The infrared spectrum of the product showed absorption at 4.44 μ characteristic of a nitrile group and in the region of 6.3 μ indicating a carboxylate ion. The multiple carbonyl absorption characteristic of amides, and the absorption characteristic of an ester group, present in the starting cyanoester, were absent.[13]

(d) **With 1,1,3,3-Tetramethylbutylamine.**—No ammonia was evolved in the reaction. The residue crystallized and 1,1,3,3-tetramethylbutylammonium β-cyanopropionate, m.p. 126–127°, was obtained in 80% yield. *Anal.* Calcd. for $C_{12}H_{24}N_2O_2$: C, 63.1; H, 10.5; N, 12.3; equiv. wt., 228. Found: C, 63.1; H, 10.4; N, 12.0; equiv. wt., 238.

Aqueous Aminolyses of Succinic Anhydride.—These reactions all were carried out in a ratio of succinic anhydride: amine:water of 1:4:12, according to the general procedure for atmospheric reactions described above. The reflux temperatures were between 95 and 105°, and the reflux times were 48 hours in each case. (a) **With Benzylamine.**—N,N′-Dibenzylsuccinamide, m.p. 210–211°, was obtained in 70% yield. A mixed m.p. with authentic sample[2] did not depress. (b) **With 1,1,3,3-Tetramethylbutylamine.**—1,1,3,3-Tetramethylbutylammonium succinate, m.p. 167–168°, was obtained in 87% yield. *Anal.* Calcd. for $C_{20}H_{44}N_2O_4$: C, 63.8; H, 11.7; N, 7.5; equiv. wt., 372. Found: C, 63.9; H, 11.5; N, 7.4; equiv. wt. (by titration with perchloric acid in acetic acid), 382. (c) **With Piperidine.**—The stripped reaction mixture remained an intractable viscous oil after standing one month in the cold. The oil then was taken up in benzene and the solution boiled to remove water. Upon cooling this solution in an ice-bath, a small amount of solid crystallized. After several recrystallizations from isopropyl alcohol, 4 g. (6%) of piperidinium acid succinate, melting at 143–144°, was obtained. *Anal.* Calcd. for $C_9H_{17}NO_4$: C, 53.3; H, 8.1; N, 6.9; equiv. wt., 203. Found: C, 53.2; H, 8.3; N, 6.7; equiv. wt. (by titration with aqueous NaOH), 204; (by titration with perchloric acid in acetic acid), 206. The major portion of the residue did not crystallize. It was water soluble and released piperidine when made alkaline, indicating it to be a piperidine salt, probably the dipiperidinium succinate.

Aqueous Aminolyses of Succinimide.—These reactions were all carried out in a ratio of succinimide:amine:water of 1:4:12, according to the general procedure for atmospheric reactions described above. The reflux temperatures were between 95 and 105°, and the reflux times were 48 hours in each case. (a) **With Benzylamine.**—N,N′-Dibenzylsuccinamide, m.p. 210°, mixed m.p. with authentic sample[2] did not depress, was obtained in 81% yield. (b) **With 1,1,3,3-Tetramethylbutylamine.**—No ammonia was evolved in the reaction. 1,1,3,3-Tetramethylbutylammonium succinamate, m.p. 180–181°, was obtained in 93% yield. A mixed m.p. with authentic sample did not depress. (c) **With Piperidine.**—No ammonia was evolved in the reaction. Piperidinium succinamate, m.p. 170–171°, identified by mixed melting point with an authentic sample,[2] was obtained in 50% yield.

Aqueous Aminolysis of Succinamic Acid with Benzylamine.—Four grams (0.039 mole) of succinamic acid, 16.6 g. (0.155 mole) of benzylamine and 8.4 g. (0.465 mole) of water were mixed and reacted according to the general procedure for atmospheric reactions described above. N,N′-Dibenzylsuccinamide, m.p. 209–210°, was obtained in 70% yield. A mixed m.p. with authentic sample did not depress. *Anal.* Calcd. for $C_{18}H_{20}N_2O_2$: C, 73.0; H, 6.8; N, 9.5. Found: C, 73.6; H, 6.8; N, 8.9.

Other Aqueous Aminolyses Carried out with Benzylamine. (a) **On Methyl Cyanoacetate.**—Methyl cyanoacetate, benzylamine and water were mixed in a 1:4:12 molar ratio according to the general procedure for atmospheric reactions described above. N,N′-Dibenzylmalonamide, m.p. 139–140°, identified by mixing melting point with an authentic sample,[2] was obtained in 92% yield. (b) **On Cyanoacetamide.**—N,N′-Dibenzylmalonamide, m.p. 138–139°, was obtained in 95% yield. A mixed m.p. with an authentic sample did not depress. (c) **On Phenylacetonitrile.**—The molar ratio used here was 1:2:6. No ammonia was evolved in the reaction. The cooled reaction mixture was acidified with concentrated hydrochloric. The phenylacetonitrile separated and was distilled to yield 46.5 g. (80% recovery) of nitrile, b.p. 122–123° (22 mm.). The yield of benzylamine hydrochloride, obtained by stripping the aqueous layer, was 126 g. (88% recovery of benzylamine).

Reactions of Aqueous 1,1,3,3-Tetramethylbutylamine. (a) **On Methyl Cyanoacetate.**—Methyl cyanoacetate, 1,1-3,3-tetramethylbutylamine and water were mixed in a 1:4:12 molar ratio according to the general procedure for atmospheric reactions described above. 1,1,3,3-Tetramethylbutylammonium cyanoacetate, m.p. 99–101°, was obtained in 52% yield. *Anal.* Calcd. for $C_{11}H_{22}N_2O_2$: C, 61.8; H, 10.3; N, 13.1; equiv. wt., 214. Found: C, 61.8; H, 10.5; N, 12.7; equiv. wt., 216 (by non-aqueous titration with perchloric acid). (b) **On Cyanoacetamide.**—1,1,3,3-Tetramethylbutylammonium cyanoacetate, m.p. 98–101° after recrystallization in good yield from petroleum ether, was obtained in 60% yield. Mixed m.p. with an authentic sample did not depress below 98°. Equiv. wt., calcd. 214, found (by non-aqueous titration) 218.

