Uncatalyzed Acetylation with Acetic Anhydride.—Two hundred grams of cellulose acetate was dissolved in two liters of acetic acid. The solution was heated by total immersion in a steam-bath and vigorously stirred during the addition of 200 g. of acetic anhydride and for one hour afterward. Samples were taken as indicated in Table II. Portions of the solution were poured into distilled water with vigorous stirring to precipitate the product, which was then washed to neutrality and dried in a current of air at 70°. The portions used for analyses were further dried at 105°.

Acetylation with Perchloric Acid Catalyst.—Two hundred grams of cellulose acetate was dissolved in two liters of acetic acid at room temperature, and 200 g. of acetic anhydride at 0° was added with good stirring. Then 80 ml. of acetic acid containing 0.10 ml. of perchloric acid was added. Samples were taken during the course of one hour at room temperature, constant stirring being maintained.

Acetylation with Sulfuric Acid Catalyst.—This acetylation was similar to the above, except that 0.70 ml. of sulfuric acid was added. The sulfuric acid combined quantitatively with the cellulose acetate during this acetylation,[5] giving products containing 0.17–0.18% sulfur. They were rendered stable to drying by adding sufficient sodium carbonate to the last wash to impart a pink color to phenolphthalein indicator.

Acetylation in Solution with Pyridine Catalyst.—Eighty grams of cellulose acetate was dissolved in 1000 ml. of acetic acid and 200 g. of pyridine. The mixture was heated to 65° and 80 g. of acetic anhydride was added with stirring. Samples were taken during the course of one hour.

Acetylation in Suspension with Pyridine Catalyst.—These acetylations were carried out in individual screw-cap bottles on a tumbler heated to 65°. Each bottle was charged with 20 g. of cellulose acetate, 280 ml. of benzene, 20 g. of pyridine and 20 g. of acetic anhydride. The products were filtered off and washed with benzene.

Acetylation with Zinc Chloride Catalyst.—Fifty grams of cellulose acetate was dissolved in 500 ml. of acetic acid, and 50 g. of acetic anhydride was added with good stirring at room temperature. This was followed by a solution of 10 g. of zinc chloride dissolved in 20 ml. of acetic acid. Samples were taken during the course of seven hours. Triacetates were prepared by acetylating several of the starting materials with two parts of acetic anhydride and one part of zinc chloride for two hours at 50°. These products contained the theoretical amount of acetyl, no free hydroxyl, and had an optical rotation of −23 ± 1°.

Acetylation with Acetyl Chloride and Pyridine.—Fifty grams of cellulose acetate was dissolved in a mixture of 60 ml. of anhydrous pyridine and 540 ml. of anhydrous dioxane. To this solution, at room temperature or slightly below, was added a slurry of the acetyl chloride–pyridine addition compound, prepared as follows: In a one-liter, three-necked flask were placed 75 ml. of pyridine and 425 ml. of dioxane, and the mixture was cooled to +3°, at which point the dioxane began to crystallize. Fifty grams of acetyl chloride was added through a dropping funnel during an interval of ten minutes, with cooling and stirring. The addition compound separated from solution immediately on adding the acetyl chloride. The temperature was maintained under 15° during this step. The solution of cellulose acetate was cooled to 15°, and the slurry of the addition compound was added as rapidly as possible with good stirring. Samples were taken during the course of 1.5 hours. Toward the end of the reaction the mixture was heated to 40° in order to obtain a greater range of acetyl content in the products.

Analyses.—Acetyl determinations were made by saponification in suspension[6] or in solution.[7] Tritylations were carried out as previously described,[2] and most of the trityl determinations were made by ultraviolet absorption. Optical rotations were determined at a concentration of 5 g. of cellulose acetate in 100 ml. of solution, using 2-dm. tubes. The solvent was chloroform:3A alcohol (85:15 by weight). Water tolerance values were determined by adding water to 125 ml. of acetone containing 125 mg. of cellulose acetate in solution[8,9] and determining photometrically the point at which turbidity appeared. The values reported in Tables II are the ml. of water required to produce turbidity. Samples too low in acetyl content to be soluble in acetone alone became soluble upon addition of water but, finally, precipitated out as water was added in excess. Samples too high in acetyl content to be soluble in acetone were first dissolved in a small amount of tetrachloroethane. In these cases a correction was applied to make the results comparable with those run in acetone alone.

