2-Bromo-5-hydroxy-1,1,3,3-tetramethylindan (XII).—A solution of 12.8 g. (0.05 mole) of dibromide I in 15 ml. of anisole was added at room temperature to a stirred slurry of 7.3 g. (0.055 mole) of aluminum chloride in 15 ml. of anisole. The reaction mixture was heated at 50–60° for 28 hr. and worked up as usual. Excess anisole was removed under vacuum, leaving a viscous liquid residue (13.1 g.). Distillation gave 5.7 g. of a liquid, b.p. 73–93° (0.05 mm.), and 3.4 g. of the indan XII, which was recrystallized from benzene: m.p. 163–164°; λ_{max} 281 mμ (ϵ 3500) and 287 mμ (ϵ 3400); ν_{max} 3170 (–OH) 1595, 1580 (C=C), 860, and 818 cm.$^{-1}$ (Ph–H). The compound gave positive silver nitrate and ferric chloride tests.

Anal. Calcd. for $C_{13}H_{17}BrO$: C, 58.00; H, 6.37. Found: C, 57.75; H, 6.44.

3-Bromo-2,4-dimethyl-1,3-pentadiene (XVII).—A solution of 25.6 g. (0.1 mole) of the dibromide I in 20 ml. of morpholine was heated under reflux for 1 hr. When cooled the reaction mixture was poured into water and acidified, and the product was extracted with ether. Distillation gave 8.7 g. (50%) of the diene XVII: b.p. 63° (33 mm.); $n^{24}D$ 1.4892; ν_{max} 1650 and 905 cm.$^{-1}$ (C=CH$_2$); λ_{max} 205.5 mμ (infl.) (ϵ 4700) and 250 mμ (ϵ 950).

Anal. Calcd. for $C_7H_{11}Br$: C, 48.02; H, 6.33. Found: C, 47.69; H, 6.31.

Alkylations of Fluorene and of 9-Fluorenylcarboxylic Acid by Means of Alkali Amides in Liquid Ammonia. Alkylations by *n*-Butyllithium[1]

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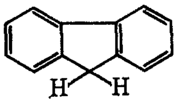
Received August 4, 1965

The extent of dialkylation accompanying monoalkylation of fluorene (1) when molecular equivalents of reactants are employed was found to be dependent on the halide and reagent. Monoalkylations of 1 by means of sodamide in liquid ammonia were accompanied by much dialkylation with *n*-butyl bromide and benzyl chloride but apparently by no dialkylation with benzhydryl and α-phenylethyl chlorides. However, monoalkylations of 1 by means of lithium amide in liquid ammonia or by *n*-butyllithium in hexane were accompanied by relatively little dialkylation, even with the *n*-butyl and benzyl halides. The four monoalkyl derivatives of 1 from these alkylations were isolated in yields of 55–83%. These methods appear preferable to earlier ones. An indirect method of preparation of the pure benzyl derivative of 1 involved benzylation of 9-fluorenylcarboxylic acid through its dianion, followed by decarboxylation. This acid was prepared by carbonation of fluorene by means of sodamide. The monobenzyl derivative of 1 was further benzylated by means of sodamide in liquid ammonia to form the dibenzyl derivative.

Fluorene (1) has previously been alkylated with various alkyl halides by means of a number of alkali bases to form the monoalkyl derivative 2. For example, 1 has been alkylated in unreported yield with benzyl chloride by phenyllithium[2] and lithium hydride[3] in hexane, triphenylmethylsodium in ether,[4] and potassium hydroxide in ethanol.[5] Benzylation of 1 by sodamide in decalin has been reported to give 2 (R = $CH_2C_6H_5$) in 63% yield,[6] but this good yield could not be duplicated in later work.[7] Monobenzylation is often accompanied by dibenzylation to afford 3, even though only molecular equivalents of the reactants are employed. Thus, the products obtained by means of lithium aluminum hydride in pyridine,[8] potassium in dioxane,[9] and lithium in heptane[9] have been shown to consist of 2 and 3 (R = $CH_2C_6H_5$) in the ratios of 48:52, 70:30, and 95:5, respectively. However, the isolated yields of the monoalkyl derivatives were apparently not determined.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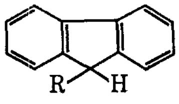
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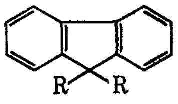
3

