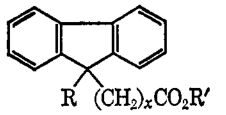
TABLE III

INFRARED SPECTRA[a] OF 9-FLUORENYLALKANOIC ACIDS AND METHYL ESTERS



R	R'	x	Primary absorption bands,[b] μ									
H	H	1	3.0–3.9 (b)	5.84 (s)	6.9, 7.0, 7.1 (t)	7.82 (m)	8.10 (m)	10.70 (m)	13.52 (s)			
H	H	3	3.0–4.0 (b)	5.85 (s)	6.9–7.09 (d)	7.75 (m)	8.05 (m)	10.70 (m)	13.53 (s)			
H	H	4	3.0–4.0 (b)	5.84 (s)	6.9–7.05 (d)	7.80 (m)	8.10 (m)	10.70 (m)	13.54 (s)			
H	H	5	3.0–4.0 (b)	5.88 (s)	6.9–7.08 (d)	7.80 (m)	8.18 (m)	10.75 (m)	13.60 (s)			
$(CH_2)_2CO_2H$	H	2[c]	3.0–4.0 (b)	5.80 (s)	6.91–6.99 (d)	7.72 (m)	8.22 (m)	10.70 (m) 10.90	13.65 (s)			
H	CH_3	3	3.25	3.39	3.45	5.71 (s)	8.10 (m)	8.35 (m)	8.55 (m)	8.71 (m)	13.0 (w)	13.50 (s)
H	CH_3	4	3.22	3.42	3.51	5.78 (s)	8.05 (m)	8.20 (m)	8.41 (m)	8.58 (m)	13.05 (w)	13.54 (s)
H	CH_3	5	3.29	3.42	3.51	5.79 (s)	8.03 (m)	8.41 (m)	8.60 (s)	8.88 (w)	13.09 (w)	13.60 (s)
$(CH_2)_2CO_2CH_3$	CH_3	2	3.30	3.40	3.50	5.72 (s)	8.02 (m)	8.39 (s)	8.55 (s)		13.15 (m)	13.55 (s)

[a] Unless otherwise designated, spectra were recorded in CCl_4 from 2.0 to 7.5 μ and in CS_2 from 7.5 to 15.0 μ. [b] b = broad, s = strong, m = medium, w = weak, d = doublet, t = triplet. [c] KBr pellet.

the organic acid product. The carboxylic acid was either recrystallized or converted into the methyl ester by refluxing in excess methanol with a catalytic amount of *p*-toluenesulfonic acid. The ester was then distilled under reduced pressure and, if the cuts solidified, was recrystallized.

Atmospheric Pressure Procedure.—The same molar ratios as used above were employed in these reactions. A stainless steel flask rather than a glass flask was used because of the deleterious effect of alkali hydroxides on glassware at high temperatures. The reaction mixture was stirred and heated at reflux and the water formed in the reaction collected in a trap. Some exothermicity was observed during the reaction and care was taken to leave plenty of empty space in the reaction flask. The work-up technique used was the same as that outlined above.

The structures of the products from the above reactions were elucidated by nmr, ir, and uv spectroscopy, elemental analysis, neutralization equivalents, and saponification equivalents. Most of these properties are found in Tables II and III and in the discussion section. The uv spectra of these materials are very similar to that of fluorene with about the only significant change being a bathochromic shift of 2–3 mμ for each additional substituent in the 9 position.

