Preparation and Diels-Alder Reaction of Some Benzoylacrylic Acids

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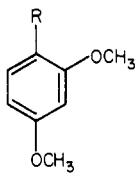
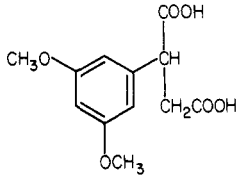
Although Friedel-Crafts acylations of the dimethyl ethers of catechol and hydroquinone with maleic anhydride give the expected products, the reaction of the dimethyl ether of resorcinol (**1a**) with maleic anhydride in the presence of aluminum chloride has been the source of some controversy.[1] Rice[2] found that the reaction in carbon disulfide gave mainly the succinic acid **2** (cf. ref 3 for a similar result with the benzoylacrylic acid **3a** as a minor product). Baddeley and co-workers[4] reported conditions under which **3a** was the main product.



1a, R = H
1b, R = $NHCOCH_3$



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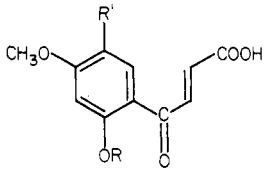
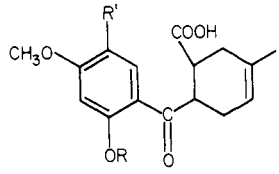
We needed the acids **3a** and **3b** to make compounds of the type **4** as intermediates for the synthesis of tetrahydroanthraquinones.[5] We confirmed Rice's results[2] but obtained, using Baddeley's conditions,[4] **2** (not **3a**[4]) in yields of up to 90%. After a careful study of the reaction, we find that adding a mixture of the reactants in tetrachloroethane to the catalyst with cooling and vigorous stirring gave an easily separable mixture of the acrylic acids **3a** and **3b** (about 55%) with **2** only present to a small extent. Compound **3b** was always the major product, and with longer reaction times no **3a** was isolated.[6] Acylation of **1b** proceeds smoothly to give **3c** as a major product. The electron-releasing effect of the acetamide group facilitates the acylation and hinders the demethylation of the methoxyl group para to it.

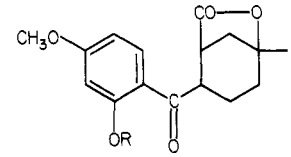


3a, R = CH_3; R′ = H
b, R = R′ = H
c, R = CH_3; R′ = $NHCOCH_3$

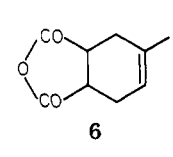


4a, R = CH_3; R′ = H
b, R = R′ = H
c, R = CH_3; R′ = $NHCOCH_3$

Addition of isoprene to **3a**, **3b**, and **3c** gave **4a**, **4b**, and **4c**, respectively. The structure of the adduct **4a** was established by its conversion to the lactone **5a**, which was also obtained by direct acylation of **1a** with **6** (see below). Similarly the γ-lactone **5b** was obtained by acid treatment of **4b**. The structure of **4c** follows by analogy with **4a** and **4b**. The regioselectivity of the Diels-Alder reaction can be explained as shown in **7**; the double bond in the acrylic acid is polarized more strongly by the ketone than by the acid group, and so C_2 is positively charged; in the diene, the presence of the methyl group leads to a negative charge on C_1.



5a, R = CH_3
b, R = H



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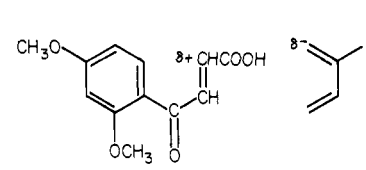

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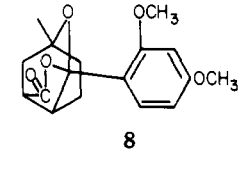
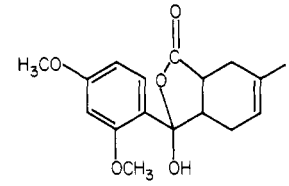


8

In an attempt to make **4a** directly, we reacted **1a** with the Diels-Alder adduct **6**[8] under the same conditions we used to prepare **3a** and **3b**. Acylation took place, but we were only able to isolate the keto lactone **5a** (15%) and tricyclic lactone **8** (32%). Compound **5a** clearly arises from **4a** by the addition of the acid group to the double bond; the more interesting product **8** comes from addition to the double bond of the hydroxyl of the pseudo-acid **9** corresponding to **4a**.