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[13] We are indebted to Dr. J. S. Stroupe and Miss Helen Miklas for obtaining and interpreting the infrared curves.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Reactions of Some Aromatic Acetylenic Carbinols[1]

BY G. F. HENNION AND B. RAYMOND FLECK[2]

RECEIVED DECEMBER 4, 1954

9-Ethynyl-9-fluorenol, diphenylethynylcarbinol and phenylmethylethynylcarbinol have been hydrated to the expected methyl ketones. Some hydroxyl group reactions of the ethynylcarbinols and of the α-ketols obtained by hydration have been studied also. In none of these reactions has rearrangement of the carbon skeleton been observed. The ethynylcarbinols underwent the Meyer–Schuster rearrangement and thus produced fluorenylideneacetaldehyde, β,β-diphenylacrolein and β-methylcinnamaldehyde, respectively, the latter in poor yield. When treated with thionyl chloride or hydrochloric acid, 9-ethynyl-9-fluorenol yielded 9-(chlorovinylidene)-fluorene.

Discussion

It is now well established that certain 17-ethynyl-17-hydroxysteroids and 17-acetyl-17-hydroxysteroids undergo skeletal rearrangement under proper conditions and lead to expanded (six-membered) D rings.[3] The present work was directed to exploring this type of rearrangement. The *t*-ethynylcarbinols, 9-ethynyl-9-fluorenol (I), diphenylethynylcarbinol (VIII) and phenylmethylethynylcarbinol (XII) together with the corresponding acetyl derivatives were chosen as model compounds.

Attempts to hydrate the triple bond of I in acetic

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[1] Paper LXI on substituted acetylenes; previous papers, *J. Org. Chem.*, **18**, 1601 (1953); THIS JOURNAL, **76**, 5160 (1954). Presented at the National A.C.S. Meeting in New York, N. Y., September, 1954.

[2] National Science Foundation Fellow, 1952–1953. Abstracted from the Ph.D. dissertation of Brother Raymond Fleck, C.S.C.

[3] A. W. Johnson, "The Chemistry of the Acetylenic Compounds, Vol. I. The Acetylenic Alcohols," Edward Arnold Co., London, 1946, p. 261; R. Turner, THIS JOURNAL, **75**, 3484 (1953).

acid under conditions used in the steroid series[3,4] gave only polymeric material. When the reaction was carried out in aqueous methanol with small amounts of mercuric sulfate and sulfuric acid as catalysts, 9-acetyl-9-fluorenol (II) was isolated in 84% yield. That the five-membered ring had not undergone expansion was shown by oxidation and by Beckmann rearrangement of the oxime, both of which yielded fluorenone.

When II was dissolved in a mixture of glacial acetic acid, acetic anhydride and boron trifluoride etherate, conditions under which 17β-hydroxy-20-ketosteroids undergo D-homoannulation, the hydroxyl group was acetylated without rearrangement. The acetate thus obtained was identical with that derived by the action of acetic anhydride and sulfuric acid and could be hydrolyzed back to II.

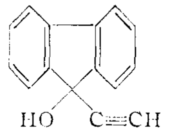
Rearrangement of 9-acetyl-9-fluorenol (II) in the presence of base was precluded by an exceptionally facile cleavage of the acetyl group with the formation of 9-fluorenol. The mechanism of the reaction is probably that proposed by Sharp and Miller[5] in their recent study of the cleavage of substituted benzoins.

In addition to II, small amounts of 9-methoxy-9-acetylfluorene (III) were consistently isolated in the hydration of I. Since 9-acetyl-9-fluorenol (II) was not converted to its methyl ether under the reaction conditions, it was concluded that etherification precedes hydration. This hypothesis was supported by the fact that I was converted to its methyl ether (IV) when allowed to stand at room temperature in acidic methanol. The hydration of IV yielded 9-methoxy-9-acetylfluorene (III) in good yield.

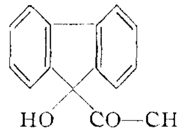
Attempts to prepare the ethyl ether V by the action of acidic ethanol on I gave V in very poor yields together with unchanged starting material. When I was converted to its acetate, however, the latter underwent solvolysis in acidic ethanol at room temperature and yielded 9-ethoxy-9-ethynylfluorene (V).

When a dilute solution of I in acidic ethanol was heated under reflux, fluorenylideneacetaldehyde (VI) was isolated in 60% yield, together with a small amount of the ethyl ether V. These results are analogous to those of Moreau, Dufraisse and Blatt[6] who found that diphenyl-(phenylethynyl)-carbinol undergoes the Meyer–Schuster rearrangement in acidic ethanol. The course of the acid-catalyzed rearrangements of terminal acetylenic carbinols of the type RR'C(OH)—C≡CH to unsaturated carbonyl compounds has long been a controversial subject, because they usually can give both an aldehyde (Meyer–Schuster rearrangement) and a ketone (Rupe reaction).[7,8] The latter reaction is ordinarily the preferred reaction path, but the ratio of aldehyde to ketone depends on the structure of the particular ethynyl carbinol. Like phenylethynylcarbinol,[9] however, I is structurally incapable of undergoing the Rupe reaction, and hence it rearranges to the aldehyde VI. Silver oxide oxidation of VI yielded the known fluorenylideneacetic acid.

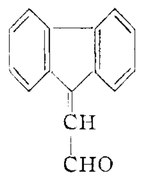
Hennion and Teach[10] treated 9-ethynyl-9-fluorenol (I) with thionyl chloride in the presence of pyridine and obtained a high-melting golden-yellow solid which was insoluble in the reaction medium. The compound contained chlorine, but its properties were inconsistent with what would be expected for 9-chloro-9-ethynylfluorene. It now has been found that the same compound is obtained in good yield by shaking an ethereal solution of I with concentrated hydrochloric acid. The structure 9-(chlorovinylidene)-fluorene (VII) is proposed for this compound. It is probably formed by a mechanism similar to that of the Meyer–Schuster rearrangement.



