and dried ($MgSO_4$). Evaporation of the methylene chloride left 0.92 g of semisolid fluorimino phosphate. The product melted at 62–63° after recrystallization from hexane; F^{19} nmr spectrum, ϕ −34.6 (>C=NF), F_A at −33.6 and F_B at 25.6 (J_{AB} = 572 cps) (CNF_2).

Anal. Calcd for $C_{13}H_{18}N_2F_8O_4P$: C, 44.07; H, 5.12; N, 7.91; F, 16.6. Found: C, 43.45; H, 5.20; N, 7.80; F, 16.35.

1-Phenyl-1,1-bis(difluoramino)-2-fluoriminopropane. A mixture of 5 ml of 100% sulfuric acid and 2.12 g (6 mmoles) of 1-phenyl-1-difluoramino-1-(O,O-diethylphosphoryloxy)-2-fluoriminopropane was degassed at −115°, and 225 cc (STP) of difluoramine was condensed into the 250-ml reaction flask. The −115° bath was removed and was replaced by an ice bath as soon as the sulfuric acid layer began to melt. The mixture was stirred until the pressure drop ceased (about 30 min of stirring). The excess difluoramine was removed from the reaction flask *in vacuo*, and the residual acid solution was quickly poured over crushed ice. The organic products were recovered by methylene chloride extraction. The residue obtained upon evaporation of the methylene chloride was chromatographed on a silica gel column packed with pentane–methylene chloride (20:1). A mixture of pentane and methylene chloride (10:1) eluted 1-phenyl-1,1-bis(difluoramino)-2-fluoriminopropane, 0.65 g, mp 56–57°, from the column.

Anal. Calcd for $C_9H_8N_3F_5$: C, 42.69; H, 3.18; N, 16.60; F, 37.52. Found: C, 43.00; H, 3.41; N, 16.30; F, 38.55.

H^1 nmr spectrum showed aromatic protons at 7.51 ppm and a CH_3 doublet centered at 2.25 ppm; coupling (about 1 cycle splitting) between the methyl and the difluoramino groups was evident; F^{19} nmr spectrum showed a singlet at ϕ −30.7 [$C(NF_2)_2$] and C=NF at −48.3.

Reaction of 1-Acetoxy-1,2-bis(difluoramino)cyclopentane and Sulfuric Acid. A solution of 2.30 g (10 mmoles) of the above acetoxycyclopentane in 10 ml of methylene chloride was added to 4 ml of frozen 100% sulfuric acid. The mixture was degassed and 110 cc (STP) of difluoramine was condensed into the 250-ml reaction flask. The −110° bath was removed and the reaction mixture was stirred at ice-bath temperature for 30 min and at ambient temperature for 30 min. Volatile materials were removed *in vacuo* and the residue was poured over ice. The organic product was extracted with methylene chloride. The residue obtained upon evaporation of the methylene chloride (1.2 g) was purified by silica gel chromatography (elution by methylene chloride–ethyl acetate, 10:1) or by distillation to give 3-difluoramino-2-fluoro-2-azacyclohexanone (**10**). The ^{19}F and ^1H nmr spectra of **10** have been reported;[9] spectral properties of crude and purified material were identical.

Anal. Calcd for $C_6H_7N_2F_3O$: C, 35.72; H, 4.19; N, 16.67; F, 33.9; mol wt, 168. Found: C, 35.78; H, 4.46; N, 17.02; F, 33.6; mol wt (ebullioscopic), 175.

Reaction of 1-Acetoxy-1,2-bis(difluoramino)cyclopentane and Difluoramine. A solution of 18 g (78 mmoles) of the crude adduct of 1-acetoxycyclopentene and tetrafluorohydrazine[2,9] in 20 ml of methylene chloride was added to a mixture of 10 ml of 30% fuming sulfuric acid, 5 ml of methylene chloride, and 400 mmoles of difluoramine (generated from aqueous difluorourea). The difluoramine was allowed to reflux off a −80° condenser. A temperature rise from −4 to +7° occurred during the 20-min addition. The mixture was stirred at 5–12° for 90 min; the excess difluoramine then was vented into a stream of nitrogen. The residue was dumped on crushed ice and diluted with methylene chloride; the methylene chloride solution was washed with water, 10% aqueous sodium bicarbonate, and water. The methylene chloride was evaporated and the residue was chromatographed on silica gel. Elution of the column with pentane–methylene chloride (5:1) gave 1,1,1-tris(difluoramino)cyclopentane (**11**), 3.53 g.

Continued elution of the column gave, in the methylene chloride–ethyl acetate (10:1) eluate, the ketone **10**, 2.18 g.

Reaction of Cyclohexenone and Difluoramine. A solution of 3.84 g (20 mmoles) of cyclohexenone in 40 ml of methylene chloride was added to a mixture of 10 ml of 30% fuming sulfuric acid, 20 ml of methylene chloride, and 200 mmoles of difluoramine at 0°. The difluoramine was allowed to reflux from a cold finger maintained at −80°. After 1 hr at 0–10°, the excess difluoramine was vented, and the residue was poured into ice–water and methylene chloride. The organic layer was washed with water and dilute aqueous sodium bicarbonate solution. The methylene chloride was removed at reduced pressure and the residue was chromatographed on a silica gel column packed in pentane–methylene chloride (98:2). Elution with the sample solvent gave 1,1,3-tris(difluoramino)cyclohexane: 1.73 g; F^{19} nmr, $C(NF_2)_2$ peaks near −800 and −1164 cps (A_2B_2 pattern) (40 Mc, CCl_3F standard) and HC–NF_2 near ϕ −40.6 (doublet) (J_{HF} = ~24 cps).

