHCl_3$) 1745 cm^{-1} (C=O); cis acetate (Ia): nmr ($CDCl_3$) τ = 8.83 (m, 2, cyclopropane CH_2) 8.38 (s, 6, CH_3 and acetate CH_3), 7.93 (dd, 1, cyclopropane CH), 2.89 (s, 5, C_6H_5); ir (CCl_4) 1755 cm^{-1} (C=O).

Synthesis of cis-2-Phenyl-1-methylcyclopropanol (Ib).--The procedure was patterned after that of DePuy et al.[16] In a dry 250-ml three-neck round-bottom flask was placed 50 ml of anhydrous ether and 2 g (0.01 mole) of the cis acetate (Ia). To the stirred solution, under nitrogen, 12 ml of 2.1 M methyllithium in ether was added dropwise over a period of 10 min. The resulting mixture was stirred for 2 hr, and rapidly added to a suspension of 25 g of boric acid in 50 ml of distilled water. Beyond this point, all glassware, etc., coming into contact with the cyclopropanol was washed with a 5% HF solution, tap water, distilled water, and then dried. The mixture was filtered, the solid washed with ether, the layers separated, and the ether layer washed with three 50-ml portions of distilled water. Pentane (100 ml) was added to the ether and a final extraction was made with 50 ml of water. After drying, the ether-pentane was removed on a rotary evaporator to yield 1.7 g of a yellow oil. Recrystallization of the crude alcohol several times from pentane-ether at Dry Ice temperatures yielded 0.6 g (42%) of a white crystalline solid which was dried under vacuum: nmr ($CDCl_3$) τ = 8.85 (m, 2, cyclopropane CH_2), 8.44 (s, 4, CH_3 and OH), 8.01 (dd, 1, cyclopropane CH), 2.74 (s, 5, C_6H_5); mass spectrum m/e (rel intensity) 148(46.6), 133(17.9), 105(83), 91(40), 77(22.9), 43(100); mp 61-63°.

Reactions of cis-2-Phenyl-1-methylcyclopropanol (Ib). A. with N-Bromosuccinimide. N-bromosuccinimide (0.13 g, 0.0006 mole) and 1 ml of $CDCl_3$ were placed in an aluminum foil-covered 50-ml erlenmeyer flask. The system was flushed with nitrogen and cooled in an ice bath. With stirring, 0.08 g (0.0006 mole) of the cis alcohol (Ib) in 1 ml of $CDCl_3$ was added in portions. After stirring 5 min, a sample of the reaction mixture was transferred to an nmr tube and nmr spectrum was recorded. In addition to singlets due to N-bromosuccinimide (τ = 7.07) and succinimide (τ = 7.27), the nmr spectrum was consistent with 4-bromo-4-phenyl-2-butanone as the sole product: τ = 7.93 (s, 3, CH_3), 6.61 (t, 2, CH_2), 4.54 (dd, 1, CH), 2.63 (m, 5, C_6H_5).[4]

B. with Base.--The procedure used was patterned after that of DePuy et al.[2] The cis alcohol (Ib) (0.1 g, 0.0007 mole) was added in portions to a 25-ml round-bottom flask containing 8 ml of 0.2 M aqueous NaOH and 8 ml of spectral grade dioxane (MCB). The system was flushed with argon, sealed, and heated at 85-90° for 61 hr. After cooling, the contents of the flask were neutralized with 3 M HCl and extracted 6 times with 20 ml of ether. The dioxane-ether was dried and removed by distillation to yield a brown oil. Analysis of the oil by gpc (Column B at 96°) indicated the presence of a single component. Comparison of the nmr spectrum of the oil with the nmr spectrum of an authentic sample proved the compound to be 4-phenyl-2-butanone.

C. with Acid.--The procedure used was patterned after that of DePuy et al.[2] A sample of the cis alcohol (Ib) (0.15 g, 0.001 mole), 6 ml of 2 M HCl, and 6 ml of dioxane were placed in a 25-ml round-bottom flask. The system was flushed with argon, sealed, and heated to 90-95° for 72 hr. The solution was cooled and neutralized with 1 N NaOH and worked up as above. Analysis of the resulting oil by nmr spectroscopy and gpc indicated the presence of 44% 4-phenyl-2-butanone and 56% 3-phenyl-2-butanone.

Synthesis of 2-Phenyl-1-methylcyclopropanol Methyl Ether (III). Crude 2-phenyl-1-methylcyclopropanol [from 13 g (0.07 mole) of 2-phenyl-1-methylcyclopropyl-acetate, cis:trans ~ 1:3] was dissolved in 200 ml of anhydrous ether in a one-liter suction flask equipped with a drying tube. The solution was cooled with an ice bath and two spatulas of aluminum chloride (anhydrous reagent) were added. The diazomethane solution was added dropwise (from a burette equipped with a drying tube) with stirring. Whenever the reaction of the diazomethane subsided as evidenced by a lack of nitrogen evolution, a spatula of fresh aluminum chloride was added. After the addition of diazomethane was complete, the solution was allowed to stir overnight while warming to room temperature. To decompose any remaining diazomethane, 50 ml of 3 N HCl was added slowly to the reaction mixture. The layers were separated and the ether layer was extracted with water until the pH of the water extract was about 5. The solution was dried ($MgSO_4$) and the ether removed with a rotary evaporator to yield a yellow oil which nmr and ir spectra indicated was cyclopropanol methyl ether (III) with little starting alcohol present. Distillation gave 8.5 g (76%) of a colorless oil (bp 51-65°/1.5 mm). The oil was chromatographed (150 g of Baker powdered silica gel) with Skellysolve-B as the eluting solvent. In general, all attempts to separate the mixture of cis and trans ethers by gpc with various columns, failed. The column chromatography, early fractions collected were always enriched in the cis ether and late fractions were enriched in the trans ether. Analysis of the ether mixture from column chromatography by gpc (Column A at 116°) yielded a single peak. The 2-phenyl-1-methylcyclopropanol methyl ether mixture (III) had the following properties: bp 46-49°/0.6 mm; ir ($CHCl_3$) 2838 (C-H of OCH_3), 1060-1090, 1230 cm^{-1} (C-O-C); nmr ($CDCl_3$) τ = 8.89 (trans CH_3 and cyclopropane CH_2), 8.52 (cis CH_3), 8.08 (cis cyclopropane CH), 7.66 (trans cyclopropane CH), 6.94 (cis OCH_3), 6.53 (trans OCH_3), 2.76 (C_6H_5); mass spectrum m/e (rel intensity) 162(15.7), 147(46.4), 130(10.2), 129(14.4), 115(27.1), 91(21.3), 77(12.1), 51(10.7), 43(100).