Acknowledgment.—We wish to thank Mr. J. R. Olson of the Physical Chemistry Department, Kodak Research Laboratories, for measuring the optical rotations reported herein.

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[5] C. J. Malm, L. J. Tanghe and B. C. Laird, *Ind. Eng. Chem.*, **38**, 77 (1946).

[6] L. B. Genung and R. C. Mallatt, *Ind. Eng. Chem., Anal. Ed.*, **13**, 369 (1941).

[7] C. J. Malm, L. B. Genung, R. F. Williams and M. A. Pile, *ibid.*, **16**, 501 (1944).

[8] D. R. Morey and J. W. Tamblyn, *J. Applied Phys.*, **16**, 419 (1945).

[9] C. J. Malm, J. W. Mench, D. L. Kendall and G. D. Hiatt, *Ind. Eng. Chem.*, **43**, 684 (1951).

ROCHESTER, N. Y.

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

Derivatives of 2,2-Diphenylcyclohexanone. II. Some Anomalous Absorption Spectra

BY WILLIAM B. BENNET AND ALFRED BURGER

RECEIVED JUNE 23, 1952

Additional derivatives of 2,2-diphenylcyclohexanone are described and the relative inertness of the parent ketone toward carbonyl reagents is discussed. 2,2-Diphenyl-5-cyclohexenone and some of its derivatives possess strikingly unexpected absorption spectra.

In continuation of previous work on cyclic analogs of methadon,[1] we have prepared further derivatives of 2,2-diphenylcyclohexanone for pharmacological testing and have noted some unexpected chemical and physical properties of certain compounds in this system.

2,2-Diphenyl-6-morpholinocyclohexanol (V) was prepared by two methods, either by reducing 2,2-diphenyl-6-morpholinocyclohexanone (III)[1] with lithium aluminum hydride or by reduction of 2,2-diphenyl-6-bromocyclohexanone (II)[1] with the same reagent followed by reaction of the resulting bromohydrin (IV) with morpholine.

Two types of addition reactions to 2,2-diphenyl-5-cyclohexenone were studied. When this unsaturated ketone VI[1] was dissolved in an excess of a secondary amine, 2,2-diphenyl-5-dialkylaminocyclohexanone derivatives (VIII) were obtained. One of these amino ketones, 2,2-diphenyl-5-piperidinocyclohexanone, was reduced to 2,2-diphenyl-5-piperidinocyclohexanol (IX) by lithium aluminum hydride. 2,2-Diphenyl-5-(*p*-acetamidobenzenesulfonyl)-cyclohexanone (VII) was pre-

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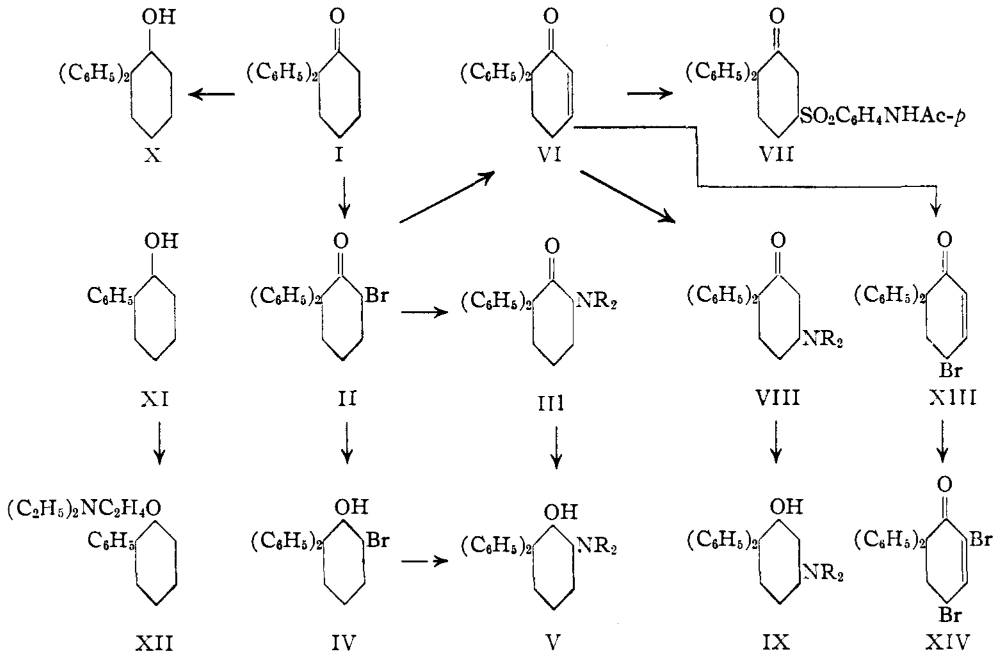
[1] A. Burger and W. B. Bennet, THIS JOURNAL, **72**, 5414 (1950).



