isopropyl ketone. From 0.5 mole of ketone and 0.5 mole of sulfuryl chloride there was obtained 57.3 g. (84%) of 2-chloro-2,4-dimethylpentanone-3, b.p. 143–145°, lit.[23] b.p. 142–143°. The n.m.r. spectrum (neat liquid) of this compound consisted of a multiplet, τ 6.55; singlet, 8.31; doublet, 8.34; in the ratio of 1:5.83:5.78, respectively. A higher boiling compound (approximately 5% yield), presumably 2,4-dichloro-2,4-dimethylpentanone-3, was detected *via* v.p.c. The yield of the main product, 2-chloro-2,4-dimethylpentanone-3 was 94% according to v.p.c.

Chlorination of Desoxybenzoin.—Sulfuryl chloride (0.5 mole) was added dropwise to 0.5 mole of desoxybenzoin over a period of 20 min. The rate of addition was such that the temperature of the reaction mixture did not exceed 40°. The viscous yellow liquid which formed was stirred at room temperature ($\sim$22°) for 2 hr. It slowly solidified to a white crystalline solid. The temperature rose to 55° during the course of the solidification ($\sim$20 min.). The yield of crude product was 117 g. A portion of this material was recrystallized from petroleum ether (b.p. 60–70°) to yield white needles, m.p. 65.0–65.5°. A mixture of this material with deoxybenzoin had m.p. 37–39°. An analytical sample (m.p. 66–66.25°) was obtained by recrystallizing the crude product three times from petroleum ether. A mixture with authentic desyl chloride melted at 66–67°.

Chlorination of Phenylacetone.—Phenylacetone (0.25 mole) was chlorinated by the dropwise addition to it of 0.25 mole of sulfuryl chloride. The reaction was exothermic and the addition was conducted over a period of 25 min. at such a rate that the temperature did not exceed 40°. Upon distillation there was obtained 40.2 g. (95%) of 1-chloro-1-phenylacetone, b.p. 123–124° at 30 mm., $n^{25}\mathrm{D}$ 1.5339. The n.m.r. spectrum of this compound consisted of two singlets, τ 4.53 and 7.42, as well as the aromatic protons below τ 3 in the intensity ratio of 1:3.12:5.34, respectively. Analysis by v.p.c. indicated that $\sim$3% of 1-phenylpropanone-2 and trace amounts of two higher boiling components, presumably 1-phenyl-3-chloropropanone-2 and 1,1-dichloro-1-phenylpropanone-2, were also present.

Chlorination of 1,1-Diphenylacetone.—Reactions were conducted with 0.05 mole of ketone and 0.05 mole of sulfuryl chloride in carbon tetrachloride solvent or without solvent. The reaction in carbon tetrachloride (50 ml.) was terminated after 6 hr. (at room temperature) by pouring the reaction solution onto 200 g. of a mixture of ice and water. The carbon tetrachloride layer was removed and then dried over anhydrous calcium chloride. Removal of the carbon tetrachloride *in vacuo* left a light yellow liquid residue which was separated by preparative gas chromatography into two components. The first of these was unconverted 1,1-diphenylacetone while the second was 1,1-diphenyl-1-chloropropanone-2. This structure was assigned on the basis of the infrared spectrum, which showed strong methyl absorption at 7.25 μ; the n.m.r. spectrum (carbon tetrachloride solution), which showed aromatic protons at τ $\sim$2.8 and a sharp singlet at 7.75, in the ratio of 3.71:1, respectively; as well as the elemental analysis which showed that the compound contained only one chlorine atom.

Anal. Calcd. for $C_{15}H_{13}ClO$: C, 73.70; H, 5.32; Cl, 14.50. Found: C, 73.58; H, 5.19; Cl, 14.48.

The yield of 1,1-diphenyl-1-chloropropanone-2 under these conditions was 53%. In a similar reaction conducted without solvent the yield of the same product was 77% after 24-hr. reaction at room temperature. Only traces (<1%) of a slightly higher boiling product, presumably 1,1-diphenyl-3-chloropropanone-2, were detected.

Synthesis of 1,2,3-triphenylpropanone-1.—Desoxybenzoin (98 g., 0.5 mole) was dissolved in 300 ml. of refluxing, anhydrous ethanol which contained 28 g. (0.5 mole) of potassium hydroxide. Benzyl chloride (64 g., 0.505 mole) was added dropwise to the refluxing solution over a period of 1 hr. The mixture was stirred and refluxed an additional 4 hr. after the addition. The reaction mixture was allowed to cool to room temperature, and then it was diluted with 1 l. of cold water. Crude 1,2,3-triphenylpropanone-1 (115 g., 80%) separated in the form of a tan crystalline solid. It was recrystallized from petroleum ether in the form of fine white needles, m.p. 125°, lit.[24] m.p. 122.

Attempted Chlorination of 1,2,3-Triphenylpropanone-1.—Attempts were made to chlorinate the compound in benzene, in carbon tetrachloride, and without solvent in a threefold excess of sulfuryl chloride. No evidence of reaction was found (no hydrogen chloride or sulfur dioxide evolution). In each case the starting ketone could be recovered without change (infrared and mixture melting point) after 24 hr. at room temperature.