Reactions of 2-Phenyl-1-methylcyclopropanol Methyl Ether (III). A. with Acid at 95-105°.--A sample of the ether mixture (III) (0.4 g, 0.0025 mole) was dissolved in 40 ml of 60:40 dioxane--8.3 N aqueous H_2SO_4 in a round-bottom flask. The system was flushed with nitrogen, sealed, and heated at 95-105°. The reaction was monitored by gpc analysis (Column A at 125°). After 24 hr, the reaction was complete and the ether peak in the gas chromatogram was replaced by two peaks with relative areas of 40% and 60%. The reaction mixture was neutralized and worked up in the usual manner. The resulting brown oil was a mixture of 62% 3-phenyl-2-butanone and 38% 4-phenyl-2-butanone identified by ir and nmr spectroscopy as well as gpc.

B. with Mercuric Acetate.--The ether mixture (III) (0.2 g, 0.001 mole) was placed in an nmr tube with 0.25 ml of CD_3COOD. An nmr spectrum indicated the ether was stable in this solvent. To the solution, 0.4 g (0.0013 mole) of mercuric acetate (MCB reagent) in 0.5 ml of CD_3COOD was added as a slurry. The reaction was monitored by nmr spectroscopy. All of the ether had reacted within 10 minutes. The solvent was removed on a rotary evaporator, the residue taken up in $CHCl_3$ and filtered to remove unreacted mercuric acetate. After removing the solvent, the resulting oil (0.367 g) gave an nmr spectrum identical to that obtained by A. DePuey for the products of the reaction of trans-2-phenyl-1-methylcyclopropanol (IIb) with mercuric acetate.[3] On this basis the products of the reaction were assigned as 75% 3-phenyl-4-acetoxymercuri-2-butanone and 25% 4-phenyl-4-acetoxymercuri-2-butanone.

C. with tert-Butylhypochlorite.--A sample of the ether mixture (III) (0.06 g, 0.0004 mole) was placed in an aluminum foil-covered 50-ml erlenmeyer flask with 1.5 ml of CCl_4. The system was flushed with nitrogen and, with cooling (ice bath), 0.08 g (0.0008 mole) of tert-butylhypochlorite prepared according to the method of Walling[17] was introduced. After 1.5 hr of stirring, a sample was removed and an nmr spectrum recorded. The only resonance in the nmr spectrum in addition to starting ether was at τ = 8.69 (tert-butylhypochlorite). After 24 hr at room temperature, there was still no evidence of reaction. The reaction was also carried out in $CDCl_3$ with no evidence of reaction after 2 days.

Reaction of trans-2-Phenyl-1-Methylcyclopropanol (IIb) with Ferric Chloride. A. Racemic Alcohol (IIb).--The alcohol (IIb) was made by methyl lithium reduction of trans-2-phenyl-1-methylcyclopropylacetate (IIa).[16] A sample of the alcohol (IIb) (0.1 g, 0.0008 mole) and 10 ml of anhydrous ether were placed in a 25-ml three-neck round-bottom flask. The solution was cooled to 0.5°, and with stirring 0.18 g (0.0011 mole) of anhydrous ferric chloride (MCB reagent) in 15 ml of ether was slowly added. Stirring was continued at 5° for 0.5 hr. The mixture was then warmed to room temperature, filtered, extracted twice with 10 ml of water, and dried ($MgSO_4$). Removal of the solvent followed by nmr analysis indicated the presence of some unreacted alcohol. The reaction was rerun in the same manner as above using an additional 0.14 g (0.0009 mole) of ferric chloride. The sole product was 4-chloro-4-phenyl-2-butanone: nmr ($CDCl_3$) τ = 7.82 (s, 3, CH_3), 6.78 (s, 2, $-CH_2CO-$), 4.58 (dd, 1, CH), 2.60 (s, C_6H_5); ir ($CHCl_3$) 1725 cm^{-1} (C=O).[4]

B. (+)-Alcohol (IV).--The (+)-alcohol (IV) was provided by D. Gibson and was made according to the procedure of DePuy et al.[2] A Rudolph Model 70 No. 709 Polarimeter with a sodium light source was used to determine optical rotations. The (+)-alcohol (IV) gave optical rotations, $[\alpha]_D$, of +39.11 ± 1° in ethanol and +39.44 ± 3.5° in $CHCl_3$. The maximum reading given for the (+)-alcohol (IV) is +41.9° (EtOH), indicating the optical purity of this alcohol was 93%. The (+)-alcohol (IV) (0.026 g, 0.0018 mole) was treated with 0.6 g (0.004 mole) of ferric chloride as described in part A. An nmr spectrum of the resulting oil indicated the presence of the chloroketone along with a small amount (~ 10%) of benzalacetone. A solution of 0.12 g of this oil in 1 ml of $CHCl_3$ gave an observed rotation of -0.25° or $[\alpha]_D$ = -1.97 ± 0.6°. An ir spectrum was taken of the solution from the polarimeter tube. A 1725 cm^{-1} (C=O) band indicated the chloroketone was still present. This solution was stirred with 1 N KOH in ethanol for 1 hr. Work-up gave a yellow oil, the nmr and ir of which, were identical to those of an authentic sample of benzalacetone.[15]

