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Sulfonation of 4*H*-Cyclopenta[*def*]phenanthrene and Its Carbonyl Derivative

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The sulfonation of 4*H*-cyclopenta[*def*]phenanthrene gave 1-sulfonic acid accompanied by formation of 2-, 3-, and 8-analogues. The reaction of 8,9-dihydro derivative with sulfuric acid in acetic anhydride yielded exclusively the 2-acid. Also, 4*H*-cyclopenta[*def*]phenanthren-4-one afforded the 8-acid as the main product, and 1- and 2-isomers as minor products. The formation of the keto 2-sulfonic acid would be controlled thermodynamically and that of the 8-isomer is controlled kinetically.

The hydrocarbon 4*H*-cyclopenta[*def*]phenanthrene (**1**) is a characteristic arene. It was the subject of some interesting studies at its active methylene[1,2] and at its C_8–C_9 bond.[3] The reactivity in electrophilic substitution of **1** differs somewhat from those of phenanthrene and of fluorene during nitration,[4] bromination,[5] and acetylation.[6] Sulfonation of phenanthrene[7] and anthracene[8] has been investigated in detail and the distribution for the reaction products has been described.

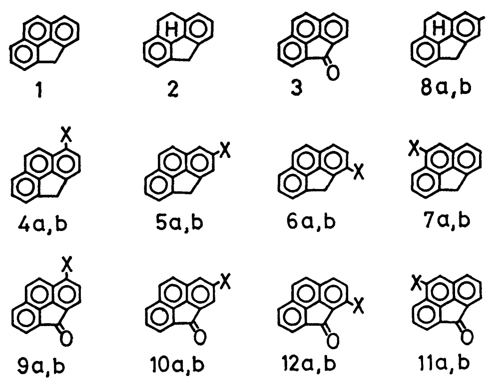
The present work deals with sulfonation of **1**, 8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene (**2**), and 4*H*-cyclopenta[*def*]phenanthren-4-one (**3**) in order to clarify the property of the skeleton of **1** toward electrophile.

Results and Discussion

The sulfonation of **1** afforded 4*H*-cyclopenta[*def*]-phenanthrene-1- (**4a**), -2- (**5a**), -3- (**6a**), and -8-sulfonic acids (**7a**), as is shown in Table 1 (Scheme 1). The assignment of these compounds was established by comparison of their ^{1}H NMR spectra with those of their nitro[4] and acetyl analogues.[6] The proportion of each isomer was determined by comparison of liquid phase chromatograms (HLPC) of the ester mixture derived from the reaction products with those of pure esters, **4b**, **5b**, **6b**, and **7b**. The error of the yield was within ±3 (%) as the average of several experiments and the error of proportion was smaller than ±1 (%) of the standard.

The predominant formation of **4a** would be explained by asserting that the electron density of the 1-position is higher than those of the other positions; this accords with the other electrophilic substitutions.[4–6]

The proportion of **4a** decreases and that of **6a** increases with elevation of the reaction temperature. In sulfonation of phenanthrene, 1-isomer is obtained moderately at low temperature.[7] These results suggest that the formation of **4a** is controlled kinetically and that of **6a** is controlled thermodynamically. Acid **6a** could be stabilized partially due to the hydrogen bond between the active methylene and the sulfonyl group at the 3-position as in the case of 9*H*-fluorene-1-carboxylic acid.[9]



Scheme 1. (Descriptions **a** shows X=SO_3H and **b** is X=SO_3Et.)

The sulfonation of **2** gave 8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene-2-sulfonic acid (**8a**) exclusively, as occurred with fluorene. Other electrophilic attacks to **2** behave in the same way. This tendency can also be seen in the reaction of 1,2,3,3a-tetrahydro-4*H*-cyclopenta[*def*]phenanthrene with electrophiles. This reaction takes place mainly at the 8-position, which corresponds to the 5-position of acenaphthene.[10]

The electron density at the 1- and 3-positions of ketone **3** would be reduced due to the carbonyl group. The reactivity at the 2- and 8-positions may be important. Sulfonation of **3** was examined using 30% oleum–

Table 1. Sulfonation of 4*H*-cyclopenta[*def*]phenanthrene (**1**)