Chlorination of a Mixture of Acetone and Phenylacetone.—Sulfuryl chloride (34 g., 0.25 mole) was added dropwise over a period of 30 min. to a well-stirred mixture of acetone (0.25 mole) and phenylacetone (0.25 mole). The temperature of reaction was kept below 40° by adjusting the rate of addition. Stirring was continued for 1 hr. after addition and then the crude mixture (a light yellow liquid) was analyzed by v.p.c. It consisted of 82% of 1-phenyl-1-chloroacetone, 14% of 1-chloropropanone-2, and traces of other components (yields are based on sulfuryl chloride).

Acknowledgment.—We are indebted to Mr. Carl Lindemann and Mr. Frank Michalek for the gas chromatographic separations, and to Dr. B. L. Shapiro for helpful discussions concerning the n.m.r. spectra and other phases of this program.

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[23] F. Asinger, M. Thiel, and V. Tesar, *Ann. Chem.*, **619**, (1958).

[24] A. McKenzie, R. Roger, and G. O. Wills, *J. Chem. Soc.*, 779 (1926)

Nitration and Acetylation of 9-Alkylfluorenes[1]

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The products from nitration and acetylation of some 9-alkylfluorenes have been investigated. Nitration gave either 2-nitro derivatives (12–38% yield) or 2,9-dinitro (tentative assignment) derivatives (33–60% yield). Monoacetylation occurred in 60–75% yield. Successive steps of oxime formation and Beckmann rearrangement converted the acetyl derivatives into acetylamino compounds. In one case (9-methylfluorene), the acetyl group was shown to occupy the 2-position. Air oxidation of the monoacetyl-9-ethylfluorene gave a crystalline product, assigned the structure of 2-acetyl-9-ethyl-9-fluorenyl hydroperoxide.

The high carcinogenic activities of 2-fluorenamine and related compounds have been recognized for some years.[4] In this respect, it seemed of interest to prepare similar derivatives of 9-alkylfluorenes for biological investigations. The present study is concerned with the syntheses and structural determinations of primary substitution products of 9-alkylfluorenes, obtained through processes of nitration and acetylation of the parent hydrocarbons Ia–d (Scheme I).

In an effort to prepare 2-nitro-9-alkylfluorenes, we followed the same general procedure (concentrated

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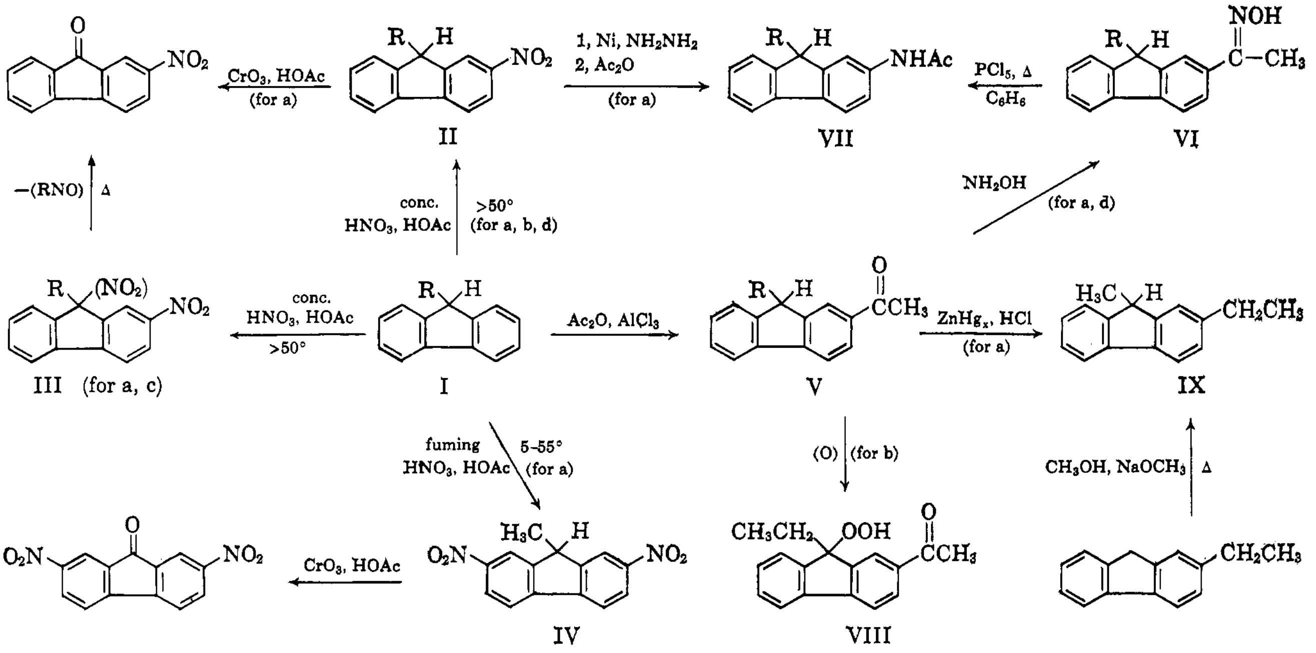
[4] E. K. Weisburger and J. H. Weisburger, "Advances in Cancer Research," Vol. 5, J. P. Greenstein and A. Haddow, Ed., Academic Press, Inc., New York, N. Y., 1958, pp. 331–431.