Preparation and Separation of cis- and trans-1,2-Diphenylcyclopropyl Acetates.--The acetate mixture was prepared according to the procedure of Freeman[5] and DePuy[9] with the modifications already described for the synthesis of 2-phenyl-1-methylcyclopropylacetates. Chalcone (75 g, 0.360 mole), prepared from condensation of acetophenone and benzaldehyde,[18] and 12.5 g (0.39 mole) of 97% hydrazine were condensed to give 3,5-diphenyl-2-pyrazaline in nearly quantitative yield. The 2-pyrazoline was treated with 230 g (0.5 mole) of lead tetraacetate to yield 98 g of the 3-acetoxypyrazoline which upon pyrolysis gave a mixture of 73% trans and 27% cis acetates. The acetates were separated and purified by a combination of spinning band distillation and recrystallization.[9] cis-1,2-Diphenylcyclopropyl acetate: mp 73.5-75° (lit. mp 74.5-75°).[9]

Synthesis of trans-1,2-Diphenylcyclopropanol (Vb).--A sample of the trans acetate (3 g, 0.01 mole) was cleaved with 13 ml (0.03 mole) of methyllithium in ether. Work-up yielded 2.6 g of a white solid. Recrystallization from Skellysolve B-ether gave 1.4 g (53%) of the pure alcohol (Vb): mp 96.5-99° (the value of the melting point varied considerably with various fractions, lit. mp 75-76.5°);[9] nmr ($CDCl_3$) τ = 2.82, 2.97 (s + m, 10, C_6H_5's), 7.23 (dd, 1, cyclopropane CH), 7.47 (s, 1, OH), 8.35 (m, 2, cyclopropane CH_2); ir ($CHCl_3$) 3610, 3430 cm^{-1} (OH).

Synthesis of cis-1,2-Diphenylcyclopropanol (Va).--A sample of the cis acetate (3.5 g, 0.014 mole) was cleaved with 14 ml (0.03 mole) of 2.3 M methyllithium to yield 3.3 g of a white solid which was recrystallized from hexane-ether mixtures at freezer or Dry Ice temperatures. The alcohol (Va) had the following properties: mp 79-82.5° (lit. mp 67-69°);[9] ir ($CHCl_3$) 3600, 3450 cm^{-1} (OH); nmr ($CDCl_3$) τ = 2.67 (d, 10, C_6H_5's), 7.51 (dd, 1, cyclopropane CH), 7.79 (s, 1, OH- which disappeared on shaking with D_2O), 8.35 (m, 2, cyclopropane CH_2).

Reactions of trans-1,2-Diphenylcyclopropanol (Vb).--A. with N-Bromosuccinimide. The trans alcohol (Vb) (0.17 g, 0.0008 mole) in 2 ml of $CDCl_3$ was added to a stirred slurry of 0.16 g (0.0009 mole) of N-bromosuccinimide (MCB) in 2 ml of $CDCl_3$ in a 50-ml erlenmeyer flask covered with aluminum foil. Immediately an aliquot was removed and nmr analysis within 5 min of mixing indicated the reaction was complete. The nmr sample was transferred back to the reaction mixture and the solvent was removed. The residual solid-oil was taken up in $CDCl_3$. In addition to singlets at τ = 7.08 and 7.28 for N-bromosuccinimide and succinimide, the nmr spectrum was consistent with 3-bromo-3-phenylpropiophenone as the sole reaction product: τ = 2.12, 2.43 (m, 10, C_6H_5's), 4.30 (t, 1, Br-C-H); 6.05.[2] Passage of the reaction mixture through a small silica gel column with CH_2Cl_2 removed the N-bromosuccinimide and succinimide. An ir spectrum of the resulting oil showed a carbonyl absorption at 1690 cm^{-1}. The N-bromosuccinimide reaction product (0.2 g) was taken up in 4 ml of dioxane, 3 ml of 1 N K_2CO_3 in dioxane-water was added, and the resulting yellow solution was stirred for 40 hr at room temperature. Methylene chloride (20 ml) was added and the solution was extracted twice with 10 ml of 5% $NaHCO_3$, and several times with water. Drying ($MgSO_4$) and removal of solvent on a rotary evaporator, yielded 0.0726 g of an oil. An nmr spectrum indicated the presence of chalcone (compared to an authentic sample)[18] and dioxane. Further water extraction removed the dioxane and yielded 0.03 g of a yellow oil which had properties identical to an authentic sample of chalcone.[18]

B. with tert-Butylhypochlorite. A 50-ml aluminum foil-covered erlenmeyer flask was charged with 0.14 g (0.0007 mole) of the trans alcohol (Vb) and 1.5 ml of $CDCl_3$. tert-Butylhypochlorite[17] (0.1 g, 0.001 mole) in 0.5 ml $CDCl_3$ was added to the stirred solution. An nmr spectrum obtained within 5 min of mixing indicated that the alcohol had been completely consumed. The reaction mixture was taken up in CH_2Cl_2 and extracted several times with water to remove the tert-butanol. After drying ($MgSO_4$) and removal of solvent, 0.1133 g of a solid was obtained. An nmr spectrum ($CDCl_3$) indicated the product was exclusively 3-chloro-3-phenylpropiophenone. The chloroketone was treated with 1 N K_2CO_3 as described in part A. The resulting product was exclusively chalcone as identified by nmr and ir spectroscopy, and gpc analysis. Reaction of the alcohol (Vb) with tert-butylhypochlorite in carbon tetrachloride was also rapid yielding the

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chloroketone. Elimination with DABCO (Aldrich), gave greater than 95% chalcone identified by nmr and ir spectroscopy, and gpc analysis versus an authentic sample.[18]

C. with Mercuric Acetate: The trans alcohol (Vb) (0.4 g, 0.002 mole) was dissolved in 15 ml of glacial acetic acid in a 50-ml erlenmeyer flask. Mercuric acetate (0.6 g, 0.002 mole, MCB reagent) was added to the stirred solution in portions. After stirring 1 hr, the solvent was removed on a rotary evaporator at 45°. The resulting cloudy oil was taken up in CH_2Cl_2 and filtered to remove some of the unreacted mercuric acetate. Removal of the solvent yielded 1.0 g of an orange semi-solid: nmr ($CDCl_3$) τ = 2.10, 2.78 (m's, C_6H_5's), 6.22 (m, CH_2 and possibly $CHHgOAc$), 8.02 (s, acetate CH_3). Further rotary evaporation removed traces of CH_2Cl_2 and HOAc to yield 0.9344 g of an orange semi-solid.