Anal. Calcd for $C_6H_9N_3F_6$: C, 30.39; H, 3.83; N, 17.72; F, 48.1. Found: C, 30.30; H, 3.84; N, 17.00; F, 49.4.

A New Method for the Directed Conversion of the Phenoxy Grouping into a Variety of Cyclic Polyfunctional Systems

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Abstract: A new synthetic process has been devised and demonstrated for the selective transformation of phenolic substances to a variety of nonbenzenoid, polyfunctional derivatives including 2,5-cyclohexadienones, 3- and 2-cyclohexenones, and cyclohexanones as well as corresponding ketals. The critical part of the method involves the conversion of the phenol to an α-phenoxy-α,α-disubstituted acetic acid derivative and the bromination of the latter as the salt in aqueous solution at 0° to form a bromo lactone in the 1,4-cyclohexadiene series.

Benzenoid rings play an extraordinarily interesting and important role in the synthesis of *nonbenzenoid* as well as benzenoid structures. The most obvious reason for this fact, the ready availability of many benzenoid compounds, is only one of the factors contributing to this importance, however. In general terms the benzenoid unit is a "complex" functional group having a considerable number of synthetically useful characteristics, including the following: (1) a wide variety of functional groups, appendages, and rings can be attached to the ring system by many types of reactions, (2) many reactions are available which allow the interconversion of functional groups, (3) several effective techniques exist for directing chemical attack at specific sites of the benzenoid unit (especially substitution), and (4) the benzenoid system may be "disrupted" or partly saturated to yield cyclic polyfunctional structures.[1]

(1) The term "complex functional group" is used here to mean a standard reactive grouping having several similar sites available for reaction.

The last of these properties, to which the research described in this paper relates, is especially important in the more subtle applications of benzenoid compounds to the synthesis of complicated nonbenzenoid structures. Perhaps the most widely used reaction for the conversion of benzenoid to cyclic, polyfunctional nonbenzenoid systems is the "Birch reduction" which generates a dihydro derivative having *two* C=C functions, usually in specific location.[2] Further transformations, for example involving amplification of functionality by addition to or oxidative scission of these double bonds, can be of value in allowing the synthesis of considerably more complicated structures. The application of the Birch reduction to the synthesis of steroids,[3] alkaloids,[4] β-polyketones,[5] nonbenzenoid aromatic compounds,[6] and a variety of other molecules[7-9] illustrates the power of the method. Unfortunately, there are limitations of the scope of the Birch reduction which circumscribe its utility, especially significant being the incompatibility of the *strongly* reducing and basic conditions which are required with many functional groups. Further, the other selective addition reactions known for benzenoid systems appear at present to be of minor importance. These include the reaction of phenols with perchloryl fluoride[10] or lead tetraacetate,[11] and certain solvolytic,[12] electrochemical,[13] photochemical,[14] and carbenoid addition[15] reactions. The present paper describes the successful development of a potentially useful new method for the selective conversion of phenols to 2,5-cyclohexadienone derivatives under especially mild conditions. The method is applicable specifically to *para*-substituted phenols and, in contrast to the Birch reduction, does not necessitate the use of reaction conditions which would affect functions such as carbonyl, cyano, or halogen.

The critical part of the process described herein consists of coupled attack on the benzenoid ring by an external electrophile and an internal nucleophile which is linked to the phenoxy function, the over-all result being 1,4 addition.[16] The carboxylate group was chosen as the internal nucleophile, and it was placed one atom away from the phenoxy oxygen to maximize its effectiveness as a neighboring group, *i.e.*, as an ArOC(<)-COO$^-$ unit. Further in order to minimize the occurrence of electrophilic attack *ortho* to the phenoxy oxygen, the carbon α to the carboxyl function was fully alkylated to allow effective steric screening against *ortho* substitution. The feasibility of the approach was studied initially using the simplest *p*-alkylated phenol, *p*-cresol, for which the desired phenoxy acid, α-*p*-tolyloxyisobutyric acid (**1**) had already been described. The conversion of *p*-cresol to **1** may be accomplished in a single step either by reaction with chloroform and sodium hydroxide in acetone[17a] or (more efficiently, 92% yield) by reaction with 2-trichloromethyl-2-propanol (chloretone) and sodium hydroxide in acetone,[17b] followed by acidification.