We have effected benzylation and certain other alkylations of 1 by means of sodamide and lithium amide in liquid ammonia. Only one example in this medium has apparently been described in the literature, and this involved dimethylation by means of sodium.[10] Our results are summarized in Table I, in which are given the percentage compositions of the products (determined by v.p.c.) and, in certain cases, the isolated yields (in parentheses).

TABLE I

ALKYLATIONS OF FLUORENE (1) WITH ALKYL HALIDES BY MEANS OF ALKALI AMIDES IN LIQUID AMMONIA

			—% composition of product[b]—		
Expt.[a]	Alkyl halide	Alkali amide	Monoalkylated (2)	Dialkylated (3)	Unalkylated (1)
1[c]	*n*-C_4H_9Br	$NaNH_2$	29	33	38
2	*n*-C_4H_9Br	$LiNH_2$	92 (83)[d]	4	4
3	$C_6H_5CH_2Cl$	$NaNH_2$	33	34 (33)[d]	33
4	$C_6H_5CH_2Cl$	$LiNH_2$	85 (55)[d]	9	6
5	$C_6H_5CH_2Cl$	$NaNH_2$[e]	45	35	20
6	$(C_6H_5)_2CHCl$[f]	$NaNH_2$	94 (79)[d]	0	Trace
7	$C_6H_5\underset{\underset{CH_3}{\vert}}{C}HCl$	$NaNH_2$	85 (81)[d]	0	Trace

[a] A 10% excess of the alkyl halide and alkali amide were employed except as indicated in note *c*. [b] Determined by v.p.c. on the crude products unless otherwise noted; the total yields of these products were 95–98%. [c] No excess halide or amide was used. [d] Isolated yield; see Experimental Section. [e] Solvent was toluene. [f] Tetraphenylethylene was obtained from this halide in 4% yield (by v.p.c.).

Table I shows that, although 1 was first converted to its sodio salt 1′ by means of 1 molecular equiv. of sodamide in liquid ammonia and 1 equiv. of *n*-

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[1] Supported by the National Science Foundation.

[2] G. Wittig, P. Davis, and G. Koenig, *Ber.*, **84**, 627 (1951).

[3] G. Wittig and A. Ruckert, *Ann.*, **566**, 101 (1950).

[4] W. Schlenk and E. Bergmann, *ibid.*, **463**, 188 (1928).

[5] W. G. Brown and B. A. Bluestein, *J. Am. Chem. Soc.*, **65**, 1082 (1943).

[6] E. J. Greenhow, E. N. White, and D. McNeil, *J. Chem. Soc.*, 2848 (1951).

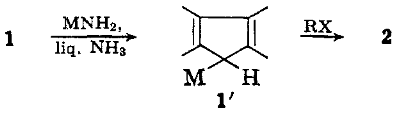
[7] G. W. H. Scherf and R. K. Brown, *Can. J. Chem.*, **38**, 697 (1960).

[8] P. T. Lansbury and R. Thedford, *J. Org. Chem.*, **27**, 2383 (1962).

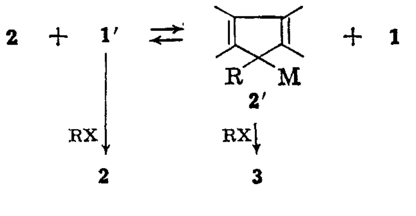
[9] G. W. H. Scherf and R. K. Brown, *Can. J. Chem.*, **39**, 1388 (1961).