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The structures of **5a** and **8** follow from their compositions ($C_{17}H_{20}O_5$) and spectra. The NMR spectra of both showed a singlet methyl signal at δ 1.5 and no vinyl protons. Each IR spectrum had a peak at 1770 cm^{-1}. However, **5a** had carbonyl absorption at 1665 cm^{-1} and a UV maximum at 303 nm (cf. **4a** UV maximum at 304 nm). By contrast, **8** had no ketonic maximum in the IR and no strong UV maximum above 281 nm. The structure of **8** is confirmed by its ^{13}C spectrum; in particular there were peaks at δ 99 (O-C-O) and 85 (O-C) (cf. ref 11).

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(3) Papa, D.; Schwenk, E.; Villani, F.; Klinsberg, E. *J. Am. Chem. Soc.* **1948**, *70*, 3356.
(4) Baddeley, G.; Makar, S. M.; Ivanson, M. G. *J. Chem. Soc.* **1953**, 3969.
(5) Wheeler, M. M.; Wheeler, D. M. S.; Peterson, G. W. *Phytochemistry* **1975**, *14*, 288.
(6) A ketone ortho to a methoxyl group facilitates demethylation of that group.[7]
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(8) A few examples[9] of the use of adducts from maleic anhydrides (including adducts related to **6**[10]) as Friedel-Crafts acylating agents have been reported.
(9) Peto, A. G. In "Friedel-Crafts and Related Reactions"; Olah, G. A., Ed.; Interscience: New York, 1964; Vol. 3, Chapter 34.IV.14.
(10) Ishibe, S.; Okumichi, T.; Matsumoto, K. *Jpn. Tokkyo Koho 79 09636* **1979**; *Chem. Abstr.* **1979**, *91*, 108873e.
(11) de Magalhaes, G. C.; Cabral, J. A. S.; Prange, T. *Tetrahedron Lett.* **1980**, *21*, 4655.

0022-3263/81/1946-3915$01.25/0

Experimental Section[12]

3-(2-Hydroxy-4-methoxybenzoyl)acrylic Acid (3b). Dimethoxybenzene (**1a**; 13.3 g, 96 mmol) and maleic anhydride (9.8 g, 100 mmol) in tetrachloroethane (40 mL) were added over 30–45 min to aluminum chloride (26.6 g, 200 mmol) at 0 °C with vigorous stirring so that the temperature did not exceed room temperature; stirring was continued for 3 h, and the stoppered flask was kept overnight. The complex at 0 °C was hydrolyzed by addition of cold dilute hydrochloric acid, and the organic layer was extracted repeatedly with saturated aqueous sodium bicarbonate (100 mL). The combined aqueous extracts were neutralized with dilute hydrochloric acid, and the precipitated **3b** was collected (11.4 g, 53%) and crystallized from ethanol: mp 172–173 °C (ethanol); IR (KBr ν_{max} 1700 (COOH), 1660 (CO), 1620 (C=C) cm^{-1}; NMR ($(CD_3)_2CO$) δ 3.8 (s, 3 H, CH_3), 6.4 (m, 2 H, arom), 6.9 and 7.95 (ABq, J_{AB} = 14 Hz, 2 H, vinyl) 7.9 (m, 1 H arom); λ_{max} (methanol) 309 nm (ϵ 9000) 228 (11 000), 206 (13 000); mass spectrum, *m/e* (relative intensity) 222.0528 (10), 177.0550 (100), 176.0469 (14), 151.0396 (37), 149.0235 (19); *m/e* calcd for $C_{11}H_{10}O_5$ (222.0528), $C_{10}H_9O_3$ (177.0551), $C_{10}H_8O_3$ (176.0474), $C_8H_7O_3$ (151.0396), $C_8H_5O_3$ (149.0239).

