the 4 position.[28] Little is known about the characteristics of such a mechanism. It would be highly coincidental that such a pathway would give rise to a positional reactivity pattern which is an imitation of that for direct deprotonation.

In light of the proposed mechanism involving carbanion formation by direct deprotonation the positional reactivity pattern indicates that the primary mode of activation by the N-oxide group is inductive. Typically, inductive effects fall off rapidly as the distance between the activating group and the reaction site is increased.

Dipole moment,[29] infrared,[30] and nmr[16] studies indicate the presence of a resonance effect in the ground states of N-oxides. However, the donation of electrons into the ring by the oxygen of the N-oxide group must have only a minor influence on exchange reactivities. The relative rates of exchange of I and of decarboxylation of N-methylpyridinium carboxylates are proportional on a logarithmic scale. These carboxylates do not contain oxygen capable of donating electrons into the ring. The minor importance of electron donation by oxygen in the exchange reactions is understandable. The orbitals of the generated carbanions are orthogonal to the orbitals of the π system and interaction between them is at a minimum.

Rate Factors.—Our determination of partial rate factors for substituents assumes that the same reaction mechanism is followed by all the reactions considered here and that the effects of the several substituents on the reaction site are additive. The general agreement of the rate factors determined from different compounds having a rate spread of about 10^4 (50°) supports these assumptions.

The magnitudes of the *ortho* and *para* N-oxide log rate factors, 9.58 and 5.88, respectively, are to be compared with those for fluorine, 5.25 and 1.13,[6] respectively. Fluorine is known to exert one of the most powerful acidifying effects on aryl hydrogens.[4] Clearly the effect of the highly polar N-oxide group is considerably greater.

The mechanism for the hydrogen exchange reactions may be written so the rate of collapse to starting materials of the hydrogen-bonded anion, A, may successfully compete with the rate of replacement of one hydrogen bond for another to give B. When this occurs the observed rates include contributions from these steps in addition to the initial step giving A. We expect this mechanism, internal return, to be important in the exchange reactions reported here. Delocalized anions are not formed and the acidity of the annular positions is considerably less than that of the solvent.[31] The observed ΔS^* values are in keeping with this suggestion. According to the internal return mechanism ΔS^* is a composite of the entropy changes of the several steps and the observed values may be less negative than those for normal second-order reactions.[6] Our ΔS^* values, Table IV, include positive and negative values and range over 16 eu.

$$\mathrm{C{-}D} + \mathrm{CH_3O^-} \rightleftarrows \underset{\mathrm{A}}{\mathrm{C^-\cdots DOCH_3}} \xrightarrow{\mathrm{HOCH_3}} \underset{\mathrm{B}}{\mathrm{C^-\cdots HOCH_3}} \longrightarrow \text{exchange}$$

In summary, pyridine N-oxides undergo hydrogen exchange by simple deprotonation reactions. Positional reactivity is determined primarily by the activating effect of the N-oxide group and secondarily by chlorine substituents. Entropies of activation suggest that a more detailed description of the exchange mechanism must include internal return.

Registry No.—I-d_5, 19639-76-0; II-4-d, 19639-77-1; II-2,6-d_2, 19639-78-2; III, 15177-57-8; III-d_3, 19639-80-6.

Acknowledgment.—We are pleased to acknowledge helpful discussions with Professor Gardiner Myers.

[28] A. San Pietro, *J. Biol. Chem.*, **217**, 579 (1955).

[29] A. R. Katritzky, E. W. Randall, and L. E. Sutton, *J. Chem. Soc.*, 1769 (1957).

[30] A. R. Katritzky, A. M. Monro, J. A. T. Beard, D. P. Dearnaley, and N. J. Earl, *ibid.*, 2182 (1958).

[31] M. Eigen, *Angew. Chem. Intern. Ed. Engl.*, **3**, 1 (1964).

Cyanation and Hydrocyanation of Unsaturated Hydrocarbons. II. Oxidation and Reduction of the Intermediate[1,2]

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Received October 16, 1968

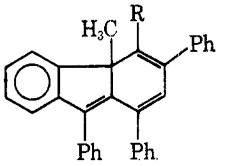
The cyanation of the heavily arylated hydrocarbon 4a-methyl-1,3,9-triphenyl-4aH-fluorene (Ia) proceeds almost quantitatively when solutions prepared from the hydrocarbon and sodium cyanide in aprotic solvents are treated with certain oxidizing agents. Of a number of oxidants studied, chromium trioxide, lead dioxide, and sodium 9,10-anthraquinone-1-sulfonate are most effective, and the last is the most conveniently used. Certain dibenzofulvenes, namely 9-benzylidenefluorene (IIa), 9-(p-bromobenzylidene)fluorene (IIc), and 9-ethylidenefluorene (IIe), are cyanated when treated with the same combinations of reagents, and the yields, especially from the arylidene compounds, are high. The roles in the cyanation process of the carbanions formed by addition of cyanide ion to the unsaturated systems, of radicals formed from such carbanions by electron exchange, and of hydrocyanation products formed by protonation of the carbanions are discussed.

The facile reaction of cyanide ion with 4a-methyl-1,3,9-triphenyl-4aH-fluorene (Ia) is attributed to the presence in this hydrocarbon of an extended, conjugated π-bond system, which stabilizes the incipient carbanion through resonance.[2a] This structural feature, as well

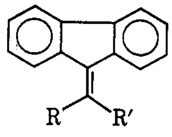
[1] Grateful acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the U. S. Army Research Office [Grants PRF-2042-A1 and DA-ARO(D)-G679 and G857] for the partial support of this work.

[2] For previous related papers, see (a) B. E. Galbraith and H. R. Snyder, *J. Org. Chem.*, **32**, 380 (1967), and (b) R. G. Landolt and H. R. Snyder, *ibid.*, **33**, 403 (1968).

as a polarized double bond, is also inherent in the nitro[2b,3] and cyano[4] derivatives of some aromatic systems, which readily undergo attack by cyanide ion, and in the dibenzofulvene compounds which we now discuss.

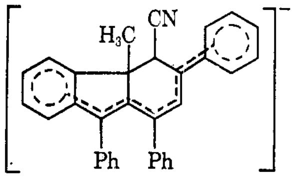


Ia, R = H
b, R = CN

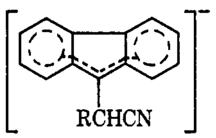


IIa, R = Ph; R' = H
b, R = Ph; R' = CN
c, R = p-C_6H_4Br; R' = H
d, R = p-C_6H_4Br; R' = CN
e, R = CH_3; R' = H
f, R = CH_3; R' = CN

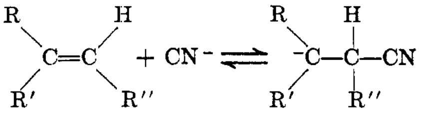
Intensely dark, almost black solutions are produced upon mixing 9-benzylidenefluorene (IIa), 9-(p-bromobenzylidene)fluorene (IIc), and 9-ethylidenefluorene (IIe) with sodium cyanide in dipolar aprotic solvents under nitrogen at room temperature. As in the reaction of cyanide ion with hydrocarbon Ia, in which the carbanion III is formed, the generation of color in these reactions is considered due, at least in part, to the initial formation of carbanion species (IVa–c), for dibenzofulvenes have long been known to be susceptible to nucleophilic attack at the 10 position.[5] However, the departure from the usual red color associated with the fluorenyl anion[6,7] and the detection of epr signals[8] in the solutions suggest the coexistence of radical species. Russell and coworkers[9] have recently cited numerous examples of electron-transfer reactions in which a carbanion spontaneously loses an electron to a molecule of the parent compound, and the electron-accepting ability of phenyl-substituted dibenzofulvenes is known to be very good.[10] Carbanion formation (reaction 1) in these cyanide–hydrocarbon mixtures will therefore likely be accompanied by electron-transfer reactions 2 and 3 between the carbanion and the hydrocarbon, or its cyanation derivative, as well as disproportionation reactions 4, 5, and 6 of the resulting radical and anion radicals.



