# The Base-catalyzed Alkylation of Fluorene with Alcohols

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The normal alcohols from $C_1$–$C_7$, inc., and also $C_{18}$, along with the respective sodium alkoxide, react at 210° with fluorene to give the corresponding 9-alkylfluorenes in from 58–92% yield.

## Introduction

The use of alcohols in the presence of base to produce new C–C or C–N bonds is a comparatively little known reaction although such reactions have been known at least since 1892.[3] Nef[4] reported the N-ethylation of aniline as have also Pratt and Frazza.[5] The alkylation of pyrrole and indole derivatives has been variously reported,[6–12] while Carroll[13–15] has reported the alkylation of ethyl acetoacetate and of ethyl malonate with cinnamyl alcohol and Haller[3,16] has reported the alkylation of camphor. Recently the first alkylation of a hydrocarbon was reported,[17] which led to the investigation of fluorene.

none, dehydration of the tertiary alcohol so formed and final hydrogenation to 9-ethylfluorene. 1,3,5-Trinitrobenzene adducts of each melted at the same temperature, which was not depressed upon admixture.[18]

Having established the course of the reaction with ethanol, it was then found that methanol, propanol, butanol, pentanol, hexanol and heptanol similarly gave the corresponding 9-alkylfluorenes. With octadecanol an excess of fluorene was used to give the 9-octadecyl derivative (see Table I).

Ultimate analyses and conversion to the 1,3,5-trinitrobenzene adducts served to characterize the compounds with three exceptions. 9-Methylfluo-

## TABLE I

### SUMMARY OF ALKYLATION REACTIONS[a]

| Fluorene | M.p. or b.p., °C. | Mm. | $n^{25}D$ | $d^{25}_4$ | Crude yield, % | Pure yield, % | Carbon, % Calcd. | Found | Hydrogen, % Calcd. | Found |
|---|---|---|---|---|---|---|---|---|---|---|
| 9-Methyl- | 96–98 | 0.6 | | | | 87.0 | 93.29 | 93.32 | 6.71 | 6.72 |
| | 45–46 | | | | | | | | | |
| 9-Ethyl- | 123–124 | 1 | 1.6180 | 1.0508 | 92.0 | 83.8 | 92.74 | 92.37 | 7.26 | 7.33 |
| 9-Propyl- | 126–128 | 1 | 1.6050 | 1.0326 | 91.0 | 72.0 | 92.26 | 92.15 | 7.74 | 7.70 |
| 9-Butyl- | 140 | 1 | 1.5956 | 1.0197 | 98.0 | 78.4 | 91.83 | 91.45 | 8.17 | 8.09 |
| 9-Amyl- | 144–146 | 1 | 1.5929 | 1.0153 | 93.5 | 66.2 | 91.47 | 91.79 | 8.53 | 8.40 |
| 9-Hexyl- | 156–159 | 1 | 1.5757 | 0.9900 | 98.0 | 68.0 | 91.14 | 91.25 | 8.86 | 9.03 |
| 9-Heptyl- | 163–165 | 1 | 1.5717 | 0.9827 | 90.0 | 58.5 | 90.85 | 90.38 | 9.15 | 9.20 |
| 9-Octadecyl- | 65.6–66.4 | | | | | 92.0 | 88.92 | 88.99 | 11.08 | 10.98 |

[a] In each alkylation, except that of fluorene with octadecanol, 0.060 mole of fluorene, 0.087 atom of sodium and an excess (40.0 ml.) of the corresponding alcohol was used. In the preparation of 9-octadecylfluorene 0.080 mole of fluorene, 0.087 atom of sodium and 0.060 mole of octadecanol was used.

## Results and Discussion

When a mixture of excess ethanol, 1.45 equivalents of sodium ethoxide and one equivalent of fluorene was heated at 210–220° for 16 hours, 9-ethylfluorene was obtained in 83% yield. Characterization of the product was effected by the identity of its physical constants with a sample made *via* the addition of ethylmagnesium iodide to fluore-

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rene is a known solid,[23–24] and the product obtained here agreed in all respects with that reported. 9-Heptylfluorene did not form a molecular compound and 9-octadecylfluorene was a solid with a sharp melting point (see Table II).