Reaction conditions				Sulfonic acid					Recovd **1**
Agent	Solvent	Temp	Time	Yield	Proportion/%				
		°C	min	%	**4a**	**5a**	**6a**	**7a**	%
H_2SO_4	Ac_2O	0	10	14	86	1	12	1	63
H_2SO_4	Ac_2O	30	10	58	77	1	21	1	10
$ClSO_3H$	dioxane	15	60	24	89	1	10	trace	53
$ClSO_3H$	dioxane	60	10	22	79	2	18	1	55
$ClSO_3H$	dioxane	100	3	29	75	2	22	1	49

Table 2. Sulfonation of 4*H*-cyclopenta[*def*]phenanthren-4-one (**3**)

Run	Reaction conditions			Sulfonic acid					Recovd **3**
	Agent	Temp °C	time min	Mono- yield %	Mono- proportion/% **9a**	**10a**	**11a**	Di- yield %	%
1	10%oleum	40	20	68	*	4	96	1	25
2	100%H_2SO_4	40	20	28	*	5	95	0	66
3	100%H_2SO_4	40	60	41	*	8	92	0	50
4	100%H_2SO_4	40	1440	98	1	8	91	1	1
5	100%H_2SO_4	60	20	67	*	8	92	0	30
6	100%H_2SO_4	80	20	98	*	9	91	2	0
7	100%H_2SO_4	100	20	83	*	10	90	6	0
8	90%H_2SO_4	120	20	74	*	18	82	9	0
9	80%H_2SO_4	160	20	43[a]	2	24	74	42	0

* The yield is smaller than 1% as the average. a) A trace amount of **12a** was found.

80% sulfuric acid at 0—160 °C for time periods between 20 min and 24 h. The formation of 4-oxo-4*H*-cyclopenta[*def*]phenanthrene-1- (**9a**), -2- (**10a**) and -8-sulfonic acids (**11a**) was confirmed by comparison of their HLPC with those of pure compounds. Table 2 shows typical runs of sulfonation of **3**. The experimental error of the yield is smaller than ±3 (%) and that of the proportion is within ±2 (%).

The major formation of **11a**, accompanied by **10a**, would be expected because of the influence of the 4-carbonyl group. The proportion of **11a** decreases with extension of the reaction time (runs 2—4), with elevation of reaction temperature (runs 2, 5—7), and with the combination of dilution of the acid and elevation of the temperature (runs 1, 6, 8, and 9). On the contrary, the proportion of **10a** increases.

The reaction of **3** using 20% oleum at 0 °C afforded **11a** (72%) and disulfonic acids (5%). Treatment of **11a** in sulfuric acid at 140 °C yielded **10a**. This finding would suggest that the formation of **11a** is kinetically controlled, that the production of **10a** is governed thermodynamically, and that **10a** forms by isomerization of **11a** under these conditions.

Notice that the positions thermodynamically controlled, that is, the 3-position of **1** and 2-position of **3**, correspond to the positions controlled thermodynamically in naphthalene[11] and phenanthrene.[12]

The π-π^* transition at *ca.* 255 nm on UV spectrum of **5a** shows a larger red shift than those of the other derivatives. This would suggest that the resonance is enlarged by replacement at the 2-position of **1**.[5,6]

The stretching vibrations on IR spectra of **6a** and **6b** show broad and complex peaks due to symmetrical and unsymmetrical S–O bonds. The NMR spectra of the 4-methylene protons of **6a** and **6b** shift to lower fields than those of the other isomers. These findings may be interpreted as due to a combination of an electronic effect and the steric factor between the SO_2 group and methylene group.

The carbonyl absorption of 4-oxo-4*H*-cyclopenta[*def*]-phenanthrene-3-sulfonic acid (**12a**) shifts in frequency about 10 cm^{-1} beyond the shifts those of the others; the UV shows a blue shift at *ca.* 370 nm, beyond that of the parent **3**. These shifts can be explained by the fact that the resonance between the 3-sulfonic acid and the 4-carbonyl group is disturbed both sterically and electronically.

Experimental

All the melting points are uncorrected. The IR spectra were measured on a JASCO IR-G spectrophotometer as KBr disks and the ^1H NMR were determined with a JEOL JNM-C60-HL spectrometer (60 MHz) in D_2O using TSP as internal reference for the sulfonic acids or in $CDCl_3$ using TMS for the esters. The UV spectra were obtained with a JASCO ORD/UV-5 apparatus in H_2O with a scanning speed of 0.76 s/nm. Mass spectra were recorded on a Hitachi RMU-6E apparatus by means of a direct inlet system.

The HLPC data were obtained on an FLC-150 instrument (JASCO) equipped with a UV detector using a reversed phase partition type SS-10-ODS column (JASCO, 25 cm). The elemental analyses of the sulfonic acids show that these crystals have waters of crystallization in the range of 1 to 3 mol, according to the degree of drying.