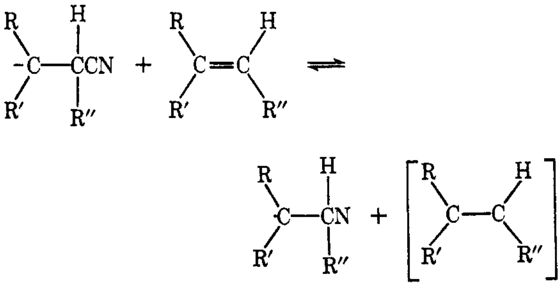
III



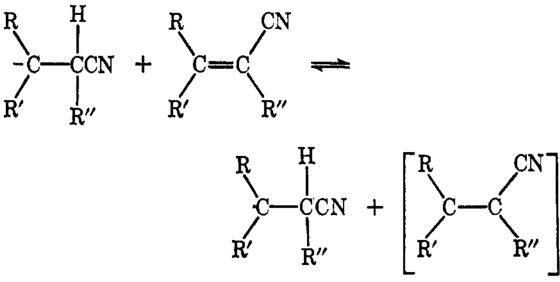
IVa, R = Ph
b, R = p-C_6H_4Br
c, R = CH_3



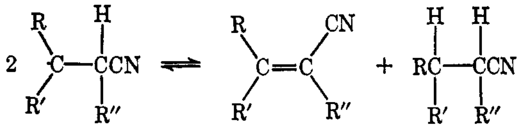
(1)



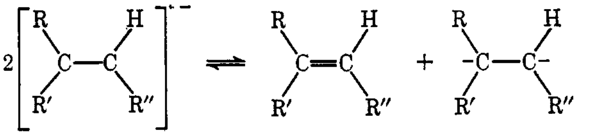
(2)



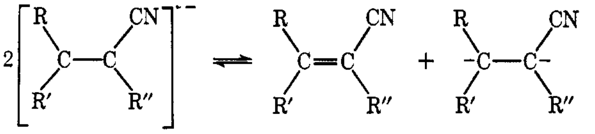
(3)



(4)



(5)



(6)

Cyanation of the hydrocarbons is achieved if the colored cyanide–hydrocarbon mixtures are treated with oxygen or air, but, although in the case of hydrocarbon Ia a 63% yield of cyanation product Ib is obtained,[2a] molecular oxygen is considerably less effective in the cyanation of dibenzofulvene IIa. When hydrocarbon IIa was treated with sodium cyanide, in dimethylformamide (DMF) or dimethyl sulfoxide (DMSO), in the presence of air, the cyanation product, 9-(α-cyanobenzylidene)fluorene (IIb), was isolated in only 28% yield. Similar reactions run under nitrogen and later exposed to air or oxygen yielded fluorenone and a colorless, high-melting compound of possible structure V.[11a] Apparently with this compound oxygenation of the intermediate occurs at the expense of hydrogen removal. The decomposition of unstable hydroperoxide anions, formed by reaction of carbanions with molecular oxygen, is well established,[11b] and the formation of fluorenone is yet another example in which such decomposition is accompanied by carbon–carbon bond scission.

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(3) R. F. Aycock, unpublished work; B. Vickery, *Chem. Ind.* (London), 1523 (1967).

(4) K. E. Whitaker, unpublished work.

(5) E. D. Bergmann in "Progress in Organic Chemistry," Vol. 3, J. W. Cook, Ed., Academic Press, New York, N. Y., 1955, p 81.

(6) D. Lavie and E. D. Bergmann, *Bull. Soc. Chim. Fr.*, **18**, 250 (1951).

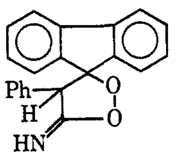
(7) D. J. Cram and D. R. Wilson, *J. Amer. Chem. Soc.*, **85**, 1249 (1963).

(8) R. G. Landolt, private communication.

(9) G. A. Russell and W. C. Danen, *J. Amer. Chem. Soc.*, **90**, 347 (1968), and previous papers here mentioned.

(10) S. Wawzonek and J. W. Fan, *ibid.*, **68**, 2541 (1946).

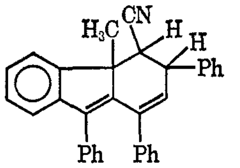
(11) (a) Structure V for compound $C_{21}H_{15}NO_2$ was suggested by a referee; it is in agreement with the analytical and spectral data. (b) G. A. Russell, E. G. Janzen, A. G. Bemis, E. J. Geels, A. J. Moye, S. Mak, and E. T. Strom, Advances in Chemistry Series, No. 51, American Chemical Society, Washington, D. C., 1965, p 112.



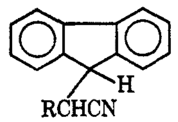
V

The facile cyanation of hydrocarbons in high yield has potential synthetic importance; so alternative oxidizing agents were investigated. Certain properties were considered necessary prerequisites for an efficient oxidizing agent. (1) It should have high solubility in the aprotic solvents. (2) Either it should be inert to attack by cyanide ion, or it should oxidize the reaction intermediate at a much faster rate than it reacts with cyanide ion. (3) It should not degrade the hydrocarbon. (4) The unreacted oxidizing agent, together with its reduced form, should be easily separated, preferably by physical means, from the anticipated cyanation product. (5) It should be readily available. Table I contains the product distributions from reactions of hydrocarbons Ia and IIa with sodium cyanide in the presence of various oxidizing agents.

The observed nonspecificity of the kind of oxidizing agent employed is understandable, for, in forming the unsaturated nitrile (cyanation product), the oxidizing agent may directly remove a hydride ion from the carbanion generated in reaction A, or it may accept an electron to give a radical, which then disproportionates (reaction 4) or undergoes further oxidation with loss of a hydrogen atom. Except in those cyanation reactions where very prolonged reaction times were employed, or the action of the oxidizing agent was very fast, hydrocyanation products were isolated. The presence of these compounds can be attributed to reactions 4 and 6, as well as to possible protonation of the carbanion during the oxidation, by traces of moisture present. With a fast oxidizing agent, oxidation of the carbanion is completed before any protonation or electron-exchange can occur; and, in the case of a prolonged reaction time, the hydrocyanation product, when formed, is apparently sufficiently acidic to be eventually completely oxidized, in the presence of cyanide ion, to the cyanation product. It has already been shown[2a] that compound VI is oxidized by oxygen to compound Ib, in the presence of sodium cyanide; and, in the present work, this oxidation was accomplished in 87% yield when compound VI was treated, under nitrogen, with sodium anthraquinone-1-sulfonate. In a similar experiment in which nitrile VIIa was the substrate, only a 24% conversion into the unsaturated nitrile (IIb) was achieved. Removal of a proton from this compound by cyanide ion is evidently more difficult, and this would explain why in many cases the over-all yield of cyanation product from 9-benzylidenefluorene (IIa) was inferior to that from the arylated triene (Ia).



VI



VIIa, R = Ph
b, R = p-C_6H_4Br
c, R = CH_3

Oxidations with chromium trioxide were exceedingly efficient, and the absence of any hydrocyanation product indicates a very rapid oxidation of the carbanion, for under similar conditions chromium trioxide failed to oxidize the hydrocyanation derivative VI, even in the presence of sodium cyanide. The rate of reaction of the hydrocarbon with cyanide ion evidently is slower than the rate of oxidation of cyanide ion by chromium trioxide, since, in an experiment in which sodium cyanide was added to a solution of hydrocarbon IIa and chromium trioxide, no cyanation took place and a complete recovery of the hydrocarbon was realized. Hexamethylphosphoramide (HMP) was chosen as the solvent for this oxidizing agent, as DMF and DMSO violently inflamed when they were dropped onto chromium trioxide. The high solubility of chromium trioxide in the reaction mixture is no doubt partially responsible for its swift oxidizing action. Potassium ferricyanide, potassium iodate, manganese dioxide, and lead dioxide are barely soluble in DMF and DMSO and they necessitate a long reaction time before the characteristic intense color of the mixtures fades. However, the yields from some of these oxidations were very good. The addition of water, to enhance the solubility of potassium ferricyanide in DMF, resulted in very little cyanation (<2%) of hydrocarbon Ia, probably because of the hydrolysis of the sodium cyanide, for hydrocarbon Ia has been shown to be unreactive to hydrogen cyanide.[2a] The failure of the ceric salts, N-bromosuccinimide, crystal violet, and Fremy's salt to oxidize effectively the cyanide–hydrocarbon mixtures is attributed to the competing reaction of these reagents with sodium cyanide, whereby the process of carbanion formation is reversed (condition 2). Triphenylformazan contaminated the products when triphenyltetrazolium chloride was used to oxidize the cyanide–hydrocarbon mixtures.