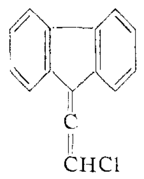
I



II



VI



VII

Attempts to hydrate diphenylethynylcarbinol (VIII) by the procedure used for 9-ethynyl-9-fluorenol were unsuccessful. The formation of a copious white mercury-containing precipitate made the catalyst ineffectual for hydration of the triple bond. Increasing the acid concentration or the length of the reaction time seemed to favor the Meyer–Schuster rearrangement with the formation of diphenylacrolein (IX). Subsequently IX was prepared in 78% yield by heating VIII under reflux in acidic ethanol. Silver oxide oxidation of IX yielded β,β-diphenylacrylic acid.

In order to hydrate the triple bond of diphenylethynylcarbinol (VIII), a modification of a technique developed by Ruzicka and co-workers[11] was employed. When VIII was mixed with one equivalent of mercuric acetate in glacial acetic acid, an exothermic reaction took place. After standing at room temperature for 16 hours, the solution was saturated with hydrogen sulfide, and diphenylacetylcarbinol acetate (X) was subsequently isolated from the reaction mixture in 58% yield. Saponification of X at room temperature gave diphenylacetylcarbinol (XI) with no observable isomerization or cleavage of the acetyl group. Temnikova[12] reported that XI does not rearrange in base, although the experimental conditions were not given.

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(4) L. Ruzicka, K. Gatzi and T. Reichstein, *Helv. Chim. Acta*, **22**, 626 (1939).

(5) D. Sharp and E. Miller, This Journal, **74**, 5643 (1952).

(6) C. Moreau, C. Dufraisse and H. Blatt, *Bull. soc. chim.*, **35**, 1412 (1924).

(7) See for example, the rearrangement of 1-ethynylcyclohexanol; J. Chanley, This Journal, **70**, 244 (1948), and references cited there.

(8) G. F. Hennion, R. Davis and D. E. Maloney, *ibid.*, **71**, 2813 (1949).

(9) W. MacGregor, *ibid.*, **70**, 3953 (1948); N. Hagihara and I. Hirao, *Mem. Inst. Sci. Ind. Research (Osaka Univ.)*, **7**, 133 (1950); *C. A.*, **45**, 8997 (1951).

(10) G. F. Hennion and E. Teach, unpublished work.

(11) L. Ruzicka, M. Goldberg and F. Hunziker, *Helv. Chim. Acta*, **22**, 707 (1939).

(12) T. Temnikova, *Vestnik Leningrad Univ.*, 138 (1947); *C. A.*, **42**, 4155 (1948).

When XI was treated with glacial acetic acid, acetic anhydride and boron trifluoride, X was obtained in good yield. There was no isomerization analogous to that observed in the 17-hydroxy-20-ketosteroids under similar conditions.

Treatment of phenylmethylethynylcarbinol (XII) with mercuric sulfate in aqueous acidic methanol gave only unchanged starting material and its methyl ether (XIII). Subsequently, XIII was prepared in 85% yield by heating XII under reflux in acidic methanol. Attempts to hydrate XIII under the usual conditions using mercuric sulfate were unsuccessful. When mercuric oxide was substituted for mercuric sulfate, however, the hydration proceeded normally, and 2-methoxy-2-phenyl-3-butanone (XIV) was obtained in 81% yield. Beckmann rearrangement of the oxime gave acetophenone, isolated as its semicarbazone.

In the presence of mercuric oxide, phenylmethylethynylcarbinol (XII) underwent hydration in aqueous acidic methanol and phenylmethylacetylcarbinol was obtained in 81% yield. Other investigators[13] recently have reported the hydration of XII in aqueous acidic ethanol and obtained XV in 28.8% yield together with a 14.5% yield of β-methylcinnamaldehyde.

When XII was heated under reflux in acidic dioxane, β-methylcinnamaldehyde (XVI) was isolated in poor yield through its bisulfite addition compound. The melting point of the semicarbazone of XVI was in agreement with the literature value and with the melting point of one of the two isomeric compounds obtained by Takeshima[14] in the formic acid-catalyzed rearrangement of XII.

Hydration of XII in glacial acetic acid, using mercuric oxide and boron trifluoride, gave phenylmethylacetylcarbinol acetate.

Experimental

9-Ethynyl-9-fluorenol (I) and diphenylethynylcarbinol (VIII) were prepared in the usual way by the action of sodium acetylide in liquid ammonia on fluorenone and benzophenone, respectively. From 135 g. (0.75 mole) of fluorenone, 128 g. of I, m.p. 105–107.5°, was obtained (87.4% yield). A sample recrystallized twice from carbon tetrachloride had a melting point of 107–108°.

Anal. Calcd. for $C_{15}H_{10}O$: C, 87.35; H, 4.89. Found: C, 86.96; H, 5.17.

Diphenylethynylcarbinol (VIII) was obtained 81% yield, m.p. 48.5–49.5°, reported[15] 49°.

Phenylmethylethynylcarbinol (XII) was supplied by Air Reduction Chemical Co.

9-Acetyl-9-fluorenol (II).—A solution of 1.0 g. of concd. sulfuric acid and 2 ml. of water in 50 ml. of methanol was placed in a 300-ml. 3-neck flask fitted with a mechanical stirrer, a thermometer, and a dropping funnel. To the solution was added 1.0 g. of mercuric sulfate and the temperature was raised to 55°. A solution of 10.30 g. (0.05 mole) of 9-ethynyl-9-fluorenol (I) in 50 ml. of methanol was added dropwise over a period of 2 hours with rapid stirring. Half-gram portions of mercuric sulfate were added at the end of the first hour and when addition was complete. The temperature was maintained at 55–57° throughout the reaction. When addition was complete, 5 ml. of water was added, and heating and stirring were continued for 2 hours. The reaction mixture was then filtered, cooled, and diluted with 400 ml. of brine. The 9-acetyl-9-fluorenol was collected, dried, and recrystallized from petroleum ether and carbon tetrachloride; m.p. 104–106°, 9.43 g. (84%). A sample recrystallized twice from petroleum ether had a melting point of 105.5–106.5°.

Anal. Calcd. for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39. Found: C, 79.92; H, 5.62.