*Sulfonation of 4*H*-Cyclopenta*[def]*phenanthrene (1). (a) Quantitative Treatment*: To a solution of **1** (190 mg, 1 mmol) in Ac_2O (9 ml) there was added a mixture of H_2SO_4 (95%, 0.1 ml) and Ac_2O (1 ml); the resulting mixture was stirred for 10 min. After dilution with cold water (100 ml), the precipitate was filtered to give unreacted **1**. The aqueous layer was treated with NaCl and the deposited materials were filtered and ion-exchanged over a cation exchange resin (Amberlite IR-120). The eluate was evaporated off and the residue was extracted with benzene (50 ml). Hexane (150 ml) was added to the solution and the precipitate was filtered. The precipitate was dissolved in water and a part of the solution was titrated with aqueous NaOH (2 mmol/l) to estimate the total yield of the sulfonic acids.

An equimolar amount of NaCl was added to the rest of the solution, which was evaporated, and the residue was treated with $POCl_3$ (2 ml) at 100 °C for 10 min. The reaction mixture was diluted with water and the precipitate was esterified with EtOH (50 ml) in the presence of pyridine (0.5 ml) at 5 °C for 3 h. The ester mixture was applied to HPLC to determine the ratio of isomers. The mobile phase used was (*a*) 2,2,4-trimethylpentane–EtOAc (89/11 volume ratio) or (*b*) hexane–dioxane (92/8). The retention time and the sensitivity were as follows: **1** (internal standard, 6.1 min for *a*, 6.2 min for *b*, 1.00), **4b** (*a*, 13.5 min, 0.69), **5b** (*a*, 12.5 min, 1.00), **6b** (*b*, 11.1 min, 0.60), and **7b** (*b*, 11.8 min, 0.70).

The reaction mixture of **1** (190 mg, 1 mmol) in dioxane (9 ml) with $ClSO_3H$ (0.2 ml, 3 mmol) in dioxane (1 ml) was treated in a manner similar to that described above.

*(b) Separation of **4a***: A solution of **1** (1.90 g, 10 mmol) in dioxane (50 ml) was refluxed with $ClSO_3H$ (1 ml, 15 mmol) for 10 min and the resulting mixture was poured into cold water (200 ml) containing NaCl (60 g). The precipitate was treated with $POCl_3$ to afford 2.208 g (77%) of the sulfonyl chlorides; these were estirified to give 2.065 g (69%) of the ethyl esters. The ester mixture was recrystallized from benzene–cyclohexane (1/1 volume ratio) to yield 1.082 g (47% based on **1**) of ethyl 4*H*-cyclopenta[*def*]phenanthrene-1-sulfonate (**4b**), mp 159.5—160.5 °C; IR, 1350 and 1165 cm^{-1}; NMR δ 1.23 (3H, t, J=7.2 Hz), 4.11 (2H, q), 4.41 (2H, s), 7.68—7.93 (4H, m), 8.04 (1H, d, J=9.0 Hz, H_8), 8.32 (1H, d, J=7.8 Hz, H_2), and 8.44 (1H, d, J=9.0 Hz, H_9); MS, *m/e*, 298 (M^+), 269, 244, and 189. Found: C, 68.51; H, 4.81%. Calcd for $C_{17}H_{14}O_3S$: C, 68.43; H, 4.73%.

The mother liquor was evaporated to dryness and the residue was dissolved in CCl_4 (100 ml) and chromatographed on a silica gel: the lower band on the column gave 15 mg (1%) of ethyl 4*H*-cyclopenta[*def*]phenanthrene-2-sulfonate (**5b**), mp 167—168 °C; IR, 1349 and 1171 cm^{-1}; NMR δ 1.30 (3H, t, J=7.2 Hz), 4.16 (2H, q), 4.39 (2H, s), 7.64—7.91 (5H, m), 8.13 (1H, s, H_3), and 8.45 (1H, s, H_1); MS, *m/e*, 298 (M^+), 269, and 189. Found: C, 68.57; H, 4.93%. Calcd for $C_{17}H_{14}O_3S$: C, 68.43; H, 4.73%.

