8-Ethyl-1-methoxybenzo[*d*]naphtho[1,2-*b*]pyran-6-one (4). A mixture of 8 (170 mg, 0.55 mmol) and 10% palladium on carbon (170 mg) was heated at 200 °C under vacuum for 10 h. During this period the reaction mixture was monitored by thin-layer chromatography (CH_2Cl_2, $R_f(8) = 0.26$, $R_f(4) = 0.56$). When the reaction was complete, the crude product was removed from the carbon by successive triturations with hot benzene and chloroform. The combined extract was evaporated to dryness, and the resulting residue was crystallized from cyclohexane–dichloromethane to yield 122 mg (72%) of 4 as fine, white needles: mp 174 °C; ^1H NMR ($CDCl_3$) δ 1.33 (t, 3 H, CH_3) 2.81 (q, 2 H, benzylic), 4.02 (s, 3 H, OCH_3), 6.79 (d, 1 H, $J_{2,3} = 7.6$ Hz, H-2), 7.41 (dd, 1 H, $J_{3,4} = 8.1$ Hz, H-3) 7.54 (dd, 1 H, $J_{9,10} = 8.1$ Hz, $J_{7,10} = 1.8$ Hz, H-9), 7.77 (d, 1 H, $J_{11,12} = 9.0$ Hz, H-11), 7.89 (d, 1 H, H-10), 7.96 (d 1 H, H-12), 7.98 (d, 1 H, H-4), 8.14 (d, 1 H, H-7); ^{13}C NMR ($CDCl_3$) δ 15.08 (CH_3), 28.51 (benzylic), 55.49 (OCH_3), 105.55 (C-2), 113.46, 114.06 (C-4), 118.01, 118.34 (C-11, C-12), 120.94, 122.02 (C-3), 124.67, 125.76, 127.00 (C-10), 128.87 (C-7), 132.80, 134.80 (C-9), 144.93, 146.34, 155.07 (C-1), 161.30 (C=O). Anal. Calcd for $C_{20}H_{16}O_3$: C, 78.93; H, 5.30. Found: C, 78.71; H, 5.29.

8-Ethyl-1-methoxy-4-(2′,3′,5′-tri-*O*-acetyl-β-D-ribofuranosyl)benzo[*d*]naphtho[1,2-*b*]pyran-6-one (1) and 8-Ethyl-1-methoxy-4-(2′,3′,5′-tri-*O*-acetyl-α-D-ribofuranosyl)benzo[*d*]naphtho[1,2-*b*]pyran-6-one (2). To a stirred solution of 4 (600 mg, 1.97 mmol) and 1,2,3,5-tetra-*O*-acetyl-β-D-ribofuranose[11] (**3**) (628 mg, 1.97 mmol) in 40 mL of dichloroethane was added stannic chloride (0.7 mL, 6 mmol). After 24 h at room temperature, the reaction mixture was poured into an aqueous sodium bicarbonate solution. The organic phase was separated and washed with water. The extract was dried (sodium sulfate), and the solvent was evaporated; the resulting residue was separated by preparative thin-layer chromatography (dichloromethane–ether, 14:1). Unreacted 4 (145 mg, 23%), 351 mg (32%) of **2**, off-white crystals (mp 200 °C), and 315 mg (29%) of 1, off-white crystals (mp 193 °C), were obtained. For 1: MS, *m/z* 562 (1.6%, $M^{\bullet+}$), 383 (100%, $M^{\bullet+} - 2AcOH - OAc$); ^1H NMR ($CDCl_3$) δ 1.29 (t, 3 H, $J = 7.6$ Hz, CH_3), 1.97, 2.19, 2.29 (3 s, 9 H, acetyl), 2.76 (q, 2 H, benzylic), 4.00 (s, 3 H, OCH_3), 4.46 (dd, 1 H, $J = 12.2$ Hz, $J = 5.0$ Hz, H-5′), 4.53 (dd, 1 H, $J = 2.6$ Hz, H-5′), 4.56 (ddd, 1 H, $J_{4',3'} = 9.5$ Hz, $J_{4',5'} = 2.6$ Hz, $J_{4',5'} = 5.0$ Hz, H-4′), 5.16 (dd, 1 H, $J_{2',3'} = 4.2$ Hz, H-3′), 5.59 (d, 1 H, H-2′), 6.58 (brs, 1 H, H-1′), 6.86 (d, 1 H, $J_{2,3} = 8.4$ Hz, H-2), 7.65 (dd, 1 H, $J_{9,10} = 8.3$ Hz, $J_{9,7} = 1.9$ Hz, H-9), 8.03 (d, 1 H, $J_{11,12} = 9.0$ Hz, H-11), 8.05 (d, 1 H, H-3), 8.09 (d, 1 H, H-10), 8.15 (d, 1 H, H-7), 8.23 (d, 1 H, H-12); ^{13}C NMR ($CDCl_3$) δ 15.19 (CH_3), 20.50, 20.95, 21.21 (acetyl), 28.56 (benzylic), 55.73 (OCH_3), 63.16 (C-5′), 69.59 (C-3′), 76.37, 76.47 (C-2′,C-4′), 82.60 (C-1′), 104.81 (C-2), 115.25 (C-4), 118.79 (C-12), 119.28 (C-11), 120.36 (C-8), 122.01, 122.43 (C-3), 125.62 (C-10), 126.77, 127.28, 128.75 (C-7), 132.80, 135.09 (C-9), 145.42 (C-6a), 147.32 (C-5), 154.97 (C-1), 160.31 (C-6), 169.72, 170.66, 170.76 (acetyl C=O). Anal. Calcd for $C_{31}H_{30}O_{10}$: C, 66.2; H, 5.38. Found: C, 66.0; H, 5.14.

