EXPERIMENTAL

The ^{1}H nmr spectra were obtained on a Varian A-60 spectrometer using tetramethylsilane as internal reference and CCl_4 as solvent. The ^{19}F nmr spectra were obtained using a Varian HA-100 spectrometer with Freon 11 as internal reference and CCl_4 as solvent. Infrared spectra were taken as neat liquid films on a Perkin-Elmer Model 137 spectrophotometer. Ultraviolet spectra were obtained on a Beckman DK-2 spectrophotometer. Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich.

General Synthetic Procedure. Dried freshly prepared sodium methoxide (0.1 mole) was suspended in anhydrous ether (100 ml), and the ethyl ester of the perfluorinated acid (0.1 mole) in anhydrous ether (15 ml) was added dropwise to the stirred suspension. During the exothermic reaction that accompanied the addition, nearly all of the sodium methoxide reacted. Acetylpentafluorobenzene (21.0 grams, 0.1 mole), prepared by the method of Vorozktsov et al. (*2*), was added dropwise in anhydrous ether (15 ml). The reaction was exothermic, and the remainder of the sodium methoxide reacted. The resultant yellow homogeneous reaction mixture was allowed to stand at room temperature for 16–20 hr under a nitrogen blanket. Work-up was effected by addition of concentrated sulfuric acid (3 ml) in water (30 ml) followed by extraction with ether and washing with water. The ethereal extract was dried over anhydrous sodium sulfate and was evaporated in vacuo to afford the crude product. Vacuum distillation afforded the pure products. The physicochemical characterization data are presented in Table I.

Copper Chelate of 4. The copper chelate, 5, was prepared by shaking aqueous copper acetate with an ether solution of Compound 4. The ether layer was washed with water to remove excess copper acetate, dried over sodium sulfate, and evaporated to dryness. The chelate was recrystallized twice from benzene to give mp 88–94° C; however, extensive drying in vacuo was required since the solid was highly solvated. Further evidence of solvation was seen when a sample of the chelate was recrystallized from dioxane to give a product of much lighter green color, mp 134–9° C. The chelate was soluble in benzene, toluene, cyclohexane, dioxane, and carbon tetrachloride at room temperature. Compound 4 could be freed from the copper by washing an ether solution of the chelate several times with 15% sulfuric acid.

A sample of the copper chelate twice recrystallized from benzene was analyzed for C, H, F, Cu. The results were in agreement with theory, and have been submitted for review.

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Synthesis and Properties of 9-(*p*-Chlorophenyl)-1,2,3-Nonanetricarboxylic Acid

JACQUES G. O'REAR and PAUL J. SNIEGOSKI[1]
Naval Research Laboratory, Washington, D. C. 20390

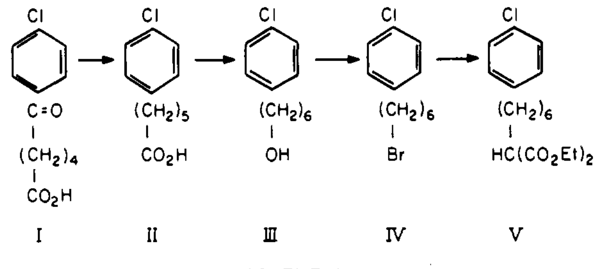
9-(*p*-Chlorophenyl)-1,2,3-nonanetricarboxylic acid was synthesized via a Michael condensation between diethyl fumarate and the appropriate α-substituted malonic acid. Analysis of the two diastereoisomers was carried out by gas-liquid chromatography. Properties of the five new intermediate compounds are also given.

In recent studies (*4–6*), several new classes of surface-active compounds have been designed and synthesized as candidate adhesion promoters for a variety of applications. These compounds feature a terminal *p*-chlorophenyl substituent, a polymethylene spacer, and either one or two carboxyl groups. Such structures form monolayers which promote adhesion between a solid substrate and an organic resin because they expose a relatively high energy chlorophenyl outer surface which is readily wet by the resin (*9*). The same structural concepts led to the design of a prototype tricarboxylic acid, 9-(*p*-chlorophenyl)-1,2,3-nonanetricarboxylic acid. This structure is designed as a coupling agent for dental restorative systems and as a finish for glass, alumina, or stainless steel.