Quinones constitute the most powerful and versatile organic oxidizing agents, being both electron acceptors and hydride ion abstractors. Although their ability to dehydrogenate organic compounds *via* a hydride ion removal mechanism has been well established,[12] no work has dealt with the use of quinones for removing a hydride ion from a preformed carbanion.[13] The cyanation reactions with the high-potential quinones, chloranil and DDQ, were only moderately successful, because of their side reactions with sodium cyanide. In order to have the quinone nucleus blocked against cyanide attack, anthraquinone was used, and the commencement of the oxidations was readily apparent by the rapid development of the magenta color, characteristic of the anthraquinone dianion.[14] Anthraquinone, however, is not very soluble in either DMF or DMSO; and its use also gave rise to the problem of separating it from the products of the reaction, since the sodium salt of the anthraquinone dianion is oxidized back to anthraquinone[14] immediately as the reaction mixture is exposed to air on work-up. As an example of a quinone-type oxidizing agent soluble in the aprotic solvents used and relatively free from cyanide ion attack, sodium anthraquinone-1-sulfonate was chosen. It gave very clean

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[12] L. M. Jackmann, *Advan. Org. Chem.*, **2**, 329 (1960).

[13] Jackmann[12] has commented on the possibility of using quinones for this purpose.

[14] L. F. Fieser and M. Fieser, "Organic Chemistry," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1956, p 766.

TABLE I

CYANATION REACTIONS OF 4a-METHYL-1,3,9-TRIPHENYL-4aH-FLUORENE (IA) AND 9-BENZYLIDENEFLUORENE (IIA)

				Hydrocarbon Ia			Hydrocarbon IIa		
Oxidizing agent	Solvent	Temp, °C	Reaction time,[a] hr	Unchanged hydrocarbon, %	Cyanation product Ib, %	Hydrocyanation product V, %	Unchanged hydrocarbon, %	Cyanation product IIb, %	Hydrocyanation product VIa, %
Potassium ferricyanide	DMSO	R.t.[b]	24	0	67	0[c]	0	39	9[d]
Potassium iodate	DMF	R.t.	70	0	80	0[c]	0	36	0[d]
Potassium metaperiodate	DMSO	R.t.	2	21	48	0[c,e]			
Manganese dioxide	DMF	R.t.	46	0	53	0[f]			
Lead dioxide	DMF	R.t.	20	0	87	0[c]	0	79	0[c,g]
Chromium trioxide	HMP	R.t.	0.5	0	87	0[c]	0	88	0[c]
Ceric sulfate	DMSO	R.t.	12	0	16	44[h]			
Ceric ammonium nitrate	DMF	R.t.	12	98	0	0[d,e]			
N-Bromosuccinimide	DMF	R.t.	1.5	61	9	5[i]			
2,3,5-Triphenyltetrazolium chloride	DMF	R.t.	1	*j*	48	0[d]			
2,3,5-Triphenyltetrazolium chloride	DMF	R.t.	5	*j*	74	0[d]			
Tetrachloro-1,4-benzoquinone (chloranil)	DMF	R.t.	2	15	51	14[d,e]	24	25	16[c,e,k]
2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)	DMF	R.t.	0.5	29	30	23[d,e]			
9,10-Anthraquinone	DMF	R.t.	5	5	53[d]	*l*	10	38[d]	*l*
Sodium 9,10-anthraquinone-2-sulfonate	DMF	R.t.	10	0	60	23[d]	0	48	21[d]
Sodium 9,10-anthraquinone-1-sulfonate	DMF	R.t.	10	0	69	18[d]			
Sodium 9,10-anthraquinone-1-sulfonate	DMSO	R.t.	10	0	80	1[d]	0	54	18[d,g]
Sodium 9,10-anthraquinone-1-sulfonate	DMSO	50	4	0	92	0[g,i]	0	64	14[g,i]
Sodium 9,10-anthraquinone-1-sulfonate	DMSO	50	6				0	68	11[g,i]
Sodium 9,10-anthraquinone-1-sulfonate	DMSO	50	12				0	72	7[g,i]
Sodium 9,10-anthraquinone-1,5-disulfonate	DMSO	R.t.	10	6	51	12[d]	0		
9,10-Phenanthraquinone	DMF	R.t.	5	0	90	0[d]	22	56	0[g,i]
Potassium nitrosodisulfonate (Fremy's salt)	DMF	R.t.	4	24	12	39[c]			
Crystal violet	DMF	R.t.	2.5	37	12	18[c,e]			

[a] Measured from the time the hydrocarbon, sodium cyanide, and oxidizing agent are all present together. [b] Room temperature of 24°. [c] 1:2 molar mixture of hydrocarbon and oxidizing agent. [d] 1:1 molar mixture of hydrocarbon and oxidizing agent. [e] Oxidizing agent added dropwise in solution. [f] Large excess of oxidizing agent. [g] Sodium cyanide added to hydrocarbon with oxidizing agent already present. [h] 1:3 molar mixture of hydrocarbon and oxidizing agent. [i] 1:1.3 molar mixture of hydrocarbon and oxidizing agent. [j] Not separated from the formazan. [k] Large excess of sodium cyanide. [l] Not separated from anthraquinone.

oxidations, and good yields of the cyanation products were obtained. Similar yields were also achieved when sodium cyanide was added to the hydrocarbon in the presence of the quinone, and in these reactions the usual intense green (hydrocarbon Ia) or black color (hydrocarbon IIa) was not observed, the deep magenta color developing immediately upon the addition of the sodium cyanide. Phenanthraquinone, a stronger oxidizing agent than anthraquinone,[15] was also very effective under conditions where cyanation of the hydrocarbons Ia or IIa had proceeded before the addition of the oxidizing agent.

The cyanation of 9-(*p*-bromobenzylidene)fluorene (IIc) with either sodium anthraquinone-1-sulfonate or phenanthraquinone was achieved with success similar to that with hydrocarbon IIa, the lack of any halogen replacement illustrating the selectivity of the cyanide ion attack under these mild conditions.

Cyanation reactions of 9-ethylidenefluorene (IIe) led even in the best case, *i.e.*, with sodium anthraquinone-1-sulfonate oxidant, to only 23% of nitrile IIf, along with 35% of hydrocyanation product VIIc. In all cases, by-product formation was serious and no starting material was recovered. Low molecular weight polymers formed in the absence of an oxidant or when the hydrocarbon was treated with sodium cyanide prior to addition of the oxidant. The nmr spectrum of a trimer isolated was complex, but a distinctive triplet near τ 3.0, which appeared in place of the quartet absorption associated with the vinyl proton of the monomeric hydrocarbon, is possible evidence for the α,β-unsaturated methylene linkage, which would be present in a trimer formed from polymerization of the hydrocarbon, following proton abstraction from its methyl group.

The efficiency of the cyanation reactions with sodium anthraquinone-1-sulfonate was markedly improved by the addition of potassium *t*-butoxide[16] to the DMSO solutions. The undesired hydrocyanation product was thereby converted into more cyanation product by proton loss and subsequent oxidation of the incipient carbanion. In the case of the 10-hr reaction listed in Table I for 9-benzylidenefluorene (IIa), the yield of the cyanation product (IIb) was raised to 78% by the addition of 1 molar equiv of potassium *t*-butoxide to the reaction mixture just prior to work-up; and, in the cyanation reaction of 9-ethylidenefluorene (IIe), the yield of cyanation product IIf was increased to 34%. A reaction in which the hydrocyanation product (VIIa) of 9-benzylidenefluorene (IIa) was itself treated with potassium *t*-butoxide, in the presence of sodium anthraquinone-1-sulfonate, resulted in a 57% conversion to the cyanation product (IIb).