SCHEME I



a, R = Me; b, R = Et; c, R = *n*-Pr; d, R = *i*-Pr

nitric acid in glacial acetic acid at 50° and above) as was used to convert fluorene into 2-nitrofluorene in good yield.[5] For the isopropyl compound Id, the reaction proceeded similarly although the yield of mononitro derivative IId was considerably smaller (38%). However, with the 9-alkylfluorenes Ia and b, the reaction proved to be sufficiently exothermic that it was difficult to control the temperature in the same manner. Although the exact reasons for the differences are not yet clear, in two runs there resulted small yields (12–16%) of mononitro derivatives IIa and b, while in another run (with Ia), the product A, m.p. 185°, isolated in 60% yield, had an elemental composition consistent with the molecular formula $C_{14}H_{10}N_2O_4$. Analogously Ic formed B, $C_{16}H_{14}N_2O_4$, in 33% yield. Direct comparison of A with a synthetic sample of the dinitro-9-methylfluorene, prepared by means of fuming nitric acid in glacial acetic acid at 5–55° according to the directions of Wawzonek, Dufek, and Sial,[6] showed that the two compounds were different. Although Wawzonek, *et al.*, assigned a structure of 2,7-dinitro-9-methylfluorene (IV) to their product, they did not prove this structure.

For structural determinations on the preceding compounds, the following procedures were used. First of all, oxidation of the Wawzonek dinitro derivative served to confirm their suggested structure since it gave 2,7-dinitrofluorenone, identical (as based on several criteria) with an authentic sample prepared similarly from 2,7-dinitrofluorene. Likewise, oxidation of our mononitro-9-methylfluorene yielded 2-nitrofluorenone.[7] Pyrolysis of A or B produced a colorless gas (which turned reddish-brown on contact with air) and left a residue of 2-nitrofluorenone (corresponding to the loss of the elements of nitroso alkane). Oxidation of B (A was not investigated) likewise gave 2-nitrofluorenone. N.m.r. spectra of A and B showed no absorption band in the immediate vicinity of δ = 3.8 p.p.m., where absorption due to the lone hydrogen atom on the 9-position of 2-nitro-9-methylfluorene and of various other 2-substituted 9-alkylfluorenes occurs. Moreover, these spectra (*vide infra*) indicate that the alkyl groups are intact. It is thus apparent that the second nitro moiety must occupy the 9-position.

The action of nitric acid on alkylarenes has been reviewed by Topchiev.[8] As applied to the formation of A or B, it would appear that nitration in the 2-position (electrophilic substitution) should occur preferentially during the early stages of the reaction, but later in the process the effects of increasing dilution (by means of the water formed) of the nitric acid and of rising temperature should be to favor free-radical substitution of the tertiary hydrogen (which is also α to both aromatic rings) in the 9-position by an –OH, –NO, –NO_2, or –ONO group. Although an OH–NO combination would fit the analytical data, it is inconsistent with the aforementioned n.m.r. spectra and the absence of any OH band in the infrared spectra. The presence of interfering absorption by the 2-nitro group, moreover, prevented use of infrared or ultraviolet spectra for distinguishing between the 9-nitro and 9-nitrite possibilities in the manner applicable to monofunctional derivatives.[9]

A survey of the literature shows that 9-nitro-,[10] 9,9-dinitro-,[11] and 2,9-dinitrofluorenes[12] have been reported and found to undergo thermal decomposition

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[5] W. E. Kuhn, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons' Inc., New York, N. Y., 1943, pp. 447, 448.

[6] S. Wawzonek, E. Dufek, and N. M. Sial, *J. Org. Chem.*, **21**, 276 (1956); see also G. B. Bachman and S. Polansky, *ibid.*, **16**, 1690 (1951).

[7] The structures of the other mononitro derivatives, IIb and d, are assigned by analogy with IIa.

[8] A. V. Topchiev, "Nitration of Hydrocarbons and Other Organic Compounds," Pergamon Press, Inc., New York, N. Y., 1959, pp. 155–179; see also A. I. Titov, *Tetrahedron*, **19**, 557 (1963).

[9] J. F. Brown, *J. Am. Chem. Soc.*, **77**, 6341 (1955); L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 17; H. E. Ungnade and R. A. Smiley, *J. Org. Chem.*, **21**, 993 (1956).

[10] W. Wislicenus and M. Waldmüller, *Ber.*, **41**, 3334 (1908); C. D Nenitzescu and D. A. Isacescu, *ibid.*, **63**, 2484 (1930).

[11] H. Wieland and C. Reisenegger, *Ann.*, **401**, 244 (1913).

[12] W. Wislicenus and H. Weitemeyer, *ibid.*, **436**, 1 (1924).

near their melting points with the evolution of oxides of nitrogen and the formation of fluorenone (in the first two cases) or 2-nitrofluorenone (in the third case). The possibility that these "9-nitrofluorenes" were actually "9-fluorenyl nitrites" instead was not considered. The thermal instability (to form initially nitrosomethane and acetone) of *t*-butyl nitrite is well known.[13] However, both triphenylmethyl nitrite and triphenylnitromethane appear to be thermally unstable.[14] Pending a thorough investigation of the various "9-nitrofluorene" cases, we tentatively designate compounds A and B by the simpler terminology of 2,9-dinitro-9-alkylfluorenes.