pared by addition of *p*-acetamidobenzenesulfinic acid to 2,2-diphenyl-5-cyclohexenone (VI) in hot acetic acid solution.[2] Attempts to hydrolyze the acetamide linkage under acid conditions reversed, in one case, the addition process, the unsaturated ketone being recovered, and in a second case caused hydrolysis of the sulfone linkage, 2,2-diphenylcyclohexanone (I) being formed.

2,2-Diphenylcyclohexanol (X) was prepared by reduction of the corresponding ketone (I) with lithium aluminum hydride. The sodium derivative of this alcohol could not be induced to react with β-chloroethyldiethylamine, while that of the analogous 2-phenylcyclohexanol (XI) did react to give β-diethylaminoethyl 2-phenylcyclohexyl ether (XII). This reduced activity of a group adjacent to two phenyl groups is also reflected in the failure of the parent ketone, 2,2-diphenylcyclohexanone (I), to form a cyanohydrin or to undergo the Reformatsky reaction as detailed in the Experimental section. These results are in accord with the observations of Newman and Mosby[3] and Horning and Finelli[4] concerning the reactivity of similarly hindered cyclic ketones.

The preparation of previously unreported compounds in this group is recorded in the Experimental part.

Ultraviolet Spectra.—The ultraviolet absorption spectra of several of these compounds exhibit anomalies. Kumler, Alpen and Strait[5,6] have noted that in some α-phenylcarbonyl compounds the carbonyl absorption peak is more intense and is shifted toward longer wave lengths than that of most ketones. They explained this phenomenon as the result of interaction between the adjacent chromophoric groups, phenyl and carbonyl, by hyperconjugation. The spectrum of 2,2-diphenylcyclohexanone (Fig. 1) shows a carbonyl absorption peak at 298 mμ with a molar extinction coefficient of 125, which is about twice the intensity of absorption noted in this region for 2-phenylcyclohexanone,[6] and much greater than the absorption normally shown by a carbonyl group.[5]

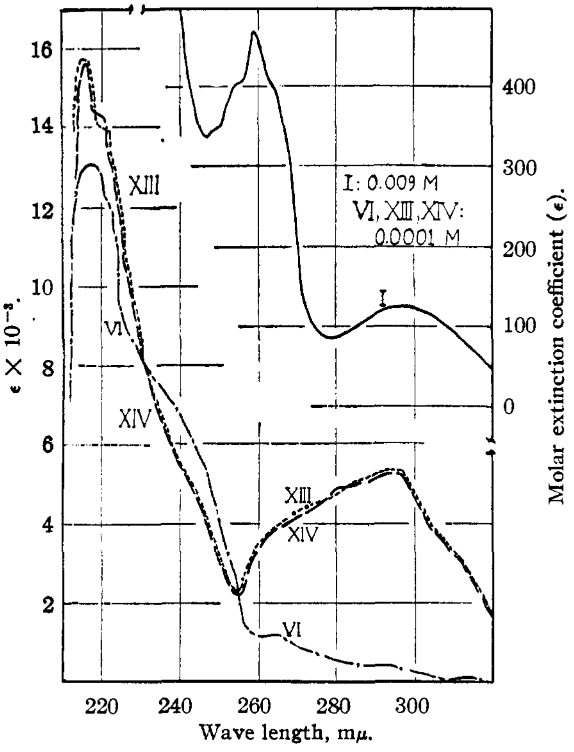


Fig. 1.—Absorption spectra in absolute ethanol at 29°.

