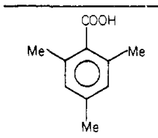
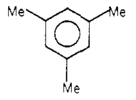
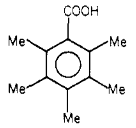
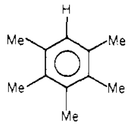
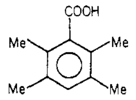
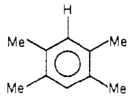
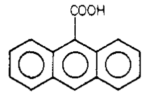
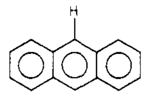
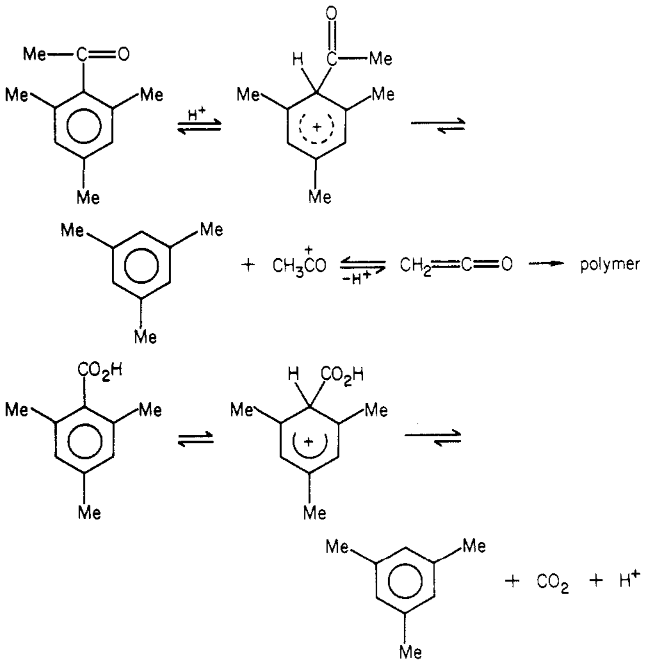
Table II. Nafion-H-Catalyzed Decarboxylation of Aromatic Carboxylic Acid[a]

acid	temp, °C	solvent	product	yield, %
	100	toluene		80
	100	toluene		~40
	100	toluene		~5
	150	anisole		~25

[a] The reaction time was 12 h in all cases.

Scheme I



benzoylmesitylene was refluxed in anisole over Nafion-H for 12 h. Transbenzoylation occurred to form both mesitylene (38%) and benzoylanisole (32%), together with small amounts (~5%) of methyl- and dimethylanisole products of competing transmethylation under the reactions conditions.

Extending our studies to arenecarboxylic acids we found that polymethylbenzenecarboxylic acids decarboxylate in refluxing toluene over Nafion-H. The effect of a *p*-methyl group in stabilizing the intermediate is reflected when comparing the yields of the decarboxylated products, since mesitylenecarboxylic acid and pentamethylbenzoic acid were decarboxylated more efficiently than 2,3,5,6-tetramethylbenzoic acid (see Table II).

In the anthracene skeleton, favorable peri interactions provide the driving force for decarboxylation, yielding 25% anthracene after overnight refluxing in anisole. In a control experiment anthracene-9-carboxylic acid was heated overnight in refluxing anisole in the absence of the catalyst and showed no decarboxylation.

It is suggested that the deacetylation and decarboxylation reactions proceed via ipso protonation of the substrate. (This process may involve dicationic species as the carbonyl/carboxyl group could also be protonated.) In a subsequent step the functional group leaves or reacts over Nafion-H (to polymerize in case of ketene; see Scheme I).

Experimental Section

Acetylmesitylene, acetyldurene, and acetylpentamethylbenzene were prepared by Friedel–Crafts acetylation of the corresponding methylbenzenes with $CH_3COCl/AlCl_3$ and were purified by fractional distillation or crystallization.

Anthracene-9-carboxylic acid (Aldrich), pentamethylbenzoic acid (Alfa), and 2,3,5,6-tetramethylbenzoic acid (Alfa) had high purity and were used as received.