Hydrocyanation of the hydrocarbons is effected when the colored cyanide–hydrocarbon mixtures are treated, in the absence of air, with such protonating agents as hydrogen cyanide,[2a] water, and ammonium chloride. The addition of 1 molar equiv of ammonium chloride, in solid form, to the colored DMF solutions caused fading of the color; and 76% of nitrile VI, 96% of nitrile VIIa, and 70% of nitrile VIIb were obtained from their respective parent compounds.

Apart from the high-yield protonation reactions, other attempts at trapping carbanion intermediates IVa and IVb were unsuccessful. Carbonation of the cyanide–hydrocarbon IIa mixture with gaseous carbon dioxide led to the isolation of only nitrile VIIa, in 46% yield. As in a similar attempt[2a] to trap carbanion III, the protonated product may be formed as a result of the reaction of sodium cyanide with carbon dioxide to give sodium cyanoformate, followed by protonation of the carbanion in the neutralized reaction solution by moisture present. Other reagents used in attempts to trap the carbanion intermediates included benzyl chloride, allyl bromide, dimethyl sulfate, sulfur dioxide, and cyanogen bromide; although all of these reagents caused fading of the colored cyanide–hydrocarbon mixtures, in no case was the anticipated product obtained.

The reversibility of cyanide ion attack (reaction 1) is considered to be the cause of the failure of the carbanion-trapping reactions, the reagent reacting with sodium cyanide and reversing the process by which the carbanion is formed. Earlier speculation[2a] on this reversibility, in the case of Ia, has now been substantiated by isolation of hydrocarbon Ia in 40% yield from its hydrocyanation derivative (VI) when a basic solution of the latter was evaporated to dryness under vacuum.

Reactions run between the hydrocarbons and sodium cyanide, in DMF under nitrogen, for extensive periods of time, in the absence of an added oxidizing agent, were anomalous. Although protonation of intermediates after 1 hr gives exclusively hydrocyanation products, cyanation products are isolated if the reactions are left for 40 hr before the ammonium chloride is added. In view of the fact that there was no apparent oxidation by the solvent, for no formaldehyde could be detected, a process of electron transfer and disproportionation of the incipient radical would appear necessary to explain the formation of a cyanation product. An electron lost from the carbanion may be transferred either to a molecule of unreacted hydrocarbon (reaction 2) or to a molecule of the unsaturated nitrile (reaction 3), once it is formed. The anion radicals so formed are then further able to disproportionate (reactions 5 and 6). If it is assumed that the hydrocarbon regenerated in reaction 5 reacts with more sodium cyanide, which is always present in excess, the over-all effect of reactions 1–6, upon final protonation, is to give rise to products from cyanation (reactions 4 and 6), hydrocyanation (reactions 4 and 6), and reduction (reaction 5) of the hydrocarbon. In the case of hydrocarbon Ia, the cyanation product (Ib) was formed in 74% yield and the hydrocyanation product (VI) in only 9% yield. A similar reaction with hydrocarbon IIa gave 13% of the cyanation product (IIb), 23% of the hydrocyanation product (VIIa), and 24% of a dinitrile. The rather high yield of cyanation product (Ib) from hydrocarbon Ia is undoubtedly due to the already mentioned ability of the hydrocyanation product (VI) to re-form carbanion III in the presence of sodium cyanide. Our inability to find any reduced hydrocarbons among the products of these reactions would be explained if reactions 2 and 5 were to take place to only a very small extent and the unsaturated nitrile itself, once formed, were to act as the principal electron acceptor (reactions

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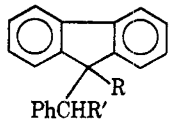
[15] W. Mansfield Clark, "Oxidation–Reduction Potentials," Williams and Wilkins, Baltimore, Md., 1960, p 386.

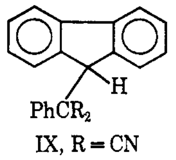
[16] The bulky *t*-butoxide ion is noted to be a very strong base in DMSO and has advantages if carbon substitution is to be avoided [A. J. Parker, *Advan. Org. Chem.*, **5**, 1 (1965)].

3 and 6). Indeed, the cyanation product might be expected to possess a greater electron affinity than the hydrocarbon, since it contains in its structure an extra component of conjugation in the form of the nitrile group.

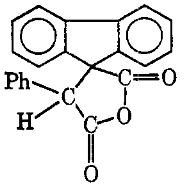
The dinitrile, isolated from prolonged treatment of hydrocarbon IIa with sodium cyanide, followed by ammonium chloride, was shown to have either structure VIIIa or IX by its preparation, in 81% yield, from hydrocyanation of nitrile IIb. Under vigorous acid hydrolysis, a dicarboxylic acid was isolated from the dinitrile in 91% yield. The acid formed a 1:1 inclusion complex with benzene, and sublimation of this complex afforded an anhydride, in 92% yield, showing strong maxima at 1865 and 1780 cm^{-1}, in close agreement with the carbonyl absorption peaks of five-membered cyclic anhydrides.[17a] The acid and anhydride were therefore given the structures VIIIb and X, respectively, and in consequence the structure VIIIa was assigned to the dinitrile. Additional proof of the dinitrile structure was furnished when the dicarboxylic acid was reduced with lithium aluminium anhydride, and the glycol (VIIIc) so formed (in 56% yield) was subsequently oxidized with Sarrett's reagent. A product was obtained in 27% yield, whose analysis, infrared spectrum (carbonyl absorption[17b] at 1770 cm^{-1}), and nmr spectrum (no aldehydic protons, but an AB quartet centered at τ 5.24 and a one-proton singlet at 5.44) were compatible with a γ-lactone having the spiro structure XI.



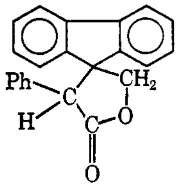
VIIIa, R = R' = CN
b, R = R' = CO_2H
c, R = R' = CH_2OH



IX, R = CN



X



XI

The structures of the nitriles IIb, IId, IIf, and VIIa–c were assigned on the basis of their infrared, nmr, and mass spectra. Nitrile IIb was also independently synthesized from 9-benzylidenefluorene by the method of Koelsch.[18] The nmr spectrum of nitrile VIIa in deuteriochloroform is anomalous; it shows, in addition to the absorption for the aromatic protons, a sharp two-proton singlet at τ 5.70. The spectrum in acetone-d_6, however, shows the four-line pattern expected for an AB system, centered at τ 5.17, with a coupling constant of 5 cps. In order to establish conclusively the identity of this nitrile, both nitrile VIIa and 9-benzyl-9-cyanofluorene were independently prepared. Catalytic hydrogenation of nitrile IIb gave a colorless nitrile, identical with nitrile VIIa, whereas benzylation of 9-cyanofluorene, by the method of Anet and Bavin,[19] gave a product whose melting point and spectra were quite different from those of nitrile VIIa. The nmr spectrum of nitrile IIf, in deuteriochloroform, contains a three-proton singlet at τ 7.53 corresponding to the vinyl methyl group, and the spectrum of nitrile VIIc contains a three-proton doublet at τ 9.21, with coupling constant 7 cps, a one-proton octet at τ 6.63, with coupling constant 3.5 cps, and a one-proton doublet at τ 5.77, also with coupling constant 3.5 cps. These spectra are in agreement with structures IIf and VIIc. The structure of nitrile VIIc was also verified by its preparation from nitrile IIf upon catalytic hydrogenation.

Experimental Section[20]

Materials.—Commercially available analytical grade solvents were employed, after they had been stored over Linde Type 4a Molecular Sieves for at least 2 weeks. Sodium cyanide (98%) was dried for 24 hr at 110°, in a vacuum oven, and stored over calcium sulfate in a tightly closed container. All gas streams were dried by sulfuric acid.