The crude organomercurial acetate from above was placed in a 125-ml erlenmeyer flask with 50 ml of MeOH to form a slurry. Sodium borohydride (0.3 g, 0.008 mole) was added in portions with cooling (ice bath) and stirring. The reaction was exothermic and mercury precipitated. After 0.5 hr of stirring, 25 ml of saturated NH_4Cl solution was added to the reaction mixture. This solution was extracted 5 times with 30 ml of CH_2Cl_2. The combined CH_2Cl_2 was extracted with saturated NH_4Cl and water. After drying ($MgSO_4$) and removing the solvent on a rotary evaporator, 0.3 g of an oil was obtained. An ir spectrum indicated both alcohol and ketone to be present. Oxidation of the mixture with a dichromate solution, yielded 0.0563 g of an oil: ir ($CHCl_3$) 1685 cm^{-1} (C=O). Analysis by gpc (Column D at 181°) yielded two peaks of 87.5% and 12.5% which had the same retention times as authentic samples of β-phenylpropiophenone and α-phenylpropiophenone respectively. These two peaks accounted for greater than 80% of the gas chromatogram. There was a small amount of material (~ 10%) with a retention time identical to chalcone. These results were supported by nmr and ir data.

Reactions of cis-1,2-Diphenylcyclopropanol (Va). A. with N-Bromosuccinimide: The cis alcohol (Va) was allowed to react with N-bromosuccinimide in $CHCl_3$ according to the procedure given for the trans alcohol (Vb) above. The reaction was rapid yielding β-chloro-β-phenylpropiophenone as the sole product identified by

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nmr and ir spectroscopy. Elimination of the bromoketone yielded exclusively chalcone identified by nmr and ir spectroscopy as well as gpc analysis.

B. with tert-Butylhypochlorite: The cis alcohol (Va) was allowed to react with tert-butylhypochlorite[17] in $CHCl_3$ according to the procedure given for the trans alcohol (Vb) above. The reaction was rapid, yielding β-chloro-β-phenylpropiophenone identified by nmr and ir spectra.

C. with Mercuric Acetate: The cis alcohol (Va) was allowed to react with mercuric acetate in HOAc according to the procedure given for the trans alcohol (Vb). Reduction of the organomercurial with sodium borohydride and oxidation with dichromate solution yielded an oil. The absence of α-phenylpropiophenone was indicated by gpc analysis (Column D at 185°). There were two major peaks with retention times identical to β-phenylpropiophenone (68%) and chalcone (32%). Spectral data (nmr and ir) indicated the presence of these two components.

β-Phenylpropiophenone: An authentic sample showed: mp 70-71° (lit. mp 72-73°).[20]

α-Phenylpropiophenone: Phenylmagnesium bromide was prepared in the usual manner from 4 g (0.16 g at.) of magnesium turnings (MCB) and 16.5 ml (25 g or 0.16 mole) of phenyl bromide. 2-Phenylpropionaldehyde (20 g, 0.150 mole, Aldrich) in 25 ml of ether was added to the Grignard over a 25-min period. After stirring for 2 hr, saturated NH_4Cl was added to the mixture until salts precipitated. The ether was decanted and the solids were washed several times with ether. The combined ether extracts were extracted twice with 100 ml of water. After drying ($MgSO_4$), the ether was removed on a rotary evaporator to yield 15 g (50%) of a yellow oil: ir ($CHCl_3$) 3620, 3480 cm^{-1} (O-H); nmr ($CDCl_3$) τ = 2.64, 2.73 (m, 10, C_6H_5's), 5.18 (d, 1, H-C-OH), 6.88 (m, 1, CH), 8.06 (s, 1, OH), 8.69, 8.91 (d, 3, CH_3's).

The alcohol (12 g, 0.06 mole) was oxidized with a dichromate solution according to the procedure used for the synthesis of isobutyrophenone. Work-up yielded 11 g of a yellow oil. Recrystallization from ethanol-Skellysolve B gave a pure sample: mp 48.5-50° (lit. mp 49-51°).[21]

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Synthesis of 2-Methyl-1-Phenylcyclopropanol (VI).--A mixture of cis- and trans-2-methyl-1-phenylcyclopropyl acetates was prepared by the method of Freeman[5] (cis:trans ~ 1.8:1). The acetate mixture (10 g, 0.05 mole) was cleaved with 56 ml of 2.3 M methyllithium[16] and worked up to give a yellow oil. The material was distilled and 7 g (88%) of a colorless oil (VI) was collected, bp 65-75°/0.8 mm): ir ($CHCl_3$) 3600, 3430 (OH); nmr ($CDCl_3$) τ = 8.7-9.4 (m, 6, cyclopropane CH_2, CH, and CH_3), 7.52 (s, 1, OH), 7.64, 7.73 (s, 5, C_6H_5).