Acetylation of three 9-alkylfluorenes (R = Me, Et, *i*-Pr) was conducted by means of the Friedel–Crafts method using acetic anhydride, aluminum chloride, and nitrobenzene. Yields of 60–75% of monoacetyl derivatives (V) were obtained. In the methyl and isopropyl cases, the ketones were first converted to oximes (80% yield of VI) by means of pyridine and hydroxylammonium chloride and then to their acetylamino derivatives (VII, 45% yield) through Beckmann rearrangement. That the acetylamino group in VIIa (and, hence, also the $CH_3C(=NOH)-$ group in VIa and the acetyl group in Va) occupies the 2-position in the fluorene ring was established[15] by comparison of the amide from Beckmann rearrangement with that derived by catalytic reduction, and subsequent acetylation, of 2-nitro-9-methylfluorene (IIa). Although the two amides were obtained in somewhat different crystalline forms, they had identical melting points (undepressed on admixture) and infrared spectra (in chloroform solution). As a synthetic pathway to VIIa from the parent hydrocarbon 9-methylfluorene the route *via* the acetyl derivative (26% over-all yield) is clearly superior to that *via* the nitro derivative (16% yield on first step).

The structural assignment of 2-acetyl-9-methylfluorene (Va) was corroborated by a second series of transformations, wherein Va was reduced by the Clemmensen method to 2-ethyl-9-methylfluorene (IX), a liquid hydrocarbon likewise available from methylation of authentic 2-ethylfluorene by means of sodium methoxide in methanol at elevated temperatures (in the manner used for the synthesis of 9-methylfluorene from fluorene).[16] Proof of identity of the two samples of IX was hampered by the fact that autooxidation slowly occurs, presumably to form mixtures of IX and oxygenated derivatives, on standing in contact with air.[17] The pure hydrocarbons, however, were separable by means of vapor phase chromatography and showed identical, expected infrared spectra when fresh.

A minor product (m.p. 161°, 4% yield) was also obtained from acetylation of 9-ethylfluorene, where vacuum distillation (using an air bubbler) was employed in processing the product. In contrast, no minor products were isolated from acetylation of the homologous methyl and isopropyl compounds, where vacuum distillation was not used. This by-product had an elemental composition consistent with the formula $C_{17}H_{16}O_3$ and exhibited an OH– stretching band in its infrared spectrum. The n.m.r. spectrum showed no absorption in the region of 3.9 p.p.m., where a triplet (ascribed to the presence of a single hydrogen on C-9) occurs in the spectrum of 2-acetyl-9-ethylfluorene (Vb). Inasmuch as this compound gave a positive test with starch–iodide paper and could be synthesized by air oxidation of Vb, it is assigned the structure of 2-acetyl-9-ethyl-9-fluorenyl hydroperoxide (VIII).[18]

In Table I are presented pertinent data on the aliphatic proton absorption patterns in the n.m.r. spectra of fluorene and various derivatives of it. Examination of the table shows, as expected, the presence of a doublet for the 9-methyl group and a quartet for the 9-hydrogen for both 9-methylfluorene and 2-nitro-9-methylfluorene. The change to a singlet (at lower field) for the 9-methyl group and the loss of absorption for the 9-hydrogen are consistent with the structural assignment given to 2,9-dinitro-9-methylfluorene. A somewhat similar, but more complex, relationship can be noted between 9-*n*-propylfluorene and 2,9-dinitro-9-*n*-propylfluorene. Thus, in the nitro derivative the multiplet for the α-methylene hydrogens of the *n*-propyl group is shifted to lower field while absorption due to the 9-hydrogen (a triplet in the hydrocarbon) is missing. The superimposed absorption bands (consisting of two intense, but unequal, peaks plus a number of weak peaks) for the β-methylene plus methyl protons have closely similar shapes in both compounds. In 2-nitro-, 2-acetyl-, and 2-acetylamino-9-isopropylfluorene the expected doublet for the 9-hydrogen occurs at *ca.* 3.8 p.p.m. However, except for the third compound in one solvent (benzene), two doublets (centered at *ca.* 0.8 p.p.m.) appear for the methyl groups when only one might have been expected. Moreover, in the 2-nitro derivative the multiplet at *ca.* 2.5 p.p.m. shows at least ten peaks. It is proposed that the occurrence of the two doublets (and possibly of the decet or higher multiplet) may be ascribed to nonequivalence of the two methyl groups in the isopropyl substituent.[19] For the acetylamino derivative (which was investigated in three solvents) the magnitude of the primary splitting in these doublets (*ca.* 7 c.p.s.) did not vary significantly with change in solvent, while that of the secondary splitting (0 in benzene, 1.2 in pyridine, and 3 c.p.s. in deuteriochloroform) was solvent dependent. In contrast, for the parent hydrocarbon 9-isopropylfluorene no secondary splitting occurs even in deuteriochloroform.