9-Benzylidenefluorene (Ia).—Colorless 9-benzylidenefluorene, mp 77–79° (lit.[21] mp 75–76°), was prepared by treatment of fluorene with benzyl alcohol and benzaldehyde in the presence of potassium hydroxide, according to the method of Sprinzak.[21]

9-(*p*-Bromobenzylidene)fluorene (IIc).—The preparation of 9-(*p*-bromobenzylidene)fluorene, mp 148–149° (lit.[22] mp 147–148°), from fluorene and *p*-bromobenzaldehyde in the presence of sodium methoxide was carried out by the method of Allen and his coworkers.[22]

9-Ethylidenefluorene (IIe).—A methanolic solution of Aldrich 9-ethylidenefluorene was treated with decolorizing charcoal and crystallized to give crystals, mp 105.5–106.5° (lit.[23] mp 103–104°).

4a-Methyl-1,3,9-triphenyl-4aH-fluorene (Ia).—The preparation of this hydrocarbon was the same as that described in a previous paper.[2a]

Reaction of 9-Benzylidenefluorene (IIa) with Sodium Cyanide. A. In DMF, in the Presence of Air.—A mixture of the hydrocarbon (1.02 g, 0.004 mol), sodium cyanide (1.96 g, 0.040 mol), and 20 ml of DMF became nearly black within 1 min when stirred under air at room temperature. After 30 min, air was led into the flask for 1.5 hr. The resulting intensely red mixture was poured into 50 ml of water, and the yellow precipitate which separated was dissolved in benzene–cyclohexane (1:1) and chromatographed through a column of neutral alumina. A benzene–cyclohexane (1:1) eluent gave 0.06 g (6%) of unchanged 9-benzylidenefluorene, mp 72–75°, and a benzene eluent gave 0.31 g (28%) of the yellow 9-(α-cyanobenzylidene) fluorene (IIb), mp 193–195°, ir 2200 cm^{-1} (CN) (lit.[18] mp 188–189°), after recrystallization of the residue from ethanol.

B. In DMF, Followed by Treatment with Air.—A mixture differing from that of A only in having two molecular equivalents of sodium cyanide (0.39 g, 0.008 mol) was stirred under nitrogen at room temperature for 30 min. Treatment of the black mixture for 2 hr with air afforded 0.08 g (7%) of nitrile IIb and 0.10 g of a colorless compound. The latter was eluted from the alumina column with ethanol and recrystallized from benzene to constant melting point (254–256° dec).

Anal. Calcd for $C_{21}H_{15}NO_2$: C, 80.48; H, 4.83; N, 4.47; mol wt, 313. Found: C, 80.05; H, 4.73; N, 4.77; mol wt, 313 (mass spectrum).

An infrared spectrum of the compound shows strong absorption at 3370 and 1685 cm^{-1}. The nmr spectrum, in DMF-d_7, shows,

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[17] (a) L. J. Bellamy in "The Infra-Red Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1957, p 128; (b) p 186.

[18] C. F. Koelsch, *J. Amer. Chem. Soc.*, **58**, 1328 (1936); **54**, 3384 (1932).

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

[20] Melting points are uncorrected and were determined with a Kofler microstage apparatus. Microanalyses were performed by Mr. J. Nemeth and his associates, and mass spectra were obtained by Mr. J. Wrona, with an Atlas CH4 spectrometer. A Perkin-Elmer 521 infrared spectrophotometer was employed for infrared spectra, which were run in potassium bromide disks, and nmr spectra were run on a Varian A-60 spectrometer, with tetramethylsilane as an internal reference.

[21] Y. Sprinzak, *J. Amer. Chem. Soc.*, **78**, 466 (1956).

[22] R. E. Allen, E. L. Schumann, W. C. Day, and M. G. Van Campen, *ibid.*, **80**, 591 (1958).

[23] J. L. Kice, *ibid.*, **80**, 350 (1958).

in addition to the complex aromatic absorption, a doublet at τ 3.95, with coupling constant 8 cps. The ratio of the areas is 14:1 (multiplet–doublet).

In a similar experiment in which the cyanide–hydrocarbon mixture was treated with oxygen instead of air, comparable yields of nitrile IIb and the compound of molecular formula $C_{21}H_{15}NO_2$ were obtained. When a cyanide–hydrocarbon mixture in DMSO was treated with air, a 19% yield of fluorenone was obtained as the sole product.

General Procedure for the Cyanation of 4a-Methyl-1,3,9-triphenyl-4aH-fluorene (Ia) and 9-Benzylidenefluorene (IIa) by Sodium Cyanide in the Presence of Oxidizing Agents Other than Molecular Oxygen (Table I).—A solution of hydrocarbon Ia (0.41 g, 0.001 mol) or hydrocarbon IIa (0.51 g, 0.002 mol) in 80 ml of the chosen solvent was placed in a 100-ml three-necked flask equipped with magnetic stirrer, a gas inlet tube dipping into the liquid, and a calcium sulfate drying tube. (In experiments with chromium trioxide, chloranil, DDQ, and ceric salts as the oxidizing agent, 30 ml of solvent was employed.) This solution was stirred under nitrogen for at least 45 min before two molecular equivalents of finely powdered sodium cyanide were added. The color of the resulting mixture was then allowed to develop for 1 hr before the oxidizing agent was added, either in solid form or as a solution in 10 ml of solvent, portionwise over a period of 30 min. (The solid ceric sulfate was added in three portions at hourly intervals, the crystal violet solution was added in two portions, with a 30-min interval between the additions, and the chloranil solution, in the case of hydrocarbon IIa, was added likewise in two portions.) At the termination of the reaction, 10 ml of water was added to the reaction mixture, the nitrogen stream was cut off, and the contents of the flask were poured into 300 ml of water. The hot aqueous mixture was agitated and acidified with a saturated solution of ammonium chloride. If a precipitate separated, it was filtered, washed with cold water, and dried, but, if an oil or an emulsion resulted, the mixture was extracted three times with benzene, the benzene fractions were combined, washed with water, dried over magnesium sulfate, and then evaporated *in vacuo*. The product from the reaction was finally dissolved in a minimum of benzene and added to a column containing silica gel (0.05–0.2 mm) suspended in cyclohexane. Elution with cyclohexane, followed by evaporation of the solvent *in vacuo*, separated any unchanged hydrocarbon present. Elution with cyclohexane and benzene (5:1) gave the unsaturated nitrile (cyanation product), and elution with benzene alone separated any saturated nitrile (hydrocyanation product) present. These compounds were isolated in a pure state from the column (as determined by their infrared spectra and melting points), and the yields quoted in Table I are calculated on the amount of material obtained directly from column chromatography, prior to any recrystallization.

The cyanation and hydrocyanation products of 4a-methyl-1,3,9-triphenyl-4aH-fluorene,[2a] and the cyanation product of 9-benzylidenefluorene,[18] have been reported. An analysis of 9-(α-cyanobenzyl)fluorene was obtained from a sample of the column product which had been recrystallized from 95% ethanol, as colorless crystals, mp 158–160°, ir 2240 cm^{-1} (CN).

Anal. Calcd for $C_{21}H_{15}N$: C, 89.64; H, 5.37; N, 4.98; mol wt, 281. Found: C, 89.57; H, 5.57; N, 4.88; mol wt, 281 (mass spectrum).

Oxidation of 4-Cyano-4a-methyl-1,3,9-triphenyl-3,4-dihydro-4aH-fluorene (VI) by Sodium 9,10-Anthraquinone-1-sulfonate in the Presence of Sodium Cyanide.—A solution of the nitrile (0.22 g, 0.0005 mol), in 80 ml of DMSO, was stirred under nitrogen for 45 min at 50°. Powdered sodium cyanide (0.10 g, 0.002 mol) was added and the mixture became faintly green after 1 hr. The quinone (0.40 g, 0.0013 mol) was then added, and the reaction mixture immediately developed a magenta color which became very intense after 30 min. After 3.5 hr, the mixture was diluted with water and acidified. The resulting yellow solid was filtered (0.21 g) and recrystallized from cyclohexane to afford orange crystals (0.19 g, 87%) of 4-cyano-4a-methyl-1,3,9-triphenyl-4aH-fluorene (Ib), mp 193–195°.