Reactions of 2-Methyl-1-Phenylcyclopropanol (VI) with Halogenating Agents. A. with N-Bromosuccinimide: N-bromosuccinimide (0.3 g, 0.002 mole, MCB) and 5 ml of $CHCl_3$ were placed in an aluminum foil-covered 50-ml erlenmeyer flask to form a slurry. The alcohol (VI) (0.2 g, 0.001 mole) in 5 ml of $CHCl_3$ was added to the stirring slurry over a few moments. The solution initially turned orange and it was stirred for 30 min. The solvent was removed on a rotary evaporator to yield 0.5 g of a solid-oil mixture which was taken up in CCl_4 and filtered to remove some of the succinimide. Removal of the CCl_4 yielded 0.3 g of an oil. An nmr spectrum ($CDCl_3$) showed phenyl absorptions at τ = 2.12 and 2.43 in the ratio of 1:1.7 assigned the ortho and meta-para protons; a series of complex absorptions in the region τ = 5.9 to 6.9 assigned to $BrCH_2$, CH-CH_3, and CH_2CO-; a weak absorption at τ = 5.29 assigned to CH-Br; and doublets at τ = 8.20 and 8.73 in the ratio of ~ 1:8 assigned to the CH_3 of β-bromo-α-methylpropiophenone and to the CH_3 of α-bromo-α-methylpropiophenone respectively. Traces of N-bromosuccinimide and succinimide were removed by silica gel chromatography with CH_2Cl_2 as the eluting solvent. An ir spectrum ($CHCl_3$) showed a carbonyl absorption at 1685 cm^{-1}. The oil was treated with K_2CO_3 for 24 hr as previously described. Pentane (50 ml) was added to the reaction mixture. The layers were separated and the pentane was extracted with 20 ml of 10% HCl, twice with 20 ml of 5% $NaHCO_3$, and twice with 20 ml of water. The pentane solution was dried ($MgSO_4$) and the solvent removed on a rotary evaporator to yield 0.0535 g of an oil. Based on comparison with nmr spectra of authentic samples, an nmr spectrum ($CDCl_3$) indicated the presence of isopropenyl phenyl ketone (VIII) and propenyl phenyl ketone (VII) with the former

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predominating. An ir spectrum showed a carbonyl absorption at 1665 cm^{-1}. Analysis by gpc (Column A at 167°) indicated the presence of two components in the amounts of 86% and 14% with retention times corresponding to authentic samples of isopropenyl phenyl ketone (VIII) and propenyl phenyl ketone (VII) respectively.

B. with Ferric Chloride: The alcohol (VI) (0.2 g, 0.002 mole) was allowed to react with 0.6 g (0.004 mole) of ferric chloride (MCB reagent) according to previously described procedures. After stirring for 30 min at 0-5°, the mixture was stirred for 2 hr at room temperature. Work-up yielded 0.2 g of a yellow oil: ir ($CHCl_3$) 1690 cm^{-1} (C=O). An nmr spectrum ($CDCl_3$) was consistent with β-chloro-β-methylpropiophenone as the sole product: τ = 8.36 (d, 3, CH_3), 6.58 (AB portion of ABX spectrum 2, CH_2), 5.32 (sextet, 1, CH), 2.01, 2.42 (m, 5, C_6H_5). These nmr assignments were confirmed by nmr spin decoupling experiments. The chloroketone was treated with 1 N K_2CO_3 as described in part A. The resulting oil had nmr, ir, and gpc properties consistent with those of an authentic sample of propenyl phenyl ketone (VII). Only a trace of the other isomer, isopropenyl phenyl ketone (VIII), was present as indicated by gpc (Column A at 167°).

C. with tert-Butylhypochlorite. No Inhibitor: The alcohol (VI) (0.2 g, 0.002 mole) was allowed to react with 0.2 g (0.002 mole) of tert-butylhypochlorite in $CHCl_3$ according to previously described procedures. After stirring 45 min, the solvent was removed on a rotary evaporator yielding 0.3 g of a colorless oil. The oil was taken up in CH_2Cl_2 and extracted several times with water. After drying ($MgSO_4$) and solvent removal, another nmr spectrum indicated the presence of β-chloro-β-methylpropiophenone. In addition a doublet at τ = 8.73 and a complex multiplet in the region τ = 5.8 to 6.5 indicated the presence of β-chloro-α-methylpropiophenone in lesser amount. An ir spectrum ($CHCl_3$) showed a carbonyl absorption at 1690 cm^{-1}. The chloroketones were treated with 1 N K_2CO_3 as described in part A. After work-up, an nmr spectrum indicated the presence of 35% isopropenyl phenyl ketone (VIII) and 65% propenyl phenyl ketone (VII). An ir spectrum ($CHCl_3$) showed carbonyl absorptions at 1655 and 1629 cm^{-1}. Analysis by gpc (Column A at 167°) indicated the presence of 42% isopropenyl phenyl ketone and 58% propenyl phenyl ketone compared with retention times of authentic samples.

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Preparation of Propenyl Phenyl Ketone (VII).--The ketone was prepared by Friedel-Crafts acylation of benzene with crotonyl chloride (Aldrich) and $AlCl_3$ according to published procedures.[22] The propenyl phenyl ketone had the following properties: bp 69-73°/0.8 mm (lit. bp 135-140°/20 mm);[23] ir ($CHCl_3$) 1660 (C=O), 1627 cm^{-1} (C=C); nmr ($CDCl_3$) τ = 8.10 (d, 3, CH_3), 2.14, 2.54, 3.04 (m, 7, C_6H_5, CH=CH); mass spectrum m/e (rel intensity) 146(54.4), 105(100), 77(82.1), 69(56.1), 51(45.8). Analysis by gpc (Column A at 167°) indicated the olefin was greater than 90% pure.