9-Acetyl-9-fluorenyl Acetate.—To a solution of 1.0 g. of 9-acetyl-9-fluorenol (II) in 5 ml. of acetic anhydride was added 3 ml. of acetic anhydride containing one drop of concd. sulfuric acid. The reaction mixture was allowed to stand at room temperature for 0.5 hour. It was then warmed on a steam-bath for 5 minutes and poured into 100 ml. of water. The 9-acetyl-9-fluorenyl acetate was crystallized from aq. ethanol; m.p. 95.5–96.5°, 0.95 g. Two recrystallizations from aq. ethanol raised the melting point to 96–97°.

Anal. Calcd. for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30. Found: C, 76.50; H, 5.17.

Oxime of II was prepared in the usual way[16]; m.p. 210–211°.

Anal. Calcd. for $C_{15}H_{13}NO_2$: N, 5.86. Found: N, 5.82.

Semicarbazone of II was prepared in the usual way[16]; m.p. 213–215° dec.

Anal. Calcd. for $C_{16}H_{15}N_3O_2$: N, 14.94. Found: N, 14.70.

Oxidation of II.—One and one-half grams of 9-acetyl-9-fluorenol (II) was added to a solution of 5 g. of sodium dichromate in 10 ml. of water. A mixture of 6 ml. of concd. sulfuric acid and 4 ml. of water was added. The reaction mixture turned black, and when the initial reaction had subsided, the solution was heated under reflux for 2 hours. It was poured into a large excess of ice-water and the yellow solid collected. Recrystallization from aq. ethanol gave bright yellow needles, m.p. 82–83°, 0.45 g. The melting point was not depressed by an authentic sample of fluorenone. Further dilution of the mother liquor yielded a second crop, m.p. 81–82°, 0.2 g.

Beckmann Rearrangement of the Oxime of II.—One gram of the oxime described above was mixed with 25 ml. of sodium-dried ether in a 125-ml. erlenmeyer flask and heated to boiling. The oxime did not dissolve completely. To this mixture was added 5 ml. of thionyl chloride in small portions over a period of a few minutes. This caused the oxime to dissolve rapidly. The ether then was removed until the volume of the solution had been reduced to *ca.* 5 ml. Heating was discontinued and the excess thionyl chloride was decomposed by adding 15 ml. of water. The mixture was heated to boiling, and the aqueous layer was decanted from the molten fluorenone. A second 15-ml. portion of water was added, heated to boiling, and decanted. Upon cooling, the fluorenone solidified, m.p. 79.5–81°, 0.8 g. Recrystallization from ether raised the melting point to 82–83°, 0.65 g.

Hydrolysis of II.—To a solution of 0.50 g. of 9-acetyl-9-fluorenol (II) in 5 ml. of methanol was added a solution of 0.25 g. of KOH in 5 ml. of methanol. The reaction mixture was allowed to stand at room temperature for 2 hours. It was then heated on a steam-bath for 15 minutes, diluted with 10 ml. of hot water and filtered. Upon cooling, a white solid was obtained, m.p. 143–146°. Recrystallization from aq. ethanol yielded 0.33 g. of 9-fluorenol, m.p. 150–152°, reported[17] 151.5–152°.

Acetate of 9-Fluorenol.—The fluorenol thus prepared was converted to 9-fluorenyl acetate using acetic anhydride and pyridine at steam-bath temperature; m.p. 68.5–69°, reported[18] 69–70°.

Action of Boron Trifluoride on II.—9-Acetyl-9-fluorenol (1.7 g.) was dissolved in 10 ml. of glacial acetic acid, containing 0.5 ml. of acetic anhydride. To this solution was added 10 ml. of glacial acetic acid containing three drops of boron trifluoride etherate. The clear solution was allowed to stand at room temperature for 24 hours. After dilution with 100 ml. of ice-water, a white solid separated from solution. The 9-acetyl-9-fluorenyl acetate so obtained was recrystallized from aq. ethanol; m.p. 96–97°, 1.6 g.

Acid-catalyzed Hydrolysis of 9-Acetyl-9-fluorenyl Acetate.—One-half gram of the above acetate was dissolved in 10

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[13] E. Venus-Danilova, A. Ivanov and I. Martynov, *J. Gen. Chem.* (*U.S.S.R.*), **21**, 1806 (1951); *C. A.*, **46**, 7070 (1952).

[14] T. Takeshima, This Journal, **75**, 4107 (1953).

[15] K. Campbell, B. Campbell and L. Eby, *ibid.*, **60**, 2882 (1938).

[16] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948.

[17] E. Bamberger and S. Hooker, *Ann.*, **229**, 157 (1885).

[18] J. Schmidt and R. Metzger, *Ber.*, **39**, 3897 (1906).

ml. of methanol. A mixture of 10 ml. of methanol, 5 ml. of water, and 2 ml. of concd. sulfuric acid was added, and the solution was heated under gentle reflux for 2.5 hours. It was then filtered and diluted with water to the cloud point. The solid which crystallized upon cooling was recrystallized from petroleum ether; m.p. 105.5–106°, 0.20 g. The melting point was not depressed by admixture with II. Concentration of the mother liquor yielded an additional 0.07 g., m.p. 102–104°.

9-Methoxy-9-ethynylfluorene (IV).—To a solution of 2.0 g. of 9-ethynyl-9-fluorenol (I) in 15 ml. of methanol was added 10 ml. of methanol containing 2 drops of concd. sulfuric acid. The reaction mixture was allowed to stand at room temperature for 15 hours. At the end of that time, the solution was poured into 50 ml. of water containing 2 g. of potassium carbonate. The 9-methoxy-9-ethynylfluorene (IV) was recrystallized from aq. ethanol; m.p. 124–125°, 0.9 g. A small sample was purified by two sublimations; m.p. 125–126°.

Anal. Calcd. for $C_{16}H_{12}O$: C, 87.24; H, 5.49. Found: C, 86.91; H, 5.72.