Oxidation of 9-(α-Cyanobenzyl)fluorene (VIIa) by Sodium 9,10-Anthraquinone-1-sulfonate in the Presence of (A) Sodium Cyanide.—The preceding reaction was repeated with 0.14 g (0.0005 mol) of nitrile VIIa, 0.20 g (0.00066 mol) of the quinone, and 0.05 g (0.001 mol) of sodium cyanide, but this time the sodium cyanide was added to a mixture of both the nitrile and the quinone, in 40 ml of DMSO. The yellow solid reaction product was chromatographed according to the general procedure and 0.03 g (24%) of nitrile IIb and 0.07 g (50%) of unchanged nitrile VIIa were isolated.

(B) Potassium *t*-Butoxide.—A reaction similar to A, with potassium *t*-butoxide (0.11 g, 0.001 mol) as the base, was run at room temperature for 30 min in 50 ml of DMSO containing 12 ml of *t*-butyl alcohol. Nitrile IIb was isolated in 57% (0.08 g) yield.

Cyanation of 9-(*p*-Bromobenzylidene)fluorene (IIc) by Sodium Cyanide in the Presence of (A) 9,10-Phenanthraquinone.—A solution of 9-(*p*-bromobenzylidene)fluorene (0.33 g, 0.001 mol) and phenanthraquinone (0.27 g, 0.0013 mol), in 80 ml of DMF, was stirred under nitrogen for 1 hr. Powdered sodium cyanide (0.10 g, 0.002 mol) was added, and the reaction mixture became dark red within 5 min. After 5 hr, the mixture was diluted with water and acidified. The yellowish brown precipitate was chromatographed according to the general procedure to give 0.01 g (3%) of unchanged starting material, mp 147.5–148°, and 0.26 g (74%) of 9-(α-cyano-*p*-bromobenzylidene)fluorene (IId), mp 166–168°. Elution with more polar solvents gave a yellow gum containing phenanthraquinone. An analytical sample of nitrile IId [mp 167–169°, ir 2185 cm^{-1} (CN)] was recrystallized from 95% ethanol.

Anal. Calcd for $C_{21}H_{12}BrN$: C, 70.39; H, 3.38; N, 3.91; Found: C, 70.47; H, 3.39; N, 3.61.

(B) Sodium 9,10-Anthraquinone-1-sulfonate.—A reaction similar to A was run for 9 hr with 0.66 g (0.002 mol) of 9-(*p*-bromobenzylidene)fluorene, 0.20 g (0.004 mol) of powdered sodium cyanide, and 0.62 g (0.002 mol) of sodium anthraquinone-1-sulfonate, in 80 ml of DMSO at 50°. Chromatography of the resulting yellow solid according to the general procedure yielded 0.41 g (58%) of nitrile IId and 0.10 g (14%) of nitrile VIIb. No starting material was recovered.

Cyanation of 9-Ethylidenefluorene (IIe) by Sodium Cyanide in the Presence of Sodium 9,10-Anthraquinone-1-sulfonate.—A solution of the hydrocarbon (0.58 g, 0.003 mol) and the quinone (0.93 g, 0.003 mol), in 80 ml of DMSO, was stirred under nitrogen for 1 hr at room temperature. Powdered sodium cyanide (0.29 g, 0.006 mol) was added and the reaction mixture became magenta within 5 min. After 5 hr, the mixture was diluted with water and acidified. Evaporation of benzene extracts at 40° gave a dark oil, which was chromatographed according to the general procedure to give 0.15 g (23%) of 9-(α-cyanoethylidene)fluorene (IIf) as a pale yellow solid and 0.23 g (35%) of 9-(α-cyanoethyl)fluorene (VIIc) as a colorless solid.

An analytical sample of nitrile IIf was recrystallized from 60–68° hexane in the form of pale yellow elongated prisms [mp 144–145°, ir 2200 cm^{-1} (CN)].

Anal. Calcd for $C_{16}H_{11}N$: C, 88.43; H, 5.10; N, 6.45; mol wt, 217. Found: C, 88.26; H, 5.18; N, 6.47; mol wt, 217 (mass spectrum).

An analytical sample of nitrile VIIc was recrystallized from 60–68° hexane in the form of colorless needles [mp 97.0–97.5°, ir 2238 cm^{-1} (CN)].

Anal. Calcd for $C_{16}H_{13}N$: C, 87.64; H, 5.97; N, 6.39; mol wt, 219. Found: C, 87.67; H, 6.09; N, 6.51, mol wt, 219 (mass spectrum).

Polymerization of 9-Ethylidenefluorene (IIe) by Sodium Cyanide.—A solution of the hydrocarbon (0.58 g, 0.003 mol) in 80 ml of DMSO was stirred under nitrogen for 45 min. Powdered sodium cyanide (0.30 g, 0.006 mol) was added and the reaction mixture became quite black after 30 min. It lightened in color to become reddish orange after 1 hr, but it then darkened and was black again by the end of the 48-hr reaction. Ammonium chloride crystals (0.159 g, 0.003 mol) were added, and the reaction mixture turned dark green. After 5 hr, the mixture was quenched with water and acidified. A pale yellow precipitate (0.58 g, mp 120–300°) was collected, dissolved in a minimum of benzene, and put on a silica gel column. Elution with cyclohexane gave no trace of unchanged hydrocarbon, but elution with cyclohexane and benzene (5:1) afforded an off-white solid (0.31 g). Benzene elution gave a yellow gum. The solid was digested with three 50-ml portions of 60–68° hexane, and the colorless residue was filtered off (0.12 g). Recrystallization from 60–68° hexane–chloroform yielded colorless, irregular prisms (0.10 g, mp 305–311°), whose analysis and molecular weight indicated a compound of molecular formula $C_{70}H_{58}N_2$. An infrared spectrum of this compound showed no nitrile absorption.

Anal. Calcd for $C_{70}H_{58}N_2$: C, 90.67; H, 6.30; N, 3.02; mol wt, 927. Found: C, 90.76; H, 6.15; N, 3.00; mol wt, 1004 (chloroform solution).

Evaporation of the 60–68° hexane solution to half-volume gave on refrigeration a crop of off-white, elongated prisms (0.03 g, mp 242–246°). An analysis and molecular weight determination of this compound were in agreement with those calculated for a trimer of the original hydrocarbon.

Anal. Calcd for $(C_{15}H_{12})_3$: C, 93.71; H, 6.29; mol wt, 577. Found: C, 93.20; H, 6.43; mol wt, 577 (mass spectrum) and 550 (chloroform solution).

Reaction of 9-Benzylidenefluorene (IIa) with Sodium Cyanide Followed by Treatment with (A) Ammonium Chloride Crystals. Preparation of 9-(α-Cyanobenzyl)fluorene (VIIa).—A solution of the hydrocarbon (1.02 g, 0.004 mol) in 80 ml of DMF was stirred under nitrogen at room temperature for 1 hr. Powdered sodium cyanide (0.80 g, 0.016 mol) was added, and the reaction mixture became black within 5 min. After 1 hr, ammonium chloride crystals (0.22 g, 0.004 mol) were added and the reaction mixture became yellow within 1 hr. After 4 hr, the mixture was diluted with water to yield 1.08 g (96%) of nitrile VIIa in the form of colorless crystals, mp 156–158°.

(B) **Carbon Dioxide.**—A mixture of the hydrocarbon (0.15 g, 0.002 mol) and sodium cyanide (0.98 g, 0.020 mol), in 20 ml of DMF, was stirred under nitrogen at room temperature. The mixture became black within 2 min. After 3 hr, stirring was interrupted and the flask was gently swept with carbon dioxide. When stirring was resumed, the mixture turned orange within 10 min and gradually became deep red. After 19 hr under carbon dioxide, the reaction mixture was diluted with water. The tan precipitate was collected and chromatographed according to the general procedure to give 0.26 g (46%) of nitrile VIIa, mp 156–158°.