3-(2,4-Dimethoxybenzoyl)acrylic Acid (3a). Compound **3a** was prepared as described above except that the complex was hydrolyzed after 3 h and worked up as above, yielding a mixture of the two acrylic acids (**3a**) and (**3b**) (11.8 g, 50%). The mixture was chromatographed on a Florsil column and elution with benzene yielded the dimethoxy acid **3a** as a yellow solid (2.36 g, 10%): mp 187–188 °C dec (MeOH) (lit.[2,3] mp 189–190 °C, 190–192 °C); IR ν_{max} 1715, 1680 cm^{-1}; NMR ($(CD_3)_2CO$) δ 3.8 (s, 3 H, OCH_3), 3.9 (s, 3 H, OCH_3), 6.5 (m, 2 H, arom), 6.7 and 7.9 (ABq, J = 14 Hz, 2 H, vinyl) 7.75, (m, 1 H, arom); λ_{max} (MeOH) 316 nm (ϵ 6300), 227 (11 000), 207 (14 000); mass spectrum, *m/e* (relative intensity) 236 (M^+, 100), 191 (90), 165 (95), and 134 (50). Anal. Calcd for $C_{12}H_{12}O_5$: C, 61.02; H, 5.08. Found: C, 61.10; H, 5.07. The monomethoxy acid **3b** (7.2 g, 37%) could be removed from the column by stripping with methanol.

2-(2-Hydroxy-4-methoxybenzoyl)-4-methyl-4-cyclohexenecarboxylic Acid (4b). Isoprene (1.36 g, 20 mmol) and **3b** (4.74 g, 21 mmol) in benzene (20 mL) were refluxed for 24 h. The benzene was evaporated, and the residue was dissolved in warm methanol (15 mL). The adduct **4b** (1.5 g, 26%) precipitated on cooling: mp 170–171.5 °C (MeOH); IR (KBr) ν_{max} 1715, 1620 cm^{-1}; NMR ($(CD_3)_2CO$) δ 1.7 (3 H, s, CCH_3), 2.1–3.2 (8 H, m), 3.8 (3 H, s, OCH_3), 5.4 (1 H, m, vinyl), 6.3 (1 H, m, arom), 6.4 (1 H, d, J = 10 Hz, arom), 7.72 (1 H, d, J = 10 Hz, arom); ^{13}C NMR ($CDCl_3$) δ 22.3, 29.6, 32.4, 38.3, 39.1, 42.1, 55.1, 100.9, 107.3, 112.8, 119.1, 131.9, 132.9, 166.0, 166.3, 207.7; λ_{max} (MeOH) 315 nm (ϵ 9100), 278 (19 000), 230 (11 000); mass spectrum, *m/e* (relative intensity) 290 (M^+, 30), 151 (100). Anal. Calcd for $C_{16}H_{18}O_5$: C, 66.21; H, 6.21. Found: C, 66.59; H, 6.38.

Lactonization of 4b. The adduct **4b** (100 mg, 0.34 mmol) was refluxed in formic acid (10 mL) for 12 h; the mixture was diluted with water (50 mL) and extracted with chloroform (25 mL). The extract was dried (Na_2SO_4) and the solvent was removed at reduced pressure, yielding the lactone **5b** as a solid (40 mg, 40%): mp 145–146 °C (MeOH); IR ($CHCl_3$) ν_{max} 1780, 1660 cm^{-1}; NMR ($CDCl_3$) δ 1.3 (s, 3 H, CH_3), 2.2 (m, 2 H), 2.5 (m, 2 H), 3.2–3.6 (m, 4 H), 3.8 (s, 3 H, OCH_3), 6.4, 6.5, and 7.4 (m, 3 H, arom).