9-Methoxy-9-acetylfluorene (III).—One-half gram of the ethynyl ether described above was dissolved in 15 ml. of methanol. Mercuric sulfate (0.20 g.) was added, and the reaction mixture was allowed to stand at room temperature for 19 hours. It was then heated on a steam-bath for 10 minutes, diluted with *ca.* 10 ml. of hot water and filtered. The filtrate was diluted with an additional 10 ml. of water and cooled in ice. Pale yellow needles of 9-methoxy-9-acetylfluorene crystallized from solution; m.p. 124–127°, 0.45 g. The compound was recrystallized once from aq. ethanol and once from petroleum ether; m.p. 131–132°.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 81.01; H, 6.16.

Alkaline Hydrolysis of III.—A solution of 0.35 g. of KOH in 3 ml. of methanol was added to a solution of 0.25 g. of 9-methoxy-9-acetylfluorene in 4 ml. of methanol, and the reaction mixture was heated under reflux for 2 hours. The solution was diluted with water to the cloud point and filtered. Upon cooling and stirring, a white solid was obtained, m.p. 41–42°, 0.15 g. Recrystallization from aq. ethanol gave 9-fluorenyl methyl ether, m.p. 42–43°, reported[19] 43.5°.

9-Ethynyl-9-fluorenyl Acetate.—9-Ethynyl-9-fluorenol (2.00 g.) was dissolved in 10 ml. of acetic anhydride containing 3 ml. of pyridine, and the solution was allowed to stand at room temperature for 16 hours. It was then heated on a steam-bath for 15 minutes and poured into a large excess of cold aq. potassium carbonate. The solid was collected and washed thoroughly with aq. potassium carbonate and then with water. Recrystallization from a mixture of carbon tetrachloride and petroleum ether gave 2.02 g. of 9-ethynyl-9-fluorenyl acetate, m.p. 129–130°. A sample recrystallized twice from the same solvent pair had a melting point of 130–131°.

Anal. Calcd. for $C_{17}H_{12}O_2$: C, 76.67; H, 5.30. Found: C, 76.50; H, 5.17.

Saponification.—One-half gram of the acetate was dissolved in 20 ml. of methanol. A solution of 0.5 g. of KOH in 5 ml. of water was added. The reaction mixture was allowed to stand at room temperature for 16 hours. It was then filtered and diluted with 100 ml. of water. Upon cooling, a crop of white needles crystallized from solution, m.p. 107–108°, 0.38 g. The melting point was not depressed by admixture with 9-ethynyl-9-fluorenol (I).

9-Ethoxy-9-ethynylfluorene.—To a solution of 0.50 g. of 9-ethynyl-9-fluorenyl acetate in 15 ml. of absolute ethanol was added 5 ml. of absolute ethanol containing a trace of concd. sulfuric acid. The reaction mixture was allowed to stand at room temperature for 20 hours. At the end of that time, it was poured into a solution of 1 g. of potassium carbonate in 75 ml. of water. Upon cooling with ice and stirring, a yellow solid precipitated, m.p. 112–116°, 0.45 g. The melting point was depressed by admixture with starting material. The 9-ethoxy-9-ethynylfluorene thus obtained was recrystallized from aq. ethanol: first crop, m.p. 122–123°, 0.29 g.; second crop, m.p. 116–119°, 0.05 g. The first crop was recrystallized from petroleum ether; m.p. 122–123°.

Anal. Calcd. for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 86.92; H, 6.09.

Fluorenylideneacetaldehyde (VI).—One-hundredth of a mole (2.06 g.) of 9-ethynyl-9-fluorenol (I) was dissolved in 50 ml. of 95% ethanol. A solution of 3.0 g. of concd. sulfuric acid in 5 ml. of water and 25 ml. of 95% ethanol was added and the reaction mixture was heated under gentle reflux. At the end of 20 minutes, an additional 25 ml. of 95% ethanol was added, and heating continued. After refluxing for a total of 2 hours, the solution was cooled and filtered. The filtrate was cooled in an ice-bath and 100 ml. of aq. 5% sodium carbonate solution was added. The orange colored solid thus obtained was recrystallized from aq. ethanol: first crop, m.p. 115–117°, 1.25 g. A sample was recrystallized twice from aq. ethanol and twice from petroleum ether; m.p. 116.5–117.5°.

Anal. Calcd. for $C_{15}H_{10}O$: C, 87.35; H, 4.89. Found: C, 87.35; H, 5.31.

Further dilution of the mother liquor from the first recrystallization from aq. ethanol gave a pale yellow solid, m.p. 106–110°, 0.25 g. The melting point was depressed by admixture with the aldehyde, but it was raised by admixture with 9-ethoxy-9-ethynylfluorene prepared by the method described above. This material was dissolved in 15 ml. of ether and washed thoroughly with two 15-ml. portions of saturated aq. sodium bisulfite solution, dried over anhydrous magnesium sulfate, and evaporated to dryness. Recrystallization from petroleum ether yielded 0.1 g. of the ether, m.p. 120–121.5°. The melting point was not depressed by admixture with 9-ethoxy-9-ethynylfluorene described above.

Fluorenylideneacetic Acid.—The method used was essentially that described by Delépine and Bonnet.[20] One-hundredth of a mole (2.06 g.) of fluorenylideneacetaldehyde was placed in a 300-ml. 3-neck flask fitted with a mechanical stirrer and a dropping funnel. To this was added 30 ml. of 95% ethanol, which was heated gently to increase the solubility of the aldehyde. A solution of 3.0 g. of silver nitrate in 3 ml. of water was added and the mixture was allowed to cool to room temperature. A solution of 2.5 g. of KOH in 30 ml. of 80% aq. ethanol was added dropwise with good stirring. Addition was complete in 15 minutes and the reaction mixture was stirred for an additional 15 minutes. The solution then was filtered and the solid residue was washed with 60 ml. of hot water. The combined filtrate and wash liquors were extracted with two 50-ml. portions of ether. The aqueous layer was then heated to boiling for 10 minutes. Upon cooling and acidifying with aq. nitric acid, fluorenylideneacetic acid precipitated from solution. The crude product was recrystallized from aq. ethanol; 1.35 g., m.p. 226–228°, reported[21] 227–228°.