[10] W. Hückel, *Angew. Chem.*, **70**, 577 (1958).

butyl bromide or benzyl chloride then being added, monoalkylation to form 2 was accompanied by much dialkylation to give 3, a corresponding amount of 1 being regenerated (expt. 1 and 3). Evidently, the monoalkyl derivative 2 entered into a rapid equilibrium with sodio salt 1′ to produce sodio salt 2′, which underwent considerable further alkylation (eq. 1 and 2, M = Na).



(1)



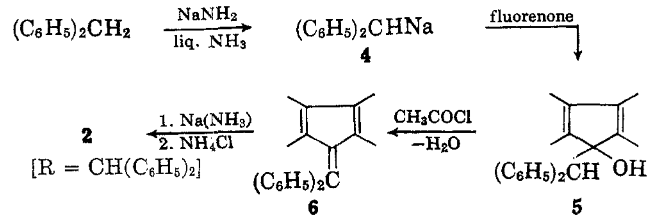
(2)

However, monoalkylation was accompanied by relatively little dialkylation when the reactions with the butyl and benzyl halides were effected by lithium amide in liquid ammonia (expt. 2 and 4, Table I), and apparently by no dialkylation when similar reactions with the larger benzhydryl and α-phenylethyl chlorides were effected even by sodamide in this medium (expt. 6 and 7). The benzhydrylation was accompanied by a little (4%) self-condensation of the halide to form tetraphenylethylene.[11]

This dependence of the extent of dialkylation on both the alkali amide and halide is interesting. The lack of appreciable dialkylation in the monoalkylation of lithio salt 1′ with the butyl and benzyl halides appears ascribable to a relatively slow equilibration of 1′ with the monoalkyl derivative 2 (see eq. 2). The absence of dialkylation in the monoalkylation of sodio salt 1′ with benzhydryl and α-phenylethyl chlorides seems attributable to a relatively slow rate of further alkylation of sodio salt 2′ (steric factor). Also, a relatively slow rate of equilibration is possible.

The structure of the benzhydryl derivative 2 was established by independent synthesis involving condensation of diphenylmethylsodium (4) with fluorenone, and dehydration and reduction of the resulting carbinol 5 and olefin 6, respectively (Scheme I)

SCHEME I



Incidentally, the addition reaction of 4 with fluorenone, which is analogous to that of 4 with benzophenone described previously,[12] is more convenient than that reported by Schlenk and Bergmann,[13] who prepared 4 from benzhydryl methyl ether and sodium in benzene. The present reduction of olefin 6 seems preferable to an earlier one employing sodium amalgam and amyl alcohol.[14]

It should be mentioned that results similar to those obtained from the alkylations of sodio salt 1′ (see eq. 1 and 2, Table I) have been observed previously for corresponding alkylations of sodiophenylacetonitrile, which affords a mixture of mono-, di-, and unalkylated nitriles with benzyl chloride but exclusively the monoalkyl derivatives with benzhydryl and α-phenylethyl chlorides.[15] On the other hand, diphenylmethylsodium (4), to which 1′ is more closely related structurally, undergoes exclusively monoalkylation with all three of these halides.[12]

Since less equilibration between the monoalkyl derivatives 2 and 1′ might be expected in a hydrocarbon solvent than in liquid ammonia (see eq. 2), a better yield of 2 (R = $CH_2C_6H_5$) was anticipated in toluene. However, the indicated yield of 2 was increased from 33 to only 45% and a 34% yield of 3 was still produced (expt. 5, Table I).