9-Carbmethoxypentyl-9-cyanoethylfluorene (5).—A solution of 109 g (0.37 mol) of methyl 6-(9-fluorenyl)caproate and 1000 ml of dioxane was charged to a reaction flask and 10 g of 32% Triton B (benzyltrimethylammonium hydroxide) in methanol was added. Acrylonitrile, 50 g (0.94 mol), was added over 5 min without any sign of reaction; therefore, the mixture was heated to reflux and stirred for 6 hr. About halfway through an additional 10 g of Triton B was added. After cooling to room temperature, the reaction mixture was treated with 2 l. of water and extracted twice with 500-ml portions of benzene. The benzene layers were combined and washed with water several times. After removal of the solvent, the solid product was recrystallized once from cyclohexane and once from methanol to yield 42 g of the methyl ester of 9-carboxypentyl-9-cyanoethylfluorene, **5** (mp 95–96°). The ir spectrum (CS_2 and CCl_4) exhibited primary absorption at 3.28, 3.41, 3.50, 4.43 (C≡N), 5.76 (C=O), 6.9, 7.45, 8.35, 8.58, 12.9, 13.2, and 13.60 μ (fluorene ring); nmr ($CDCl_3$), δ 4.58 for the methyl group, δ 7.32 and 7.70 for the ring protons, and two groups from δ 1.20 to 1.70 and from 1.85 to 2.55 representing the other protons. The integrated areas were consistent with the structure assignments.

Anal. Calcd for $C_{23}H_{25}O_2N$: C, 79.50; H, 7.69; N, 4.23. Found: C, 79.70; H, 7.49; N, 4.04.

Methyl 6-(3-Indenyl)caproate (6) and 1,3-Bis(carbomethoxypentyl)indene (8).—There were charged to a 3-l. stainless steel rocker autoclave 129 g (1.1 mol) of indene, 139 g (1.2 mol) of ε-caprolactone, and 100 g (1.5 mol) of 85% potassium hydroxide pellets and this mixture was heated to 200° for 20 hr. The solid reaction product was treated with water and extracted with isopropyl ether to remove any unreacted indene. The aqueous layer was cooled with ice and acidified with concentrated hydrochloric acid releasing 191 g of an oil which became semisolid on standing. This material was esterified by refluxing for 20 hr with 2 l. of methanol and 5 g of *p*-toluenesulfonic acid. The reaction mixture was treated with 1 l. of water and extracted twice with 250-ml portions of isopropyl ether. The combined ether layers were washed once with 100 ml of 5% sodium hydroxide solution and with water until neutral. The ether was removed and the ester mixture distilled under reduced pressure giving 42 g (15.7%) of methyl 6-(3-indenyl)caproate (**6**) [bp 145° (0.45 mm); $n^{20}D$ 1.5327] and 61 g (27%) of the dimethyl ester of 1,3-bis(carboxypentyl)indene (**8**) [bp 222° (0.4 mm); $n^{20}D$ 1.5250]. The ir (CS_2 and CCl_4) of both **6** and **8** exhibited bands at 5.73 μ (C=O); nmr of **6** (CCl_4), δ 1.4–1.85 (m, six protons), 2.1–2.58 (m, four protons), 3.2 (q, two protons), 4.55 (s, three protons), 6.08 (one proton), and 7.05–7.38 (m, four protons).

Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.36; H, 8.37.

Anal. Calcd for $C_{23}H_{32}O_4$: C, 74.16; H, 8.66; mol wt, 372.5. Found: C, 74.47; H, 8.51; mol wt (by freezing point depression of benzene), 372.

Registry No.—Fluorene, 86-73-7; indene, 95-13-6; 9-fluorenylacetic acid, 6284-80-6; **1a,** 16425-43-7; **1a** methyl ester, 16425-44-8; **1b,** 16425-45-9; **1b** methyl ester, 16425-46-0; **1b** 2,2,4-trimethylpentyl ester, 16425-47-1; **1c,** 16425-48-2; **1c** methyl ester, 16425-49-3; **2,** 4425-95-0; **2** dimethyl ester, 13098-97-0; **5,** 16605-83-7; **6,** 16425-52-8; **8,** 16452-33-8.

Acknowledgment.—The authors wish to thank Dr. W. T. Pace for the nmr spectra, as well as Mr. A. H. DuVall and Mr. S. B. Gottlieb for elemental analysis and other analytical services and Mr. M. A. Eccles for technical assistance.

The Michael Reaction of Acrylate Salts

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The Michael reaction[2] has been well reviewed and is an important synthetic tool. Briefly, it consists of the reaction of a carbanion with an electron-deficient unsaturated system.