9-(Chlorovinylidene)-fluorene (VII).—One-eighth mole (25.8 g.) of 9-ethynyl-9-fluorenol was dissolved in 100 ml. of absolute ether in a 500-ml. 3-neck round-bottom flask fitted with a mercury seal stirrer, a reflux condenser, and a dropping funnel. One-half gram of pyridine was added and a solution of 18 g. of freshly distilled thionyl chloride in 25 ml. of absolute ether was added dropwise with stirring. The reaction was exothermic and the temperature was maintained at 28–30° by occasional cooling. The addition of thionyl chloride was complete in 20 minutes. Stirring was continued and a few minutes after addition had been completed, a yellow solid began to separate from solution. After the reaction mixture had been stirred for one hour, the solid was filtered off and dried. The yield was 14.8 g. Concentration of the mother liquor gave only tarry materials. The solid was recrystallized from methyl Cellosolve; yield 10.5 g. It darkened at 210° and melted with decomposition at 223–225°.

Anal. Calcd. for $C_{15}H_9Cl$: Cl, 15.78. Found: Cl, 15.51.

The assigned structure (VII) appears justified by the analysis, oxidation to fluorenone and spectral evidence. A solution in chloroform revealed the typical allenic bands at 5.15 and 5.25 μ (weak) and no absorption at 3.1 and 4.7 μ (terminal acetylenes). The ultraviolet absorption also indicated unusual unsaturation: $\lambda_{\max}$ 273 mμ (ϵ 21,400), $\lambda_{\max}$ 365 mμ (shoulder), $\lambda_{\max}$ 375 mμ (ϵ 13,400) in chloroform, 6.41×10^{-5} mole/liter.

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(19) A. Kliegl, *Ber.*, **62**, 1334 (1929).

(20) M. Delépine and P. Bonnet, *Compt. rend.*, **149**, 39 (1909).

(21) A. Sieglitz and H. Jassoy, *Ber.*, **54**, 2135 (1921).

A solution of 5.0 g. of 9-ethynyl-9-fluorenol in 30 ml. of ether was placed in a 200-ml. flask and 15 ml. of concentrated hydrochloric acid was added. The mixture was allowed to stand at room temperature for 16 hours. The solid material then was filtered off and washed with ether; m.p. 224–227° dec., yield 4.5 g. (83%). Recrystallization from methyl Cellosolve did not change the melting point, nor was any depression of melting point observed upon admixture with the compound obtained by the thionyl chloride procedure.

Oxidation of VII.—Five grams of sodium dichromate was dissolved in 20 ml. of glacial acetic acid. To the cold solution was added 1.5 g. of the chloroallene (VII). The temperature was increased slowly to the boiling point and the reaction mixture was allowed to reflux for 4 hours. It was then poured into 100 ml. of cold 2% aq. hydrochloric acid and allowed to stand for 24 hours. The fluorenone was filtered off and recrystallized from aq. ethanol; m.p. 78–80°, 0.95 g. Recrystallization from ether gave 0.40 g. of fluorenone, m.p. 82–82.5°, not depressed by an authentic sample. Evaporation of the mother liquor yielded an additional 0.25 g., m.p. 75–78°.

β,β-Diphenylacrolein (IX).—Diphenylethynylcarbinol (10.0 g.) was dissolved in 25 ml. of 95% ethanol and added dropwise to a refluxing solution of 50 ml. of 95% ethanol, 15 ml. of water and 5.0 g. of concd. sulfuric acid. Addition required 0.5 hour and refluxing was continued for 15 minutes after all of the ethynylcarbinol had been added. The solution was then cooled and poured into 250 ml. of ice-water and further cooled in an ice–salt-bath. The oil which initially separated from solution solidified upon stirring. Recrystallization from a mixture of ligroin and ether gave 7.8 g. of β,β-diphenylacrolein, m.p. 44.5–45.5°, reported[22] 44–45°.

Semicarbazone.—The semicarbazone was made in the usual manner,[16] and melted at 214–214.5°, reported[23] 214–215°.

β,β-Diphenylacrylic Acid.—β,β-Diphenylacrylic acid was prepared by the silver oxide oxidation of β,β-diphenylacrolein as described above for the oxidation of fluorenylideneacetaldehyde. One-hundredth of a mole (2.08 g.) yielded 1.88 g. of acid melting at 158–159.5°. Recrystallization from aq. ethanol raised the melting point to 159–160°, reported[24] 162°.

Diphenylacetylcarbinol Acetate (X).—The procedure was adapted from one devised by Ruzicka and co-workers.[11] Two-hundredths of a mole (4.16 g.) of diphenylethynylcarbinol was dissolved in 25 ml. of glacial acetic acid containing 1 ml. of acetic anhydride. Mercuric acetate (7.0 g.) was added in portions with shaking. The clear solution was allowed to stand at room temperature for 16 hours, saturated with hydrogen sulfide and allowed to stand for 3 hours. It was then filtered through a layer of Norit A decolorizing charcoal, and the solid material was washed with 10 ml. of hot glacial acetic acid. The acetic acid filtrates were poured into 100 ml. of water and allowed to stand for 2 hours. Since the oily reaction product could not be induced to solidify, it was taken up in 150 ml. of ether–petroleum ether (1:6) and the aqueous mother liquor was extracted with 50 ml. of ether. The combined organic layers were washed with five 100-ml. portions of water and dried over anhydrous magnesium sulfate. The solution was then concentrated to 100 ml. and chromatographed on a 20 × 250 mm. column packed with Eimer and Amend adsorption alumina which had been activated by heating at *ca.* 200° for one hour. The column was then eluted with ether–petroleum ether (1:4) and evaporation of the solvent from the various fractions gave an oil which readily solidified. The acetate of diphenylacetylcarbinol thus obtained melted at 48.5–52°. The yield was 3.09 g. (58%). Recrystallization from a mixture of petroleum ether and carbon tetrachloride raised the melting point to 52.5–53°.

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 75.18; H, 6.11.