Preparation of Isopropenyl Phenyl Ketone (or Methacrylophenone) (VIII). A. Preparation of Isopropylphenylcarbinol: Phenyl magnesium bromide was prepared in the usual manner from 24 g (1.4 g at.) of magnesium turnings (MCB) and 218 g (1.4 mole) of bromobenzene (MCB). Isobutyraldehyde (100 g, 1.4 mole, MCB) in 250 ml of anhydrous ether was added dropwise to the Grignard over a period of 2 hr. The mixture was then stirred under reflux for 0.5 hr. Saturated aqueous NH_4Cl was then added until a precipitate formed. The ether was decanted and the precipitate washed with ether. The combined ether was extracted with water and dried. Removal of the ether by distillation yielded a liquid which upon distillation gave 174.2 g (91%) of isopropylphenylcarbinol: bp 61-67°/~0.7 -1mm (lit. bp 101-104°/7 mm).[23]

B. Preparation of Isobutyrophenone: In a 500-ml three-neck round-bottom flask was placed 30 g (0.3 mole) of the above alcohol and 100 ml of ether. To this stirred solution was added 150 ml of dichromate solution (prepared from 55 g of sodium dichromate dihydrate and 41.5 ml of concentrated H_2SO_4 diluted to 225 ml with water) over a 70-min period at room temperature. Some cooling with an ice bath was necessary. The mixture was then stirred for 16 hr. The ether and green chromate layers were separated and the chromate layer was extracted with ether. The combined ether was extracted with 50 ml of 5% $NaHCO_3$, 50 ml of water, and dried ($MgSO_4$). Removal of the ether and distillation yielded 47.0 g (94%) of isobutyrophenone: bp 60-65°/1.6 mm (lit. bp 120°/20 mm).[24]

C. Preparation of α-Bromo-α-Methylpropiophenone: The procedure followed was patterned after that for the preparation of α-bromoacetophenone from acetophenone.[25] A 250-ml three-neck

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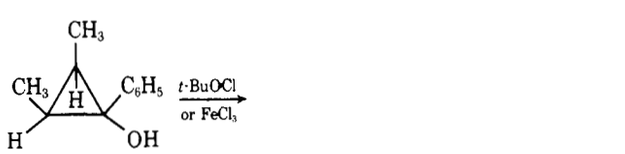
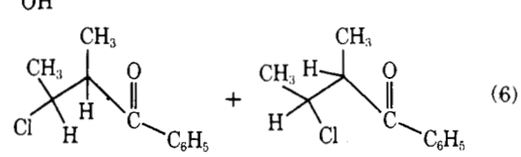
round-bottom flask was charged with 10 g (0.07 mole) of isobutyrophenone and 50 ml of anhydrous ether. This mixture was cooled with an ice bath and about 0.1 g of aluminum chloride (MCB reagent) was added. Bromine (3.3 ml, 10.3 g, 0.07 mole, MCB reagent) was added dropwise to the cold solution with stirring over a 5-min period. No reaction seemed to occur, so two spatulas of aluminum chloride were added and the ice bath was removed. After stirring 30 min the reaction was complete as evidenced by the disappearance of the bromine color. The solvent was removed on a rotary evaporator to leave an orange oil which was taken up in ether and extracted twice with 25 ml of water. The water layer was extracted with ether. The ether solutions were combined and dried ($MgSO_4$). The ether was removed on a rotary evaporator to yield 14 g (89%) of a yellow oil. Treatment of a few drops of the oil with silver nitrate-ethanol produced a yellow precipitate (AgBr). Spectral properties were consistent with those expected for α-bromo-α-methylpropiophenone: nmr ($CDCl_3$) τ = 1.93 (m, 2, ortho protons), 2.48 (m, 3, meta and para protons), 7.96 (s, 6, CH_3's); ir ($CHCl_3$) 1680 cm^{-1} (C=O).

D. Preparation of Isopropenyl Phenyl Ketone (or Methacrylophenone VIII): Heating of α-bromo-α-methylpropiophenone with an equivalent of DABCO (Air Products or Aldrich) in dioxane at 100-106° for 12 hr resulted in the formation of a precipitate (DABCO·HBr) which was filtered and washed with CH_2Cl_2. The dioxane-CH_2Cl_2 was extracted with water several times. The solution was dried ($MgSO_4$) and the solvent removed on a rotary evaporator to yield an oil which an nmr spectrum indicated was fairly pure isopropenyl phenyl ketone (VIII). The oil was taken up in pentane and extracted with 20 ml of 2 N HCl, 20 ml of 5% $NaHCO_3$, and twice with 20 ml of water. After drying ($MgSO_4$) and removal of solvent, the resulting oil was distilled and a fraction (bp 49-51°/1 mm, lit. bp 60°/3 mm)[26] was collected. It had spectral properties consistent with those expected for isopropenyl phenyl ketone (VIII): ir ($CHCl_3$) 1660 (C=O), 1630 cm^{-1} (C=C); nmr ($CDCl_3$) τ = 2.31 (m, 2, ortho protons), 2.45 (m, 3, meta and para protons), 4.10, 4.38 (m's, 2, CH_2=C), 7.90 (s, 3, CH_3); mass spectrum m/e (rel intensity) 146(40), 105(100), 77(65.8), 58(16.3), 51(28.6), 43(57.3), 41(12.1), 39(16.1), 32(16.4). Analysis by gpc (Column A at 167°) indicated the olefin was pure.

this hypothesis optically active *trans*-2-phenyl-1-methylcyclopropanol (IV)[2] was allowed to react with NBS, *tert*-butyl hypochlorite, and $FeCl_3$. Cleavage with NBS and *tert*-butyl hypochlorite in $CDCl_3$ proceeds with predominant or exclusive inversion at the benzylic carbon yielding optically active 4-halo-4-phenyl-2-butanone (eq 7).[8] In contrast, cleavage with $FeCl_3$ in ether yields racemic 4-chloro-4-phenyl-2-butanone.

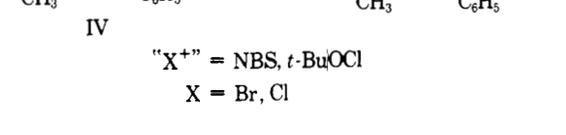




50% 50% (6)

***cis*- and *trans*-1,2-Diphenylcyclopropanol (Va and Vb).** A mixture of *cis*- and *trans*-1,2-diphenylcyclopropylacetates was prepared and separated according to the method of Freeman[5] and DePuy.[9] Cleavage with methyllithium produces the corresponding alcohols Va and Vb. These alcohols melt over a relatively wide range even after numerous recrystallizations even when it appeared by nmr and ir spectroscopy that they were pure. Perhaps they melt with some ring opening induced by air or glass.