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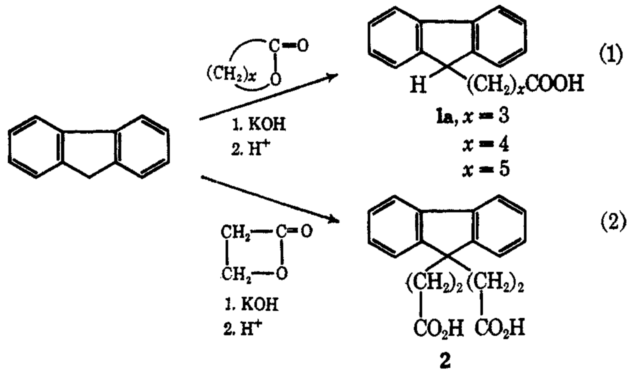
[1] To whom inquiries should be addressed.

[2] E. B. Bergmann, D. Ginsburg, and R. Pappo, *Org. Reactions*, **10**, 179 (1959).

During the investigation[3] of the reaction of lactones with fluorene and potassium hydroxide to form ω-(9-fluorenyl)alkanoic acids (**1**), it was observed that all the lactones used gave monosubstituted fluorene derivatives except propiolactone, which gave 9,9-bis(carboxyethyl)fluorene.[3] Although most lactones were postulated to react with fluorene through a hydroxy acid salt intermediate, the potassium 3-hydroxypropionate which would form from propiolactone could dehydrate to an acrylate under the reaction conditions. Acrylate salts are not reported as acceptors in the Michael reaction, except in the case of the reaction of indole[4] with acrylate and methacrylate salts to form 1- and 3-indolepropionic acid. The mechanism of 3-indole acid formation probably involves a rearrangement of the 1-indolepropionic acid.[5] This communication extends the Michael reaction of acrylate salts to more common hydrocarbon donor systems and reports the synthesis of several unknown compounds. Also, the reaction of potassium phenylacetate with acrylate salts is reported and provides an example of a new class of donor molecules.



Fluorene was treated with potassium or sodium acrylate,[3] formed *in situ* by the reaction of acrylic acid with the alkali metal hydroxide, using excess base as catalyst to give **2** in 50–60% yield and 90–100% efficiency based on fluorene. The normal reaction was conducted either in a rocker autoclave or at atmospheric pressure at 210–235° for about 20 hr. No improvement in the reaction was observed when tetralin, naphthalene, or diphenylmethane were employed as solvents. All of the experiments are outlined in Table I. The diacid (**2**) prepared by this technique had previously been made by Bruson[6] *via* cyanoethylation of fluorene followed by hydrolysis of the corresponding dinitrile derivative.

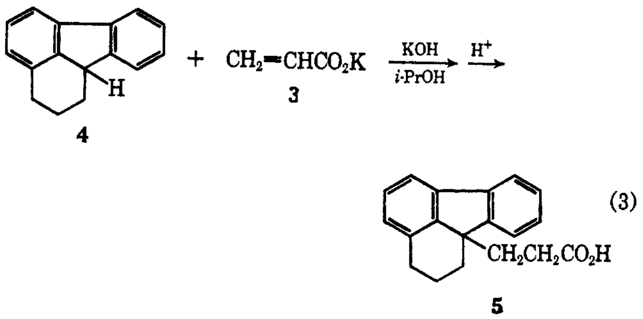
Tetrahydrofluoranthene, **4**, also reacted with potassium acrylate and potassium hydroxide to yield 3-[6a(4H)-5,6-dihydrofluoranthenyl]propionic acid, **5**, in 33% yield and 70% efficiency based on **4**. This product, **5**, has been synthesized[7] *via* cyanoethylation of **4** followed by hydrolysis to the acid.