(C) **Allyl Bromide.**—A mixture of the hydrocarbon (0.51 g, 0.002 mol) and sodium cyanide (0.98 g, 0.020 mol), in 20 ml of DMF, was stirred at room temperature under nitrogen. The reaction mixture became black within 4 min and was stirred under nitrogen for 30 min. The solution was then siphoned into a separatory funnel and added dropwise over a 10-min period to a stirred solution of allyl bromide (15 ml, 0.23 mol) in 10 ml of DMF. Distillation of the solvent and excess allyl bromide under reduced pressure and Soxhlet extraction of the resulting residue with benzene for 4 hr gave, after evaporation of the benzene, a reddish orange residue. Recrystallization of this residue from ethanol afforded 0.17 g (33%) of unchanged hydrocarbon, mp 75–76°.

Similar experiments were run in which mixtures of the hydrocarbon and sodium cyanide in DMF were treated with excesses of benzyl chloride and cyanogen bromide. In the case of benzyl chloride, 0.06 g (12%) of unchanged hydrocarbon was isolated as the only product, and, with cyanogen bromide, 0.28 g (55%) of unchanged hydrocarbon was recovered, together with 0.07 g (13%) of nitrile IIb.

Reaction of 9-(*p*-Bromobenzylidene)fluorene (IIc) with Sodium Cyanide Followed by Treatment with (A) Ammonium Chloride Crystals. Preparation of 9-(α-Cyano-*p*-bromobenzyl-fluorene (VIIb).—In an experiment similar to the hydrocyanation of hydrocarbon IIa, 0.25 g (70%) of nitrile VIIb was obtained from 0.33 g (0.001 mol) of bromo compound IIc in the form of colorless crystals, mp 200–202°. A second recrystallization of the nitrile from 95% ethanol afforded an analytically pure sample [mp 202–203°, ir 2230 cm^{-1} (CN)].

Anal. Calcd for $C_{21}H_{14}BrN$: C, 70.00; H, 3.92; 3.89; Found: C, 70.08; H, 3.96; N, 3.80.

(B) **Sulfur Dioxide.**—Treatment of a mixture of sodium cyanide (0.49 g, 0.010 mol) and 9-(*p*-bromobenzylidene)fluorene (0.67 g, 0.002 mol) in 15 ml of DMF, at room temperature under nitrogen, after 3.5 hr, with gaseous sulfur dioxide for 5 hr gave 0.10 g (15%) of starting material and 0.09 g (12%) of nitrile IId.

(C) **Dimethyl Sulfate.**—From a reaction similar to B, in which compound IIc in DMF was treated with sodium cyanide and then 1 ml of freshly distilled dimethyl sulfate, 0.41 g (61%) of unchanged hydrocarbon was recovered, together with 0.04 g (6%) of nitrile VIIb.

Reaction of 4a-Methyl-1,3,9-triphenyl-4aH-fluorene (Ia) with Sodium Cyanide Followed by Treatment with Ammonium Chloride. Preparation of 4-Cyano-4a-methyl-1,3,9-triphenyl-3,4-dihydro-4aH-fluorene (VI).—In an experiment similar to the hydrocyanation of hydrocarbon IIa, 0.41 g (0.001 mol) of hydrocarbon Ia yielded 0.33 g (76%) of nitrile VI, mp 274–276°.

Reaction of 4-Cyano-4a-methyl-1,3,9-triphenyl-3,4-dihydro-4aH-fluorene (VI) with Potassium *t*-Butoxide in DMF, Followed by Vacuum Evaporation of the Solvent.—A solution of the nitrile (0.33 g, 0.00075 mol) in 50 ml of DMF, contained in a flask equipped with a condenser set for distillation, was flushed with nitrogen for 1 hr. Potassium *t*-butoxide (0.165 g, 0.0015 mol) was added, and the intensely green color of the reaction mixture was developed for 3 hr. A receiving flask, immersed in Dry Ice–isopropyl alcohol and connected to a vacuum line, was then attached to the condenser, and the DMF was evaporated under nitrogen at 40° over a 25-hr period, leaving a dark residue. The residue was treated with an excess of water and an orange-yellow solid separated, which was completely soluble in cyclohexane (indicating the absence of any starting material). Chromatography of this solution on silica gel afforded 0.13 g (40%) of 4a-methyl-1,3,9-triphenyl-4aH-fluorene (Ia) as the only identifiable product.

Prolonged Reaction of 4a-Methyl-1,3,9-triphenyl-4aH-fluorene (Ia) with Sodium Cyanide in DMF.—A solution of the hydrocarbon (0.41 g, 0.001 mol) in 80 ml of DMF was stirred under nitrogen, at room temperature, for 2 hr before powdered sodium cyanide (0.20 g, 0.004 mol) was added. The green reaction mixture was stirred under nitrogen for 42 hr, and then ammonium chloride crystals (0.053 g, 0.001 mol) were added. Stirring was resumed and the reaction mixture became reddish brown within 2 min. After 5 hr, the reaction mixture was diluted and acidified to give a copious yellow precipitate which was chromatographed according to the general procedure; 0.32 g (74%) of nitrile Ib, mp 193–194°, and 0.04 g (9%) of nitrile VI, mp 273–274°, were isolated.

In an attempt to detect any possible formation of formaldehyde during this experiment, outflowing gases from the stirred mixture of hydrocarbon Ia and sodium cyanide in DMF were passed through a trap containing a dimedone solution. The DMF was then removed from the reaction mixture and treated with alkaline phloroglucinol (Jorissen's test[24]). In each case a negative result was obtained. (Jorissen's test was found satisfactory in DMF solutions by tests with trace amounts of formaldehyde.)

Prolonged Reaction of 9-Benzylidenefluorene (IIa) with Sodium Cyanide in DMF.—In a reaction similar to the preceding one, hydrocarbon IIa (0.51 g, 0.002 mol) in 80 ml of DMF was treated with powdered sodium cyanide (0.40 g, 0.008 mol) for 35 hr. Ammonium chloride crystals (0.11 g, 0.002 mol) were then added. Six hours later, 100 ml of degassed benzene was run into the dark brown reaction mixture. The reaction mixture was finally diluted with water and the two layers were allowed to separate. The benzene extract was chromatographed according to the general procedure to give 0.075 g (13%) of nitrile IIb, 0.13 g (23%) of nitrile VIIa, recrystallized from 95% ethanol, in the form of colorless fluffy needles, mp 156–158°, and 0.15 g (24%) of 9-cyano-9-(α-cyanobenzyl)fluorene (VIIIa) recrystallized from 95% ethanol as colorless prisms, mp 163–164°, ir 2250 cm^{-1} (CN).

Anal. Calcd for $C_{22}H_{14}N_2$: C, 86.26; H, 4.61; N, 9.15; mol wt, 306. Found: C, 86.07; H, 4.70; N, 9.17; mol wt, 306 (mass spectrum).

Reaction of 9-(α-Cyanobenzylidene)fluorene (IIb) with Sodium Cyanide in DMF Followed by Treatment with Ammonium Chloride. Preparation of 9-Cyano-9-(α-cyanobenzyl)fluorene (VIIIa).—A solution of the nitrile (0.84 g, 0.003 mol) in 200 ml of DMF was stirred under nitrogen for 1 hr. Powdered sodium cyanide (0.60 g, 0.012 mol) was added, and the reaction mixture became dark orange after 4 hr. Ammonium chloride crystals (0.32 g, 0.006 mol) were then added, and the reaction mixture was left stirring under nitrogen at room temperature. After 27 hr, the reaction mixture was diluted with water and acidified to give an off-white precipitate which was chromatographed on silica gel. Elution with cyclohexane and benzene (5:1) gave 0.025 g (3%) of unchanged nitrile IIb, and elution with benzene alone afforded 0.74 g (81%) of dinitrile VIIIa, mp 161–163°. This reaction was carried out on ten times the scale without loss of yield.