We have also effected certain monoalkylations of fluorene (1) by means of n-butyllithium in hexane (eq. 3, Table II). This base has previously been employed in xylene for the n-butylation of 1, but no yield was reported.[16]

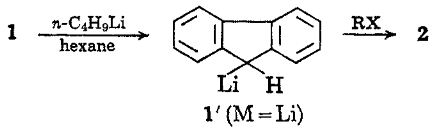
TABLE II

ALKYLATIONS OF FLUORENE (1) WITH ALKYL HALIDES BY MEANS OF *n*-BUTYLLITHIUM IN HEXANE

Expt.	Alkyl halide	% composition of product[a] Monoalkylated (2)	Dialkylated (3)	Unalkylated (1)
1	n-C_4H_9Br	79[b]	...	...
2	$C_6H_5CH_2Cl$	84 (58)[c]	8	8
3	$(C_6H_5)_2CHCl$[d]	29	0	22
4	$(C_6H_5)_2CHCl$[e]	47	0	17

[a] Determined by v.p.c. on the crude products unless otherwise noted; the total yields of these products were 95–98%. [b] Isolated by distillation; this product was pure by v.p.c. [c] Isolated by recrystallization. [d] Tetraphenylethylene was obtained in 17% yield (by v.p.c.). [e] Tetraphenylethylene was obtained in 26% yield; this reaction was effected in hexane–ether.

Table II shows that monoalkylations (eq. 3) were accompanied by relatively little or no dialkylation with the butyl, benzyl, and benzhydryl halides. However, the yield of the monobenzhydryl derivative 2 was only fair, and appreciable self-condensation of the halide was observed.[11]



(3)

It may be concluded from our results that both lithium amide in liquid ammonia and n-butyllithium in hexane are superior to sodamide in liquid ammonia or toluene for the mono-n-butylation and monobenzylation of fluorene (1), but that sodamide in liquid ammonia is preferable to n-butyllithium for the benzhydrylation and probably also for the α-phenylethylation. These methods, which have afforded the v.p.c.

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[11] C. R. Hauser, W. P. Brasen, P. S. Skell, S. W. Kantor, and A. E. Brodhag, *J. Am. Chem. Soc.*, **78**, 1653 (1956).

[12] P. J. Hamrick and C. R. Hauser, *ibid.*, **81**, 2096 (1959).

[13] W. Schlenk and E. Bergmann, *Ann.*, **464**, 20 (1928).

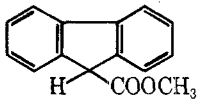
[14] V. Kaufmann, *Ber.*, **29**, 73 (1896).

[15] C. R. Hauser and W. R. Brasen, *J. Am. Chem. Soc.*, **78**, 494 (1956).

[16] H. F. Miller and G. B. Bachmann, *ibid.*, **57**, 766 (1935).

pure monoalkyl derivatives **2** in isolated yields of 55–83% (see Tables I and II), appear better than earlier procedures.[2–9,16] In particular, our procedures for the preparation of 9-fluorenyllithium (**1′**, M = Li), which is more suitable for butylation and benzylation than the sodio or potassio intermediate, are more convenient than that of Scherf and Brown[7,9] who prepared this lithio intermediate by means of lithium metal in ether, and isolated it by precipitation with heptane.

Although direct monoalkylation of fluorene may be accompanied by dialkylation, only monoalkylation is possible with ester **7**[17] and formylfluorene **8**,[5] which may be converted to the monoalkylfluorene **2** by hydrolysis–decarboxylation and reverse-aldol-type condensation, respectively.



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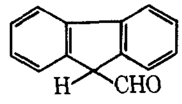
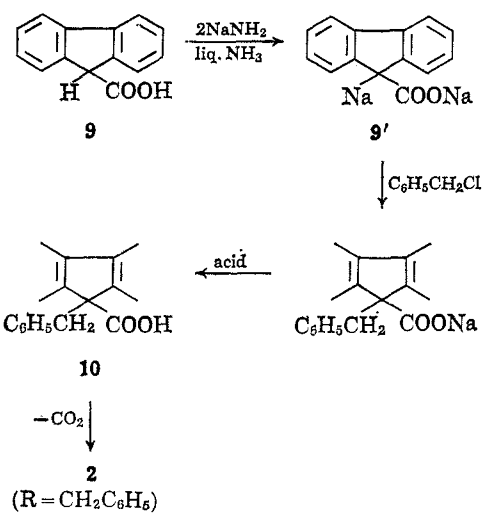


8

We have effected benzylation of carboxylic acid **9** through its disodio salt **9′** to form **10**, which was decarboxylated to give v.p.c. pure **2** (R = $CH_2C_6H_5$) in 84% over-all yield (Scheme II). Acid **9** is readily available through carbonation of fluorene (see below).