The ultraviolet absorption spectra of three α,β-unsaturated ketones prepared in this series show a further anomaly. On the basis of the observation by Woodward,[7] 2,2-diphenyl-5-cyclo-

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[2] *Cf.* H. Gilman and L. F. Cason, THIS JOURNAL, **72**, 3469 (1950).

[3] M. S. Newman and W. L. Mosby, *ibid.*, **73**, 3738 (1951).

[4] E. C. Horning and A. F. Finelli, *ibid.*, **73**, 3741 (1951).

[5] W. D. Kumler, L. A. Strait and E. L. Alpen, *ibid.*, **72** 1463 (1950).

[6] E. L. Alpen, W. D. Kumler and L. A. Strait, *ibid.*, **72**, 4458 (1950).

[7] R. B. Woodward, *ibid.*, **63**, 1123 (1941); **64**, 76 (1942).

hexenone (VI) and 2,2-diphenyl-4-bromocyclohexen-5-one (XIII) should have an absorption peak in the neighborhood of 225 mμ and 2,2-diphenyl-4,6-dibromo-5-cyclohexenone (XIV) near 239 mμ. Instead (Fig. 1), all three ketones absorb strongly in the neighborhood of 215 mμ, a much shorter wave length than would have been predicted.

Compounds XIII and XIV also show a strong absorption peak at about 295 mμ. In order to exclude the possibility of a rearrangement in the dehydrobromination of 2,2-diphenyl-6-bromocyclohexanone, we have oxidized 2,2-diphenyl-5-cyclohexenone[1] unequivocally to benzophenone.

Acknowledgment.—We wish to express our thanks to the Central Research Laboratories of Monsanto Chemical Company, Dayton, Ohio, for the ultraviolet spectra of the unsaturated ketones, and to Smith, Kline and French Laboratories, Philadelphia, Pa., for financing many of the microanalyses reported in this paper.

Experimental

All melting points are corrected. Most of the microanalyses were performed by Clark Microanalytical Laboratory, Urbana, Illinois.

Oxidation of 2,2-Diphenyl-5-cyclohexenone.—An 0.3-g. sample of the unsaturated ketone was oxidized with an excess of chromic acid in acetic acid solution, the reaction being completed by heating for five hours at 100° after the initial reaction had subsided. The mixture was hydrolyzed on ice, filtered, and the product was dried. It melted at 48.5° and did not depress the melting point of an authentic sample of benzophenone.

2,2-Diphenyl-6-bromocyclohexanol (IV).—To a rapidly stirred suspension of 0.2 g. of lithium aluminum hydride in 35 ml. of dry ether was added dropwise a solution of 0.82 g. of 2,2-diphenyl-6-bromocyclohexanone[1] in 50 ml. of ether. Stirring was continued for 30 minutes after completion of the addition. The precipitated complex was hydrolyzed by dropwise addition of water and dilute hydrochloric acid, the ether layer was washed, dried, and the solvent evaporated. A yield of 0.65 g. (79%) of colorless crystals was obtained by recrystallization from ligroin, m.p. 123–124.5°.

Anal. Calcd. for $C_{18}H_{19}BrO$: C, 65.26; H, 5.78. Found: C, 65.17; H, 5.88.

2,2-Diphenyl-6-morpholinocyclohexanol (V). (a).—To a solution of 0.64 g. of 2,2-diphenyl-6-bromocyclohexanol in 25 ml. of dry toluene was added 2 ml. of freshly distilled morpholine and the solution refluxed for 3.5 days. The solution was decanted from the precipitated morpholine hydrobromide and the solvent and excess morpholine were removed *in vacuo*. The residue was recrystallized from benzene and methanol, yielding colorless crystals, m.p. 189–190°.

Anal. Calcd. for $C_{22}H_{27}NO_2$: C, 78.30; H, 8.07. Found: C, 78.47; H, 7.98.