For **2**: MS, *m/z* 562 (7.1%, $M^{\bullet+}$), 383 (100%, $M^{\bullet+} - 2AcOH - OAc$); ^1H NMR ($CDCl_3$) δ 1.31 (t, 3 H, $J = 7.6$ Hz, CH_3), 1.53, 2.02, 2.17 (3 s, 9 H, acetyl), 2.80 (q, 2 H, benzylic), 4.02 (s, 3 H, OCH_3), 4.34 (dd, 1 H, $J_{5',5'} = 12.2$ Hz, $J_{5',4'} = 5.1$ Hz, H-5′), 4.48–4.52 (m, 2 H, H-4′, H-5′), 5.69 (dd, 1 H, $J_{3',2'} = 4.8$ Hz, $J_{3',4'} = 7.6$ Hz, H-3′), 6.35 (dd, 1 H, $J = 3.5$ Hz, H-2′), 6.72 (d, 1 H, H-1′), 6.93 (d, 1 H, $J_{3,2} = 8.4$ Hz, H-2), 7.68 (dd, 1 H, $J_{9,7} = 1.9$ Hz, $J_{9,10} = 8.3$ Hz, H-9), 7.94 (d, 1 H, H-3), 8.02 (d, 1 H, $J_{11,12} = 9.1$ Hz, H-11), 8.11 (d, 1 H, H-10), 8.23 (d, 1 H, H-12), 8.24 (d, 1H, H-7); ^{13}C NMR ($CDCl_3$) δ 15.21 (CH_3), 20.14, 20.55, 20.93 (acetyl), 28.59 (benzylic), 55.68 (OCH_3), 64.40 (C-5′), 73.02, 73.66, 77.71 (C-2′, C-3′, C-4′), 80.59 (C-1′), 104.83 (C-2), 114.81 (C-4), 118.44 (C-12), 118.99 (C-11), 120.41 (C-8), 122.43 (C-3 and quaternary), 124.09, 126.60, 126.98 (C-10), 128.82 (C-7), 132.99, 135.10 (C-9), 145.42 (C-6a), 147.41 (C-5), 154.68 (C-1), 160.35 (C-6), 169.04, 169.54, 171.00 (acetyl C=O). Anal. Calcd for $C_{31}H_{30}O_{10}$: C, 66.2; H, 5.38. Found: C, 66.0; H, 5.10.