Reaction of the salt of **1** in aqueous potassium bicarbonate solution at 0° with 1 equiv of aqueous bromine–potassium bromide solution led to immediate precipitation of the bromo lactone **2** which, though not very stable, could be purified by recrystallization. Attempts to replace the bromine substituent in **2** by hydrogen, *e.g.*, using zinc–acetic acid, aluminum amalgam, methanolic sodium borohydride, catalytic hydrogenation, or dibutyltin dihydride, led uniformly to formation of the phenoxy acid **1**. However, treatment of the bromo lactone **2** with methanolic silver nitrate smoothly afforded the methoxy lactone **3**. Similarly, the acetate **4** was formed from **2** using silver acetate in acetic acid, and the hydroxy lactone **5** resulted using aqueous silver nitrate. Catalytic reduction of the methoxy lactone **3**, the acetoxy lactone **4**, or the hydroxy lactone **5** produced cleanly the corresponding saturated lactones **6**, **7**, and **8** using rhodium-on-alumina catalyst and hydrogen in dioxane solution. Alkaline hydrolysis of the saturated methoxy lactone **6** gave 4-methoxy-4-methylcyclohexanone (**9**), and the saturated acetoxy and hydroxy lactones **7** and **8** similarly yielded 4-hydroxy-4-methylcyclohexanone (**10**). Reaction of 4-methoxy-4-methylcyclohexanone with boron trifluoride furnished 4-methyl-3-cyclohexenone (**11**). Thus, the conversion of *p*-cresol to the bromo lactone **2** makes possible the synthesis of a wide variety of substances which possess the functionality required for structural elaboration. From a preparative standpoint the generation of the methoxy, acetoxy, and hydroxy lactones from **1** was best carried out without purification of the intermediate bromo lactone **2**, in which case over-all yields on the order of 50% have been obtained.

The conversion of the salt of **1** to the bromo lactone **2** represents the first case, as far as the authors are aware, of internal nucleophilic participation during electrophilic aromatic substitution.[18] The chlorolactonization

(2) For a review of the Birch reduction, see H. Smith, "Organic Reactions in Liquid Ammonia," Interscience Publishers, New York, N. Y., 1963.

(3) For example, the hydrochrysene approach of W. S. Johnson, B. Bannister, and R. Pappo, *J. Am. Chem. Soc.*, **78**, 6331 (1956).

(4) For example, the synthesis of lycopodine by G. Stork, R. A. Kretchmer, and R. H. Schlessinger, *ibid.*, **90**, 1647 (1968), in which the Birch reduction is employed at two stages.

(5) D. C. C. Smith and P. Fitton quoted in ref 2, p 245.

(6) For example, the synthesis of heptalene: H. J. Dauben and D. J. Bertelli, *J. Am. Chem. Soc.*, **83**, 4657 (1961), and the synthesis of 1,6-methano[10]annulene: E. Vogel and H. D. Roth, *Angew. Chem. Intern. Ed. Engl.*, **3**, 228 (1964).

(7) Cecropia juvenile hormone: E. J. Corey, J. A. Katzenellenbogen, N. W. Gilman, S. A. Roman, and B. W. Erickson, *J. Am. Chem. Soc.*, **90**, 5618 (1968).

(8) Kaurene: R. A. Bell, R. E. Ireland, and R. B. Partyka, *J. Org. Chem.*, **31**, 3530 (1966).

(9) Conessine: J. A. Marshall and W. S. Johnson, *J. Am. Chem. Soc.*, **84**, 1485 (1962).

(10) J. S. Mills, J. Barrera, E. Olivares, and H. Garcia, *ibid.*, **82**, 5882 (1960).

(11) (a) F. Wessely and F. Sinwel, *Monatsh. Chem.*, **81**, 1055 (1950); (b) E. Hecker and E. Meyer, *Angew. Chem. Intern. Ed. Engl.*, **3**, 229 (1964).

(12) R. Baird and S. Winstein, *J. Am. Chem. Soc.*, **84**, 788 (1962).

(13) B. Belleau and N. L. Weinberg, *ibid.*, **85**, 2525 (1963).

(14) M. Bellas, D. Bryce-Smith, and A. Gilbert, *Chem. Commun.*, 862 (1967).

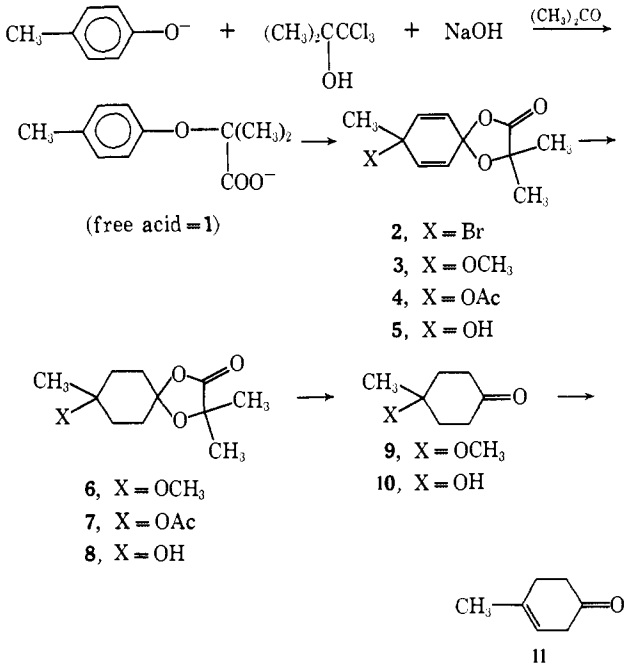
(15) E. Müller, H. Fricke, and H. Kessler, *Tetrahedron Letters*, 1525 (1964).