2-(2,4-Dimethoxybenzoyl)-4-methyl-4-cyclohexenecarboxylic Acid (4a). A mixture of the dimethoxy acid **3a** (4.74 g, 20 mmol) and isoprene (1.36 g, 20 mmol) in benzene (20 mL) was refluxed for 24 h. The reaction was worked up as for the reaction with **3b**, and the solid **4a** was collected (1.3 g, 21%): mp 175–176 °C (MeOH); IR (KBr) ν_{max} 1725, 1660 cm^{-1}; NMR ($(CD_3)_2CO$) δ 1.7 (s, 3 H, $C\text{-}CH_3$), 2.25–3.2 (m, 6 H), 3.85, 3.9 (2 s, 6 H, OCH_3), 5.4 (m, 1 H, C=C-H) 6.5 (s, 2 H, arom), 7.75 (1 H, arom); ν_{max} (MeOH) 303 nm (ϵ 12 000), 260 (18 000), 229 (19 000), 214 (19 000); mass spectrum, *m/e* (relative intensity) 304.1312 (8), 165.0552 (100), 138.079 (12); *m/e* calcd for $C_{17}H_{20}O_5$ (304.1310), $C_9H_9O_3$ (165.0552); heating this compound with formic acid gives lactone **5a** (see below).

Acylation of 1a with 6. A solution of **1a** (3.4 g, 25 mmol) and **6** (3.3 g, 20 mmol) in methylene chloride (50 mL) was added with vigorous stirring to anhydrous aluminum chloride (6.5 g, 50 mmol). The orange-brown mixture was stirred at room temperature for 4.5 h and then poured over ice, and dilute hydrochloric acid was added. Methylene chloride was added and the organic layer was separated. The aqueous layer was extracted twice more with methylene chloride. The combined methylene chloride solutions were washed twice with water and dried (Na_2SO_4). The combined aqueous layers were extracted with ethyl acetate (3 times); the ethyl acetate solutions were washed with water and dried (Na_2SO_4). Evaporation of the combined ethyl acetate and methylene chloride extracts yielded an oily residue (6.02 g). Addition of methanol gave a sticky oil; the methanol was removed, and the next day crystals separated from the residue. These were purified by washing with methanol to give lactone **8**; mp 176–181 °C (0.88 g, 2.9 mmol). Recrystallization from ethyl acetate gave **8**: mp 182–183 °C; UV (MeOH λ_{max} 209 nm (ϵ 16 000), 230 (10 500), 275 (2700), 281 (2600); IR (CH_2Cl_2) ν_{max} 1770, 1610, 1585 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.49 (s, 3H), 1.6–2.2 (m, 6 H), 2.9–3.6 (m, 2 H) 3.82 (s, 6 H), 6.5–6.7 (m, 2 H), 7.57 (d, J = 9 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 180.3, (C=O), 161.6, 157.6 (OC_{Ar}), 128.6, 118.9, 113.7, 103.4 (C_{Ar}), 99.2 (OCO), 84.7 (OC_{Al}), 55.7, 55.3 (OCH_3), 45.8, 40.2, 34.1, 33.8, 26.1, 21.2 (CH_3); mass spectrum, *m/e* (relative intensity) 304.1309 (6), 260.1418 (11), 165.0551 (100); *m/e* calcd $C_{17}H_{20}O_5$ (304.1311), $C_{16}H_{20}O_3$ (260.1413), $C_9H_9O_3$ (165.0551).

The methanolic solutions, from which **8** was obtained, were evaporated. A portion (2.92 g) of the residue (5.03 g) was dissolved in methanol (5 mL)**8** and the crystals (0.39 g, mainly **5a** by TLC), which separated on cooling, were flash chromatographed on silica gel. Elution with CH_2Cl_2/EtOAc (19/1) gave the keto lactone **5a**, mp 135–138 °C (0.15 g), which crystallized from methanol with mp 137–139 °C: UV (MeOH) λ_{max} 215 nm (ϵ 11 500), 228 (12 000), 268 (11 700), 302 (8600); IR (CH_2Cl_2) ν_{max} 1770, 1665, 1600 cm^{-1}; NMR ($CDCl_3$) δ 1.46 (s, 3 H), 1.5–2.4 (m, 6 H), 3.03 (d, J = 6 Hz, 1 H), 3.57 (t, J = 8 Hz, 1 H), 3.83 (s, 3 H), 3.87 (s, 3 H), 6.3–6.6 (m, 2 H), 7.7 (d, J = 9 Hz, 1 H), ($(CD_3)_2CO$) 1.40 (s, 3 H), 1.7–2.4 (m, 6 H), 2.92 (d, J = 4 Hz, 1 H), 3.63 (t, J = 8 Hz, 1 H), 3.83 (s, 3 H), 3.93 (s, 3 H), 6.5–6.7 (m, 2 H), 7.63 (d, J = 9 Hz, 1 H); mass spectrum, *m/e* (relative intensity) 304.1317 (2), 276.1010 (3), 165.0555 (100), 122.0368 (6); *m/e* calcd for $C_{17}H_{20}O_5$ (304.1311), $C_{15}H_{16}O_5$ (276.0998), $C_9H_9O_3$ (165.0552), $C_7H_6O_2$ (122.0368).

