The analytical sample crystallized from methanol as long yellow-green plates, m.p. 288–290°, (C) λ_{max} (log ϵ), 247-(3.93), 283 mμ(3.69); λ_{min} 233(3.74), 271(3.61), 327 mμ-(3.16).

Anal. Calcd. for $C_{16}H_{14}ClNO_6$: C, 54.63; H, 4.01; N, 3.98. Found: C, 54.67; H, 4.17; N, 3.96.

DURHAM, N. C.

[CONTRIBUTION FROM THE CHEMISTRY RESEARCH LABORATORY, AERONAUTICAL RESEARCH LABORATORIES, AIR FORCE RESEARCH DIVISION, AIR RESEARCH AND DEVELOPMENT COMMAND AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Synthesis of Spiro[cyclohexane-1,9′-fluorene] and Related Compounds[1]

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The synthesis of the title compound (VI) is described (Chart I). A more direct route to the key intermediate spiro [cyclohexane-1,9′-fluoren]-4-one (V) is provided by the cyclization of 9,9-fluorenedipropionitrile (II) to 3-cyano-4-aminospiro-[Δ^3-cyclohexene-1,9′-fluorene] (VII) by a catalytic quantity of potassium *t*-butoxide in *t*-butyl alcohol followed by hydrolysis to the spiro ketone V in an acetic-phosphoric acid mixture. Infrared and ultraviolet spectral evidence is presented for the entirely enolic structures of 3-carbomethoxyspiro [cyclohexane-1,9′-fluoren]-4-one (IVa) and 3-carboxamidospiro-[cyclohexane-1,9′-fluoren]-4-one (VIII), respectively. The structure and spectra of the interesting diketo spirane, 11,12-dihydro-1H,10H-benzo[*h,i*]fluoranthene-3,10-(2H)-dione (XI), are also discussed.

Because spiranes are rigid molecules they may show unusual transport properties in the liquid state. It was therefore decided to investigate this class of compounds, initially restricted to five- or six-membered carbocyclic rings, as part of a general program to correlate physical properties with certain structural features.

A search of the literature at the inception of this work revealed no generally applicable method for the synthesis of spirocyclohexane compounds.[2] It occurred to us that an attractive synthetic route to these compounds is offered *via* the dicyanoethylation[3a] of the active methylene group contained in the ring of a cyclic compound, followed by cyclization of the resulting γ,γ-disubstituted dinitrile or diacid or diester derived therefrom.[4] Other workers have employed similar sequences with acyclic active methylene compounds to obtain 4-substituted cyclohexanones[5a–d] and piperidones.[5e–i] We report here the application of this method to the synthesis of spiro[cyclohexane-1,9′-fluorene] (VI) and related compounds as outlined in Chart I.[6] The dinitrile II obtained by cyanoethylation of fluorene[3b,7] was converted directly to the dimethyl ester IIIa by hydrogen chloride in methanol and

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[1] Presented before the Division of Organic Chemistry at the 137th meeting of the American Chemical Society, Cleveland, Ohio, April, 1960, Abstr. p. 29-O.