Table I

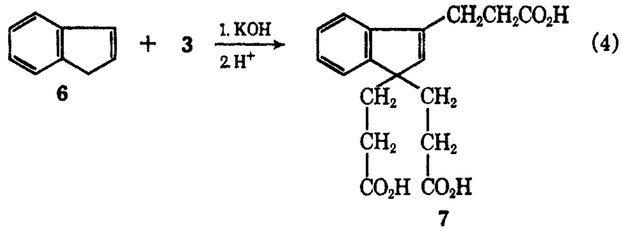
Synthesis of 9,9-Bis(carboxyethyl)fluorene[a]

Run no.	Temp, °C	Time, hr	Yield,[b] %	Efficiency,[b] %
1[c]	230	20	64	98
2[c]	112	20	0	0
3[c]	230	6	49	. . .
4[c]	225	1	50	100
5[d–f]	228	20	0	0
6[d,e,g]	228	20	32	. . .
7[d,h,i]	214	14	11	. . .

[a] Unless otherwise noted, the molar ratio of fluorene–acrylic acid–KOH was 1.0:2.1:2.7. [b] Based on fluorene. [c] Reacted in a 3-l. stainless steel rocker autoclave. [d] Reacted in a stainless steel flask. [e] Molar ratio 1.0:3.0:4.1. [f] Tetralin used as solvent. [g] Naphthalene used as solvent. [h] Molar ratio 1.0:2.1:3.0. [i] Diphenylmethane used as solvent.



Indene, **6**, reacted with acrylate salts to give the trisubstituted product 1,1,3-tris(carboxyethyl)indene, **7**. This material was isolated as its trimethyl ester in about 10% yield. Some material thought to be due to disubstitution was isolated but contained impurities that could not be removed by standard techniques. These results are analogous to the cyanoethylation of indene[6] where 1,1,3-tris(cyanoethyl)indene was the primary product.



Diphenylmethane and 9,10-dihydroanthracene failed to react with potassium or sodium acrylate. Neither of these worked in the reaction of lactones[3] with compounds containing activated methylene groups.

The use of acrylate salts as acceptors in the Michael reaction has been extended to a new class of donors—compounds with active hydrogens also containing an acid salt in the molecule. The specific examples are potassium phenylacetate, **8**, and the potassium salt of ω-substituted (9-fluorenyl)alkanoic acids, **1a** and **1c**.

Phenylacetic acid was treated with acrylic acid and potassium hydroxide to give a 40% yield of 2-phenylglutaric acid, **9**. The acid was identified by conversion to its dimethyl ester, **10**, and to 2-phenylgutaric anhydride, **11**. The best reported synthesis of 2-phenylglutaric acid[8,9] involves cyanoethylation of phenyl-

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(3) H. E. Fritz, D. W. Peck, and K. E. Atkins, *J. Org. Chem.*, **33**, 2575 (1968).

(4) (a) H. E. Johnson and D. G. Crosby, *ibid.*, **28**, 2030 (1963); (b) W. Reppe and H. Ufer, U. S. Patent 2,195,974 (1940).

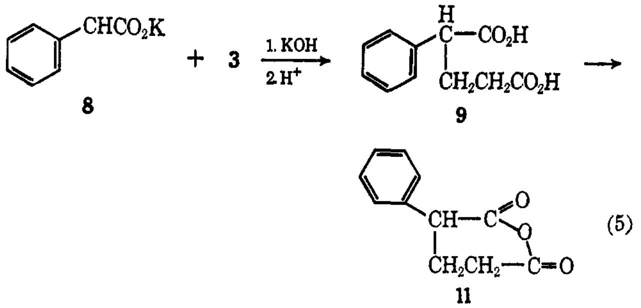
(5) H. E. Fritz, *J. Org. Chem.*, **28**, 1384 (1963).

(6) (a) H. A. Bruson, *J. Amer. Chem. Soc.*, **64**, 2457 (1942); (b) H. A. Bruson, U. S. Patent 2,339,218 (1944); (c) H. A. Bruson, U. S. Patent 2,339,373 (1944).

(7) CIBA Ltd, British Patent 666,713 (1952); *Chem. Abstr.*, **47**, 7547e (1953).

(8) E. C. Horning and A. F. Finelli, *Org. Syn.*, **30**, 81 (1950).