(b).—To a rapidly stirred suspension of 0.1 g. of lithium aluminum hydride in 35 ml. of dry ether was added dropwise a solution of 1 g. of 2,2-diphenyl-6-morpholinocyclohexanone[1] in 50 ml. of ether. Stirring was continued for one-half hour after the addition was complete, and the complexes were destroyed by addition of 20 ml. of water and a few drops of 10% sodium hydroxide solution. The ether layer was separated, the aluminum hydroxide suspension extracted with ether, and the ether extracts were washed, dried and evaporated to dryness. The product, crystallized from benzene–methanol, gave no depression of the melting point of a sample prepared by method (a) above.

2,2-Diphenyl-5-piperidinocyclohexanone (VIII).—A solution of 1.0 g. of 2,2-diphenyl-5-cyclohexenone[1] in 10 ml. of piperidine was allowed to stand at room temperature for five days and taken up in ether. The ethereal solution was washed with water until neutral, dried and the ether was evaporated. Recrystallization of the residue from isoöctane gave an 82% yield of colorless crystal clusters melting at 104.5–106°.

Anal. Calcd. for $C_{23}H_{27}NO$: C, 82.84; H, 8.16. Found: 82.85; H, 8.17.

In an exactly analogous manner **2,2-diphenyl-5-morpholinocyclohexanone** was prepared from morpholine and 2,2-diphenyl-5-cyclohexenone. The colorless crystals melted at 156–157°.

Anal. Calcd. for $C_{22}H_{25}NO_2$: C, 78.77; H, 7.51. Found: C, 79.12; H, 7.02.

2,2-Diphenyl-5-piperidinocyclohexanol (IX).—To a suspension of 0.05 g. of lithium aluminum hydride in 10 ml. of ether was added dropwise a solution of 0.20 g. of 2,2-diphenyl-5-piperidinocyclohexanone in 20 ml. of ether. After stirring for an additional 30 minutes, 5 ml. of water was added dropwise, followed by a few drops of saturated sodium carbonate solution. The layers were separated, the aqueous suspension was extracted with ether, and the combined ether extracts were washed, dried and evaporated. The yield was 0.14 g. (67%). Recrystallization from ligroin gave colorless crystals of m.p. 127.5–128°.

Anal. Calcd. for $C_{23}H_{29}NO$: C, 82.34; H, 8.71. Found: C, 82.48; H, 8.49.

2,2-Diphenyl-5-(*p*-acetamidobenzenesulfonyl)-cyclohexanone (VII).—A solution of 1 g. of 2,2-diphenyl-5-cyclohexenone in 10 ml. of glacial acetic acid was added to a suspension of 0.8 g. of *p*-acetamidobenzenesulfinic acid in 20 ml. of glacial acetic acid, and the mixture was heated on the steam-bath until solution was complete. After two hours standing at room temperature, the reaction product began to crystallize. It weighed 1.0 g. (56%), and was recrystallized from methyl ethyl ketone and isoöctane. The colorless crystals melted at 192–193°.

Anal. Calcd. for $C_{26}H_{25}NO_4S$: C, 69.77; H, 5.63. Found: C, 69.40; H, 5.65.

A solution of 0.4 g. of this sulfone in 100 ml. of a mixture of equal volumes of water, glacial acetic acid and concd. hydrochloric acid was refluxed for five hours in an attempt to hydrolyze the amide linkage. The cooled solution was neutralized, extracted with ether, the extract dried, and the solvent evaporated to give a product which did not depress the melting point of the starting ketone, 2,2-diphenyl-5-cyclohexenone.

A second hydrolysis consisted of a 10-hour reflux in 15% aqueous sulfuric acid. The precipitate obtained from the neutralization of this solution was shown to be 2,2-diphenylcyclohexanone by analysis, and by its failure to depress the melting point of an authentic sample.