The residue (2.52 g) from the evaporation of the mother liquors from the crystallization of **5a** was subjected to medium-pressure liquid chromatography[13] on silica gel using CH_2Cl_2/EtOAc (19/1) as the eluting agent. The following products were obtained from the column: **1a** (0.67 g), **8** (0.36 g), and **5a** (0.39 g). Another 0.8 g of material was obtained in later fractions; TLC indicated that several compounds were present but these substances were not identified. The overall yields of **8a** and **5a** (allowing for recovered **1a**) were 32% and 15%, respectively.

3-(2,4-Dimethoxy-5-(methylcarboxamido)benzoyl)acrylic Acid (3c). Aluminum chloride (2.6 g, 10 mmol) was added to a stirring solution of 2,4-dimethoxyacetanilide (**1b**; 1 g, 5 mmol) and maleic anhydride (0.5 g, 4.8 mmol) in tetrachloroethane (20 mL) at 0 °C. The stirring was continued for 1 h and the mixture was kept for 2 h at room temperature. Dilute hydrochloric acid was added at 0 °C and the precipitated acid **3c** (750 mg, 53%) was crystallized: mp 220–222 °C (EtOH); NMR ($CDCl_3$) δ 2.1 (s, 3 H, $COCH_3$), 3.95 (s, 6 H, OCH_3), 6.8 (s, 1 H, arom), 6.56 and

(12) Melting points (uncorrected) were obtained in capillary tubes by using a Mel-Temp apparatus. NMR spectra were recorded on a Varian Associates A-60D, XL 100, or EM 390 spectrometer. All chemical shifts are reported in parts per million (δ) downfield from $(Me)_4Si$ as the internal standard. IR spectra were recorded on a Perkin Elmer 137 or 237 spectrometer or a Beckman Acculab 4 grating spectrometer. UV spectra were determined on a Cary 14 recording spectrometer or a Hewlett-Packard 8450. Mass spectra were determined on an A.E.I. MS-50 mass spectrometer. Elemental analyses were performed by Micro-Tech Laboratories, Inc., Skokie, IL. Analytical TLC was done on E. Merck 5775 silica gel sheets. Column chromatography used Merck 9385 silica gel (400–230 mesh) or Baker 1-3405 silica gel.

(13) Meyers, A. I.; Slade, J.; Smith, R. K.; Mihelich, E. D.; Kershenson, F. M.; Liang, C. D. *J. Org. Chem.* **1979**, *44*, 2247.

(14) Note Added in Proof: When **5a** was kept with aluminum chloride in methylene chloride for 2 h at room temperature **8** and an unidentified product were formed (TLC). The latter material was also present when **8** was treated under similar conditions (TLC) and in the mixture from the reaction of **1a** and **6** (medium-pressure chromatography and TLC). The easy conversion of **5a** into **8** supports the close structural relationship of these compounds.

7.72 (ABq, J = 15 Hz, 2 H, vinyl), 8.35 (s, 1 H, arom).