(9) M. F. Ansell and D. H. Hey, *J. Chem. Soc.*, 1683 (1950).



malonic or phenylcyanoacetic esters, followed by hydrolysis with cleavage of one carboxyl group.

The reactivity of potassium phenylacetate in this system was surprising. Since the carboxylate salt does not have good electron-withdrawing properties, it would have been reasonable to predict that the methylene hydrogens would not be acidic enough to form a carbanion that would enter into the Michael reaction. The fact that these reactions were conducted in solid phase, free of solvent, may have changed some of these factors.

Other acids salts which participate as donors are **1a** and **1c** which yield the corresponding unsymmetrical diacids in 40–50% yields when treated with potassium acrylate in the presence of potassium hydroxide. The compounds were previously unknown and no other simple synthesis can be immediately envisioned. The carboxylate salt groups are far enough away from the active hydrogen that they should not affect the initial carbanion formation.

Experimental Section

Melting points were obtained on a Fisher-Johns instrument. Infrared spectra were recorded by Beckman IR-4, ultraviolet spectra by a Cary Model 21 spectrophotometer, and nuclear magnetic resonance spectra by a Varian Associates Model A-60 spectrometer. Elemental analyses were performed by the UCC Chemicals and Plastics R and D analytical group.

9,9-Bis(carboxyethyl)fluorene (2).—Into a 1-l. stainless steel rocker autoclave were charged 166 g (1.0 mol) of fluorene, 80 g (1.1 mol) of acrylic acid, and 100 g (1.5 mol) of 85% potassium hydroxide pellets and this mixture was heated to 220° for 20 hr. The cooled product was treated with 1 l. of water and extracted with 1 l. of isopropyl ether. The ether was removed by distillation and 86 g (0.52 mol) of unreacted fluorene was recovered. Acidification of the aqueous layer with concentrated hydrochloric acid released 128 g of 9,9-bis(carboxyethyl)fluorene, **2**. The infrared, ultraviolet, and nmr spectra were identical with those of an authentic sample[3] and there was no depression of a mixture melting point. This represented a 75% yield of diacid based on the acrylic acid charged and an 85% yield based on reacted fluorene.

3-[6a(4H)-5,6-Dihydrofluoranthenyl]propionic Acid (5).—To a 3-l. stainless steel rocker autoclave were charged 200 g (0.98 mol) of 1,2,3,10b-tetrahydrofluoranthene,[10] **4**, 100 g (1.4 mol) of glacial acrylic acid, 100 g (1.5 mol) of 85% potassium hydroxide pellets, and 500 ml of isopropyl alcohol. This mixture was heated to 240° and held for 20 hr. Water, 1 l., was added to the reaction mixture and the solution was filtered to recover 109 g of unreacted **4**. The filtrate was acidified with concentrated hydrochloric acid, releasing a white solid. After recrystallization from 1 l. of benzene, 92 g of **5** (33%) were obtained. An analytical sample was obtained by a recrystallization from methanol, mp 181–182° (lit.[7] mp 176–176.5°). A mixture melting point with authentic material was not depressed. The ir spectrum of the acid (KBr) showed bands at 3.3, 3.42 (broad), 5.87, 6.95 (doublet), 7.67, 7.94, 10.7, and 13.25 μ. The band at 13.25 μ is consistent with an *ortho*-substituted aromatic ring with four adjacent H atoms.[11] The acid was converted into its methyl ester by refluxing in methanol in the presence of *p*-toluenesulfonic acid catalyst. Upon recrystallization from benzene white crystals, mp 115–117, were obtained.

Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52; neut equiv, 278.3. Found: C, 82.10; H, 6.59; neut equiv, 274.

Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.90. Found: C, 82.31; H, 6.84.