Attempted Carbonyl Reactions of 2,2-Diphenylcyclohexanone (I).—This ketone was recovered unchanged from attempts to form the cyanohydrin by the method of Lapworth[8] and from an attempted Reformatsky reaction with zinc and ethyl bromoacetate under the usual conditions. The ketone does form a semicarbazone[9] and, under drastic conditions, an oxime.[1]

2,2-Diphenylcyclohexanol (X).—A solution of 2.5 g. of 2,2-diphenylcyclohexanone in 50 ml. of ether was dropped slowly into a stirred suspension of 0.4 g. of lithium aluminum hydride in ether and stirring was continued for another 30 minutes. Water and dilute hydrochloric acid were then added slowly, and the ether layer was separated, dried and evaporated. The yield was 2.4 g. (95%). To obtain a sample of analytical purity, a benzene–ligroin solution of the alcohol was chromatographed through alumina. The colorless crystals (from isoöctane) melted at 80.5–81°, b.p. 160–162° (2 mm.).

Anal. Calcd. for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.40; H, 7.98.

β-Diethylaminoethyl 2-Phenylcyclohexyl Ether (XII).—To a solution of 12.60 g. of 2-phenylcyclohexanol in 200 ml. of dry toluene was added 1.65 g. of sodium, the mixture refluxed for 24 hours and excess sodium removed. Ten grams of β-chloroethyldiethylamine was added to the solution along with a trace of copper bronze powder as catalyst, and reflux was continued for nine hours. The solution was cooled, washed with water and the solvent was removed under reduced pressure. A colorless, mobile liquid was obtained by vacuum distillation, b.p. 153–155° (2 mm.), n^{29}D 1.5032.

Anal. Calcd. for $C_{18}H_{29}NO$: C, 78.49; H, 10.61; N, 5.09. Found: C, 78.69; H, 10.39; N, 5.10.

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(8) A. Lapworth and E. Wechsler, *J. Chem. Soc.*, **97**, 41 (1910).

(9) H. Meerwein, *Ann.*, **396**, 231 (1913).

2,2-Diphenyl-4-bromo-5-cyclohexenone (XIII).—A solution of 2.15 g. of 2,2-diphenyl-5-cyclohexenone in 50 ml. of carbon tetrachloride was refluxed for 32 hours with 1.55 g. of N-bromosuccinimide. Crude succinimide separated in quantitative yield (0.85 g.) and a crude yield of 2.5 g. (85%) of the bromo ketone was left after evaporation of the solvent. Colorless needles were obtained from isoöctane–benzene, m.p. 135–136°, b.p. 135–138° (0.006 mm.). Its acetone solution decolorized 2% aqueous potassium permanganate.

Anal. Calcd. for $C_{18}H_{15}BrO$: C, 66.07; H, 4.62. Found: C, 66.02; H, 4.89.

2,2-Diphenyl-4,6-dibromo-5-cyclohexenone (XIV).—To a solution of 2 g. of 2,2-diphenyl-4-bromo-5-cyclohexenone in 50 ml. of carbon tetrachloride was added a solution of 0.31 ml. of bromine in 15 ml. of the same solvent. Decolorization required about 48 hours. After removal of the solvent a quantitative crude yield (2.5 g.) of colorless felted needles was obtained which, on recrystallization from isoamyl alcohol, melted at 165–166°. The product decolorized aqueous potassium permanganate.

Anal. Calcd. for $C_{18}H_{14}Br_2O$: C, 53.23; H, 3.47. Found: C, 53.18; H, 3.67.

Absorption Spectra.—A modified Beckman spectrophotometer was used for ultraviolet absorption measurements. Results are reported graphically in Fig. 1. Absolute ethanol solutions of the compounds were used in the following strengths: for 2,2-diphenylcyclohexanone, 0.009 molar; for the unsaturated ketones, 0.0001 molar.

CHARLOTTESVILLE, VA.

[CONTRIBUTION FROM THE RESEARCH INSTITUTE OF TEMPLE UNIVERSITY AND THE MATERIALS LABORATORY, WRIGHT AIR DEVELOPMENT CENTER]

Fluorinated Esters. I. Esters of Perfluoro Monocarboxylic and Dicarboxylic Acids with 1,1-Dihydroperfluoroalcohols and α,α,ω,ω-Tetrahydroperfluoroglycols