Experimental[20]

2-Nitro-9-methylfluorene (IIa).—To a stirred solution of 18 g. (0.1 mole) of 9-methylfluorene[16] in 140 ml. of glacial acetic acid at 50–55° was added dropwise, over a period of 15 min., 22 ml. of concentrated nitric acid (69%). The temperature rose spontaneously to 65–70°. After 10 min. at this temperature, the mixture was gradually (over 2 hr.) cooled to room temperature and then poured into 2 l. of water. The pasty precipitate which formed on standing was dissolved in 50 ml. of

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(13) J. B. Levy, *Ind. Eng. Chem.*, **48**, 762 (1956); P. Gray, *Chem. Ind.* (London), 120 (1960).

(14) W. Schlenk, L. Mair, and C. Bornhardt, *Ber.*, **44**, 1169 (1911); J. N. Ray, *J. Chem. Soc.*, **117**, 1335 (1920).

(15) By analogy with Va, the acetyl groups in Vb and d are also assumed to occupy the 2-position of the fluorene nucleus.

(16) K. L. Schoen and E. I. Becker, *Org. Syn.*, **39**, 43 (1959).

(17) Y. Sprinzak, *J. Am. Chem. Soc.*, **80**, 5449 (1958); see also ref. 27.

(18) For a review of the literature on alkyl hydroperoxides, see A. G. Davies, "Organic Peroxides," Butterworths, London, 1961, Chapter 1.

(19) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, pp. 18–19.

(20) Microanalyses were performed by Micro-Tech Laboratory, Skokie, Ill. Ultraviolet absorption spectra were obtained by means of a Cary Model 11 spectrophotometer, infrared spectra, by means of a Beckman IR-7 instrument.

TABLE I

MAGNETIC RESONANCE CHARACTERISTICS AND ASSIGNMENTS FOR PROTONS ON AL'PHATIC CARBON ATOMS IN SOME SUBSTITUTED FLUORENES

Substituent(s) on fluorene			Characteristics and assignments,[b] δ, p.p.m.[c] (multiplicity),[d] J, c.p.s.		
9-Position	2-Position	Solvent[a]	9-H[e]	9-Alkyl substituent	2-Substituent
H, H	H	A	(s)		
H, H	Ac	A	(s)		2.44 (s)
H, Me	H	A	(q) 7.5	1.40 (d) 7.5	
H, Me	NO_2	A	(q) 7.5	1.38 (d) 7	
NO_2, Me	NO_2	B	*f*	2.26 (s)	
H, Me	Ac	A	(q) 7.5	1.49 (d) 7.5	2.51 (s)
H, Me	Et	A	(q) . . .[g]	1.5 (d) 7	2.7 (q) 7[h] 1.2 (t) 7[i]
H, Me	NHAc	C	(q?) . . .[g]	1.43 (d) 7	2.14 (s)
H, Et	Ac	A	(t) 6	2.07 (m) . . .[g, h]; 0.67 (t) 7.5[i]	2.52 (s)
H, Et	NO_2	A	(t) 6	2.04 (m) . . .[g, h]; 0.66 (t) 7.5[i]	
HOO, Et	Ac	B	*f*	*ca* 2.4 (m) . . .[g, l]; 0.60 (t) 7.5[i]	2.49 (s)[l]
H, *n*-Pr	H	A	(t) 6	*ca.* 1.8 (m) . . .[g, j]; *ca.* 0.8 (m) . . .[g, k]	
NO_2, *n*-Pr	NO_2	A	*f*	*ca.* 2.5 (m) . . .[g, j]; *ca.* 0.8 (m) . . .[g, k]	
H, *i*-Pr	H	C	(d) 3.5	*ca.* 2.5 (m) . . .[g]; 0.82 (d) 7	
H, *i*-Pr	Ac	A	(d) 3.5	*ca.* 2.5 (m) . . .[l]; 0.82 (2d)[m]	2.5 (s)[l]
H, *i*-Pr	NO_2	A	(d) 4	*ca.* 2.5 (m) 4; 0.82 (2d)[n]	
H, *i*-Pr	NHAc	B	(d) 3.5	*ca.* 2.5 (m) . . .[g]; 0.81 (2d)[n]	2.23 (s)
H, *i*-Pr	NHAc	C	(d) 3.5	*ca.* 2.4 (m) . . .[g]; 0.77 (2d)[o]	2.14 (s)
H, *i*-Pr	NHAc	D	(d) 3.5	. . .[p]; 0.77 (d) 7	1.78 (s)

[a] A represents carbon tetrachloride; B, pyridine; C, deuteriochloroform; D, benzene. [b] Using tetramethylsilane as internal standard. [c] Given for 9-alkyl and 2-substituents only. [d] Singlet, s; doublet, d; triplet, t; quartet, q; multiplet, m. [e] $\delta = 3.58$ p.p.m. for the 9-hydrogen atoms in fluorene itself and 3.8 ± 0.1 for those in all of the other compounds listed. [f] No absorption near 3.8 p.p.m. [g] Resolution or concentration was inadequate to allow a suitable determination of *J*. [h] Methylene. [i] Methyl. [j] α-Methylene in the substituent. [k] Methyl plus β-methylene in the substituent. [l] Intense singlet (2-acetyl) superimposed on weak multiplet (methylene hydrogens on ethyl group or lone hydrogen on isopropyl group). [m] Two doublets: $J = 7.5$ c.p.s. for primary splitting and 2 c.p.s. for secondary splitting. [n] Two doublets: $J = 7$ c.p.s. for primary splitting and 1.2 c.p.s. for secondary splitting. [o] Two doublets: $J = 7$ c.p.s. for primary splitting and 3 c.p.s. for secondary splitting. [p] No absorption was detected above the noise level in the spectrum.