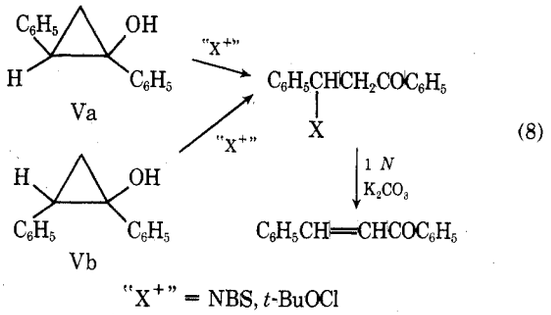
Both of these alcohols react rapidly with NBS or *tert*-butyl hypochlorite in CCl_4 solution to yield a single halo ketone whose nmr spectrum is consistent with the struc-



IV (7)

"X+" = NBS, *t*-BuOCl

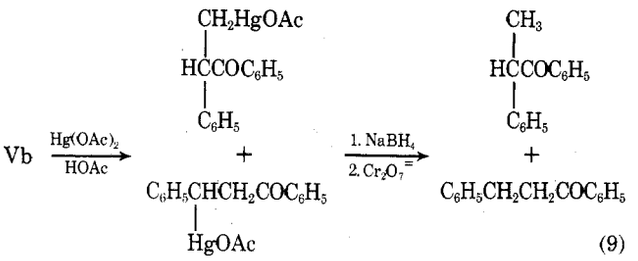
X = Br, Cl



"X^+" = NBS, *t*-BuOCl

ture of β-halo-β-phenylpropiophenone (eq 8). This structure was confirmed when it was found that stirring with 1 *N* potassium carbonate solution converted the product exclusively to chalcone.

When either Va or Vb is stirred with an equivalent of mercuric acetate in acetic acid at room temperature, ring cleavage occurs within an hour, giving rise to a mixture of organomercurials (eq 9). To determine the relative amount



(9)

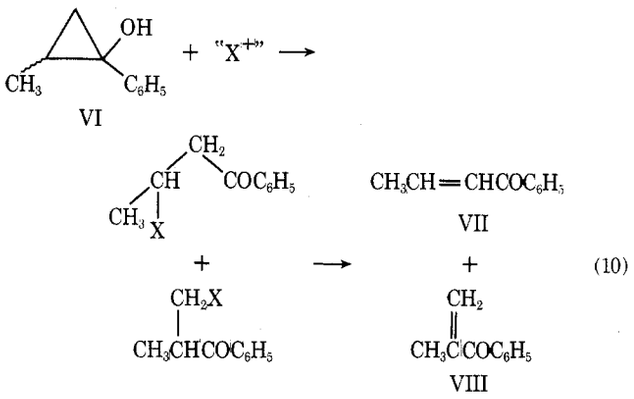
of C_1–C_2 compared to C_1–C_3 bond cleavage, the carbon–mercury bond was reduced with sodium borohydride and the resulting mixture of alcohols was reoxidized to a mixture of α- and β-phenylpropiophenone. Analysis of the mixture of ketones was made by gpc and comparison was made with authentic samples which were synthesized by standard methods (see Experimental Section). Both the cis and trans isomers gave mainly or exclusively C_1–C_2 cleavage; from the former no α-phenylpropiophenone was formed, the ketone fraction being 68% β-phenylpropiophenone and 32% chalcone while the latter gave 88% β-phenyl- and 12% α-phenylpropiophenone together with chalcone. The chalcone must have arisen by elimination of the highly reactive benzylic organomercurial either by solvolysis or during reduction.[10] In any event it could only have arisen from the products of C_1–C_2 cleavage so that cleavage in this direction occurs to the extent of 90–100%. We have also shown that cleavage of these isomers by H^+ leads to 93–95% C_1–C_2 cleavage.[9] These results confirm scattered literature results which indicate that in a 1,2-diphenylcyclopropane the ring bond between two phenyl groups is cleaved preferentially. Levina[11] reported that cleavage of 1,2-diphenylcyclopropanes occurs between the two phenyls upon reaction with bromine at −7°. LaLonde[12] also found exclusive C_1–C_2 cleavage of the 1,2-diphenylcyclopropanes with bromine in CCl_4 at −20°. Young[13] has noted a similar direction of cleavage for 1,2-diphenylcyclopropanes with ceric ammonium nitrate.

2-Methyl-1-phenylcyclopropanol (VI). In previous work we had determined that this compound undergoes 99% C_1–C_3 cleavage with mercuric acetate, 53% C_1–C_3 cleavage with H^+, and 83% C_1–C_3 cleavage with OH^-.[3] To complete our comparison with the 1,2-diphenyl and 2-phenyl-1-methyl systems, we wished to determine the product composition upon ring opening with halogenating compounds (eq 10). Brominations were carried out with NBS in chloroform and chlorinations with *tert*-butyl hypochlorite in chloroform and ferric chloride in ether. The results are given in Table I.

Table I
Product Distributions from Cleavage of 2-Methyl-1-phenylcyclopropanol (VI) with Halogenating Agents[a]

Reagent/solvent	% C_1–C_2 cleavage	% C_1–C_3 cleavage
NBS/$CHCl_3$	14	86
t-BuOCl/$CHCl_3$	58	42
$FeCl_3$/ether	100	0

[a] Based on elimination of the β-halo ketones to isopropenylphenyl ketone (VIII) and propenylphenyl ketone (VII).



"X^+" = NBS, *t*-BuOCl

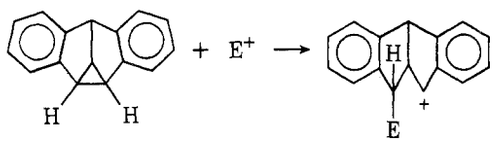
These results for NBS and $FeCl_3$ are those expected on the basis of earlier studies. For example, bromination of 1,2,2-trimethylcyclopropanol gives 100% C_1–C_3 bond cleavage, by attack of the electrophile on the least substituted carbon, while $FeCl_3$ oxidation gives 100% C_1–C_2 opening with the generation of the most stable radical.[4] The reaction products with *tert*-butyl hypochlorite are difficult to account for. When the reaction was carried out in the presence of hydroquinone or *p*-cresol, the product mixture did not change. These inhibitors did not interrupt any radical chain reaction.