2-(2,4-Dimethoxy-5-(methylcarboxamido)benzoyl)-4-methyl-4-cyclohexenecarboxylic Acid (4c). A mixture of the acrylic acid **3c** (4.0 g, 13.7 mmol) and isoprene (5 mL) in ethanol (100 mL) was refluxed overnight. The adduct **4c** (2.5 g, 50%) was isolated in the same manner as in the previous additions and the solid was collected: mp 190–191 °C (EtOH); IR (KBr) ν_{max} 3400, 1725, 1640, 1600 cm^{-1}; NMR ($(CD_3)_2CO$) δ 1.6 (s, 3 H, C=CCH_3), 2.1 (s, 3 H, $COCH_3$), 2.1–3.0 (m, 6 H), 3.9 (2 s, 6 H, OCH_3), 5.3 (m, 1 H, C=CH), 6.6 (s, 1 H, arom), 7.8 (m, 1 H, arom); λ_{max} (MeOH) 315 nm (ϵ 1200), 270 (3000), 240 (4700); mass spectrum, m/e (relative intensity) 361.1521 (5), 222.0771 (100), 180.0658 (17), 165.0524 (25); m/e calcd for $C_{19}H_{23}NO_6$ (361.1525), $C_{11}H_{12}NO_4$ (222.0767), $C_9H_{10}NO_3$ (180.0661).

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Registry No. 1a, 151-10-0; **1b**, 23042-75-3; **3a**, 78149-70-9; **3b**, 78149-71-0; **3c**, 78149-72-1; **4a**, 78149-73-2; **4b**, 78149-74-3; **4c**, 78149-75-4; **5a**, 78149-76-5; **5b**, 78149-77-6; **6**, 3425-89-6; **8**, 78149-78-7; maleic anhydride, 108-31-6; isoprene, 78-79-5.

Geminal Fluorination of Diazo Compounds

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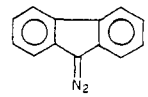
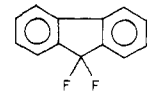
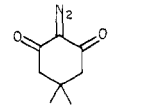
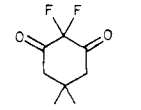
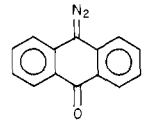
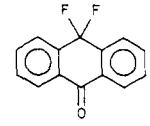
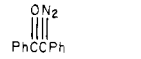
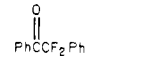
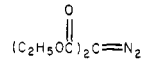
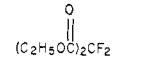
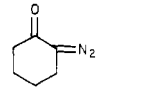
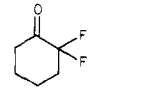
The utility of diazo compounds as intermediates in preparative organic chemistry has proven of great value.[2] Conversion of diazo compounds to halocarbons is a long known process dating back to nearly a century ago when Curtius reported the reaction between diazo compounds and hydrogen halides.[3a] Subsequently, considerable attention has been focused on the halogenation of various diazo substrates with both hydrogen halides and molecular halogen.[3-7]

The preparation of fluorocarbon compounds from diazo precursors has received much less attention. Olah in 1956 first reported the conversion of diazo compounds into fluorocarbons on reaction with hydrogen fluoride.[8a] A few reports on the reaction of hydrogen fluoride with diazo substrates have emerged subsequently, including reactions in the presence of haloamides to produce mixed halofluorocarbon compounds.[8-10] Olah recently introduced the use of pyridinium poly(hydrogen fluoride) as a more effective source of HF in the hydrofluorination of diazo compounds.[8c]

Leroy and Wakselman in 1976 made the only reports on the reaction of diazo compounds with molecular fluorine. However, their studies were mostly concerned with the use of trifluoromethyl hypofluorite as a fluorinating reagent; and their studies with molecular fluorine were less detailed.[11]

We report now an efficient and selective preparation of geminal difluoro compounds by reaction of diazo substrates with dilute molecular fluorine in Freon-11 solution at −70 °C. The results given in Table I show that very respectable yields (65–94%) of geminal difluoro compounds are obtained. Moreover, neither the carbon–hydrogen bonds nor the keto function is affected in the fluorination. The overall enthalpy change of −154 kcal/mol for conversion of a diazo function to a geminal difluoro function would indeed favor the selectivity observed.[12] However, the low

Table I. Fluorination of Diazo Compounds

diazo substrate	product	% yield[a]	^{19}F NMR[b]
$Ph_2C{=}N_2$	Ph_2CF_2	71	87
		88	110
		80	169
		94	81
		79	81
		70	109
		65	111

[a] Isolated yields of pure product. [b] ϕ (ppm) upfield relative to $CFCl_3$.

(1) Taken in part from the Master of Science thesis of J.J.S. submitted to Southern Illinois University, 1980.

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