Scheme II

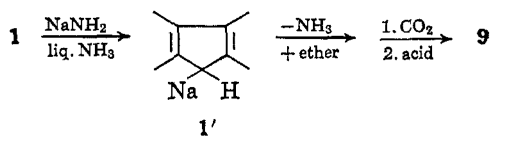


Similarly, disodio salt **9′** was alkylated with α-phenylethyl chloride to form, after decarboxylation, **2** (R = α-phenylethyl) contaminated with fluorene (see Experimental Section). The direct α-phenylethylation of fluorene was more satisfactory (see eq. 1, Table I).

The present indirect method (Scheme II) appears preferable to the earlier ones since the use of ester **7** requires the additional step of its preparation and that of formyl derivative **8** is hampered by its instability.[5]

Carboxylic acid **9**, which was the starting compound in our indirect method, was prepared in 93% yield by carbonation of fluorene by means of sodamide in liquid ammonia, the ammonia being replaced by ether before treatment with carbon dioxide (eq. 4).

Similarly, carbonation of **1** was effected in 64% yield by means of lithium amide; previously the reaction was



(4)

realized in 89% yield by means of potassium amide.[18] Also, carbonations of **1** by means of phenyllithium[19] and *n*-butyllithium[20] in hydrocarbon solvents have been reported. Such carbonation methods appear comparable with that involving cyclization of benzilic acid by aluminum chloride.[21]

Finally, 9-benzylfluorene was alkylated with benzyl chloride by means of sodamide in liquid ammonia to form 9,9-dibenzylfluorene in 87% yield (eq. 5).

$$\mathbf{2}\ (\text{R = benzyl}) \xrightarrow[\text{2. } C_6H_5CH_2Cl]{\text{1. } NaNH_2(NH_3)} \mathbf{3}\ (\text{R = benzyl}) \qquad (5)$$

This alkylation has previously been effected by means of potassium in dioxane.[7]

Experimental Section[22]

Alkylations of Fluorene (1) with Alkyl Halides by Alkali Amides.—In Table I are summarized the results obtained from these alkylations in liquid ammonia or toluene. The details are described below.

A. With *n*-Butyl Bromide.—To a stirred suspension of 0.05 mole of sodamide[23] or 0.055 mole of lithium amide[24] in 300 ml. of commercial, anhydrous liquid ammonia was added 8.3 g. (0.05 mole) of fluorene (**1**), followed by 150 ml. of dry ether, to produce a brown solution of the sodio or lithio salt **1′**; this color appeared immediately. After 30 min., 7.3 g. (0.05 or 0.055 mole, see Table I) of *n*-butyl bromide in 50 ml. of dry ether was added. When the color was discharged (about 1 hr.), the liquid ammonia was allowed to evaporate at room temperature or was removed on the steam bath, and 100 ml. each of ether and water were added. The mixture was shaken to dissolve solids, and the two layers were separated. The ethereal layer (with which was combined an ethereal extract of the aqueous layer) was dried over magnesium sulfate, and the solvent was removed. The crude residue was analyzed by v.p.c.

In the experiment with lithium amide, the crude product was distilled through a 12-cm. Vigreux column to give 9-*n*-butylfluorene (**2**, R = C_4H_9), b.p. 162.5–165° (4.5 mm.) [lit.[16] b.p. 195° (33 mm.)], in 83% yield.

B. With Benzyl Chloride.—Alkylations of fluorene with this halide were effected by means of sodamide and lithium amide in liquid ammonia essentially as described above for *n*-butyl bromide. The brown color of sodio or lithio salt **1′** was discharged within 90 min. In the experiment with sodamide, the crude product was recrystallized once from 95% ethanol to give 9,9-dibenzylfluorene (**3**, R = $CH_2C_6H_5$), m.p. 145–148° (lit.[9] m.p. 146°), in 33% yield.