The upper band afforded 152 mg (7%) of ethyl 4*H*-cyclopenta[*def*]phenanthrene-3-sulfonate (**6b**), mp 98.5—99.5 °C; IR, 1354 and 1178 cm^{-1}; NMR δ 1.30 (3H, t, J=7.2 Hz), 4.17 (2H, q), 4.67 (2H, s), and 7.67—8.14 (7H, m); MS, *m/e*, 298 (M^+), 269, 253, 244, 205, and 189. Found: C, 68.37; H, 4.86%. Calcd for $C_{17}H_{14}O_3S$: C, 68.43; H, 4.73%.

*Sulfonation of 8,9-Dihydro-4*H*-cyclopenta*[def]*phenanthrene (**2**).* A solution of H_2SO_4 (100%, 0.2 ml) and Ac_2O (1 ml) was added to **2** (576 mg, 3 mmol) in Ac_2O (14 ml). The resulting mixture was stirred for 10 min at room temperature. By a treatment similar to that given above, 506 mg (56% based on **2**) of ethyl 8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene-2-sulfonate (**8b**) was isolated, mp 144—145 °C; IR, 1357 and 1168 cm^{-1}; NMR δ 1.46 (3H, t, J=7.2 Hz), 3.40 (4H, s), 4.13 (2H, s), 4.30 (2H, q), 7.07—7.40 (3H, m), 7.64 (1H, s, H_1), and 7.78 (1H, s, H_3); MS, *m/e*, 300 (M^+), 271, 245, 207, and 191. Found: C, 67.80; H, 5.29%. Calcd for $C_{17}H_{16}O_3S$: C, 67.97; H, 5.37%.

*Sulfonation of 4*H*-Cyclopenta*[def]*phenanthren-4-one (**3**).* *(a) Quantitative Treatment*: A mixture of **3** (204 mg, 1 mmol) and H_2SO_4 (1 ml) was shaken for a prescribed time at a suitable temperature. After dilution with water, the precipitate was filtered to give unreacted **3**. The aqueous layer was treated with NaCl and the deposited materials were ion-exchanged. The eluate was evaporated off and the residue was extracted with EtOAc (50 ml). Hexane (150 ml) was added to the EtOAc solution. The precipitate formed was dissolved in water (200 ml) and submitted to titration and HLPC to estimate the yield of acids and the ratio of isomers, respectively. The mobile phase used in HLPC comprised dioxane (35%) and aqueous Bu_4NBr (5 mmol/l, 65%). The retention time and sensitivity were as follows: **9a** (13.0 min, 45.5), **10a** (14.8 min, 47.1), **11a** (11.5 min, 35.3), **12a** (9.8 min, 36.1), disulfonic acids (*ca.* 5 min, 38.5), and *p*-toluenesulfonic acid (as reference sample, 5.3 min, 1.0).

*(b) Separation of **11b**.* A mixture of **3** (2.04 g, 10 mmol) and H_2SO_4 (85%, 10 ml) was stirred for 50 min at 140 °C. After treatment with aqueous NaCl, the sodium salt was refluxed gently with $POCl_3$ (40 ml) for 15 min, giving 2.58 g (85%) of the sulfonyl chloride.

The resulting chloride (3.0 g, 10 mmol) was esterified with dry EtOH (1000 ml) in the presence of pyridine (40 ml) at 5 °C for 7 h and the reaction mixture was poured into cold water. The precipitate was chromatographed on a silica-gel column. The lower band afforded 2.24 g (74% based on sulfonyl chloride) of ethyl 4-oxo-4*H*-cyclopenta[*def*]-phenanthrene-8-sulfonate (**11b**), mp 218—219 °C; IR, 1710 (C=O), 1352, and 1167 cm^{-1}; NMR δ 1.29 (3H, t, J=7.2 Hz), 4.17 (2H, q), 7.51—8.09 (5H, m), 8.42 (1H, d, J=7.8 Hz, H_7), and 8.55 (1H, s, H_9); MS, *m/e*, 312 (M^+), 283, 257, 220, 219, 204, and 203. Found: C, 65.27; H, 3.67%. Calcd for $C_{17}H_{12}O_4S$: C, 65.37; H, 3.87%.

The upper band on the column gave 637 mg (22%) of ethyl 4-oxo-4*H*-cyclopenta[*def*]phenanthrene-2-sulfonate (**10b**) mp 208—209 °C; IR, 1710 (C=O), 1360 and 1173 cm^{-1}; NMR δ 1.33 (3H, t, J=7.2 Hz), 4.21 (2H, q), 7.64—8.03 (5H, m), 8.17 (1H, s, H_3), and 8.53 (1H, s, H_1); MS, *m/e*, 312 (M^+), 283, 257, 220, 219, 204, and 203. Found: C, 65.29; H, 3.93%. Calcd for $C_{17}H_{12}O_4S$: C, 65.37; H, 3.87%.