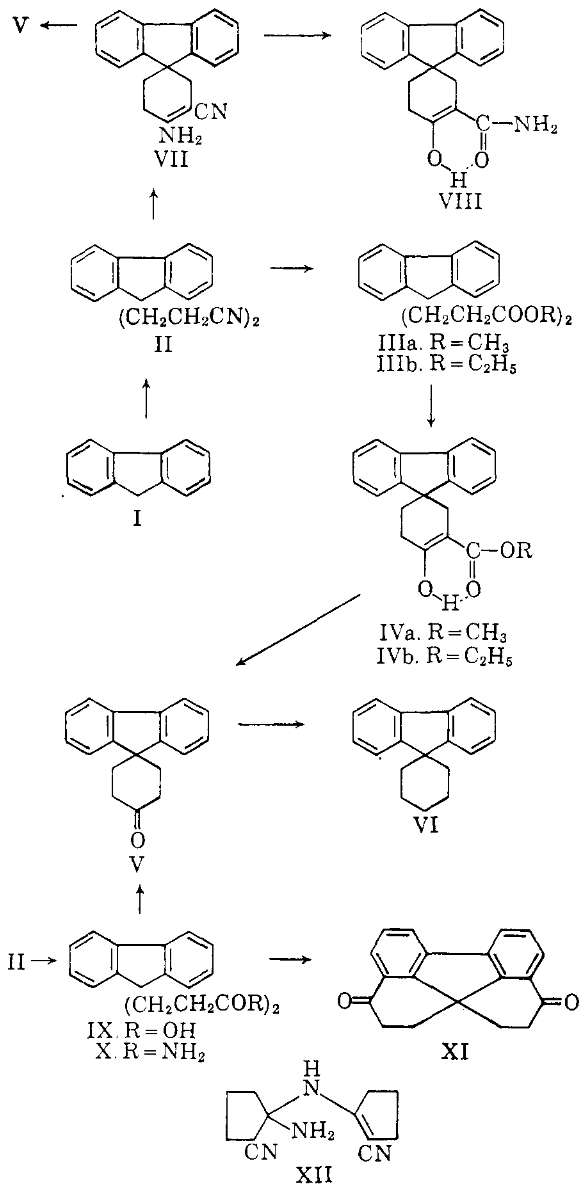
[2] Recently methods differing from those reported herein for the synthesis of spirocyclohexane-type compounds have been published. *Cf.* (a) M. Mousseron, R. Jacquier, and H. Christol, *Compt. rend.*, **239**, 1805 (1954); *Bull. soc. chim. France*, 346 (1957); M. Mousseron, H. Christol, and F. Plenat, *Compt. rend.*, **245**, 1281 (1957); (b) K. Heyns and A. Heins, *Angew. Chem.*, **68**, 414 (1956); *Ann.*, **604**, 133 (1957); (c) S. Winstein and R. Baird, *J. Am. Chem. Soc.*, **79**, 756 (1957); R. Baird and S. Winstein, *J. Am. Chem. Soc.*, **79**, 4238 (1957); (d) W. R. Hatchard, *J. Am. Chem. Soc.*, **80**, 3640 (1958).

[3] (a) H. S. Bruson, *Org. Reactions*, **V**, 79 (1949); (b) 112 (1949).

[4] When this work was started in July 1951, there were no recorded references to the use of this method for spirane synthesis. Subsequently, however, other workers have used this same approach in the synthesis of various spirocyclohexane compounds. The method of ring closure is indicated in parentheses. (a) R. Ya. Levina, N. P. Shusherina, and T. A. Kaminskaya, *Doklady Akad. Nauk, S.S.S.R.*, **86**, 79 (1952), *cf. Chem. Abstr.*, **47**, 4849 (1953) (pyrolysis of diacid with barium hydroxide). Reference to spirane synthesis appears as a footnote only in the original article without experimental details or physical constants; (b) R. P. Mariella and R. J. Clutter, Abstracts of Papers, 126th Meeting, American Chemical Society, 59-O (1954), *cf.* R. P. Mariella, R. Clutter, and H. G. Ebner, *J. Org. Chem.*, **20**, 1702 (1955) (pyrolysis of diacid with lead oxide); (c) R. H. Burnell and W. I. Taylor, *J. Chem. Soc.*, 3486 (1954) (Dieckmann condensation); (d) D. A. Stauffer and O. E. Fancher, U. S. Pat. **2,647,896** (1953), *cf. Chem. Abstr.*, **48**, 9405 (1954) and *J. Org. Chem.*, **25**, 935 (1960) (Dieckmann condensation), (sodium-potassium sand on dinitrile—*i.e.*, Thorpe reaction); (e) G. D. Johnson, W. B. Lindsey, and B. R. Jones, *J. Am. Chem. Soc.*, **78**, 461 (1956) (Dieckmann condensation); (f) K. Sheng and H. Chi-Yi, *Acta Chim. Sinica*, **22**, 138 (1956) (Dieckmann condensation). The latter journal is not abstracted by Chemical Abstracts Service. A reproduction of this article was obtained from the library of the Chemical Society, London, England; (g) F. M. Dean and K. Manunapichu, *J. Chem. Soc.*, 3112 (1957). The following cyclization attempts were unsuccessful; (lithium ethylanilide on dinitrile—*i.e.*, Ziegler-Thorpe reaction), (Dieckmann condensation on diester), (acetic anhydride on diacid); (h) P. McCloskey, *J. Chem. Soc.*, 4732 (1958) (Dieckmann condensation).

[5] (a) M. Rubin and H. Wishinsky, *J. Am. Chem. Soc.*, **68**, 838 (1946); (b) R. L. Frank and J. B. McPherson, Jr., *J. Am. Chem. Soc.*, **71**, 1387 (1949); (c) F. F. Blicke and E. Tsao, *J. Am. Chem. Soc.*, **75**, 3999 (1953); (d) E. C. Horning, M. G. Horning, N. J. Fish, and M. W. Rutenberg, *J. Am. Chem. Soc.*, **74**, 773 (1952); (e) G. B. Bachman and R. S. Barker, *J. Am. Chem. Soc.*, **69**, 1535 (1947); (f) R. C. Fuson, W. E. Parham, and L. J. Reed, *J. Am. Chem. Soc.*, **68**, 1239 (1946); (g) S. M. McElvain and G. Stork, *J. Am. Chem. Soc.*, **68**, 1049 (1946) and earlier references cited therein; (h) A. A. Cook and K. J. Reed, *J. Chem. Soc.*, 399 (1945); (i) S. M. McElvain and R. E. McMahon, *J. Am. Chem. Soc.*, **71**, 901 (1949).