1,1,3-Tris(carboxyethyl)indene (7).—To a 3-l. stainless steel rocker autoclave were charged 116 g (1.0 mol) of indene, 230 g (3.2 mol) of glacial acrylic acid, and 280 g (4.2 mol) of 85% potassium hydroxide pellets. This mixture was heated to 240° for 20 hr, then the cooled reaction product was treated with 2 l. of water. The solution was extracted with 1 l. of isopropyl ether to remove unreacted indene. The aqueous layer was acidified with concentrated hydrochloric acid to release 206 g of tan taffylike material which was treated with 500 ml of methanol and 20 g of *p*-toluenesulfonic and refluxed for 10 hr. The methanol solution was treated with water releasing a brown oil which was removed by extraction with 1 l. of isopropyl ether. The ether solution was washed with 100 ml of 10% sodium hydroxide and then with water. The ether was evaporated leaving 189 g of brown oil which was distilled at reduced pressure to yield 37 g of the trimethyl ester of 1,1,3-tris(carboxyethyl)indene (10%). In a similar experiment, the taffylike material obtained upon acidification was recrystallized from benzene to yield the triacid, mp 148–150°.

Anal. Calcd for $C_{21}H_{26}O_6$: C, 67.37; H, 7.00; sapon equiv, 125. Found: C, 67.61; H, 7.15; sapon equiv, 130.

Anal. Calcd for $C_{18}H_{20}O_6$: C, 65.05; H, 6.07; neut equiv, Found: C, 65.28; H, 6.27; neut equiv, 110.0.

2-Phenylglutaric Acid (9).—There was charged to a 3-l. stainless steel rocker autoclave 136 g (1.0 mol) of phenylacetic acid, 200 g (2.8 mol) of glacial acrylic acid, and 300 g (4.6 mol) of 85% potassium hydroxide pellets. This mixture was heated to 240° for 20 hr and the product was recovered from the autoclave by dissolving in water. The clear, brown solution was acidified with concentrated hydrochloric acid. The aqueous solution was extracted twice with 500-ml portions of isopropyl ether and, after evaporation of the ether, 134 g of acidic product was obtained. This material was esterified by refluxing with 500 ml of methanol and 5 g of *p*-toluenesulfonic acid for 10 hr. The reaction mixture was diluted with water and worked up in the normal manner. Distillation of the crude product at reduced pressure yielded 80 g of dimethyl 2-phenylglutarate: bp 167–168° (10 mm); $n^{20}D$ 1.5011.

Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.07; H, 6.83; mol wt, 236.3. Found: C, 66.08; H, 6.90; mol wt (by freezing point depression of benzene method), 237.

2-Phenylglutaric Acid Anhydride (11).—The reaction above was repeated and 152 g of crude acid product was obtained. This material was distilled under reduced pressure and 89 g of **11** was obtained: bp 177–182° (1.0–1.6 mm); afte rrecrystallization from ether, mp 95.0–95.5° [lit.[8] bp 178–188° (0.5–1.0 mm), mp 95–96°]. Infrared spectrum (CS_2) showed a carbonyl doublet centered at 5.56 μ indicative of anhydride.

9-(Carboxyethyl)-9-(carboxypropyl)fluorene (12a).—To a 1-l. stainless steel rocker autoclave was charged 126 g (0.5 mol) of 4-(9-fluorenyl)butyric acid,[12] **1a**, 108 g (1.5 mol) of acrylic acid, and 200 g of 85% potassium hydroxide pellets (3.0 mol). This mixture was heated to 260° and held for 10 hr. The product was recovered by dissolving in 2 l. of water and the aqueous solution was acidified with concentrated hydrochloric acid. Isopropyl ether, 1 l., was used to extract the crude acid product. The ether was evaporated and the resulting solid recrystallized from a benzene–isopropyl alcohol mixture yielding 69 g of **12a**, mp 187–187.5°, representing a 42% yield. There was recovered 47 g of 4-(9-fluorenyl)butyric acid making the efficiency, based on **1a**, 80%. The dimethyl ester of **12a** was prepared by refluxing in methanol containing a catalytic amount of *p*-toluenesulfonic acid. After recrystallization from ether the dimethyl ester melted 70–70.5°.