The solvents were high purity (>98% as determined by GLC) commercial samples.

GLC analysis was performed on a Varian Model 3700 instrument equipped with a capillary column and an on-line automatic integrator.

Proton NMR spectra were recorded on a Varian 60 instrument.

In a typical experiment, to a mixture of the aryl methyl ketone (0.007 mol) and Nafion-H (400–800 mg), was added toluene or anisole (15–20 mL), and the mixture was heated under reflux for a specified period of time. Aliquots were withdrawn for GLC analysis, and the products were characterized on the basis of their retention times by comparison and coinjection with authentic samples.

For acetylpentamethylbenzene the progress of reaction was monitored by TLC with hexane as the solvent. The reaction mixture was cooled to room temperature, filtered and washed repeatedly with ether (5 × 10 mL). The combined filtrate was concentrated, and the residual solid was crystallized with MeOH, to give pentamethylbenzene (80% yield).

For 9-acetylanthracene the progress of reaction was followed by ^1H NMR. The anthracene formed in this reaction was purified by crystallization from hexane.

For arenecarboxylic acids, to the reaction mixture, after filteration of the catalyst, was added a saturated solution of sodium bicarbonate, and the mixture was stirred at room temperature overnight, during which unreacted arenecarboxylic acids were completely dissolved. The organic layer was separated and dried ($MgSO_4$), and the solvent was removed. The decarboxylated arene products were analyzed by GLC and NMR.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

Registry No. **1**, 1667-01-2; **2**, 2040-01-9; **3**, 15517-58-5; **4**, 2142-78-1; **5**, 784-04-3; 2,4,6-trimethylbenzoic acid, 480-63-7; 2,3,4,5,6-pentamethylbenzoic acid, 2243-32-5; 2,3,5,6-tetramethylbenzoic acid, 2604-45-7; 9-anthracenecarboxylic acid, 723-62-6; Nafion-H, 63937-00-8.

Reaction of Dimethyl 3-Oxoglutarate with 1,3-Dicarbonyl Compounds

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Dimethyl 3-oxoglutarate, **1**, reacts with 1,2-dicarbonyl compounds to produce a variety of cyclic, bicyclic, and

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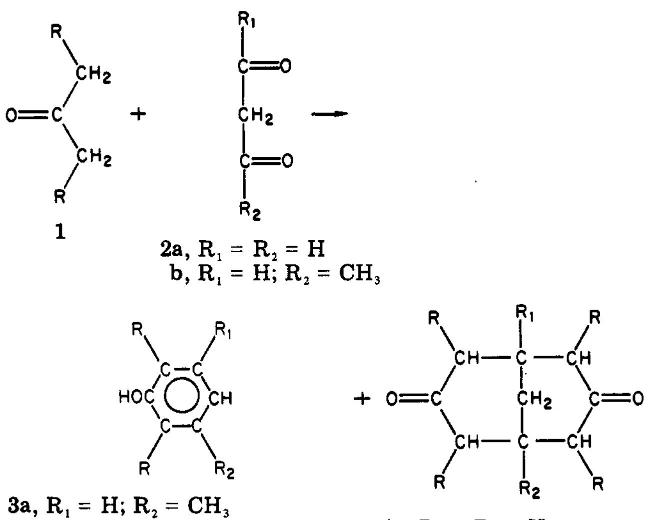
Scheme I[a]



1

2a, $R_1 = R_2 = H$
b, $R_1 = H$; $R_2 = CH_3$

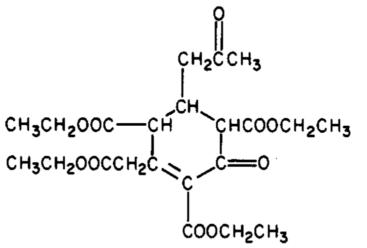
3a, $R_1 = H$; $R_2 = CH_3$
b, $R_1 = R_2 = C_6H_5$
c, $R_1 = OH$; $R_2 = CH_2COOCH_3$