(16) Preliminary reports of this work have been given in two lectures. See (a) E. J. Corey, Abstracts, 19th National Organic Symposium, American Chemical Society, June 1965, p 7, and (b) E. J. Corey, *Pure Appl. Chem.*, **14**, 19 (1967).

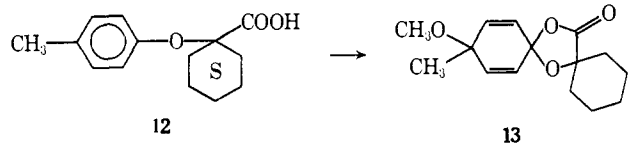
(17) (a) G. Bargellini, *Gazz. Chim. Ital.*, **36** [II], 337 (1906). (b) This procedure was based on considerations of mechanism and the finding by Ch. Weizmann, M. Sulzbacher, and E. Bergmann, *J. Am. Chem. Soc.*, **70**, 1153 (1948), that α-alkoxyisobutyric acids are produced in good yield from chloretone and alcohols (in excess) in the presence of base. The reaction of chloretone with base would appear to result in the generation of the α-lactone of α-hydroxyisobutyric acid which undergoes nucleophilic attack by alkoxide or phenoxide to form the α-alkoxy- or α-phenoxyisobutyric acid salt.

(18) (a) There is no strong evidence at the present time as to whether the electrophilic and nucleophilic steps are concurrent or sequential. The stereochemistry of the bromolactonization of **1** is also unknown, as is the stereoselectivity. The nmr spectrum of the bromo lactone **2** is consistent with expectations for a single stereoisomer (see Experimental Section); however, it would not be unreasonable for the *cis*

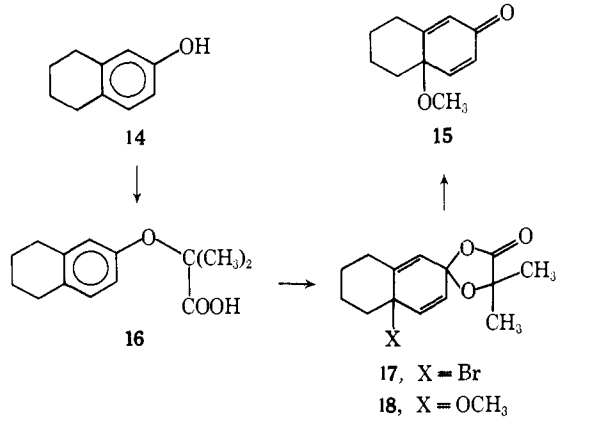
of the salt of **1** appears to be considerably less efficient than the reaction with bromine to form **2**. In addition, only low yields (<20%) of bromo lactone are obtained by the bromination of potassium *p*-tolyloxyacetate under a variety of conditions indicating that α substitution is crucial to the success of the bromolactonization process.



1-Tolyloxycyclohexane-1-carboxylic acid (**12**) was prepared from 1,1,1-trichlorocyclohexanol and subjected to bromolactonization followed by silver-promoted methanolysis. The expected methoxy lactone **13** was obtained in 46% yield from **12**.



5,6,7,8-Tetrahydro-2-naphthol (**14**) was transformed readily into the methoxydienone **15** using the new process *via* the acid **16** and the lactones **17** and **18**.



The results obtained in this investigation would appear to indicate that the method for the selective reduction of phenols which is described herein can be a useful alternative to the Birch reduction, especially with those phenolic substances bearing functional groups incompatible with alkali metal–ammonia solutions.

Experimental Section

General. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Spectrometers used were Varian A-60 (nmr), Cary Model 14 (ultraviolet), and Perkin-Elmer Infracord (infrared). Nmr chemical shifts are given in parts per million (ppm) downfield from tetramethylsilane as internal standard.

Preparation of α-*p*-Tolyloxyisobutyric Acid (1) from *p*-Cresol and Chloretone. Procedure A. A solution of 216 mg (2 mmol) of *p*-cresol and 852 mg (4 mmol) of chloretone dihydrate in acetone (4 ml) was placed in an ice bath, and a total of 640 mg (16 mmol) of sodium hydroxide powder was added in three equal portions with stirring at 2-hr intervals. Before each addition the reaction mixture was cooled to 0°, and after the addition the mixture was allowed to warm to 25°. Prior to the addition of the last portion of base, an additional 4 ml of acetone was added to the thick suspension. After 16 hr (final pH 10–11) the solvent was removed *in vacuo*, and the residue was taken up in water, acidified with hydrochloric acid, and extracted with ether. The acid was separated by extraction of the ethereal solution with aqueous sodium bicarbonate. The aqueous extract was acidified with hydrochloric acid, and the acid was obtained by extraction with ether as an oil (385 mg) which gave 358 mg (92.3%) of crystalline acid **1**, mp 77–78°[17a] on recrystallization from benzene–*n*-pentane. An experiment using dimethylformamide as solvent with chloretone hemihydrate under the same conditions gave 321 mg (82.7%) of crude **1**. Various runs have been made in aqueous mixtures of dimethyl sulfoxide or dimethoxyethane using potassium hydroxide, lithium hydroxide, or Triton B as base, but yields were below 20% in each case.