The ir spectrum of 12a (KBr pellet) showed major bands at 2.90, 3.3, 3.4, 5.82, 6.9, 7.05, 7.7, 8.1, 8.2, 8.62, 12.85, 12.95, and 13.55 μ. The major bands of the dimethyl ester of **12a** (CS_2

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[10] Obtained by sodium metal catalyzed hydrogenation of fluoranthene.

[11] E. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., p 77.

[12] Prepared from the base-catalyzed reaction of fluorene with γ-butyrolactone (see ref 3).

and CCl_4) are 3.40, 5.76, 6.90, 6.95, 7.35, 7.79, 8.03, 8.40, 8.60, 13.0, 13.18, and 13.60 μ. The nmr of **12a** showed absorption at δ 0.4–3.6 (m, ten protons), 7.3, 7.8 (eight protons), and a broad absorption at 9.9 ppm for acid protons (two protons). The nmr of **12a** dimethyl ester (CCl_4) showed absorption at δ 1.4–2.5 (m, ten protons), singlets at 3.40 and 3.53 (six protons), and 7.3 and 7.7 (m, eight protons).

Anal. Calcd for $C_{20}H_{20}O_4$: C, 74.1, H, 6.3. Found: C, 74.4, H, 6.4.

Anal. Calcd for $C_{22}H_{24}O_4$: C, 75.0; H, 6.9; sapon equiv, 176. Found: C, 74.9; H, 7.00; sapon equiv, 176.

9-(Carboxyethyl)-9-(carboxypentyl)fluorene (12b).—A 3-l. stainless steel rocker autoclave was charged with 526 g of methyl 6-(9-fluorenyl)caproate[13] (1.8 mol), 225 g (3.1 mol) of glacial acrylic acid, and 450 g (6.8 mol) of 85% potassium hydroxide pellets. This mixture was heated to 220° for 20 hr. The product was dissolved in 3 l. of water and filtered, and the filtrate was acidified with concentrated hydrochloric acid liberating a white viscous oil. Upon dissolving this crude oil in 2 l. of methanol approximately 110 g was insoluble. This apparently polymeric material was separated by decantation. To the methanol solution was added 15 g of *p*-toluenesulfonic acid; this mixture was refluxed for 24 hr. After the usual work-up 398 g of the dimethyl ester was isolated by distillation [bp 215–218° (0.3 mm), $n^{25}D$ 1.5604]. The ir spectrum of the dimethyl ester of **12b** (CS_2 and CCl_4) showed major bands at 3.3 (w), 3.41 (s), 3.50, 5.75, 6.90, 6.95, 7.31, 7.70, 8.05, 8.40, 8.60, 13.0, 13.17, and 13.62 μ. The infrared spectrum of **12b** (KBr pellet) showed major bands at 3.0, 3.32, 3.48, 4.18, 5.88, 6.93, 7.0, 7.65, 8.0, 8.31, 10.7, 12.86, and 13.58 μ.

Anal. Calcd for $C_{24}H_{28}O_4$: C, 75.76; H, 7.42; sapon equiv, 190. Found: C, 75.95; H, 7.42; sapon equiv, 202.

Registry No.—**5**, 13099-00-8; **7**, 974-60-7; dimethyl 2-phenylglutarate, 10436-86-9; **12a**, 13098-95-8; **12a** dimethyl ester, 13098-96-9; **12b** dimethyl ester, 13098-99-2; **5** methyl ester, 16423-39-5.

Acknowledgment.—The authors wish to thank Dr. W. T. Pace for the nmr analysis as well as Mr. A. H. DuVall and Mr. S. B. Gottlieb for elemental analysis, Mr. B. Romine for saponification equivalents, and Mr. M. A. Eccles for experimental assistance.

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[13] Prepared by the base-catalyzed reaction of fluorene with ϵ-caprolactone (see ref 3).