toluene. Addition of 150 ml. of cyclohexane to the toluene solution gave a precipitate which was recrystallized twice from methanol, yielding 3 g. of yellow crystals, m.p. 82–83°. Residues from evaporation of the organic layers were dissolved in the minimal quantity of chloroform and chromatographed on a 3.8 × 30 cm. column of Mallinckrodt silicic acid using 30–60° petroleum ether–benzene (4:1 v./v.) as eluent. The effluent furnished 0.7 g. more of product, m.p. 83–84° (total yield 16%). Recrystallization from absolute ethanol gave a sample for analysis, m.p. 84–85°, slightly yellow needles; $\lambda_{\max}^{\mathrm{Et_2O}}$ 237 mμ (log ε 4.25) and 327 (4.67).

Anal. Calcd. for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.22. Found: C, 74.61; H, 4.96; N, 6.38.

2-Nitro-9-ethylfluorene (IIb).—Nitration of 0.1 mole of 9-ethylfluorene[16] was conducted by the preceding method. The temperature rose more rapidly but was prevented from exceeding 83°. The toluene layer was washed with water, dried, and evaporated to leave a residue which was recrystallized from methanol, yielding 12%, m.p. 69–70°. Further recrystallizations gave yellow shiny leaves, m.p. 70–71°.

Anal. Calcd. for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N, 5.85. Found: C, 75.09; H, 5.36; N, 6.20.

2-Nitro-9-isopropylfluorene (IId).—This was prepared from 9-isopropylfluorene[21] in the manner used for IIb, except that it was necessary to apply external heat in order to bring the reaction temperature up to 80°, yield 38%, m.p. 78–80°. Recrystallization from absolute ethanol gave faintly yellow prisms, m.p. 79.5–80.5°.

Anal. Calcd. for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.68; H, 5.99; N, 5.57.

2,9-Dinitro-9-methylfluorene (IIIa).—The nitration was conducted using 2.5 times the quantities of reagents employed for the preparation of IIa, but the same period of 15 min. for addition. Over *ca.* 40 min. the temperature of the reaction mixture was increased to 80°, where it was kept for 5 min. Then it was allowed to decrease to 20° over a period of 2.5 hr. The red-brown crystals which precipitated from the reaction mixture were separated, washed twice (using a solution of 0.5 g. of sodium acetate in 25 ml. of glacial acetic acid each time), and dried *in vacuo*. A second crop was obtained on pouring the mother liquor into water, to give a total yield of 40.3 g. (60%), m.p. 175–179°. Four recrystallizations from glacial acetic acid and one from toluene gave yellow needles, m.p. 184–185°; $\lambda_{\max}^{\mathrm{Et_2O}}$ 214 mμ (log ε 4.63), 241 (4.25), and 322 (4.57).

Anal. Calcd. for $C_{14}H_{10}N_2O_4$: C, 62.22; H, 3.73; N, 10.37. Found: C, 62.04; H, 4.01; N, 10.22.

2,9-Dinitro-9-*n*-propylfluorene (IIIc).—Following the preceding method, 52 ml. of concentrated nitric acid was added to a solution of 50 g. (0.24 mole) of 9-*n*-propylfluorene[16] in 330 ml. of glacial acetic acid. As the temperature was raised to 80°, however, an exothermic reaction suddenly occurred and the reaction temperature rose spontaneously to 110°. The mixture was cooled to 75° over a period of 2 min. and then subsequently to room temperature over a period of 2 hr. The pasty precipitate which formed on pouring the mixture into 1.5 l. of water was collected and recrystallized once from ethanol, yielding 23.6 g. (33%), m.p. 95–108°. Four recrystallizations from toluene and one from ethanol gave yellow prisms, m.p. 111–112°; $\lambda_{\max}^{\mathrm{Et_2O}}$ 216 mμ (log ε 4.71), 241 (4.35), and 324 (4.62).

Anal. Calcd. for $C_{16}H_{14}N_2O_4$: C, 64.42; H, 4.73; N, 9.39. Found: C, 64.66; H, 4.87; N, 9.35.

Oxidation of Nitrofluorenes. A.—Synthetic 2-nitrofluorenone, m.p. 220–221°, was obtained by nitration of fluorene[5] and subsequent oxidation with chromium trioxide in glacial acetic acid.[22] 2,7-Dinitrofluorene (Aldrich Chemical Co., Milwaukee, Wis.) was converted to 2,7-dinitrofluorenone (m.p. 291–292°) in a similar manner.[23] When dissolved in concentrated sulfuric acid, 2-nitrofluorenone gave a red color[24] and 2,7-dinitrofluorenone gave a yellow-green color.