Procedure B. α-*p*-Tolyloxyisobutyric acid was also prepared essentially according to the procedure of Bargellini.[17a] In a three-necked flask fitted with a dropping funnel, a mechanical stirrer, and a condenser was placed a solution of 60 g of *p*-cresol in 600 ml of acetone. Powdered sodium hydroxide (135 g) was added in small portions with stirring. The mixture became warm and was cooled to about 35°, and 90 g of chloroform was added within 1.5 hr with stirring. The mixture was then refluxed for 5 hr. The solvent was removed *in vacuo*, and the residue was dissolved in water, acidified with dilute hydrochloric acid, and extracted with ether. The acidic material was isolated as described above to give 44.6 g (41.5%) of **1** as colorless crystals, mp 77–79°.

Bromo Lactone 2. A solution of bromine was prepared from 8 g of bromine and 24 g of potassium bromide in 100 ml of water (0.5 *M*). To a solution of 1.94 g (0.01 mol) of α-*p*-tolyloxyisobutyric acid and 2 g of potassium bicarbonate in 20 ml of water at 0° was added slowly 20 ml of precooled bromine solution with rapid stirring. The bromo lactone **2** precipitated immediately upon addition of bromine and was extracted with ether 3 min after the addition was complete. The organic solution was dried with magnesium sulfate and evaporated *in vacuo* without heating to give 2.067 g of colorless crystals. The crude product was recrystallized from ether–*n*-pentane to give 1.38 g (50.6%) of **2** as colorless needles which melted at 89–90.5°.

Anal. Calcd for $C_{11}H_{13}BrO_3$: C, 48.37; H, 4.80; Br, 29.25. Found: C, 48.30; H, 4.83; Br, 29.25.

The infrared spectrum (CCl_4) showed a carbonyl peak at 5.54 μ. The nmr spectrum (CCl_4) showed peaks at (ppm): 1.48 (6 H), 1.90 (3 H), and 5.61, 5.78, 6.33, and 6.50 (4 H, AB pattern).

Methoxy Lactone 3. To a solution of 2.037 g of unrecrystallized bromo lactone **2** obtained directly from the reaction as described above (75.5% yield) in 40 ml of methanol at 0° was added with rapid stirring an ice-cold solution of 1.5 g of silver nitrate in 60 ml of methanol. After 3 min 2 g of potassium acetate (solid) was added, and the mixture was stirred for an additional 3 min. The precipitated silver halide was removed by filtration, and the methanol was removed *in vacuo* at 30° from the filtrate. The residue was taken up in water and extracted with ether. The ethereal layer was extracted with ammonium hydroxide (pH 10) to remove acidic compounds, washed with water until neutral, dried with magnesium sulfate, and concentrated *in vacuo*. Colorless crystals were obtained (1.305 g) which on recrystallization from ether–*n*-pentane

and *trans* forms of 2 to exhibit essentially identical nmr spectra, and therefore, the nmr data do not allow stereochemical conclusions. (b) For examples of internal nucleophilic attack concomitant with phenol oxidation, see E. J. Corey and L. F. Haefele, *J. Am. Chem. Soc.*, **81**, 2225 (1959), also G. Schmir, L. A. Cohen, and B. Witkop, *ibid.*, **81**, 2228 (1959), and G. G. Gallo, C. R. Pasqualucci, and A. Diena, *J. Org. Chem.*, **30**, 1657 (1965).

gave 1.114 g of methoxy lactone **3** (66.7% from **2**, 50.5% over-all from the acid **1**) with mp 108–109°.

Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.22; H, 7.23.

The infrared spectrum (CCl_4) exhibited a carbonyl peak at 5.54 μ. The nmr spectrum (CCl_4) showed peaks at (ppm): 1.25 (3 H), 1.47 (6 H), 3.02 (3 H), and 5.82, 5.84, 5.85 (4 H).

Saturated Methoxy Lactone 6. Rhodium-on-alumina catalyst (5%) (180 mg) suspended in 2 ml of dioxane was prehydrogenated, and a solution of 1 g of the methoxy lactone **3** in 6 ml of dioxane was added. The mixture was stirred with hydrogen at 12–15° until 2 equiv of hydrogen were consumed. The crude product was distilled at 110° bath temperature (0.3 mm) to give 740 mg of **6** as a colorless oil (72.8%). The analytical sample was obtained by preparative gas chromatography (gc).

Anal. Calcd for $C_{12}H_{20}O_4$: C, 63.13; H, 8.83. Found: C, 63.06; H, 8.86.

Nmr spectrum (ppm) ($CDCl_3$): 1.13 (3 H), 1.41 (6 H), multiplet 1.61–1.75 (8 H), 3.13 (3 H), infrared absorption due to carbonyl at 5.54 μ (CCl_4).

4-Methoxy-4-methylcyclohexanone (9). The crude saturated methoxy lactone **6** (740 mg) was stirred at 20° for 2 hr with 60 ml of 5% potassium hydroxide until the solution was clear. The reaction mixture was then exhaustively extracted with *n*-pentane. The solution was dried with magnesium sulfate and then concentrated at 20–30° *in vacuo* to give 327 mg of an oil. Distillation at a bath temperature of 105° (13 mm) gave 307 mg (66.7%) of spectroscopically pure ketone **9**. The analytical sample was obtained by preparative gc.