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Registry No. **1**, 116596-78-2; **2**, 116596-79-3; **3**, 13035-61-5; **4**, 114862-65-6; **5**, 83-56-7; **6**, 116596-80-6; **7**, 114862-61-2; **8**, 114862-62-3.

Aryl Exchange via Reversible Friedel–Crafts Reaction in the Synthesis of a Diarylacetic Acid

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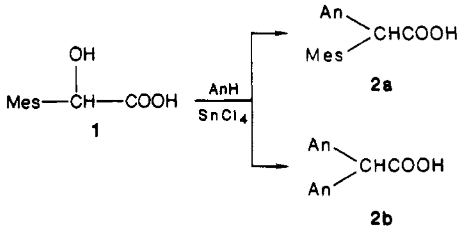
Friedel–Crafts alkylations are reversible processes as judged by transalkylation and reorientation reactions and the formation of the thermodynamically more stable product if the processes take place for sufficient time.[1]

In the course of an attempted preparation of a diarylacetic acid via a Friedel–Crafts type alkylation of an aromatic substrate by an arylglycolic acid, we observed a product which suggests that exchange of an aryl group between the two precursors takes place. We believe that this is due to the reversibility of the Friedel–Crafts reaction after an initial proton transfer. Alkyl transfers are known,[1] and aryl "replacement" reactions were reported in the $AlCl_3$-catalyzed reaction of few β,β-diarylpropionic acids with aromatic solvents[2] or in the $AlCl_3$-catalyzed addition of ArH to cinnamic acids, which presumably proceeds via the β,β-diarylpropionic acids.[2] Since we did not find a precedent for this behavior in our particular system, we report this interesting variant of the reaction here.

Reflux of mesitylglycolic acid (**1**)[3] with anisole as the solvent (16-fold excess over 1) in the presence of excess anhydrous stannic chloride gave 70% yield of an acid, which is not the expected anisylmesitylacetic acid (**2a**) since it showed no mesityl-methyl signals in the NMR. The acid was identified as 2,2-di-*p*-anisylacetic acid (**2b**) (eq 1).



(1)

Mes = 2,4,6-$Me_3C_6H_2$; An = 4-$MeOC_6H_4$

In order to see if this results from the large concentration of anisole, the same reaction was conducted in refluxing CS_2 with only a slight excess of anisole and with the same or a different order of mixing the reagents. Both **2a** and **2b** were formed under these conditions, either in a 1:1 ratio when $SnCl_4$ is dripped into the anisole–CS_2 solution, or in a 4.8-fold excess of **2a** when the anisole is dripped into the $SnCl_4$–CS_2 solution (eq 1).

The reaction conditions are those of a Friedel–Crafts reaction where the carbenium ion **3a** generated from **1** with the Lewis acid catlayst $SnCl_4$ electrophilically attacks the activated anisole to give cation **4a**. The parallel formation of **2a** and **2b** and the exclusive formation of **2b** with excess

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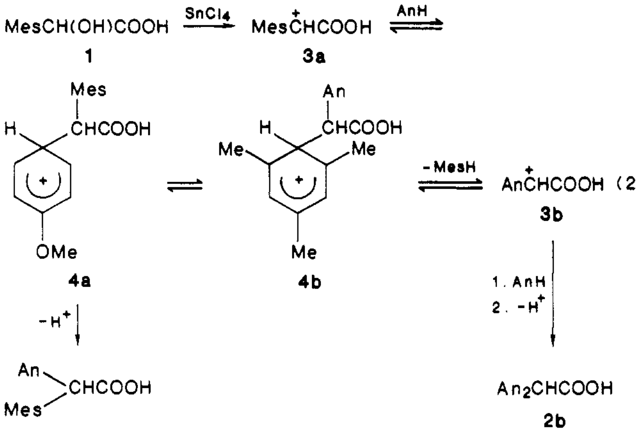
anisole suggests that the electrophilic attack step is reversible. Whereas simple reversibility, i.e. **4a** → **3a** is a hidden process and does not affect product formation, when another aromatic ring in **4a** (e.g., mesityl) can serve as the nucleofuge after a proton transfer to it (cf. **4b**) this overall step would amount to an aryl group exchange on the arylglycolic acid residue or the cation generated thereof. This is presented in eq 2.