Diphenylacetylcarbinol (XI).—A 1.30-g. portion of the hydration product described above was dissolved in 15 ml. of 5% methanolic KOH and allowed to stand at room temperature for 2 hours. The solution was then filtered and cooled in an ice-bath. Cold water was added gradually with stirring and cooling. Diphenylacetylcarbinol crystallized from solution and the addition of water was continued until 100 ml. had been added. The product was collected and dried; m.p. 65–66.5°, 1.00 g. (91%). Recrystallization from a mixture of ligroin and carbon tetrachloride raised the melting point to 66–67°, as reported by Stevens and Sherr.[25]

Acetylation.—To a solution of 0.50 g. of XI in 4 ml. of acetic anhydride was added 3 ml. of acetic anhydride containing 1 drop of concd. sulfuric acid. The reaction mixture was allowed to stand at room temperature for 0.5 hour, heated on a steam-bath for 5 minutes and then poured slowly into 75 ml. of water with vigorous stirring. Upon cooling and stirring, a solid was obtained which melted at 45–48°, 0.54 g. The melting point was depressed by admixture with XI, but not by the original hydration product (X). Recrystallization from petroleum ether raised the melting point to 52–53°.

Oxime.—The oxime of XI was prepared in the usual way,[16] m.p. 158.5–160°, reported[26] 159–160°.

Action of Boron Trifluoride on Diphenylacetylcarbinol (XI).—A solution of 3 drops of boron trifluoride etherate, 0.7 ml. of acetic anhydride and 3 ml. of glacial acetic acid was added to a solution of 0.30 g. of diphenylacetylcarbinol in 4 ml. of glacial acetic acid and the reaction mixture was allowed to stand at room temperature for 24 hours. It then was poured into 50 ml. of cold water with vigorous stirring. The oil which separated from solution solidified upon prolonged standing at room temperature. After 10 days, it was collected and dried, m.p. 43–48°; crystallization from petroleum ether raised the melting point to 50.5–52.5°, 0.27 g. The melting point was depressed by admixture with XI but not with the original hydration product, diphenylacetylcarbinol acetate.

2-Methoxy-2-phenyl-3-butyne (XIII).—To a solution of 21.9 g. (0.15 mole) of phenylmethylethynylcarbinol (XII) in 40 ml. of methanol was added 10 ml. of methanol containing 1.0 g. of concd. sulfuric acid and 5 ml. of water. The resulting solution was heated under reflux for 1.5 hours. At the end of that time, it was cooled and poured into 100 ml. of brine and extracted with 200 ml. of ether in three portions. The combined ethereal layers were washed with 100 ml. of brine solution containing 5 g. of sodium carbonate, and then with two 100-ml. portions of water. The ethereal solution was dried over anhydrous magnesium sulfate and distilled through a modified Claisen flask; b.p. 63–64° at 3.5 mm. The yield of 2-methoxy-2-phenyl-3-butyne was 20.4 g. (85%). A sample which was fractionally distilled had the following physical constants: b.p. 62–63° at 3 mm., $n^{25}D$ 1.5059, d^{25} 0.9173.

Anal. Calcd. for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.03; H, 7.92.

2-Methoxy-2-phenyl-3-butanone (XIV).—A solution of 1.0 g. of concd. sulfuric acid in 25 ml. of methanol was placed in a 300-ml. 3-neck round-bottom flask fitted with a mechanical stirrer, a thermometer, and a dropping funnel. Red mercuric oxide (1.0 g.) was added and the temperature was raised to 55°. A solution of 24.0 g. of the ethynyl ether XIII in 25 ml. of methanol was added dropwise with stirring over a period of 45 minutes. The reaction was noticeably exothermic and the temperature was maintained at 55°. Half-gram portions of red mercuric oxide were added when half of the ethynyl compound had been added and when addition was complete. The reaction mixture was stirred at 55° for 2 hours after addition had been completed. During this time 10 ml. of water was added. The dark colored solution was then filtered into 100 ml. of brine, and the product was extracted with 200 ml. of ether in three portions. The combined ethereal layers were washed with 100 ml. of brine, 75 ml. of water, 75 ml. of 5% sodium carbonate solution and two 75-ml. portions of water. The ethereal solution was dried over anhydrous magnesium sulfate and then distilled through a modified Claisen flask; b.p. 89–90° at 3 mm. The yield of 2-methoxy-2-phenyl-3-butanone was 21.7 g. (81%). A sample which was fractionally distilled had the following physical constants: b.p. 89–90° at 3 mm., $n^{25}D$ 1.5041, d^{25} 1.0305.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.35; H, 7.43.

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[23] K. Ziegler and P. Tiemann, *ibid.*, **55**, 3413 (1922).

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[25] C. Stevens and A. Sherr, *J. Org. Chem.*, **17**, 1228 (1952).

[26] T. Temnikova, *J. Gen. Chem.* (*U.S.S.R*), **15**, 514 (1945); *C. A.*, **40**, 4695 (1946).

Oxime.—The oxime of XIV was prepared in the usual way,[16] m.p. 66.5–67.5° after two crystallizations from aq. ethanol.

Anal. Calcd. for $C_{11}H_{15}NO_2$: N, 7.25. Found: N, 6.94.

Semicarbazone.—The semicarbazone was prepared in the usual way,[16] m.p. 164–165° after two crystallizations from aq. ethanol.

Anal. Calcd. for $C_{12}H_{17}N_3O_2$: N, 17.86. Found: N, 17.72.

Beckmann Rearrangement of the Oxime of XIV.—To a solution of 2.0 g. of the oxime in 10 ml. of sodium-dried ether was added 1 ml. of thionyl chloride in 3 ml. of ether. After a few minutes, 10 ml. of ice-water was added, followed by 10 ml. of ethanol. The reaction mixture was heated to boiling and ethanol was added until the oily layer dissolved. The solution was then neutralized with 10% sodium hydroxide and buffered with 3 g. of sodium acetate. After adding 2.0 g. of semicarbazide hydrochloride, the solution was filtered and allowed to cool slowly to room temperature. A large excess of ice-water then was added and the semicarbazone precipitated from solution, m.p. 192–195°, 1.2 g. After two crystallizations from aq. ethanol, the melting point was 198–200°, and was not altered by admixture with an authentic sample of acetophenone semicarbazone.