4a, $R_1 = R_2 = H$
b, $R_1 = H$; $R_2 = CH_3$
c, $R = R_1 = R_2 = H$
d, $R = R_1 = H$; $R_2 = CH_3$

[a] For 1-4b, $R = COOOCH_3$.

tricyclic compounds.[1-4] 1 reacts with 1,3-dicarbonyl compounds, 2, to give isophthalates 3.[5,6] In this study, 1 gave bicyclo[3.3.1]nonanes 4a[7] and 4b (Scheme I) in addition to the isophthalates, with two 1,3-dicarbonyl compounds, malonaldehyde (2a) and acetylacetaldehyde (2b). 1 failed to react with dibenzoylmethane at room temperature and reacted, mainly, with itself on heating, forming 3c and only a trace of 3b.

While Prelog[6] certainly obtained the ethyl ester of 4b, along with diethyl 4-methyl-2-hydroxyisophthalate, by reaction of diethyl 3-oxoglutarate with acetylacetaldehyde, he incorrectly identified it as 5.



5

Not only does the mass spectrum support structure 4b and fail to support the tetramethyl ester of structure 5 but removal of the four carbomethoxy groups from 4a gave bicyclo[3.3.1]nonane-3,7-dione 4c a known compound.[8] That the same ring system forms with either the ethyl or the methyl ester of 3-oxoglutaric acid was established when removal of the four carbomethoxy groups from the acetylacetaldehyde reaction product, 4b, gave the same material (mixed melting point) Prelog obtained from the material he identified as 5.

Experimental Section

Tetramethyl 1-Methyl-3,7-dioxobicyclo[3.3.1]nonane-2,4,6,8-tetracarboxylate (4b). In a 400-mL beaker, 1.10 g of potassium hydroxide was dissolved in 200 mL of methyl alcohol, and then 17.4 g (0.10 mol) of dimethyl 3-oxoglutarate (Aldrich) was added. In another beaker, 10 g (0.068 mol) of acetylacetaldehyde dimethyl acetal (Aldrich, 90%) was treated with 25 mL of 0.27 M hydrochloric acid with heating and stirring for 10 min—until the mixture seemed to be steaming a little. The hydrolyzed acetal was then poured into the alcohol solution, and the mixture was left to stir in the open beaker.

Some solid was filtered off each day for several days, giving a total of 5.5 g of crude material. Recrystallization from methyl alcohol gave pure white 4b: mp 132–133 °C; mass spectrum, m/e 398 (M^+, 10%), 366 (M^+ -32, 40%), 334 ($M^+ - 64$, 100%), 302 ($M^+ - 96$, 19%), 277 (48%), 275 (38%).

Anal. Calcd for $C_{18}H_{22}O_{10}$: C, 54.27; H, 5.53. Found: C, 54.14; H, 5.61.

The filtrate was stirred with 1:1 glacial acetic acid/hydrochloric acid and then extracted with ether. Evaporation of the ether gave 12.5 g of residue. A portion of the residue was heated with 30% potassium hydroxide in methyl alcohol, worked up, and vacuum sublimed to give snow-white 4-methyl-2-hydroxyisophthalic acid, mp 225 °C.[6] A second portion of the residue was chromatographed and then distilled at 150–160 °C (5 mm) to give 3a, mp 46–48 °C.

Tetramethyl 3,7-Dioxobicyclo[3.3.1]nonane-2,4,6,8-tetracarboxylate (4a). Malonaldehyde bis(dimethyl acetal) (Aldrich) by the above procedure gave 4a, a white, granular solid melting at 179.1 °C: mass spectrum, m/e 384 (M^+, 17%), 352 ($M^+ - 32$, 55%), 320 ($M^+ - 64$, 100%), 292 (24%), 288 ($M^+ - 96$, 40%), 260 (43%), 225 (24%).