Hydrolysis of 9-Cyano-9-(α-cyanobenzyl)fluorene (VIIIa). Preparation of 9-Carboxy-9-(α-carboxybenzyl)fluorene (VIIIb) and Its Anhydride X.—A suspension of the dinitrile (0.30 g, 0.001 mol) in a mixture of concentrated sulfuric acid (5.0 ml), glacial acetic acid (3.0 ml), and water (5.0 ml) was refluxed at 130° for 5 hr. On dilution of the reaction mixture with water, 0.31 g (91%) of 9-carboxy-9-(α-carboxybenzyl)fluorene, mp 208–210°, was obtained. Recrystallization of the dicarboxylic

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[24] M. Jorissen, *J. Pharm. Chim*, **6**, 167 (1897).

acid, from petroleum ether (bp 90–110°)-acetone, gave an analytical sample in the form of colorless elongated prisms [0.28 g, mp 212–213°, ir 1700 cm^{-1} (CO)].

Anal. Calcd for $C_{22}H_{16}O_4$: C, 76.70; H, 4.68; mol wt, 344. Found: C, 76.62; H, 4.65; mol wt, 344 (mass spectrum).

A sample of the dicarboxylic acid (mp 208–210°) was recrystallized from benzene–acetone, and the analysis of the crystalline product (mp 207–210°) was in agreement with that calculated for a 1:1 inclusion complex between the acid and benzene.

Anal. Calcd for $C_{22}H_{16}O_4 \cdot C_6H_6$: C, 79.60; H, 5.25. Found: C, 79.91; H, 5.25.

Sublimation of this inclusion complex (0.04 g) at 125° and 3.00 mm, yielded a sublimate of the acid anhydride (X) in the form of colorless crystals (0.035 g, 92%, mp 183.5–185°).

Anal. Calcd for $C_{22}H_{14}O_3$: C, 80.97; H, 4.32; mol wt, 326. Found: C, 80.67; H, 4.31; mol wt, 326 (mass spectrum).

Reduction of 9-Carboxy-9-(α-carboxybenzyl)fluorene (VIIIb). Preparation of 9-Hydroxymethyl-9-(α-hydroxymethylbenzyl)fluorene (VIIIc).—A solution of the dicarboxylic acid (1.40 g, 0.004 mol) in anhydrous ether (100 ml) was added dropwise, over a period of 1 hr, to a stirred suspension of lithium aluminum hydride (1.60 g, 0.04 mol) in anhydrous ether (250 ml). The reaction mixture was refluxed for 4 hr. It was then cooled in an ice and salt bath and treated carefully with 20 ml of water and 200 ml of a 10% hydrochloric acid solution; the layers were separated. The aqueous layer was extracted three times with ether and the extracts were combined with the ether layer. Evaporation of the ether left a colorless semisolid gum which, on trituration with 60–68° hexane containing a trace of benzene, afforded a white crystalline solid, 0.84 g. This solid was recrystallized from hexane (bp 60–68°)–benzene to give 0.72 g (56%) of 9-hydroxymethyl-9-(α-hydroxymethylbenzyl)fluorene (VIIIc) as colorless irregular prisms [mp 123–125°, ir 2925 and 2880 cm^{-1} (CH_2)].

Anal. Calcd for $C_{22}H_{20}O_2$: C, 83.49; H, 6.37; mol wt, 316. Found: C, 83.67; H, 6.53; mol wt, 316 (mass spectrum).

Oxidation of 9-Hydroxymethyl-9-(α-hydroxymethylbenzyl)fluorene (VIIIc). Preparation of 9-(α-Carboxybenzyl)-9-hydroxymethylfluorene Lactone (XI).—A solution of the glycol (0.30 g, 0.00095 mol) in anhydrous pyridine (3 ml) was added dropwise to a slurry of Sarett's reagent (5 ml), prepared from chromium trioxide and anhydrous pyridine.[25] The mixture was stirred at room temperature for 10.5 hr; then it was treated with 20 ml of water to complete the separation of the product. The resulting tan solid had very little solubility in a wide range of organic solvents. It was extracted with boiling chloroform and a nearly colorless gum was obtained upon evaporation of the solvent. The gum crystallized from hexane (bp 60–68°)–benzene, and the product was recrystallized from the same solvent mixture to give colorless crystals, 0.08 g (27%), of the lactone (XI), mp 172–175°.

Anal. Calcd for $C_{22}H_{16}O_2$: C, 84.55; H, 5.16; mol wt, 312. Found: C, 84.38; H, 5.26; mol wt, 312 (mass spectrum).

Catalytic Hydrogenation of 9-(α-Cyanobenzylidene)fluorene (IIb).—The nitrile (0.28 g, 0.001 mol), in 100 ml of ethanol, was stirred in a 125-ml hydrogenation flask and hydrogenated at atmospheric pressure with 30% palladium–charcoal as catalyst (0.015 g) for 3.5 hr. The filtered solution afforded a colorless residue, on evaporation, which was recrystallized from ethanol to give 0.14 g (50%) of nitrile VIIa, mp 157–159°.

Benzylation of 9-Cyanofluorene with Benzyl Chloride and Sodium Methoxide. Preparation of 9-Benzyl-9-cyanofluorene.—The procedure used is that described by Anet and Bavin[19] for the benzylation of methyl fluorene-9-carboxylate.

To a stirred solution prepared from sodium (0.68 g, 0.030 g-atom) and 25 ml of methanol was added, at room temperature, 9-cyanofluorene (1.91 g, 0.010 mol), prepared according to the method of King and his coworkers.[26] Benzyl chloride (6 ml, 0.052 mol) was added dropwise over a 5-min period to the orange-brown solution, and the reaction mixture was stirred at room temperature for 12 hr. It was then poured into 60 ml of a mixture of ice and 5% hydrochloric acid solution. The mixture was extracted twice with chloroform and the extracts were washed with 5% sodium bicarbonate solution and evaporated. The liquid residue was then dissolved in ether and the solution washed with 15% aqueous ammonia solution. Evaporation of the ether solution gave crystals which were washed with acetone and recrystallized from ethanol to give 1.70 g (61%) of the colorless 9-benzyl-9-cyanofluorene, mp 120–122°. A second recrystallization from ethanol gave an analytically pure sample [mp 122–123°, ir 2230 cm^{-1} (CN)].

Anal. Calcd for $C_{21}H_{15}N$: C, 89.63; H, 5.37; N, 4.98; mol wt, 281. Found: C, 89.53; H, 5.64; N, 4.95; mol wt, 281 (mass spectrum).

An nmr spectrum of the compound in deuteriochloroform shows a singlet at τ 6.66, for the two methylene protons.

Catalytic Hydrogenation of 9-(α-Cyanoethylidene)fluorene (IIf). Preparation of 9-(α-Cyanoethyl)fluorene (VIIc).—A solution of the nitrile (0.10 g, 0.00046 mol) in ethanol (50 ml) was hydrogenated at 20 lb/in.^{2} for 2 hr, in the presence of 30% palladium on charcoal (0.02 g). The filtered solution afforded a brown, oily residue, on evaporation, which was charcoaled in hexane (bp 60–68°). The hexane solution was then concentrated and 9-(α-cyanoethyl)fluorene (VIIc) separated in the form of colorless crystals (0.05 g, 50%, mp 96–96.5°).

Registry No.—Ib, 19656-46-3; IIb, 19656-47-4; IId, 19656-48-5; IIf, 19656-49-6; VI, 10229-35-3; VIIa, 19656-51-0; VIIb, 19656-52-1; VIIc, 19656-53-2; VIIIa, 19656-54-3; VIIIb, 19656-55-4; VIIIc, 19656-56-5; X, 19656-57-6; XI, 19656-58-7; 9-benzyl-9-cyanofluorene, 19656-59-8.

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(25) W. J. Hickinbottom in "Reactions of Organic Compounds," Longmans, Green and Co., London, 1959, p 132.

(26) J. A. King, R. I. Meltzer, and J. Doczi, *J. Amer. Chem. Soc.*, **77**, 2217 (1955).