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.93. Found: C, 67.13; H, 9.91.

Nmr spectrum (ppm) (CCl_4): 1.20 (3 H), 1.56–2.56 (8 H), 3.13 (3 H), infrared absorption due to carbonyl at 5.82 μ (neat).

The product was further characterized by the 2,4-dinitrophenylhydrazone, mp 148–149°.

Anal. Calcd for $C_{14}H_{18}O_5N_4$: C, 52.17; H, 5.63; N, 17.38. Found: C, 52.03; H, 5.70; N, 17.41.

Elimination of methanol from **9** was effected by treatment with boron trifluoride–etherate in methylene chloride solution at 20° to give 4-methyl-3-cyclohexenone (**11**) which was identified by gc and infrared comparison with an authentic sample.[19]

4-Methyl-4-methoxy-2,5-cyclohexadienone. To a solution of 600 mg of the methoxy lactone **3** in 3 ml of dioxane was added 1.1 equiv of potassium hydroxide in 15 ml of water, and the mixture was stirred for 3 hr at 0° until clear. The aqueous solution was extracted with *n*-pentane, and the solution was dried with magnesium sulfate and concentrated *in vacuo* at 20° to give 345 mg of yellow crystals. The product was purified by sublimation at 20° (0.5 mm) using a Dry ice cooled collector to give 320 mg of the dienone (86.8%) as plates, mp 67–68°.[20]

Anal. Calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.49; H, 7.31.

The nmr spectrum (CCl_4) showed peaks at (ppm): 1.39 (3 H), 3.16 (3 H), and 6.07, 6.26, 6.55, 6.72 (4 H). The infrared spectrum (CCl_4) showed peaks due to C=O at 5.96 μ and C=C at 6.10 and 6.20 μ.

Acetoxy Lactone 4. A solution of the bromo lactone **2** (1 g) in glacial acetic acid (12 ml) was stirred at 20° for 1 hr with silver acetate (1.9 g). The precipitated silver bromide was filtered and was washed with ether. The filtrate was extracted with saturated sodium bicarbonate solution to remove the acid. The ethereal layer was dried with magnesium sulfate, and the solvent was removed *in vacuo* to give 648 mg (67%) of crystalline product. An analytical sample of the acetoxy lactone **4** was prepared by recrystallization from ether–*n*-pentane (243 mg, mp 146–148°).

Anal. Calcd for $C_{13}H_{16}O_5$: C, 61.89; H, 6.39. Found: C, 61.85; H, 6.41.

The remaining product (375 mg) melted at 85–87°. The nmr spectrum showed the presence of two isomers in the crude product. The nmr spectrum ($CDCl_3$) of the analytical sample showed peaks at (ppm): 1.54 (9 H), 2.01 (3 H), and 5.72, 5.89, 6.21, 6.25, 6.38 (4 H). The infrared spectrum exhibited carbonyl absorption (CCl_4) at 5.54 and 5.74 μ.

Hydroxy Lactone 5. To a solution of bromo lactone **2** (600 mg) in dioxane (2 ml) was added a solution of silver nitrate (450 mg) in water (6 ml) at 0° with stirring. After 5 min, 1 g of solid potassium acetate was added, and the mixture was stirred for an additional 3 min. The precipitated silver salts were filtered off and washed with ether. The ethereal solution was extracted with sodium bicarbonate solution. The organic phase was dried with magnesium sulfate and removed *in vacuo* to give 430 mg of crystalline product. Recrystallization from carbon tetrachloride–*n*-pentane gave 350 mg (75.8%) of crude hydroxy lactone **5** with a melting range from 70 to 85°. Two crystallizations from ether–*n*-pentane gave 103 mg of **5**, mp 108–109.5°.

Anal. Calcd for $C_{11}H_{14}O_4$: C, 62.84; H, 6.71. Found: C, 62.81; H, 6.69.

The remaining product had an identical infrared spectrum and a melting range between 80 and 85°.

Nmr spectrum (CCl_4) of the analytical sample (ppm): 1.36 (3 H), 1.52 (6 H), 2.25 (1 H), 5.62, 5.78, 6.09, and 6.27 (4 H). Infrared absorption at 2.69 and 2.85 μ (OH) and 5.54 μ (C=O) in CCl_4 solution.

Hydrogenation of the Hydroxy Lactone 5. The hydroxy lactone **5** (145 mg) was hydrogenated at 12–15° in dioxane (1.5 ml) with prehydrogenated rhodium-on-alumina (5%) catalyst in 3 ml of dioxane until 2 equiv of hydrogen were consumed. The product was distilled at 110° bath temperature (0.3 mm). The solidified product, evidently a mixture of isomers of **8**, had mp 81–102°.

Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.69; H, 8.40.

Nmr peaks (CCl_4) (ppm): 1.27 (3 H), 1.48 (6 H), 1.68, 1.76, 1.83 (8 H), 2.10 (1 H).