1-Methylbicyclo[3.3.1]nonane-3,7-dione (4d). 4b (2.3 g) was heated overnight with a 1:1 mixture of glacial acetic and concentrated hydrochloric acids. Liquids were removed at reduced pressure, and the residue was taken up in methylene chloride. The methylene chloride solution was washed with sodium bicarbonate solution, dried, and evaporated. Vacuum sublimation and recrystallization from cyclohexane gave 4d, a white solid melting at 84 °C,[6] 2,4-Dinitrophenylhydrazone, mp 250 °C.[6] The same material (mixed melting point) was obtained from the tetraethyl ester. Similar treatment of 4a gave a white solid, 4c, melting 240–242 °C.[8]

Dimethyl 2-Hydroxy-4,6-diphenylisophthalate (3b). A solution of 1.0 g of potassium hydroxide in 125 mL of methyl alcohol, 11.2 g (0.05 mol) of dibenzoylmethane (Aldrich), and 17.4 g (0.10 mol) of 1 was heated under reflux for 3 days. Distillation of the alcohol, treatment with 10% sodium hydroxide, ether extraction, evaporation of the ether, and recrystallization from methyl alcohol gave 0.5 g of pure white solid 3b: mp 156–157 °C; mass spectrum, m/e 362 (M^+, 67%), 330 ($M^+ - 32$, 100%), 298 ($M^+ - 64$, 82%), 273 (31%), 246 (15%), 217 (40%).

Anal. Calcd for $C_{22}H_{18}O_5$: C, 72.92; H, 4.97. Found: C, 72.89; H, 5.00.

Acidification of the sodium hydroxide wash, followed by recrystallization from methyl alcohol, gave pure white needles of 3c:[9] mp 136–137 °C; mass spectrum, m/e 298 (M^+, 25%), 266 ($M^+ - 32$, 100%), 239 ($M^+ - COOCH_3$, 25%), 234 ($M^+ - 64$, 50%), 207 ($M^+ - (COOCH_3, CH_3OH)$, 75%), 202 ($M^+ - 96$, 33%).

Anal. Calcd for $C_{13}H_{14}O_8$: C, 52.35; H, 4.70. Found: C, 51.85; H, 4.80.

Registry No. 1, 1830-54-2; 2a, 542-78-9; 2a bis(dimethyl acetal), 102-52-3; 2b, 625-34-3; 2b dimethyl acetal, 5436-21-5; 3a, 75716-69-7; 3b, 35044-30-5; 3c, 6512-25-0; 4a, 86668-67-9; 4b, 86668-68-0; 4c, 770-15-0; 4d, 86668-69-1; 5, 86688-48-4; diethyl 3-oxoglutarate, 105-50-0; 4-methyl-2-hydroxyisophthalic acid, 86668-70-4; tetraethyl 1-methyl-3,7-dioxobicyclo[3.391]nonane-2,4,8-tetracarboxylate, 86668-71-5; dibenzoylmethane, 120-46-7.

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(1) Weiss, U.; Edwards, J. M. *Tetrahedron Lett.* **1968**, 4885.

(2) Yang, S.; Cook, J. M. *J. Org. Chem.* **1976**, *41*, 1903.

(3) Yang, S.; Mueller-Johnson, M.; Oehldrich, J.; Wichman, D.; Cook, J. M. *J. Org. Chem.* **1976**, *41*, 4053.

(4) White, D. M. *J. Org. Chem.* **1974**, *39*, 1951.

(5) Ansell, M. F.; Nash, B. W.; Wilson, D. A. *J. Chem. Soc.* **1963**, 3028.

(6) Prelog, V.; Metzler, O.; Jeger, O. *Helv. Chem. Acta.* **1947**, *30*, 675.

(7) Bertz and Dabbagh (Bertz, S. H.; Dabbagh, G. *Angew Chem., Int. Ed. Engl.* **1982**, *21*, 306) reported the formation of 4a by this reaction while the present note was in the hands of the editor.

(8) Gangeur, A. R.; Meier, R. *Tetrahedron Lett.* **1969**, 1365.

(9) Dootson, F. W. *J. Chem. Soc.* **1900**, 77, 1196.