## TABLE II

### 1,3,5-TRINITROBENZENE ADDUCTS OF THE ALKYLFLUORENES

| 1,3,5-Trinitrobenzene adduct of fluorene | M.p., °C. | Carbon, % Calcd. | Found | Hydrogen, % Calcd. | Found | Nitrogen, % Calcd. | Found |
|---|---|---|---|---|---|---|---|
| 9-Ethyl- | 88–89 | 61.91 | 61.82 | 4.21 | 4.11 | 10.32 | 10.45 |
| 9-Propyl- | 40.7–41.4 | 62.70 | 62.61 | 4.54 | 4.62 | 9.97 | 9.99 |
| 9-Butyl- | 61.5–62.5 | 63.44 | 63.40 | 4.86 | 5.01 | 9.65 | 9.67 |
| 9-Amyl- | 64–65 | 64.13 | 64.01 | 5.16 | 5.10 | 9.35 | 9.47 |
| 9-Hexyl- | 48–48.5 | 64.79 | 64.83 | 5.44 | 5.50 | 9.07 | 9.30 |

From the physical constants for the 9-alkylfluor-

(18) This independent synthesis was necessary because 9-ethylfluorene had been reported as a solid[19–21] and, in a careful correction of earlier work, by Wislicenus as a liquid.[22]

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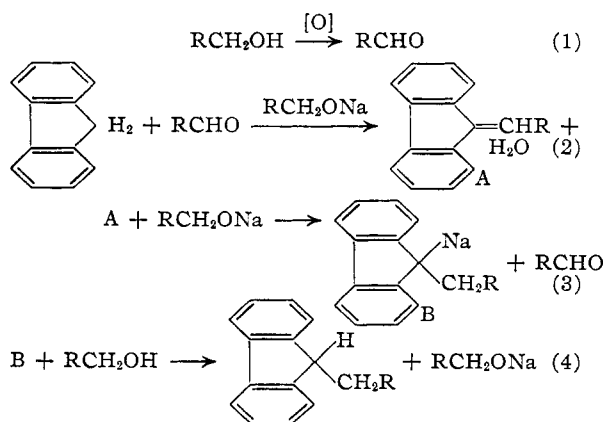(24) M. Orchin, THIS JOURNAL, **68**, 5712 (1946).

enes, their molecular refractions were determined. From a comparison of the found values with the calculated ones fluorene is shown to manifest a positive exaltation. From a plot of the molecular refraction against alkyl chain length and extrapolation to no alkyl chain the molecular refraction of fluorene was estimated to be 55.27 ml.-mole$^{-1}$ (see Table III).

### TABLE III
#### MOLAR REFRACTIONS OF 9-ALKYLFLUORENES

| Fluorene | $M^{25}$D, ml.-mole$^{-1}$ | |
| --- | --- | --- |
| | Found | Calcd. |
| 9-Ethyl- | 64.77 | 62.07 |
| 9-Propyl- | 69.47 | 66.69 |
| 9-Butyl- | 74.14 | 71.30 |
| 9-Amyl- | 78.87 | 75.92 |
| 9-Hexy- | 83.65 | 80.54 |
| 9-Heptyl- | 88.49 | 85.16 |

The mechanism of this reaction appears to be related to that of the Guerbet reaction as reviewed by Machemer[25] or written by Pratt and Frazza.[5] However, certain steps are different. The following mechanism is essentially that arrived at independently by Sprinzak.[26]

From the lack of any precautions to exclude oxygen or oxidizing agents, it can be assumed that at least a trace of aldehyde corresponding to the alcohol would be present at the high temperature of the reaction mixture (eq. 1).[27] In the presence of base it is well established that an aldehyde will condense with fluorene to give a dibenzofulvene[28] (eq. 2). Sodium alkoxide then reduces the exo-double bond with attendant formation of a molecule of aldehyde (eq. 3). This step may formally be regarded as a type of Meerwein–Ponndorf–Verley[27–29] reduction in which the exo-double bond of the dipolar fulvene[30,31] plays the role of the hydrogen acceptor. Finally, the sodium derivative of the product can react with solvent to give the 9-alkylfluorene and sodium alkoxide (eq. 4).



