

also were carried out in isopropyl alcohol solution, under conditions recently used for the alkylation of alkylidene cyanoacetic esters.³⁰ In both cases the yields were higher in isopropyl than in ethyl alcohol (see footnotes to Table I). This is evidence that alcoholysis is an important factor influencing the yields in this synthesis.

B.—Ethyl butylidenemalonate reacts with powdered sodium in ether or benzene solution, just as isopropylidene malonic ester does,³¹ giving a soluble sodium derivative. Methylation with dimethyl sulfate gave a 50–60% yield of ethyl (1-butenyl)-methylmalonate, b. p. 130–132° (24 mm.). The ester was purified by shaking with ammonia and refractionation, but quantitative reductions required only 86% of the theoretical quantity of hydrogen, showing the presence of a saturated ester in the product. In preparing a disubstituted barbituric acid derivative from this partially reduced ester, by condensation with urea, in one case a small amount of 5-methyl-5-butylbarbituric acid, m. p. 179–179.5° (uncor.), was isolated,⁷

(7) *Summaire, Bull. soc. chim.*, **33**, 189 (1923), reports m. p. 181°.

proving the presence of ethyl butylmethylmalonate in the ester prepared by this method.

C.—Ethyl butylidenemalonate was treated with sodamide, in liquid ammonia solution and suspended in both ether and toluene. A sodium derivative was formed in each case, but alkylation in ether or toluene with both diethyl sulfate and allyl bromide gave poor yields (10 to 40%) of impure esters.

Summary

Primary alkylidene malonic esters, $RCH_2CH=C(COOEt)_2$, react with sodium ethoxide and sodium isopropoxide to give sodium derivatives of primary 1-alkenylnalonic esters, $[RCH=CHC(COOEt)_2]^-Na^+$. These sodium derivatives may be alkylated readily, giving substituted vinyl alkyl malonic esters of the type, $RCH=CH-C(R')(COOEt)_2$.

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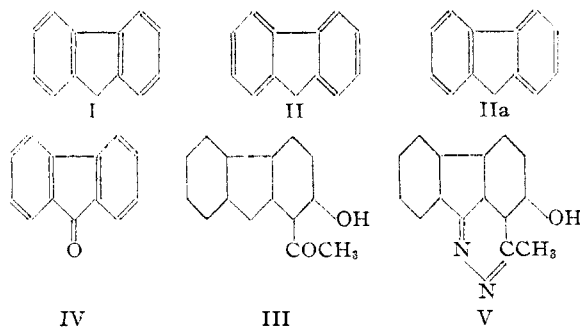
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Remarks on the Structure of Fluorene

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W. C. Lothrop has published¹ an interesting paper on the fine structure of fluorene. Some time ago, we experimented on similar lines.² Agreeing with the conclusions drawn by Lothrop to the effect that fluorene is not to be represented by exclusively one of the formulas I or II (and possibly IIa), we should like to supplement his evidence by reporting briefly some of our results.



In addition to the rearrangement of 2-allyloxyfluorene, we have also studied that of 2-acetoxyfluorene. Under the influence of aluminum chloride, an isomer is formed in moderate yield, to which we ascribe the formula III of 1-acetyl-2-hydroxyfluorene on the basis of its unreactivity to

ward hydroxylamine, III being an *o,o'*-disubstituted acetophenone.³ This rearranging reaction appears to take place on form I, which, by the way, is also responsible for the formation of the 9-sodium derivative of fluorene.⁴ On the other hand, it has been shown before,⁵ that the Kolbe reaction with 2-hydroxyfluorene leads to two isomeric 2-hydroxyfluorene-carboxylic acids, most probably the 1- and the 3-compounds. By the same reasoning as above, they would owe their formation to the fine structures I and II, respectively.

Similar observations have been made in the series of fluorenones, the quinone-like properties of which would be accounted for most fittingly by formula (IV).⁶ The rearrangement product of 2-acetoxyfluorene is 1-acetyl-2-hydroxyfluorenone, as it forms with hydrazine hydrate a pyridazine (V), analogous to that we could obtain from 1-benzoylfluorenone. The rearrangement of 2-allyloxyfluorenone, however, gave two isomers,

(3) See, e. g., Claus and Foeking, *Ber.*, **20**, 3101 (1887); Baum, *ibid.*, **28**, 3207 (1895); V. Meyer and co-workers, *ibid.*, **29**, 830, *seq.* (1896).

(4) Compare Hueckel, *Z. Elektrochem.*, **43**, 779 (1937).

(5) German Patent 350,293; Friedlaender, *Fortschritte der Teerfarben-Industrie*, **18**, 599.

(6) Color! For the spectrum, see Böeseken and co-workers, *Rec. trav. chim.*, **44**, 188 (1925).

(1) Lothrop, *THIS JOURNAL*, **61**, 2115 (1939).

(2) T. Berlin, Thesis, Jerusalem University, 1939.

forming a well-crystallized molecular compound. After hydrogenation of the allyl double bond, two hydroxypropylfluorenones were separated, apparently the 1- and the 3-propyl-2-hydroxy compounds. This indicates that in fluorenone, too, the double bonds have no fixed position, the form represented by (IV) perhaps being somewhat favored.