A proton transfer from the protonated anisole moiety to the mesityl group in **4a** can be either intra- or intermolecular, in which case cation **4b** is formed. This is followed by expulsion of mesitylene, i.e. **4b** → **3b**. Anisyl and mesityl have similar base strengths. Their reactivities in aromatic substitution are similar as well, as judged by the σ^+ values of *p*-MeO and *p*-Me[4] (assuming that $\sigma^+_{o\text{-Me}} \sim \sigma^+_{p\text{-Me}}$), when reactivity reduction by the *o*-Me groups due to steric effect is taken into account. It is interesing that mesityl stabilizes a vinyl cation better than anisyl: the solvolytic reactivity of $ArC(Br){=}CH_2$ is 17-fold higher for Ar = Mes than for Ar = *p*-An.[5]

The aryl groups play a dual role in this mechanism. They stablize the benzylic positive charge in **3a** and **3b**, and their substituents stabilize the positively charged *r*-complexes **4a** and **4b** by electron donation. At the same time, their conjugate acids transfer a proton (i.e. **4a** ⇌ **4b**) and are lost as neutral species (i.e., **4b** → **3b**). The delicate balance between these roles and the similar basicities of the two aryl groups probably enables the formation of a reasonable amount of both **4a** and **4b** in their equilibrium and the observation of the reaction in our case. However, the observed ratios of products under the various conditions cannot be rationalized without knowing the rate-determining step and how far the reactions are from being under thermodynamic control.

The role of the excess anisole seems to be to increase the rate of formation of **2b** by taking away **3b** from the equilibrium mixture. Corroboration of this speculation requires additional experiments.

It is of interest that this aryl exchange reactin was not observed previously when the aromatic reagent had either identical basicity or smaller basicity than mesitylene. The reaction of mesitylglycolic acid with mesitylene-*Me*-d_9 (Mes*H), which was studied previously[6] under H_2SO_4 catalysis, resulted only in monolabeled dimesitylacetic acid (Mes*CH(Mes)COOH), and the reaction of **1** with excess 1-*tert*-butyl-3,5-dimethylbenzene and $SnCl_4$ gave only 4-*t*-Bu-2,6-$Me_2C_6H_2CH$(Mes)COOH.[6] Apparently, under these specific conditions even the almost identical basicity of the two aryl groups does not ensure the occurrence of exchange. Likewise, the reaction of **1** with excess of C_6D_6 and $SnCl_4$ gives only MesCH(C_6D_5)COOH and not $(C_6D_5)_2$CHCOOH,[7] whereas with toluene as a solvent only MesCH(*p*-Tol)COOH was formed,[8] indicating again that a suitable combination of effects is required for this exchange to be observed.

We note also that the aryl replacement in β,β-diarylpropionic acids also proceeds only with certain substituents (e.g., Ph, *p*-ClC_6H_4),[2] which are much less capable of stabilizing a positive charge than anisyl and mesityl.

A detailed knowledge of the mechanism and of the optimal conditions may turn the reaction to a useful method for generating new diarylacetic acids from the appropriate arylglycolic and aromatic precursors. We plan to study this question.