$$RCH_2OH \xrightarrow{[O]} RCHO \qquad (1)$$

In accord with equations 1–4 are the facts: (1) that very little pressure, if any, is generated during the reaction, indicating the feasibility of steps 3 and 4 which show regeneration of aldehyde and of alkoxide (2) that triphenylmethane is not alkylated under the same conditions speaking for the double bond intermediate[32]; (3) that a 9,9-disubstituted fluorene is not obtained speaking to the same point; (4) that 1,2,3,4-tetraphenylfulvene, a related molecule, is reduced with either ethanol and sodium ethoxide or butanol and sodium butoxide under the same conditions to 1,2,3,4-tetraphenyl-5-methylcyclopentadiene.[33]

### Experimental

**Base-catalyzed Alkylations.**—The procedures were similar for all of the alcohols. The alkylation with ethanol is used as an example. To a solution of 2.0 g. (0.087 atom) of sodium in 40 ml. of absolute alcohol in a Carius tube 10 g. (0.060 mole) of fluorene was added. The tube was sealed and heated for 16 hr. at 210°. After cooling, the contents of the tube were neutralized with 1:1 hydrochloric acid and then 50 ml. of benzene was added. The organic layer was washed with water and then distilled. Redistillation gave three fractions which were included in the crude yield, while the center one was considered as the pure material. The latter was used directly as the analytical sample.

In the case of methanol a 1300-ml. stainless steel reaction vessel was used in order to carry out the reaction on a $^2/_1$ molar scale. Stirring gave a lighter colored product than without. Duplicate experiments gave 81 and 84% of twice-distilled 9-methylfluorene.

The alkylation with octadecanol was carried out at atmospheric pressure in a flask equipped with a water condenser and heated in an oil-bath.

**9-Ethylidenefluorene.**—A solution of 55.7 g. (0.31 mole) of fluorenone in ether was added to a flask containing ethylmagnesium iodide (from 8.5 g. (0.35 atom) of magnesium and 60 g. (0.387 mole) of ethyl iodide). The solution was refluxed for 40 minutes and was then poured onto a mixture of 150 g. of ice and 15 ml. of sulfuric acid. The aqueous layer was separated, extracted with two 25-ml. portions of ether and the combined organic layers were washed once with 50 ml. of water. Distillation of the ether and crystallization of the residue from methanol gave 36 g. (0.187 mole, 61%) of white crystals of 9-ethylidenefluorene, m.p. 103–104.5° (reported[34] 104°). On standing exposed to air, the compound decomposes to fluorenone and acetaldehyde, which has been previously observed.[35,36]

**9-Ethylfluorene.**—Thirty-six grams (0.187 mole) of 9-ethylidenefluorene in ethyl acetate at 45 p.s.i. of hydrogen in the presence of 2 g. of 5% palladium-on-charcoal absorbed the theoretical amount of hydrogen in 0.5 hour. Filtration of the catalyst, distillation of the solvent and then distillation of the product gave 9-ethylfluorene, b.p. 123–124° (1 mm.).

*Anal.* Calcd. for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: C, 92.44; H, 7.36.

**1,3,5-Trinitrobenzene Adduct of 9-Ethylfluorene.**—Hot, saturated solutions containing equimolar quantities of 1,3,5-trinitrobenzene and of 9-ethylfluorene (from reduction) in alcohol were combined and allowed to cool. The yellow crystals were collected and recrystallized from methanol.

*Anal.* Calcd. for $C_{21}H_{17}N_3O_6$: C, 61.91; H, 4.21; N, 10.32. Found: C, 61.72; H, 4.07; N, 10.34.

Other 1,3,5-trinitrobenzene adducts were prepared similarly. 9-Ethylfluorene and 9-amylfluorene did not form isolable molecular compounds with trinitrotoluene, trinitrobenzene or picric acid in any of a variety of solvents, and 9-heptylfluorene did not form a compound with the last two of these or with picrolonic acid, picramic acid or chloranil.

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