In the experiment with lithium amide, the crude product was recrystallized four times from 95% ethanol to give 9-benzylfluorene (**2**, R = $CH_2C_6H_5$), m.p. 131–134° (lit.[9] m.p. 134°), in 55% yield.

In another experiment, 0.05 mole of 9-fluorenylsodium (**1′**) was prepared in liquid ammonia by means of sodamide, and the ammonia was evaporated as an equal volume of dry toluene was added. To the resulting suspension of **1′** was added 6.98 g.

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(17) F. A. L. Anet and P. M. G. Bavin, *Can. J. Chem.*, **34**, 991 (1956).

(18) R. S. Yost and C. R. Hauser, *J. Am. Chem. Soc.*, **69**, 2325 (1947).

(19) G. Wittig, F. T. Meyer, and G. Lange, *Ann.*, **571**, 167 (1951).

(20) R. R. Butner and J. W. Cusic, *J. Am. Chem. Soc.*, **65**, 262 (1943).

(21) H. J. Richter, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p. 482.

(22) Melting points (UniMelt capillary melting point apparatus) and boiling points are uncorrected. An F and M Model 500 programmed-temperature gas chromatograph equipped with a Disc chart integrator with a 2-ft column of 10% silicone gum rubber SE 30 (Wilkins Instrument and Research, Inc.) on 60–80 mesh Chromosorb W was used. The carrier gas was helium.

(23) See C. R. Hauser, F. W. Swamer, and J. T. Adams, *Org. Reactions*, **8**, 122 (1954).

(24) See W. R. Dunnevant and C. R. Hauser, *J. Org. Chem.*, **25**, 503 (1960).

(0.055 mole) of benzyl chloride, and the reaction mixture was refluxed for 2.5 hr. After cooling, the mixture was shaken with 100 ml. of water, and the layers were separated. The toluene layer was dried and the solvent was removed. The crude residue was analyzed by v.p.c.

C. With Benzhydryl Chloride.—Alkylation with this halide was effected by means of sodamide in liquid ammonia as described for *n*-butyl bromide under A. The suspension of the reaction product obtained on replacing the liquid ammonia by ether was filtered, and the filtrate was evaporated. The residue from the filtrate was combined with the solid on the funnel. Two recrystallizations from benzene afforded 13.1 g. (79%) of 9-benzhydrylfluorene [2, R = $CH(C_6H_5)_2$], m.p. 216–218° (lit.[14] m.p. 217–218°). The melting point was undepressed on admixture with a sample of 9-benzhydrylfluorene prepared independently as described below. Also, the infrared spectra of the two samples were identical.

D. With α-Phenylethyl Chloride.—Alkylation with this halide was effected by means of sodamide in liquid ammonia as described for *n*-butyl bromide under A. The ethereal suspension of the reaction product was filtered, and the solid was combined with the residue left on evaporation of the filtrate. Two recrystallizations from methanol afforded 11.59 g. (81%) of 9-α-phenylethylfluorene (2, R = α-phenylethyl), m.p. 88–91°.

Anal.[25] Calcd. for $C_{21}H_{18}$: C, 93.33; H, 6.67. Found: C, 93.37; H, 6.81.

The melting point was undepressed on admixture with a sample prepared by α-phenylethylation of 9-fluorenecarboxylic acid followed by decarboxylation as described below. In addition, the infrared spectra of the two samples were identical.

Independent Synthesis of 9-Benzhydrylfluorene.—To a stirred solution of 0.05 mole of diphenylmethylsodium (4) in 300 ml. of liquid ammonia was added 9 g. (0.05 mole) of fluorenone in 50 ml. of dry ether (color of **4** was discharged immediately) as described previously for the addition reaction of **4** with benzophenone.[12] The reaction mixture was neutralized inversely with 0.1 mole of ammonium chloride in liquid ammonia and worked up to give 12.01 g. (69%) of 9-hydroxy-9-benzhydrylfluorene (5), m.p. 183–186° (lit.[13] m.p. 183°).