Experimental Section

Anisylmesitylacetic Acid (2a). (a) To a solution of mesitylglycolic acid[3] (5 g, 0.028 mol) and freshly distilled anisole (3.69 mL, 0.034 mol) in CS_2 (25 mL) at 45 °C was added $SnCl_4$ (4.62 mL, 0.039 mol) dropwise during 30–40 min. The solution turned orange and then dark red. After being refluxed for 8 h, the solution was poured onto ice–water (100 mL), extracted with ether (3 × 30 mL), and dried ($MgSO_4$), and the ether was evaporated. The TLC showed two spots of equal intensity, and ^1H NMR analysis showed the formation of **2a** to **2b** in a 1:1 ratio. Chromatography on a silica gel (Merck 230–400 mesh) pressure column using 4:1 petroleum ether (40–60 °C)–ethyl acetate (v/v) as the eluent gave four fractions: mesitylene (0.66 g), **2b** (1.14 g), a 4:1 **2b**:**2a** mixture (0.84 g), and nearly pure **2a** (0.88 g, 12%). Recrystallization from MeOH gave pure anisylmesitylacetic acid (**2a**): mp 177 °C; UV λ_{max} (EtOH) 206 nm (ϵ 8600), 222 (6500), 274 (660); IR ν_{max} (Nujol) 2820–2480 (w, sh, COOH), 1710–1690 (m, CO) cm^{-1}; NMR (200 MHz) ($CDCl_3$) δ 2.20 (6 H, s, Me), 2.29 (3 H, s, Me), 3.77 (1 H, s, OMe), 5.36 (1 H, s, CH), 6.78, 6.83, 7.03, 7.07 (4 H, AA′BB′ q, *J* = 8.8 Hz, An), 6.91 (2 H, s, Mes-H); MS (EI, 75 °C, 68 eV), *m/z* (relative abundance, assignment) 284 (32, M), 239 (B, M – COOH), 223 (9, M – CH_3 – H – COOH), 209 (7, M – 2Me – COOH), 192 (9, M – MeCOOH – MeOH), 165 (9, M – Mes), 133 (8, $MesCH_2$), 119 (10, Mes), 91 (3, $C_7H_7^+$), 77 (3, Ph). Anal. C, 75.91; H, 6.87. Calcd for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09.

(b) To a refluxing mixture of mesitylglycolic acid (10 g, 0.057 mol) and $SnCl_4$ (9.24 mL, 0.079 mol) in CS_2 (130 mL) was added dropwise distilled anisole (7.38 mL, 0.068 mol) in CS_2 (40 mL), and the reflux was continued overnight. On workup as above, 9.81 g of a **2a**/**2b** mixture according to the TLC was formed in a 4.8:1 **2a**:**2b** ratio (according to the NMR). Chromatography under the conditions as above gave **2a** (4.13 g, 28%), which on recrystallization from MeOH gave white crystals of pure **2b** (3.57 g, 24%), mp 176 °C.

2,2-Di-*p*-anisylacetic Acid (2b). To a solution of mesitylglycolic acid (10 g, 0.057 mol) in distilled anisole (100 mL, 0.91 mmol) at 70 °C was added anhydrous $SnCl_4$ (9.16 mL, 0.078 mol) dropwise. The solution was heated at 70 °C for 8 h, poured into water (60 mL), extracted with ether (3 × 50 mL), and washed with dilute HCl (50 mL). The ethereal solution was extracted with 10% aqueous Na_2CO_3 solution (3 × 40 mL), the extract was acidified with concentrated HCl, and the solid obtained was filtered. The adsorbed anisole was distilled, leaving a white solid (9.85 g, 70%), mp 102 °C. Recrystallization from ethanol gave pure 2,2-di-*p*-anisylacetic acid: mp 109 °C (lit.[9] mp 110 °C); IR (Nujol) 2800–2400 (br, COOH), 1700 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.78 (6 H, s, OMe), 4.94 (1 H, s, CH), 6.83, 6.88 7.21, 7.26 (4 H, AA′BB′, *J* = 8.8 Hz, Ar); molecular peak in the mass

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spectrum, *m/z* 272. Anal. C, 70.32; H, 5.85. Calcd for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92.

Acknowledgment. We thank Dr. Silvio Biali for discussions. This work was supported by The Israel Commission for Basic Research, The Israel Academy for Sciences and Humanities, to which we are grateful.

Registry No. 1, 20797-56-2; **2a**, 116437-29-7; **2b**, 4541-73-5; anisole, 100-66-3.

Parameterization of Cyano Group MM2 Constants in Peracetylated Aldononitriles

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Allinger's MM2 program[1] includes bending and torsional constants related to alkyl cyano groups; however, it does not permit the direct application to combinations of cyano and other functional groups. One of these is an acyloxy group α to the cyano group. This combination is typical in peracetylated aldononitriles, derivatives extensively used in the analysis of sugars.[2] Accordingly, the bending C_{sp}–C_{sp^3}–O_{sp^3} (type 4-1-6) and the torsional constants C_{sp}–C_{sp^3}–O_{sp^3}–C_{sp^2} (type 4-1-6-3) and C_{sp}–C_{sp^3}–O_{sp^3}–LP (type 4-1-6-20)[3] are here parameterized; PAAN compounds can be studied with the MM2 approach.