Saponification of the Saturated Hydroxy Lactone 8. The hydroxy lactone **8** (300 mg) was suspended in 15 ml of sodium hydroxide solution (5%) and was stirred for 3.5 hr at 20° until the crystals dissolved. The aqueous solution was extracted with ether, and the solvent was dried with magnesium sulfate and removed to give 143 mg (80%) of crude ketone as an oil. The compound was identified as 4-hydroxy-4-methylcyclohexanone (**10**) by its infrared and nmr spectra. The nmr spectrum (CCl_4) showed peaks at (ppm): 1.32 (3 H), 1.86–2.67 (8 H, with a sharp peak at 1.95), 3.13 (1 H). The 2,4-dinitrophenylhydrazone derivative melted at 146–147°.

Saponification of the Acetoxy Lactone 4. To a solution of 126 mg of **4** in 1 ml of dioxane cooled to 12°, an ice-cold solution of 66 mg of potassium hydroxide, 90% purity (1.05 equiv), was added with stirring under N_2. The crystals which separated on addition of the aqueous solution dissolved within 4.5 hr at 0°. Extraction with *n*-pentane, drying with magnesium sulfate, concentration *in vacuo*, and recrystallization gave 48 mg (77.4%) of a solid product, mp 76–77°, identified by infrared and nmr spectra as 4-methyl-4-hydroxy-2,5-cyclohexadienone.[21] The nmr spectrum ($CDCl_3$) showed peaks at (ppm): 1.47 (3 H), 3.10 (1 H), and 5.97, 6.14, 6.78, 6.94 (4 H). The infrared spectrum (CCl_4) showed carbonyl absorption at 5.96 μ. The saponification of the hydroxy lactone **5** led to the same product.

1-*p*-Tolyloxycyclohexane-1-carboxylic Acid (12). To an ice-cold solution of 4.350 g (0.02 mol) of 1,1,1-trichloromethylcyclohexanol[22] and 1.081 g (0.01 mol) of *p*-cresol in 30 ml of cyclohexanone was added one-third of 3.2 g (0.08 mol) of powdered sodium hydroxide with stirring. The mixture was warmed to room temperature and stirred for 1 hr before the slurry was cooled to 0° and the next one-third portion of the sodium hydroxide was added. After another hour the rest of the base was added under the same conditions, and the mixture was stirred for 9 hr at 20° (final pH 10–11) and thereafter heated to 50–60° for 75 min until the pH was 8–9. The mixture was diluted with ether and was extracted with sodium bicarbonate solution. The aqueous phase was extracted four times with ether and acidified with hydrochloric acid, and the acid **12** was then extracted with ether and dried with magnesium sulfate, and the ether was removed *in vacuo* to give 562 mg of an oil. On addition of carbon tetrachloride 122 mg of crystalline product was obtained. The oil from the mother liquor was distilled at 100° (0.3 mm), and another crop of 190 mg of crystalline product was obtained. The total yield of **12** was 312 mg (13.3%) with mp 125–127°. The analytical sample was prepared by thick layer chromatography on silica gel with chloroform as eluent, mp 130–131°.

Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.06; H, 7.69.

(19) E. A. Braude, A. A. Weble, and M. U. S. Sultanbawa, *J. Chem. Soc.*, 3328 (1958).

(20) E. Hecker and R. Lattrell, *Ann. Chem.*, **662**, 48 (1963), report mp 62–63° for this compound.

(21) S. Goodwin and B. Witkop, *J. Am. Chem. Soc.*, **79**, 179 (1957), report mp 76–78°.

(22) D. G. Kundiger, E. A. Ikenberry, E. B. W. Ovist, J. G. Peterson, and C. R. Dick, *ibid.*, **82**, 2953 (1960).

Nmr spectrum ($CDCl_3$) (ppm): 1.51–2.09 (10 H), 2.27 (3 H), and 6.72, 6.87, 6.98, 7.13 (4 H).

Methoxy Lactone 13. To a solution of 204 mg (0.87 mmol) of the acid **12** and 400 mg (4 mmol) of potassium bicarbonate in 3 ml of water was added at 0° with rapid stirring bromine (0.87 mmol) in aqueous potassium bromide solution. After 3 min Celite 545 was added, and the insoluble bromo lactone was collected by filtration, washed with water, and dissolved in methanol at −20°. The solution was filtered by suction immediately into a solution of 510 mg (3 mmol) of silver nitrate in 25 ml of methanol at −50°. The mixture was allowed to warm slowly to room temperature, and 1 g of sodium acetate (solid) was added. The solid material was filtered, and the methanol was removed at 30° *in vacuo*. The residue was taken up in water, extracted with ether, and the ethereal solution was extracted with sodium bicarbonate solution, dried with magnesium sulfate, and evaporated to give 197 mg of a partly crystalline product. An analytical sample was prepared by thick layer chromatography on silica gel with chloroform as eluent to give 107 mg (46.6%), mp 110–112°.

Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.19; H, 7.65.

The infrared spectrum showed carbonyl absorption ($CHCl_3$) at 5.58 μ. The nmr spectrum ($CDCl_3$) showed peaks at (ppm): 1.33, 1.37 (3 H), 1.75 with a shoulder at 1.57 (10 H), 3.11, 3.15 (3 H), and 5.95 (4 H).