Discussion

The results reported in this paper complement and reinforce those reported earlier[1,3,4,9] without affording final answers to several striking aspects of the reactions of cyclopropanols with electrophiles. The most puzzling anomalies lie in ring opening with various halogenating agents. We might take 1,2,2-trimethylcyclopropanol as a "well behaved" compound. This molecule reacts rapidly with NBS or *tert*-butyl hypochlorite giving quantitative yields of products resulting from attack on the methylene ring carbon.[4] 2-Phenyl-1-methylcyclopropanols reacts equally rapidly, but exclusively at the benzylic carbon, and completely, or nearly so, with inversion of configuration at C_2. This high stereospecificity would seem to rule out any radical–chain mechanism, especially so since $FeCl_3$ oxidation leads to nearly racemic chloride, and, while ionic chain mechanisms are conceivable, they do not give any clear-cut explanation for the differences found on halogenation of 2-methyl-1-phenylcyclopropanols nor for the differing stereochemical results reported earlier for the 2,3-dimethyl-1-phenylcyclopropanols and cyclopropyl acetates.[4] Further work will be needed to clear up these differences in behavior which are especially interesting because cyclopropanes in general are not reactive toward halogenating agents, cyclopropanols being a notable exception.

Our results also confirm that 1,2-diphenylcyclopropanes are especially susceptible to cleavage of the ring bond between the phenyl groups, no matter what the electrophile.

The effect is observed whether the two aromatic rings are cis to one another or trans, and thus cannot be due to a steric relief of strain. We do not have any stereochemical results in a diphenyl system, so we cannot say whether the electrophile is entering with retention or inversion, but in the system studied by Cristol and coworkers[14] ring opening always occurred on the bond between the aromatic rings and with retention (eq 11). It will be interesting to see if this stereochemistry will hold for simple cyclopropanes.



(11)

The independence of product composition with cyclopropane stereochemistry is also clearly shown by the reactions of *cis*- and *trans*-2-phenyl-1-methylcyclopropanols, and the product composition is also unchanged when the much less reactive methyl ethers are used in place of the alcohols. Additional work is now in progress which may shed light on some of these puzzling observations.

Acknowledgment. The authors wish to thank the National Science Foundation for support of this research by Grant GP 13783X.

Registry No.—Ia, 52306-22-6; Ib, 52438-83-2; IIa, 52306-23-7; IIb, 10606-71-0; *cis*-III, 52306-24-8; *trans*-III, 52306-25-9; (+)-IV, 52306-26-0; Va, 43187-69-5; Vb, 43187-79-7; *cis*-VI, 52374-29-5; *trans*-VI, 52306-27-1; VII, 495-41-0; VIII, 769-60-8; benzalacetone, 122-57-6; hydrazine, 302-01-2; 3-methyl-5-phenyl-2-pyrazoline, 939-03-7; 3-acetoxy-3-methyl-5-phenyl-1-pyrazoline, 52306-28-2; *N*-bromosuccinimide, 128-08-5; mercuric acetate, 1600-27-7; *tert*-butyl hypochlorite, 507-40-4; ferric chloride, 7705-08-0; 4-chloro-4-phenyl-2-butanone, 52306-29-3; 4-bromo-4-phenyl-2-butanone, 52306-30-6; *cis*-1,2-diphenylcyclopropyl acetate, 43187-69-5; *trans*-1,2-diphenylcyclopropyl acetate, 43187-79-7; β-bromo-β-phenylpropiophenone, 52306-31-7; α-phenylpropiophenone, 2042-85-5; 2-phenylpropionaldehyde, 93-53-8; 1,2-diphenyl-1-propanol, 28795-94-0; β-chloro-β-methylpropiophenone, 34880-85-8; isobutyraldehyde, 78-84-2; isopropylphenylcarbinol, 611-69-8; isobutyrophenone, 611-70-1; α-bromo-α-methylpropiophenone, 10409-54-8.

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Activation of Dimethyl Sulfoxide by Electrophiles and Use of the Reactive Intermediates in the Preparation of Iminosulfuranes[1a]

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Received June 11, 1974

Dimethyl sulfoxide (DMSO) reacts at oxygen with SO_3, P_4O_{10}, BF_3, and H_2SO_4 at or below room temperature. With the first two electrophiles, intermediates are obtained that generally react readily with sulfonamides, amides, and aromatic amines to give iminosulfuranes in good to excellent yields (60–90%). Although intermediate complex formation is necessary for the formation of iminosulfuranes, it is not a sufficient condition for successful reaction, as a good leaving species must also be provided to facilitate cleavage of the S–O bond of DMSO. Acetic anhydride does not form significant quantities of "activated" intermediate with DMSO at room temperature but does at elevated temperatures and, if sulfonamides or carboxamides are present, iminosulfuranes are obtained. The activation of DMSO with SO_3 has received detailed study; SO_3 is especially useful in the preparation of iminosulfuranes from DMSO and aromatic amines; and it can also be used with the other nitrogen compounds. Salts have been prepared from selected iminosulfuranes and hydrogen chloride. Mechanistic considerations are also discussed.

In this paper we are reporting (a) the "activation" of DMSO by liquid SO_3 and, for comparison, P_4O_{10}, acetic anhydride, concentrated sulfuric acid, and boron trifluoride; (b) the scope and limitations of the reaction of "activated" DMSO with a variety of nitrogen compounds (sulfonamides, amides, and aryl amines) to prepare iminosulfuranes with a wide range of structures (R_2S^+–N^-–R'); (c) certain mechanistic aspects of the iminosulfurane preparative reaction; and (d) some spectral and other miscellaneous characteristics of iminosulfuranes. As a corollary of (a),