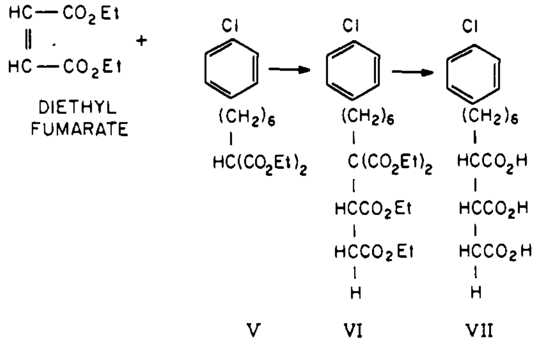
This compound, 9-(*p*-chlorophenyl)-1,2,3-nonanetricarboxylic acid (VII, Scheme 2), was synthesized via a Michael condensation between diethyl fumarate and the appropriate α-substituted malonic ester. Major steps in the synthesis are shown in Schemes 1 and 2. Compounds III through VII are reported for the first time.

The two diastereoisomers of VII, analyzed by gas-liquid chromatography (glc) of their methyl esters, were designated according to their retention times: VIIA elutes

SCHEME 1



SCHEME 2



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[1] To whom correspondence should be addressed.

first and VIIB last. Diastereoisomer, VIIB, was isolated in high purity by means of recrystallization. Infrared spectra indicated that the anhydride produced by heating, VII, forms a five-membered ring. High temperature tends to drive the anhydride to the form corresponding to diastereoisomer, VIIB.

EXPERIMENTAL

All melting points and boiling points are uncorrected. Elemental assays (carbon, hydrogen, and halogens) are in agreement with theoretical values and were submitted for review.

5-(*p*-Chlorobenzoyl)pentanoic acid, I, was prepared according to the method of Fieser et al. (*3*): mp 132–4° C [lit. (*3*), mp 133° C]; N.E. calcd, 240.7; found, 241.0.

6-(*p*-Chlorophenyl)hexanoic acid, II, resulted from the Wolff-Kishner reduction (*2*), of I (361.0 grams, 1.5 moles). Work-up and recrystallization from heptane at −10° C gave a 93% yield: mp 43–4° C [lit. (*3*), mp 43–3.5° C]; N.E. calcd, 226.7; found, 229.6.

6-(*p*-Chlorophenyl)-1-hexanol, III, was obtained from the reduction of II by lithium aluminum hydride, followed by vacuum distillation: 90% yield, bp 182° C at 0.5 mm, n_D^{20} 1.5245.

6-(*p*-Chlorophenyl)-1-bromohexane, IV, was prepared from III by the Collins and Davis method (*1*): 86% yield, bp 185° C at 0.5 mm, n_D^{20} 1.5390, d_4^{20} 1.2936.

6-(*p*-Chlorophenyl)-1,1-heptanedicarboxylic acid diethyl ester, V, was prepared by reacting sodium diethyl malonate (0.81 mole) and IV (0.58 mole) using the method of Ramart-Lucas and Papadakis (*7*): 84% yield, bp 182° C at 0.5 mm, n_D^{20} 1.4910, d_4^{20} 1.0789.

9-(*p*-Chlorophenyl)-1,2,3,3-nonanetetracarboxylic acid tetraethyl ester, VI, was prepared by a modification of the method due to Schlogl and Pelousek (*8*). Sodium ethoxide solution, prepared by reacting absolute ethanol (200 ml) and sodium (7.92 grams, 0.344 g-atom), was treated at room temperature first with V (122.2 grams, 0.344 mole), and then with diethyl fumarate (77.1 grams, 0.448 mole). After stirring for 24 hr, the mixture was diluted with water and extracted with ether. The ether extract was dried and concentrated in vacuo (200° C/1 mm) to yield the tetraester (175 grams, 0.332 mole, 96.5% yield) as a viscous orange oil, which was used without further purification.