α-Tetrahydro-β-naphthyloxyisobutyric Acid (16). To a solution of 445 mg (3 mmol) of tetrahydro-β-naphthol (**14**)[23] and 1.281 g (6 mmol) of chloretone dihydrate in 4 ml of acetone was added with stirring 960 mg (24 mmol) of sodium hydroxide powder in small portions in intervals of *ca.* 30 min over a period of 4 hr. Before each addition the mixture was cooled to about 5° and was then allowed to warm to room temperature. Each time the slurry became solid, 2 ml of acetone was added (total amount of acetone 26 ml). After stirring at 25° for 21 hr (final pH 8–9), the solvent was removed *in vacuo*, and the residue was taken up in water, acidified with hydrochloric acid, and extracted with ether. Extraction of the ethereal solution with sodium bicarbonate, acidification with hydrochloric acid, and extraction of the aqueous phase with ether gave the acid **16** as an oil (650 mg) which crystallized on standing. Recrystallization from benzene–*n*-pentane gave 580 mg (82.4%), mp 98–101°. The analytical sample melted at 100–101°.

(23) H. Brown, H. W. Durand, and C. S. Marvel, *J. Amer. Chem. Soc.*, **58**, 1594 (1936).

Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.72; H, 7.92.

The nmr spectrum ($CDCl_3$) showed peaks at (ppm): 1.58 (6 H), 1.70, 1.75, 1.78, 1.86 (4 H), 1.68 (4 H), and 6.64, 6.67, 6.72, 6.87, 7.03 (3 H).

Methoxy Lactone 18. To a solution of 234 mg (1 mmol) of the acid **16** and 400 mg (4 mmol) of potassium bicarbonate in a mixture of 8 ml of water and 2 ml of dimethyl sulfoxide was added at −22° with rapid stirring 2 ml (1 mmol) of aqueous sodium bromide–bromine solution. As soon as the reaction was finished (2–3 min), Celite 545 was added, the mixture was diluted to 25 ml with ice-cold water and was filtered through a Büchner funnel. The insoluble bromo lactone **17**–Celite mixture was treated with methanol (−20°) and was filtered by suction immediately into a solution of 510 mg (3 mmol) of silver nitrate in 25 ml of methanol (−50°) with stirring. The mixture was allowed to warm to room temperature over 0.5 hr. Solid potassium acetate (1 g) was then added, and the solid material was filtered off after 3 min. The solvent was removed *in vacuo*, the residue was taken up in water and extracted with ether. The ethereal solution was extracted with sodium bicarbonate solution to remove acidic components, dried with magnesium sulfate, and evaporated to give 140 mg (53%) of methoxy lactone **18** as an oil. The nmr spectrum of **18** in $CDCl_3$ showed peaks at (ppm): 1.25–2.12 (8 H), 1.54 (6 H), 3.01 (3 H), and 5.67, 5.89, 5.92 (3 H).

Methoxy Dienone 15. Methoxy lactone **18** (620 mg) was stirred for 5.5 hr at 0° under nitrogen in a solution of 223 mg (1.5 equiv based on 90% purity) of potassium hydroxide in 14 ml of dimethyl sulfoxide and 5 ml of water. The mixture was then extracted with ether, and the organic phase was washed with water, dried with magnesium sulfate, and evaporated to give 357 mg of a yellow oil. The compound was purified by preparative layer chromatography on silca gel with chloroform to yield 256 mg of a colorless oil (61.2% or 32.4% based on the acid **16**). The analytical sample was distilled at a bath temperature of 85–90° (0.05 mm). It solidified to colorless crystals, mp 42° (lit.[20] mp 42–43°).

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.19; H, 7.89.

The nmr spectrum of **15** in $CDCl_3$ showed peaks at (ppm): 1.22–2.40 (8 H), 2.97 (3 H), and 6.10, 6.17, 6.52, 6.69 (3 H).

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Intramolecular Excitation Transfer in 1,4-Dimethoxy-5,8-Methano-6,7-*exo*-[fluorene-9′-spiro-1″-cyclopropane]naphthalene

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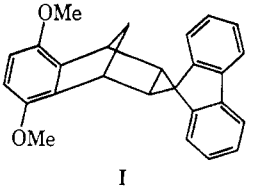
Abstract: The recent reports[1,2] that no excitation transfer takes place between the chromophores in the title compound (I) are unexpected from theory and past experience, and, indeed upon investigation we found entirely different results. Because of the nature of the absorption spectrum of I, it is dangerous to consider excitation transfer within that molecule, at least in the very weak coupling limit. However, assuming that such considerations are legitimate our measurements of the emissions from I and proper models are consistent with a scheme which requires very efficient singlet excitation transfer from the *p*-methoxybenzene group to the fluorene moiety in I.

Filipescu reported[1] that there is neither singlet excitation transfer nor triplet transfer between the chromophores in the title compound I and that the spectral characteristics of the fluorene and *p*-dimethoxybenzene chromophores in I are very similar to what they are for the individual chromophores in appropriate



I

(1) N. Filipescu in "Molecular Luminescence," E. C. Lim, Ed., W. A. Benjamin, New York, N. Y., 1969, p 697.