Experimentally determined structural data (bond lengths and angles and dihedral angles) have been reported for molecules 1–13.[4–16] Molecules 4–13 were studied by X-ray diffraction, 1 was studied by electron diffraction,[4] and 2 and 3 by microwave spectroscopy.[5,6]

In general, good agreement was obtained between the reported experimental structural values and our own calculated values with the MM2(77) program;[17] however, the MM2 nitrogen(sp)–carbon(sp) bond lengths were appreciably and systematically longer than the experimental values (σ 0.0260). Readjustment of the reported 4-10 (C_{sp}–N_{sp}) stretching values led to the following parameters: l_0 = 1.135 Å and k_s = 18.500 mdyn/Å, in a better concordance with the experimental results (σ 0.0123). Experimental and calculated bond and angles related to the cyano group were in good agreement.

The correctness of torsional constants is confirmed by comparing experimental and calculated conformational energy (enthalpy) differences; in fact, the torsional contribution to the energy may overshadow all other energetic contributions. However, the experimental energy differences between conformers in acyclic molecules are scarce; indeed, experimental data were only available for **17**[18] and **21**.[19] The necessary values were obtained by following Allinger's practice[20] using MO calculations. The present study has been carried throughout within the MNDO approximation.[21] Our attention was centered on two groups of molecules: nitriles **17–20** (to evaluate the 4-1-1-1 (C_{sp}–C_{sp^3}–C_{sp^3}–C_{sp^3}) torsion parameters) and hydroxy nitriles **21–25** (to evaluate the 4-1-1-6 (C_{sp}–C_{sp^3}–C_{sp^3}–O_{sp^3}) torsion parameters).

Because of symmetry factors, molecules **17**, **19**, **20**, **23**, and **25** have only two energetically different conformers. The MNDO ΔH_f's of these conformers are collected in Table I; they lead directly to the conformational enthalpy differences shown in Table II. A correction factor of 0.84 kcal/mol was introduced to get acceptable agreement between experimental and theoretically[22] evaluated conformational enthalpy differences. The values $\Delta\Delta H_f$("exp") are the differences to be used in substitution of the experimentally unavailable ones when parameterization is done.

Empirical calculations on molecules **17–25** with the current MM2 values led to anti–gauche enthalpy differences smaller than they should be. The calculation of the standard deviation (root mean square, rms) with current MM2 values for the 4-1-1-1 and 4-1-1-6 torsion parameters gave the unsatisfactory values 0.68 and 0.61, respectively; consequently, a reparameterization process of 4-1-1-1 and 4-1-1-6 torsion values was undertaken.

Values of ΔH_f of gauche conformers more negative than those of the anti ones forces either V_1 or V_2 to be smaller or negative. Assigning negative values to V_1 is not convenient because it leads to a simultaneous stabilization for the eclipsed (w = 0°) conformer; consequently, values of V_2 more negative than the (already negative) current ones were studied. Best results were attained by making V_2 = –1.1 and readjusting the V_3 parameter. A larger V_3 value leads to a smaller σ but, simultaneously, to a higher energy for the eclipsed conformer and to an incorrectly high C_{sp^3}–C_{sp^3} rotation barrier. The compromise set of values provisionally adopted for the 4-1-1-1 torsional parameters was V_1 = 0.2, V_2 = –1.1 and V_3 = 0.2; this leads to a σ value of 0.20.

Hydroxy nitriles **21–25** were used to reparameterize the 4-1-1-6 constants and to refine the 4-1-1-1 constants, which also intervene in the empirical MM2 conformational energy calculations of those molecules. The *experimental* ΔH_f differences between the gauche and anti conformers in **17** (0.42 kcal/mol) and **21** (≥0.72 kcal/mol) show that V_2-

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