Experimental

1-Acetyl-2-hydroxyfluorene (III).—2-Acetoxyfluorene (4.1 g.), prepared from 2-hydroxyfluorene⁷ with acetic anhydride according to Claborn and Haller,⁸ was heated at 80° for three hours with a solution of aluminum chloride (3.6 g.) in nitrobenzene (30 cc.). The reaction product was decomposed with cold dilute hydrochloric acid, the nitrobenzene removed with steam and the residue dried and extracted with carbon tetrachloride in a Soxhlet apparatus. The product soluble in carbon tetrachloride was triturated with methyl alcohol and some acetone and recrystallized from butyl alcohol or 25% acetic acid as long yellowish needles, m. p. 159°; yield, 0.6 g. *Anal.* Calcd. for C₁₆H₁₂O₂: C, 80.3; H, 5.4. Found: C, 79.8; H, 5.3. With hydroxylamine in alcohol, no reaction occurred.

1-Acetyl-2-hydroxyfluorenone.—2-Acetoxyfluorenone⁸ (3 g.) was treated with aluminum chloride (2.8 g.) in nitrobenzene (20 cc.) as above. After removal of the solvent, the product was recrystallized from xylene as red, bent crystals, m. p. 206°. *Anal.* Calcd. for C₁₅H₁₀O₃: C, 75.6; H, 4.2. Found: C, 76.0; H, 4.3.

Pyridazine Derivative (V).—The diketone (300 mg.) was heated with hydrazine hydrate (64 mg.) in alcoholic solution (5 cc.), for three hours. The solvent was evaporated and the residue, after trituration with toluene containing some methyl ethyl ketone, recrystallized from toluene as yellow crystals, m. p. 197° (dec.). The combustion analysis was unsatisfactory (Calcd. for C₁₅H₁₀ON₂: C, 76.9; H, 4.3. Found: C, 75.0; H, 4.6); so was that of the pyridazine derivative of 1-benzoylfluorenone; 1-benzoyl-fluorenone⁹ (500 mg.; b. p. 245°/0.4 mm.; m. p. 114–116°) was boiled with hydrazine hydrate (56 mg.) in alcohol (5 cc.) for two hours. The product obtained by evaporation of the solvent was triturated with acetone and recrystallized from benzene as yellow platelets, m. p. 181°. *Anal.* Calcd. for C₂₀H₁₂O₂: C, 85.7; H, 4.3. Found: C, 84.6; H, 4.5.

It may be mentioned that the rearrangement of 2-acetoxyfluorenone, when carried out at 115°, gave a substance different from the 1-acetyl-2-hydroxyfluorene

described above; it crystallized from butyl alcohol, had m. p. 249° and gave analytical figures pointing to the formula C₁₆H₁₂O₃ (instead of C₁₅H₁₀O₃) (Calcd. C, 75.0; H, 5.0. Found: C, 75.3, 75.4; H, 5.4, 4.9). The structure of this compound (which might be bimolecular) has not been dealt with.

2-Allyloxyfluorenone.—2-Hydroxyfluorenone⁷ (4 g.) was heated with allyl bromide (2.7 g.) and potassium hydroxide (2 g.) in alcohol (40 cc.) until neutrality (ten hours). The reaction product, separating on cooling, was dissolved in ether and extracted several times with concentrated potassium hydroxide solution. From light petroleum, containing some acetone, it gave crystals, m. p. 84–85°, yield, 2.2 g. *Anal.* Calcd. for C₁₆H₁₂O₂: C, 81.3; H, 5.1. Found: C, 80.7; H, 5.6.

Molecular Compound of 1-Allyl-2-hydroxy- and 3-Allyl-2-hydroxyfluorenone.—The foregoing compound (1 g.) was heated at 200° for three hours and then distilled under 0.05 mm. pressure. The red oil, distilling at 186°, was triturated with light petroleum (b. p. 130°) and recrystallized from benzene or 25% acetic acid as orange-red needles, m. p. 125–126°; yield, 0.6 g. *Anal.* Calcd. for C₁₆H₁₂O₂: C, 81.3; H, 5.1. Found: C, 80.9; H, 5.2.

1-Propyl- and 3-Propyl-2-hydroxyfluorenone.—The foregoing compound (2 g.) was treated with a current of hydrogen in boiling propyl alcohol (50 cc.), containing the palladous hydroxide catalyst (1 g.) of Kuhn and Stroebel,¹⁰ for eighteen hours. The solvent was evaporated and the residue recrystallized from aqueous alcohol (1:1) as clusters of yellow needles, m. p. 202° (after repeated recrystallization from the same solvent) crystallized spontaneously (*Anal.* Calcd. for C₁₆H₁₄O₂: C, 80.7; H, 6.0. Found: C, 79.3; H, 6.4), while the darker-yellow isomer, m. p. 155°, appeared, when the mother liquor was concentrated. *Anal.* Calcd. for C₁₆H₁₄O₂: C, 80.7; H, 6.0. Found: C, 79.6; H, 5.8.

Summary

2-Acetoxyfluorene and 2-acetoxyfluorenone, on Fries rearrangement, give the 1-acetyl-2-hydroxy compounds.

From 2-allyloxyfluorenone, both 1- and 3-allyl-2-hydroxyfluorenones are obtained in the form of a molecular compound.

These facts support the conclusion drawn by Lothrop¹ that no fixed "fine structure" exists in fluorene; the dibenzocyclopentadiene formula, however, seems to prevail.

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(7) Diels, *Ber.*, **34**, 1758 (1901).

(8) Claborn and Haller, *THIS JOURNAL*, **59**, 1055 (1937).

(9) Koelsch, *ibid.*, **54**, 4744 (1932).

(10) Kuhn and Stroebel, *Ber.*, **70**, 785 (1937).