BY MURRAY HAUPTSCHEIN, JOSEPH F. O'BRIEN, CHARLES S. STOKES AND ROBERT FILLER

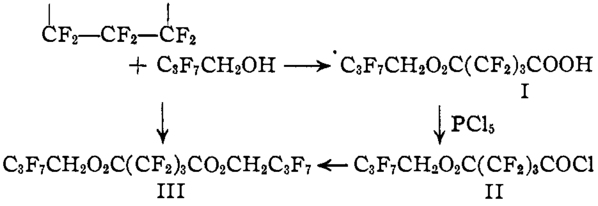
RECEIVED JUNE 20, 1952

A general method for the synthesis of the almost completely fluorinated esters and diesters of 1,1-dihydroperfluoro alcohols and α,α,ω,ω-tetrahydroperfluoro glycols with perfluoromono- and dicarboxylic acids, by the action of perfluoro acid chlorides and anhydrides on the fluorinated alcohols and diols, is described. Several physical and chemical properties of these new compounds, as well as of certain intermediates, are given.

This is the introductory paper to studies which are being carried out for the purpose of relating and correlating various properties with the molecular structure and constitution of several series of fluorinated diesters. Since no general method is as yet available for the preparation of totally fluorinated esters,[1] it was decided to investigate first a series of esters of 1,1-dihydroperfluoro alcohols with perfluorocarboxylic acids, the only member of which to be reported is trifluoromethyl trifluoroacetate, obtained by Swarts.[2] It was found that the representative alcohol, 1,1-dihydroperfluorobutanol did not esterify at a practical rate *n*-perfluorobutyric acid either when the latter strong acid was employed in excess or when chloroform was used for the azeotropic removal of the water of esterification.[3] This chemically stable alcohol, however, did react slowly with the low boiling *n*-perfluorobutyryl chloride to form 1,1-dihydroperfluorobutyl perfluorobutyrate. In a similar manner, the higher boiling perfluoroöctanoyl chloride reacted more rapidly with 1,1-dihydroperfluorobutanol to give 1,1-dihydroperfluorobutyl perfluoroöctanoate. 1,1-Dihydroperfluoroethyl perfluorobutyrate was obtained on treating 1,1-dihydroperfluoroethanol with perfluorobutyryl chloride.

This method has been extended to the synthesis of α,α,ω,ω-tetrahydroperfluoroglycol esters of perfluoro acids. Excess perfluorobutyryl chloride reacted with 1,1,5,5-tetrahydro-1,5-perfluoropentanediol and with 1,1,6,6-tetrahydro-1,6-perfluorohexanediol to yield 1,1,5,5-tetrahydro-1,5-perfluoropentanediol di-*n*-perfluorobutyrate and 1,1,6,6-tetrahydro-1,6-perfluorohexanediol di-*n*-perfluorobutyrate, respectively.

The method is also applicable to the preparation of bis-1,1-dihydroperfluoroalkanol esters of perfluorodicarboxylic acids, although certain difficulties are still to be overcome in this case. These shortcomings arise from the fact that good methods are needed for the production of satisfactory yields of the intermediate acid chlorides of perfluorodicarboxylic acids. The difficulty in synthesizing perfluoroglutaryl chloride has been previously cited.[4] In the present study crude perfluoroadipyl chloride did form a diester with 1,1-dihydroperfluorobutanol, but its purity is questionable. On the other hand, the easily preparable perfluoroglutaric anhydride[4] made possible an excellent synthesis of bis-(*n*-1,1-dihydroperfluorobutyl) perfluoroglutarate in accordance with the scheme



Perfluoroglutaric anhydride was treated with *n*-1,1-dihydroperfluorobutanol in the molar ratio of 1:2, respectively. There was obtained 58.8% of the desired diester III and 26.1% of the half ester (I). I is readily converted into III by treating the acid chloride II with an equimolar quantity of the alcohol. The acidic monoester I was very stable

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(1) See M. Hauptschein and A. V. Grosse, THIS JOURNAL, **74**, 4454 (1952).

(2) F. Swarts, *Bull. soc. chim. Belg.*, **43**, 476 (1934).

(3) E. E. Burgoyne and F. E. Condon, THIS JOURNAL, **72**, 3276 (1950).

(4) M. Hauptschein, C. S. Stokes and E. A. Nodiff, *ibid.*, **74**, 4005 (1952).