*Isomerization of **11a**.* Acid **11a** (323 mg, 1 mmol) in H_2SO_4 (85%, 1 ml) was heated at 140 °C for 30 min. Upon similar treatment to that described above, 5% of **10a** and 92% of **11a** were detected by HLPC.

Oxidation of Sulfonic Acid Mixture. Hydrocarbon **1** (1.90 g, 10 mmol) was sulfonated with 20% oleum (2 ml) in dioxane (50 ml) under refluxing for 2 h, followed by salting-out, chlorination, and esterification. The yield was 787 mg (26% based on **1**) of the ethyl esters. In addition, 845 mg (44%) of **1** was recovered.

The ester mixture in aqueous EtOH (90%, 110 ml) was heated for 6 h and the solution was evaporated off. The residue was refluxed with MnO_2 (1 g) in water (50 ml) for 30 min. After filtration, the filtrate was added to a solution of $BaCl_2$ (20 g) in water (100 ml) to form the barium salt, which was treated with $POCl_3$, followed by esterification with EtOH. The keto ester was chromatographed on a silica-gel column with benzene. The first eluate afforded 151 mg (5.1% based on **1**) of ethyl 4-oxo-4*H*-cyclopenta[*def*]phenanthrene-1-sulfonate (**9b**), mp 185—186 °C; IR, 1712 (C=O), 1362, and 1172 cm^{-1}; NMR δ 1.30 (3H, t, J=7.2 Hz), 4.16 (2H, q), 7.50—8.04 (5H, m), 8.21 (1H, d, J=7.2 Hz, H_2), and 8.40 (1H, d, J=9.0 Hz, H_9); MS, *m/e*, 312 (M^+), 283, 257, 220, 219, 204, and 203. Found: C, 65.44; H, 3.83%. Calcd for $C_{17}H_{12}O_4S$: C, 65.37; H, 3.87%.

The second eluate gave 8 mg (0.3%) of **10b**, mp 208—209 °C.

The third eluate yielded 43 mg (1.4%) of ethyl 4-oxo-4*H*-cyclopenta[*def*]phenanthrene-3-sulfonate (**12b**), mp 182.5—183.0 °C; IR, 1722 (C=O), 1360, and 1182 cm^{-1}; NMR δ 1.40 (3H, t, J=7.2 Hz), 4.46 (2H, q), and 7.48—8.04 (7H, m); MS, *m/e*, 312 (M^+), 283, 220, 204, and 203. Found: C, 65.43; H, 3.66%. Calcd for $C_{17}H_{12}O_4S$: C, 65.37; H, 3.87%.

*Reduction of **11b**.* Ester **11b** (312 mg, 1 mmol) in EtOH (100 ml) was refluxed with $N_2H_4 \cdot H_2O$ (90%, 0.5 ml) for 12 h to give the corresponding hydrazone. The hydrazone was warmed in ethylene glycol (40 ml) containing KOH (2 g) at 170 °C for 3 min and the mixture was poured into water. The precipitate was treated with $POCl_3$ and the chloride was converted into ethyl 4*H*-cyclopenta[*def*]phenanthrene-8-sulfonate (**7b**), yield 164 mg (55%), mp 137—138 °C; IR, 1351 and 1171 cm^{-1}; NMR δ 1.25 (3H, t, J=7.2 Hz), 4.12 (2H, q), 4.37 (2H, s), 7.64—8.00 (5H, m), 8.19—8.44 (1H, m, H_7), and 8.64 (1H, s, H_9); MS, *m/e*, 298 (M^+), 269, 243, and

189. Found: C, 68.70; H, 4.67%. Calcd for $C_{17}H_{14}O_3S$: C, 68.43; H, 4.73%.

By a similar procedure, **10b** (312 mg, 1 mmol) was reduced to **5b** (196 mg, 66%), and **9a** (312 mg, 1 mmol) afforded **4a** (154 mg, 52%).

Hydrolyses of the Esters into the Corresponding Sulfonic Acids. Ester **4b** (298 mg, 1 mmol) was refluxed in EtOH (100 ml) containing water (10 ml) for 6 h to give acid **4a**, yield 287 mg (94%), mp 191—194 °C (dec); IR, 1222, 1165, 1082, and 1034 cm^{-1}; UV$_{max}$ 225 nm (log ε 4.47), 249 (4.62), 293 (3.86), 305 (3.85), 331 (2.95), and 347 (2.87); NMR δ 3.52 (2H, s), 7.01—7.51 (4H, m), 7.71 (1H, d, J=9.0 Hz, H_8), 8.09 (1H, d, J=7.2 Hz, H_2), and 8.28 (1H, d, J=9.0 Hz, H_9); MS, *m/e*, 270 (M$^+$), 205, and 189.

