grams of product, bp 70–74°C (23 mm) assayed at 3.5% benzene, 93% *exo*-, and 3.5% *endo*-brevicomin by gas-liquid chromatography. Redistillation yielded 516 grams (55%) at bp 72–73°C (21 mm). Gas-liquid chromatography analysis showed 95% *exo*- and 5% *endo*-brevicomin with only a faint (<0.2%) amount of benzene. The material was identical to exo-brevicomin prepared previously (*1*) and the natural material, with regard to chemical and biological parameters.

ACKNOWLEDGMENT

David Wood, University of California at Berkeley, performed the bioassays.

LITERATURE CITED

(1) Bellas, T. E., Brownlee, R. G., Silverstein, R. M., *Tetrahedron*, **25**, 5149 (1969).
(2) Silverstein, R. M., Brownlee, R. G., Bellas, T. E., Wood, D. L., Browne, L. E., *Science*, **159**, 889 (1968).
(3) Wasserman, H. H., Barber, E. H., *J. Amer. Chem. Soc.*, **91**, 3674 (1969).

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Synthesis and Spectral Characterization of Beta-Diketones Containing Perfluorophenyl and Perfluoroalkyl Groups

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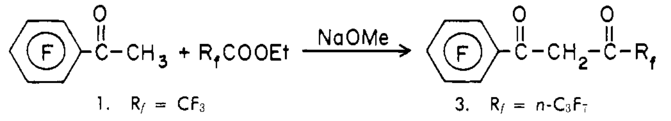
Four β-diketones containing perfluorophenyl groups and perfluoroalkyl groups have been synthesized and characterized by ir, uv, and ^1H and ^{19}F nmr.

Four β-diketones containing perfluorophenyl groups and perfluoroalkyl groups have been synthesized and characterized:



1. $R_f = CF_3$
2. $R_f = C_2F_5$
3. $R_f = n\text{-}C_3F_7$
4. $R_f = n\text{-}C_7F_{15}$

The Claisen condensation of acetylpentafluorobenzene with the ethyl ester of the appropriate perfluorinated aliphatic acid in the presence of sodium methoxide afforded the products in good yield.

The chemical shifts and peak shapes of the enolic protons in the proton magnetic spectra were in agreement with the generalization set forth by Lintvedt and Holtzclaw (*1*). Thus, the chemical shift of the hydrogen-bonded enolic proton of 1 was shifted to a lower δ value than the other three, indicating less basicity, because of the greater electron withdrawing power of the trifluoromethyl group compared to other perfluoroalkyl groups. The chemical shifts of all four compounds, however, were of greater δ values than that reported (*1*) for 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, indicating that the perfluorophenyl group is not so strong an electron withdrawing group as the trifluoromethyl group. Also, in every case, the enolic proton peaks of the β-diketones were sharp (peak width ca. 8 cps), which is characteristic of electron-withdrawing substituent groups. It was interesting to note as well, that the keto-enol equilibrium was shifted completely to the enol form in the nmr solvent (CCl_4).

Table I. β-Diketones[a]

Compd no.	Name	Yield, %	Bp °C, mm Hg	Ir, cm^{-1}		Uv *n*-hexane, mμ, ε	Nmr	
				C=O	C—F		^1H, δ (position)	^{19}F, ppm (position)
1	4,4,4-Trifluoro-1-pentafluoro phenyl-1,3-butanedione	48	77–79 4.7	1620	1180	289 (10,820)	13.7 (enolic H) 6.2 (olefinic H)	76.8 (CF_3), 137.6 (*o* ring F's), 146.7 (*p* ring F), 159.3 (*m* ring F's)
2	4,4,5,5,5-Pentafluoro-1-pentafluorophenyl-1,3-pentanedione	27	83–98 (2.9)[b]	1620	1200	292 (12,120)	13.9 (enolic H) 6.3 (olefinic H)	82.9 (CF_3), 124.6 (CF_2), 139.3 (*o* ring F's), 148.0 (*p* ring F), 161.0 (*m* ring F's)
3	4,4,5,5,6,6,6-Heptafluoro-1-pentafluorophenyl-1,3-hexanedione	62	88–89 (3.4)	1625	1220	292 (12,550)	13.9 (enolic H) 6.2 (olefinic H)	80.7 (CF_3), 121.5 and 126.7 (CF_2), 138.0 (*o* ring F's), 147.6 (*p* ring F), 160.1 (*m* ring F's)
4	4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Pentadecafluoro-1-pentafluorophenyl-1,3-decanedione	37	107–110 (1.2)	1620	1220	293 (11,650)	13.9 (enolic H) 6.2 (olefinic H)	80.7 (CF_3), 119.8–125.4 (CF_2), 137.1 (*o* ring F's), 146.3 (*p* ring F), 159.3 (*m* ring F's)

[a] Elemental analyses (C, H, F) in agreement with theoretical values were obtained and submitted for review. [b] Gas chromatography (150°, 2 m. 20% SF-96 on Chromosorb P, 15 psig) showed higher boiling impurities. Purification was effected by chromatography on silica gel with benzene as eluent. Flash distillation removed colored impurities from the chromatographed product.

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EXPERIMENTAL

The ^1H 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.

LITERATURE CITED

(1) Lintvedt, R. L., Holtzclaw, H. F., Jr., *Inorg. Chem.*, **5**, 239 (1966).
(2) Vorozktsov, N. N., Jr., Barkhash, V. A., Ivanova, N. G., Anichkina, S. A., Andreevskaya, O. I., *Dokl. Akad. Nauk* (SSSR), **159**, 125 (1964); *CA*, **62**, 4045 (1965).

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

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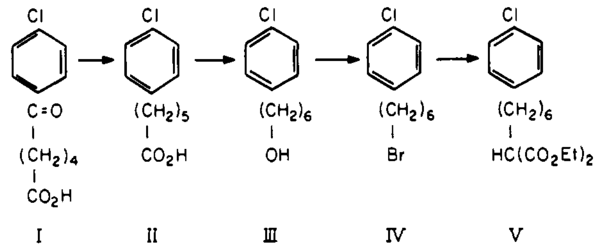
9-(*p*-Chlorophenyl)-1,2,3-nonanetricarboxylic acid was synthesized via a Michael condensation between diethyl fumarate and the appropriate α-substituted malonic acid. Analysis of the two diastereoisomers was carried out by gas-liquid chromatography. Properties of the five new intermediate compounds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

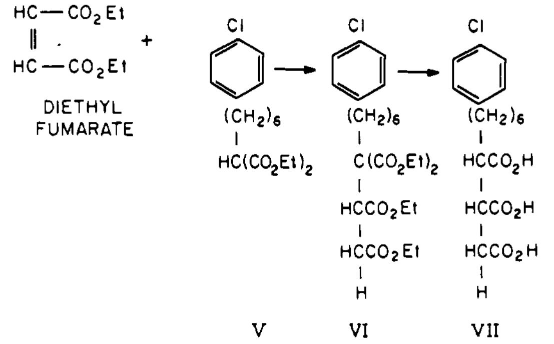
This compound, 9-(*p*-chlorophenyl)-1,2,3-nonanetricarboxylic acid (VII, Scheme 2), was synthesized via a Michael condensation between diethyl fumarate and the appropriate α-substituted malonic ester. Major steps in the synthesis are shown in Schemes 1 and 2. Compounds III through VII are reported for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