Phenylmethylacetylcarbinol (**XV**).—A solution of 1.0 g. of concd. sulfuric acid and 2 ml. of water in 50 ml. of methanol was placed in a 300-ml. 3-neck round-bottom flask fitted with a mechanical stirrer, a dropping funnel, and a thermometer. The temperature was raised to 55°, and 1.0 g. of red mercuric oxide was added. A solution of 20.0 g. of phenylmethylethynylcarbinol (XV) in 50 ml. of methanol and 5 ml. of water was added dropwise over a period of 1.5 hours. When half of the acetylenic carbinol had been added, 0.5 g. of mercuric oxide also was added. The reaction was slightly exothermic, and the temperature was maintained at 55–57°. When addition of the ethynylcarbinol was complete, another 0.5-g. portion of catalyst was added, and the reaction mixture was stirred at 55° for one hour. During this time, 10 ml. of water was added. The reaction mixture was then worked up in the manner described above for XIV. Distillation through a modified Claisen flask yielded 18.1 g. (81%) of phenylmethylacetylcarbinol boiling at 100–102° at 3.2 mm. A sample which was fractionally distilled had the following physical constants: b.p. 99–100° at 3 mm., $n^{25}D$ 1.5215, d^{25} 1.0764. The literature gives the following physical constants: b.p. 122–123° at 8 mm., 88–90° at 2 mm., d^{17} 1.0801, d^{20}_4 1.0915, $n^{20}D$ 1.5340.[27]

Oxime.—The oxime of XV was prepared in the usual way.[16] A sample recrystallized twice from dilute aq. ethanol melted at 105.5–106.5°.

Anal. Calcd. for $C_{10}H_{13}NO_2$: N, 7.82. Found: N, 7.85.

Semicarbazone.—The semicarbazone of phenylmethylacetylcarbinol melted at 183–184°, in agreement with the literature value.[28]

Acetate.—Phenylmethylacetylcarbinol (1.0 g.) was dissolved in 5 ml. of acetic anhydride and to it was added 3 ml. of acetic anhydride containing 1 drop of concd. sulfuric acid. The solution was allowed to stand at room temperature for 0.5 hour, heated on a steam-bath for 10 minutes and then poured into 60 ml. of brine. The oil which separated from solution was extracted with 30 ml. of ether and the ethereal layer was washed with two 25-ml. portions of water. The ether was removed on a steam-bath and the residual oil was dissolved in 10 ml. of 95% ethanol. A solution of 4.0 g. of sodium acetate and 3.0 g. of semicarbazide hydrochloride in 4 ml. of water was added and the hot solution was allowed to cool slowly to room temperature. After 10 hours, it was filtered, diluted with 50 ml. of water, and cooled in an ice-bath. In this way, 0.8 g. of the semicarbazone was obtained. Its melting point upon heating slowly was 172–175° and it was depressed by admixture with the semicarbazone of phenylmethylacetylcarbinol. Recrystallization from aq. ethanol raised the melting point to 177–178° when heated slowly from below 170°. When heated rapidly to 180°, the semicarbazone showed no sign of melting. Upon raising the temperature slowly from 180°, it melted sharply at 182.5–183°. Von Auwers and Mauss[28] report 183° for the melting point of the semicarbazone of the acetate of phenylmethylacetylcarbinol. Admixture with the semicarbazone of phenylmethylacetylcarbinol depressed the melting point below 170°.

Hydration of XII in Glacial Acetic Acid.—Red mercuric oxide (0.2 g.) was added to a solution of 1.0 g. of phenylmethylethynylcarbinol (XII), 0.5 ml. of acetic anhydride and 3 drops of boron trifluoride etherate in 10 ml. of glacial acetic acid. An exothermic reaction took place, and the solution darkened rapidly. After standing at room temperature for 24 hours, it was poured into 50 ml. of water and extracted with 50 ml. of ether. The ethereal layer was washed with two 50-ml. portions of water and dried over anhydrous magnesium sulfate. The ether then was removed by heating on a water-bath and 25 ml. of 95% ethanol was added to the residual oil. A solution of 2.0 g. of semicarbazide hydrochloride and 3.0 g. of sodium acetate in 5 ml. of water was added and heated to boiling. The hot solution was then filtered and allowed to cool slowly to room temperature. After 6 hours, it was filtered again and diluted with a large excess of water. The slightly discolored product thus obtained melted at 180–182°. Upon recrystallization from aq. ethanol, 0.35 g. of an almost colorless solid was obtained, m.p. 182.5–183° when heated slowly from 180°, not depressed by admixture with the semicarbazone of the acetate of phenylmethylacetylcarbinol prepared above.

β-Methylcinnamaldehyde (**XVI**).—To a mixture of 60 ml. of dioxane, 20 ml. of water and 10.0 g. of concd. sulfuric acid, was added 5.0 g. of phenylmethylethynylcarbinol. The two-phase system was heated under reflux for 45 minutes. It was then poured into 50 ml. of water, cooled, and extracted with 100 ml. of ether. The ether layer was washed with two 50-ml. portions of water and then with two 50-ml. portions of 40% sodium bisulfite solution. The combined bisulfite layers were filtered, cooled in ice, and made basic with cold 40% KOH. The aldehyde was extracted with 100 ml. of ether and the ether layer was washed with two 100-ml. portions of water and then dried over anhydrous magnesium sulfate. The ether was removed, and 0.85 g. of oil was obtained. This had a sharp, pleasant odor and gave a red precipitate when tested with 2,4-DNP test reagent. The oil was dissolved in 8 ml. of 95% ethanol and a solution of 2.5 g. of semicarbazide hydrochloride and 3 g. of sodium acetate in 8 ml. of water was added. A copious white precipitate separated from solution. The mixture was heated on a steam-bath for one hour and then allowed to cool slowly to room temperature for an additional 5 hours. It was then diluted with 100 ml. of ice-water and the solid material was collected and dried, m.p. 190–197°. Recrystallization from aq. ethanol yielded two crops of crystals: first crop, m.p. 205–207°, 0.7 g.; second crop, m.p. 194–196°, 0.1 g. The melting point of each crop was depressed by admixture with the semicarbazone of acetophenone, and the melting point of the second crop was raised by admixture with the first crop. Recrystallization of the first crop from aq. ethanol did not raise the melting point. The literature reports 206° for the melting point of β-methylcinnamaldehyde semicarbazone.[29]

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