B.—A refluxing solution of 1 g. of 2,7-dinitro-9-methylfluorene (m.p. 246–247°, synthesized by the method of Wawzonek, Dufek, and Sial)[6] in 70 ml. of glacial acetic acid was treated with 7 g. of chromium trioxide, added in three portions over a period of 1.5 hr. After 1 hr. of additional refluxing, the mixture was

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[21] D. N. Matthews and E. I. Becker, *J. Org. Chem.*, **21**, 1317 (1956).

[22] J. Strasburger, *Ber.*, **17**, 107 (1884).

[23] G. T. Morgan and R. W. Thomason, *J. Chem. Soc.*, 2691 (1926).

[24] I. Heilbron, "Dictionary of Organic Compounds," Vol. III, Oxford University Press, New York, N. Y., 1953, p. 688.

poured into water and the collected precipitate was recrystallized first from glacial acetic acid and then from toluene, m.p. 286–290°, undepressed on admixture with a sample of synthetic 2,7-dinitrofluorenone from A. The two samples were also identical in infrared spectra and color test with concentrated sulfuric acid.

Thermal Decomposition of 2,9-Dinitro-9-alkylfluorenes.—Heating 2,9-dinitro-9-methylfluorene at 210° in a small-diameter glass tube for 5 min. gave evolution of a colorless gas which turned reddish brown (probably to form nitrogen dioxide) on contact with air. When evolution of gas had ceased, the residue was recrystallized first from glacial acetic acid and then from absolute ethanol, m.p. 219–221°, identified as 2-nitrofluorenone by direct comparison (mixture melting point, infrared spectrum, color test) with the preceding synthetic sample.

Similar treatment of 2,9-dinitro-9-*n*-propylfluorene at 220–230° gave a residue which (after one recrystallization from pyridine) gave an infrared spectrum identical with that of 2-nitrofluorenone.

Acetylation of 9-Alkylfluorenes.—To a cold (−5°) stirred mixture of 14.6 ml. of acetic anhydride, 34.6 g. of anhydrous aluminum chloride, and 150 ml. of nitrobenzene was added 0.12 mole of 9-alkylfluorene in portions. The mixture was stirred for 3 hr. at 0° and then for 3 hr. at 20°. It was poured into a mixture of ice and 10% hydrochloric acid. For R = Me, the nitrobenzene was removed by steam distillation and the residual solid was recrystallized from acetone (using decolorizing charcoal), m.p. 116–118°, 20-g. (75%) yield. Further recrystallization from methanol gave leaves of 2-acetyl-9-methylfluorene (Va), m.p. 116.5–117.5°, which produced a greenish yellow color when dissolved in concentrated sulfuric acid.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.24; H, 6.46.

For R = *i*-Pr, there resulted a 60% yield of crude product, obtained as needles of 2-acetyl-9-isopropylfluorene (Vd), m.p. 77–78° after four recrystallizations from methanol.

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.71; H, 7.26.

For R = Et, the nitrobenzene layer was separated, washed successively with concentrated hydrochloric acid, dilute aqueous sodium carbonate solution, and water, dried, and distilled *in vacuo* (first at 18 mm.), yielding 67% of yellow viscous liquid, b.p. 165–168° (0.6 mm.). Recrystallization from absolute ethanol gave needles of 2-acetyl-9-ethylfluorene (Vb), m.p. 86–87°.

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.45; H, 6.74.

2-Acetyl-9-ethyl-9-fluorenyl Hydroperoxide (VIII).—Also isolated from the recrystallization solvent for Vb was a 4% yield of yellow by-product, m.p. 159–161°; on recrystallization from ethanol it was converted to yellow flakes of VIII, m.p. 160–161°.

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 76.39; H, 6.18.

To a cold (−20°) solution of 67 mg. of Vb in 3 ml. of anhydrous pyridine was added 1 drop of Triton B solution. Dry air was passed over the rapidly stirred, deep blue mixture for 1 hr. (After 15 min. the color had become pale green). The reaction mixture was warmed to room temperature, treated with excess dilute hydrochloric acid, and extracted with chloroform. Evaporation of the dried solvent gave 40 mg. of VIII (m.p. 155–156°), identical (after further recrystallization) with the previously described by-product as based on infrared spectra.

Methyl 9-Methyl-2-fluorenyl Ketoxime (VIa).—A mixture of 15 g. of 2-acetyl-9-methylfluorene, 15 g. of hydroxylammonium chloride, 75 ml. of absolute ethanol, and 75 ml. of pyridine was refluxed for 3 hr. Removal of solvents and stirring the residue with water yielded 13 g. (81%) of crystals. Four recrystallizations from methanol gave cubes, m.p. 167–168°.

Anal. Calcd. for $C_{16}H_{15}NO$: N, 5.90. Found: N, 5.89.

Methyl 9-Isopropyl-2-fluorenyl Ketoxime (VId).—In the preceding manner was obtained an 84% yield of crude oxime, m.p. 160–161°. Recrystallization gave long, cotton-like needles, m.p. 161–162°.

Anal. Calcd. for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.28. Found: C, 81.45; H, 7.11; N, 5.05.