The Mills Nixon Effect. II[1]

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Received December 27, 1967

In an earlier paper[1] we reported a quantitative examination of product distributions in bromination and nitration of *o*-xylene, indan, and tetralin. The results revealed a higher *ar*-β/*ar*-α substitution ratio for indan than for tetralin and it was assumed that this order, which is the reverse of that to be expected on steric grounds, and is also inexplicable on any standard electronic basis, could be explained in terms of the strain developed in the five-membered ring system of indan. We now report work on aromatic hydrogen exchange of the three hydrocarbons in anhydrous trifluoroacetic acid. This system was chosen because it has probably the lowest steric requirement of any electrophilic substitution reaction and any steric masking of the effect of ring strain should therefore be minimized. The results are shown in Table I.

TABLE I

RATE CONSTANTS FOR HYDROGEN EXCHANGE OF TRITIATED HYDROCARBONS IN ANHYDROUS TRIFLUOROACETIC ACID AT 70°

Hydrocarbon	10^5k, sec^{-1}	Registry No.
3-[^{3}H]-*o*-Xylene	1.10 ± 0.02	16408-68-7
4-[^{3}H]-*o*-Xylene	1.55 ± 0.03	16408-69-8
4-[^{3}H]-Indan	0.82 ± 0.01	16408-70-1
5-[^{3}H]-Indan	3.34 ± 0.04	16408-71-2
5-[^{3}H]-Tetralin	3.10 ± 0.02	16408-72-3
6-[^{3}H]-Tetralin	3.35 ± 0.03	16408-73-4

The rate constants for detritiation of indan confirm that the two aromatic positions have markedly different reactivities. The ratio of the two rate constants *ar*-α/*ar*-β is 0.25, of the same order as the ratios of the percentages of α-bromo and β-bromoindans,[1] which range from 0.19 to 0.28. The two positions in tetralin are almost equally reactive, and again this result is in line with the bromination and nitration studies and with the results for *o*-xylene.[2] It seems clear, therefore, that indan reflects in its electrophilic substitution reactions the strain imposed on the aromatic ring by the fused, five-membered ring. Tetralin does not show this difference in reactivity, and it is probable that the buckled six-membered ring imposes little strain on the aromatic ring.

One further point should be made. In our previous detailed explanation,[1] we assumed that an increase in the double-bond character of the common bond in indan will results in a less stable system. This is undoubtedly a useful practical assumption but in making it we were directly applying a conclusion drawn by Brown from his results on nonaromatic derivatives of cyclopentane and cyclohexane.[3] This we now believe was not justifiable because the kind of interference (involving methylene hydrogens) that allowed Brown to explain his generalization is absent in our compounds. While, therefore, the assumption correlates our results, it does not provide a satisfactory explanation for them.

Experimental Section

Anhydrous trifluoroacetic acid was prepared by fractional distillation of commercial acid from sulfuric acid and then from silver oxide.

Tritiated hydrocarbons were prepared from the corresponding bromo compounds.[1] The bromo compounds were shown to be pure by glpc analysis under conditions known to separate isomeric pairs; the Grignard reagents formed from them were treated with tritiated water (specific activity 10 mCi/ml), and the resulting hydrocarbons were purified by fractional distillation. These showed no impurity on glpc analysis.

Rate Measurements.—These were carried out in anhydrous trifluoroacetic acid solvent at 70° as described previously,[4] using hydrocarbon concentrations of about 0.05 *M*. First-order rate plots of log count rate *vs.* time were linear over at least three half-lives in all cases; rate constants calculated from the equation $k = 2.303 \times$ slope of rate plot, were determined at least twice for each substrate and were reproducible to within ±2%. The rate constants were not converted into partial rate factors because the rate constant obtained for *p*-[^{3}H]-toluene in this study was 7% lower than that previously reported[4] and used as standard.

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[1] Part I: J. Vaughan, G. J. Welch, and G. J. Wright, *Tetrahedron*, **21**, 1665 (1965).

[2] R. Taylor, G. J. Wright, and A. J. Homes, *J. Chem. Soc., Sect. B*, 780 (1967).

[3] H. C. Brown, J. H. Brewster, and H. Shechter, *J. Amer. Chem. Soc.*, **76**, 467 (1954).

[4] R. Baker, C. Eaborn, and R. Taylor, *J. Chem. Soc.*, 4927 (1961).