9-(*p*-Chlorophenyl)-1,2,3-nonanetricarboxylic acid, VII, resulted from the saponification of VI, followed by acidification and decarboxylation. A mixture of water (400 ml) and propylene glycol (1600 ml), potassium hydroxide (1.33 mole), and VI (87.5 grams, 0.166 mole) was refluxed for 72 hr. The saponified mixture was diluted with water (1400 ml) and acidified (200 ml 12*N* hydrochloric acid). The resulting precipitate was collected, washed with water, suspended in 2*N* hydrochloric acid (2000 ml), and the acidic mixture refluxed for 12 hr. Crystals from the cooled mixture were collected and recrystallized from water (2000 ml) to afford the crude tricarboxylic acid, VII: 59.7 grams (97% yield); mp 100–20° C; N.E. calcd, 123.6; found, 130.0. The crude VII was purified via the triethyl ester, VIII, described later in this section. Saponification of VIII required a 72-hr reflux in 100% excess of 0.5*N* potassium hydroxide solution (propylene glycol–water, 80–20 by volume). Acidification, work-up, and recrystallization from water led to a 98% yield of VII: mp 100–24° C; N.E. calcd, 123.6; found, 127.9. Glc of the trimethyl esters of VII showed them to consist of 36% of the faster-eluting diastereoisomer, VIIA, and 64% of the slower-eluting VIIB.

VIIB from VII by Recrystallization. The analytical product, VII (10 grams), was dissolved in acetone (125 ml). Successive additions of ether (500 ml) and pentane (500 ml) gave a clear solution which slowly deposited crystals. After 8 hr, 6 grams of crystals were collected (mp 135–42° C). Two similar recrystallizations led to 4.0 grams of the diastereoisomer analyzing 100%, VIIB, by glc; mp 139–44° C; N.E. calcd, 123.6; found, 127.9.

9-(*p*-Chlorophenyl)-1,2,3-nonanetricarboxylic acid triethyl ester, VIII, was prepared from the crude VII by standard methods and distilled: 90% yield; bp 220° C at 0.5 mm; n_D^{20} 1.4911; S.E. calcd, 151.7; found, 150.1.

Formation of Anhydride. A sample of VII was heated for 30 min at 120° C under a reduced pressure of 10 mm. N.E. calcd for the anhydromonoacid, 118.6; found, 117.6; molecular weight calcd, 352.8; found (in camphor), 360.

The infrared spectra (in a potassium bromide pellet) of the anhydride prepared at 120° C clearly indicate a carboxylic acid and an anhydride. The broad OH stretching frequency of 3100 cm^{-1} and the $C=O$ stretching vibration at 1710 cm^{-1} are definite indications of a carboxylic acid. The doublet at 1785 and 1855 cm^{-1} is characteristic of anhydrides and particularly five-membered rings, since in acyclic anhydrides and six-membered rings, the high-frequency component of the doublet consistently lies in the range 1790–830 cm^{-1}, and almost never as high as 1850 cm^{-1}.

Glc of the methyl esters prepared from this anhydride indicated a composition 22%, VIIA, and 78%, VIIB. The original composition of VII was 36%, VIIA, and 64%, VIIB. When the anhydride was prepared from VII at 200° C, glc showed a final composition of 3%, VIIA, and 97%, VIIB.

Analysis by Gas-Liquid Chromatography. Chromatography was carried out with a Beckman GC 4 equipped with a thermal conductivity detector. The 20-ft × ⅛-in. stainless steel column, containing 3% XE-60 on Gas Chrom Q 80–100 mesh, was operated at 250° C with a helium flow of 22 ml/min. Retention times for the methyl esters are 22.5 min for VIIA and 24.0 min for VIIB.

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