2-Acetylamino-9-methylfluorene (VIIa). A. From the Nitro Derivative.—To a warm (50°), stirred solution of 4.3 g. of 2-nitro-9-methylfluorene in 75 ml. of toluene and 25 ml. of absolute ethanol was added 3.1 ml. of hydrazine (95%) and then (in four equal portions over a period of 1 hr.) 20 mg. of Raney nickel.[25] The colorless mixture was distilled until the distillate no longer gave an alkaline test. The filtered residual mixture was concentrated to *ca.* 13 ml., diluted with 9 ml. of absolute ethanol, and cooled to 0° to give hygroscopic crystals of amine (dried in a desiccator). A solution of 1 g. of this amine in 5 ml. of anhydrous pyridine and 10 ml. of acetic anhydride was left at room temperature for 24 hr. and then evaporated. The residue was triturated with water and recrystallized repeatedly from methanol to give faintly cream platelets, m.p. 173.5–174.5°.

Anal. Calcd. for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 81.19; H, 6.53; N, 6.00.

B. From the Oxime Derivative.—To a cold (10°) solution of 12 g. of oxime VIa in benzene was added 13 g. of phosphorus pentachloride. The mixture was refluxed for 15 min. and then poured into ice and water. The residue remaining from evaporation of benzene extracts of the aqueous mixture was recrystallized twice from methanol (5.2-g. yield, 43%) and then sublimed at 0.3 mm. and 150° to give a cotton-like product, m.p. 173–174°, undepressed on admixture with product from A. Infrared absorption spectra in chloroform solution of amides from A and B were identical.

2-Acetylamino-9-isopropylfluorene (VIId).—Following the preceding Beckmann rearrangement method B, there was obtained (from 6.1 g. of oxime VId) 2.6 g. (43%) of once-recrystallized product, m.p. 145–147°. Repeated recrystallizations from methanol gave faintly yellow prisms, m.p. 148–149°.

Anal. Calcd. for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.28. Found: C, 81.21; H, 7.29; N, 5.49.

2-Ethyl-9-methylfluorene (IX). A. From 2-Ethylfluorene.—2-Ethylfluorene was obtained by Clemmensen reduction of 2-acetylfluorene (Aldrich Chemical Co.)[26] according to the directions of Campbell and Wang.[27] A mixture of 11 g. of analytically pure 2-ethylfluorene, m.p. 99.5–100.5°,[28] and a solution made from 2 g. of sodium metal and 40 ml. of absolute methanol was heated at 170–180° for 16 hr. in a 500-ml. rocking autoclave. The mixture was then processed in the manner used for similar synthesis of 9-alkylfluorenes,[16] yielding 5.6 g. (48%) of liquid, b.p. 110–120° (0.2 mm.). Redistillation at 0.2 mm. gave a central fraction of slightly yellow liquid, b.p. 114°, for an analytical sample.

Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.13; H, 7.85.

A **1,3,5-trinitrobenzene complex** was obtained as bright yellow needles from absolute methanol, m.p. *ca.* 78°.[29]

Anal. Calcd. for $C_{16}H_{16} \cdot C_6H_3N_3O_6$: N, 9.97. Found: N, 10.03.

B. From Va.—Clemmensen reduction, in the preceding manner, on 4.7 g. of Va gave 3 g. of crude product. Two fractional distillations gave an analytically pure sample of light yellow liquid, b.p. 112° (0.15 mm.), n^{25}_{D} 1.4968.

Anal. Found: C, 92.56; H, 7.75.

Infrared spectra on freshly prepared samples from A and B were identical, as were those on samples which had stood in stoppered containers for a few months. The older samples, however, showed strong OH bands and gave positive tests with starch–iodide paper. Gas chromatography of older samples using Apiezon L as stationary phase and 250° gave two major fractions. Infrared analysis indicated that the fraction of shorter retention time was nearly pure IX while the second fraction was a ketone, not further identified.

N.m.r. Spectra.—Proton magnetic resonance spectra were obtained by means of a Varian Associates A-60 spectrometer using tetramethylsilane as internal standard. Data relative to absorption by aliphatic protons for selected compounds are presented in Table I. All compounds also exhibited multiple absorptions at $\delta > 6$ p.p.m. for the aromatic protons present.

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[25] Adapted from the procedure of T. L. Fletcher and M. J. Namkung [*J. Org. Chem.*, **23**, 680 (1958)] for reduction of 2-nitrofluorene to 2-aminofluorene. Note that our hydrazine was nearly anhydrous and not 64% as employed by Fletcher and Namkung.

[26] Melting point undepressed on admixture with product from direct acetylation of fluorene by the method of W. E. Bachmann and J. C. Sheehan [*J. Am. Chem. Soc.*, **62**, 2687 (1940)].

[27] N. Campbell and H. Wang, *J. Chem. Soc.*, 1513 (1949).

[28] E. Sawicki, *J. Am. Chem. Soc.*, **76**, 2269 (1954); see also J. D. Dickinson and C. Eaborn, *J. Chem. Soc.*, 2337 (1959).

[29] Near this temperature it was difficult to decide from visual observation if the sample were a solid, a liquid, or both.