A solution of 11.5 g. (0.033 mole) of carbinol **5** in 100 ml. of acetyl chloride was refluxed gently for 13 hr., and the solvent was then removed.[13] The residue was washed with petroleum ether (b.p. 30–60°) and recrystallized from ethyl acetate to give 10.0 g. (92%) of 9-benzhydrylidene (6), m.p. 226–228° (lit.[13,14] m.p. 224–225°).

To a stirred suspension of 7.0 g. (0.02 mole) of olefin **6** in 300 ml. of liquid ammonia was added 110 ml. of dry ether followed by 1.06 g. (0.04 g.-atom) of sodium. The resulting blue solution was stirred for 2 hr. and then neutralized with 5.0 g. (0.09 mole) of ammonium chloride (color was discharged). The ammonia was evaporated and the residue was shaken with 100 ml. of water. The mixture was filtered to give 6.03 g. (86%) of 9-benzhydrylfluorene (2, R = benzhydryl), m.p. 213–216°, and 219–220° after several recrystallizations from benzene.

Alkylations of Fluorene (1) with Alkyl Halides by *n*-Butyllithium.—In Table II are summarized the results obtained from these alkylations. The details are described below.

A. With *n*-Butyl Bromide.—To a stirred solution of 8.3 g. (0.05 mole) of fluorene in 200 ml. of dry hexane under a dry nitrogen atmosphere was added 40 ml. of 1.6 *M* *n*-butyllithium in hexane,[26] to produce a yellow suspension of lithio salt 1′. The reaction mixture was refluxed gently for 3 hr. under positive nitrogen pressure. Yellow lithio salt 1′ had precipitated after about 0.5 hr. After cooling, a solution of 7.3 g. (0.05 mole) of *n*-butyl bromide in 50 ml. of dry hexane was added, and the resulting mixture was stirred at room temperature under nitrogen for 3 hr. The reaction mixture was shaken with water, and the two layers were separated. The hexane layer was dried over magnesium sulfate and, after filtering, the solvent was removed. The residue was distilled to give 8.83 g. (80%) of 9-*n*-butylfluorene (2, R = C_4H_9), b.p. 139–144° (0.1 mm.), [lit.[16] b.p. 192–195° (33 mm.)]. The distilled product was pure by v.p.c.

B. With Benzyl Chloride.—Alkylation of fluorene (1) with this halide was effected as described in A for *n*-butyl bromide, employing 0.064 mole of *n*-butyllithium and 0.055 mole of benzyl chloride to 0.05 mole of fluorene. The product obtained on removing the hexane was recrystallized three times from 95% ethanol to afford 7.45 g. (58%) of v.p.c. pure 9-benzylfluorene, m.p. 131–134° (lit.[9] m.p. 134°).

C. With Benzhydryl Chloride.—Alkylation with this halide was effected as described above for *n*-butyl bromide. The crude product, on removing the hexane, was analyzed by v.p.c. (see Table II).

Alkylations of 9-Fluorenecarboxylic Acid through Its Dianion. A. With Benzyl Chloride.—To a stirred suspension of 0.11 mole of sodamide[23] in 300 ml. of liquid ammonia was added 10.5 g. (0.05 mole) of 9-fluorenecarboxylic acid (9), followed by 200 ml. of dry ether, to produce a green mixture of the disodio salt 9′. After 1 hr., 6.9 g. (0.055 mole) of benzyl chloride in 50 ml. of dry ether was added, and the stirring was continued for 4 hr. (a slight green color still persisted). The liquid ammonia was removed, and 100 ml. of water was added. The two layers were separated. The aqueous layer (after being extracted with 100 ml. of ether) was acidified with dilute hydrochloric acid and the resulting precipitate was collected to give, after drying, 13.3 g. (89%) of presumably 9-benzyl-9-carboxyfluorene (9), m.p. 190–205°.