Acid **5a** was obtained from **5b**, by a method similar to that described above, in a 76% yield, mp 180—183 °C (dec); IR, 1205, 1178, 1095, and 1040 cm^{-1}; UV, 216 (4.52), 256 (4.79), 299 (3.88), 331 (2.54), and 350 (2.40); NMR δ 3.50 (2H, s), 7.03—7.36 (5H, m), 7.90 (1H, s, H_3), and 8.14 (1H, s, H_1); MS, *m/e*, 270 (M$^+$) and 189.

Acid **6a** was derived from **6b**, yield 95%, mp 175—179 °C (dec); IR, 1257—1128 (broad), 1081, and 1036 cm^{-1}; UV, 225 (4.66), 250 (4.55), 292 (3.96), 304 (3.95), 332 (2.77), and 348 (2.65); NMR δ 4.24 (2H, s), 7.08—7.51 (5H, m), 7.64 (1H, d, J=7.8 Hz, H_1), and 8.02 (1H, d, J=7.8 Hz, H_2); MS, *m/e*, 270 (M$^+$), 222, 205, and 189.

Acid **7a** was prepared from **7b**, yield 78%, mp 179—183 °C (dec); IR, 1198, 1080, and 1030 cm^{-1}; UV, 226 (4.73), 254 (4.58), 294 (3.78), 304 (3.75), 333 (2.85), and 351 (2.81); NMR δ 3.53 (2H, s), 7.05—7.84 (5H, m), 8.24 (1H, s, H_9), and 8.29 (1H, d, J=7.8 Hz, H_7); MS, *m/e*, 270 (M$^+$), 205, and 189.

Acid **8a** was obtained from **8b**, yield 86%, mp 179.5—181.0 °C (dec); IR, 1205, 1180, 1097, and 1035 cm^{-1}; UV, 211 (4.58) and 282 (4.16); NMR δ 2.83 (4H, s), 3.46 (2H, s), 6.96—7.23 (3H, m), 8.03 (1H, s, H_1), and 8.21 (1H, s, H_3); MS, *m/e*, 272 (M$^+$) and 191.

Acid **9a** was derived from **9b**, yield 98%, mp 254—256 °C (dec); IR, 1708 (C=O), 1256, 1224, 1172, 1084, and 1034 cm^{-1}; UV, 235 (5.29), 300 (3.79), and 381 (2.58); NMR δ 6.11—6.93 (5H, m), 7.37 (1H, d, J=9.0 Hz, H_9), and 7.47 (1H, d, J=7.2 Hz, H_2); MS, *m/e*, 284 (M$^+$), 204, and 203.

Acid **10a** was prepared from **10b**, yield 93%, mp 225—227 °C (dec); IR, 1708 (C=O), 1195, 1188, 1094, and 1049 cm^{-1}; UV, 239 (5.22) and 386 (2.59); NMR δ 6.09—6.81 (6H, m) and 7.23 (1H, s, H_1); MS, *m/e*, 284 (M$^+$), 204, and 203.

The acid **10a** was also obtained by the acidic hydrolysis of the corresponding sulfonyl chloride in a 79% yield.

Acid **12a** was derived from **12b**, yield 95%, mp 249—255 °C (dec); IR, 1716 (C=O), 1222, 1204, 1094, and 1034 cm^{-1}; UV, 238 (4.96), 275 (4.03), 320 (3.76), and 370 (2.37); NMR δ 6.60—6.89 (5H, m), 7.23 (1H, d, J=8.4 Hz, H_1), and 7.48 (1H, d, J=8.4 Hz, H_2); MS, *m/e*, 284 (M$^+$), 204, and 203.

Acid **11a** was prepared from **11b**, yield 99%, mp 245—251 °C (dec); IR, 1706 (C=O), 1231, 1202, 1061, and 1021 cm^{-1}; UV, 236 (5.27), 279 (3.94), and 366 (2,38); NMR δ 5.98—7.20 (5H, m), 7.29 (1H, s, H_9), and 7.68 (1H, d, J=7.8 Hz, H_7); MS, *m/e*, 284 (M$^+$), 204, and 203.

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