This acid (13.3 g.) was dissolved in 200 ml. of dimethylformamide, and the solution was refluxed for 12 hr. After cooling, the reaction mixture was stirred with 300 ml. of water for 30 min. The resulting precipitate was collected by filtration to give 10.72 g. (97.5%, over-all yield 84%) of 9-benzylfluorene (2, R = $CH_2C_6H_5$), m.p. 130–133°, which was pure by v.p.c. One recrystallization from ethanol raised the melting point to 131–133° (lit.[7] m.p. 134°). This melting point was not depressed on admixture with a sample of 9-benzylfluorene prepared by direct benzylation of fluorene (see above).

B. With α-Phenylethyl Chloride.—This alkylation was effected essentially as described above with benzyl chloride employing 0.06 mole of potassium amide in 300 ml. of liquid ammonia, 0.025 mole of acid 9, 0.03 mole of α-phenylethyl chloride, and 100 ml. of dry ether. The reaction mixture was allowed to stir overnight (green color was still present), and then worked up to give, after decarboxylation, 4.5 g. of product consisting of 73% of 2 (R = α-phenylethyl) and 27% of fluorene (by v.p.c.). A sample was heated at 50° and 0.2 mm. for 3 days to sublime the fluorene, leaving a residue, which on recrystallization from methanol gave 0.5 g. of 2 (R = α-phenylethyl), m.p. 88–91°; this melting point was not depressed on admixture with a sample of the product prepared by direct α-phenylethylation of 1 (see above).

Carbonation of Fluorene by Alkali Amides. A. By Sodamide.—To a stirred suspension of 0.05 mole of sodamide in 300 ml. of liquid ammonia was added 8.3 g. (0.05 mole) of fluorene, followed by 300 ml. of dry ether. After stirring for 30 min., the liquid ammonia was evaporated on the steam bath, as more ether was added. The resulting brown, ethereal suspension of sodio salt 1′ was poured onto a large excess of pulverized, Dry Ice. After the excess Dry Ice had evaporated, the residue was shaken with 200 ml. of water, and the two layers were separated. The aqueous layer was carefully acidified with dilute hydrochloric acid. The resulting precipitate was collected by filtration and dried to give 9.78 g. (93%) of 9-fluorenecarboxylic acid (8), m.p. 221–226.5°, and at 227–229° (72%) after recrystallization from glacial acetic acid (lit. m.p. 221–222°,[20] 228–230°[21]). Our product, m.p. 221–226.5°, appeared to be about as pure as that described by Richter.[21]

B. By Lithium Amide.—This experiment was effected as described above for sodamide. The brown solution of lithio salt 1′ in liquid ammonia retained its color on replacing the ammonia by ether. There was obtained 6.7 g. (64%) of 9-fluorenecarboxylic acid (8), m.p. 217–226°.

Benzylation of 9-Benzylfluorene.—To a stirred suspension of 0.0167 mole of sodamide in 200 ml. of liquid ammonia was added 4.3 g. (0.0167 mole) of 9-benzylfluorene (2, R = $CH_2C_6H_5$) in 100 ml. of dry ether. A red color developed immediately. After stirring for 30 min., 2.63 g. (0.02 mole) of benzyl chloride in 30 ml. of dry ether was added, and the ammonia was removed on the steam bath. The resulting ethereal suspension was shaken with water, and the mixture was filtered. The ethereal layer of the filtrate was evaporated, and the residue (5.44 g.) was recrystallized from 95% ethanol to give 4.95 g. (89%) of 9,9-dibenzylfluorene (2, R = benzyl), m.p. 145–148° (lit.[9] m.p. 146°).

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(25) Performed by Janssen Pharmaceutica, Belgium.

(26) Obtained from Foote Mineral Co., New Johnsonville, Tenn.