CHART I



to the diethyl ester IIIb by sulfuric acid in ethanol respectively. Alternatively, the elegant method of Clinton and Laskowski[8] was used to esterify the diacid IX, derived from the alkaline hydrolysis of II, to the dimethyl ester IIIa. The Dieckmann reaction was then used to cyclize these esters with sodium-potassium sand in xylene without isolation of the intermediate β-keto esters IVa or IVb.[9a] The latter were hydrolyzed and decarboxylated in hydrochloric-acetic acid solution in 23% over-all yield to the spiro ketone V[9b] which was reduced to the spirane VI by the modified Wolff-Kishner method.[10] The spirane VI has been reported by Wieland and Probst[11] who prepared the intermediate spiro[Δ^3-cyclohexene-1,9′-fluorene] from 9-methylenefluorene and butadiene in ether at 140° in a sealed tube. They then hydrogenated this compound over platinum oxide in acetic acid to the spirane VI, m.p. 80.0–80.5°. This melting point coincides with that observed for VI prepared herein and thus confirms the structures assigned to V and VI. These workers did not indicate any elemental analysis for VI or any yield data for either step in their synthesis.

The spiro ketone V was also obtained in 48% yield by treatment of the diacid IX with acetic anhydride followed by pyrolysis of the resulting anhydride at 250° under reduced pressure (Blanc reaction). The spiro ketone could also be produced in low yield by heating the diacid IX with barium hydroxide under reduced pressure.

When the direct cyclization of the dinitrile II to the spiroenaminonitrile VII was attempted with a catalytic quantity of sodium ethoxide in ethanol, i.e. according to Thorpe's[12] original reaction conditions, only starting material was recovered.[13] Similarly, none of the desired product VII was produced from the reaction of II with a catalytic quantity of sodium-naphthalene addition complex in hot dioxane under nitrogen.[5e] The simplicity of the original Thorpe reaction is appealing without its necessity for an inert atmosphere or high-dilution apparatus. It was surmised that a stronger base would be necessary to effect cyclization of II as well as a solvent in which both the base and II were soluble. Accordingly, the variation wherein a catalytic quantity of sodium *t*-butoxide in boiling *t*-butyl alcohol was used to cyclize substituted adiponitriles[14] was applied to the cyclization of the dinitrile II to the spiroenaminonitrile VII. Po-

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(6) Most of the work reported herein was essentially completed and submitted to The Journal of the American Chemical Society on October 14, 1953. At the suggestion of the referee and the editor, publication was withheld pending conversion of the intermediate enaminonitrile VII to the ketone V. Now the details of this successful hydrolysis as well as the difficulties that other workers have experienced in similar hydrolyses are included in the main text. Subsequently, there appeared an abstract of U. S. Pat. **2,647,896** (*cf.* ref. 4d) which contained some results similar to those in this manuscript. Any such overlap of our work with that in the patent is clearly indicated in the main text.

(7) H. A. Bruson, *J. Am. Chem. Soc.*, **64**, 2457 (1942).

(8) R. O. Clinton and S. C. Laskowski, *J. Am. Chem. Soc.*, **70**, 3135 (1948).

(9) (a) Stauffer and Fancher (ref. 4d) obtained a 90% yield of IVa, 3-carbomethoxyspiro[cyclohexane-1,9′-fluoren]-4-one, from IIIa with a 2:1 mole ratio of sodium methoxide in toluene, a procedure for the Dieckmann reaction similar to that employed by W. Bachmann, W. Cole, and A. L. Wilds, *J. Am. Chem. Soc.*, **62**, 835 (1940); (b) These workers (ref. 4d) obtained an 83% yield of spiro ketone V from keto ester IVa by hydrolysis in hydrochloric-acetic acid solution.

(10) Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).

(11) H. Wieland and O. Probst, *Ann.*, **530**, 274 (1937).

(12) J. F. Thorpe, *J. Chem. Soc.*, **95**, 1903 (1909).

(13) Recently, Q. E. Thompson, *J. Am. Chem. Soc.*, **80**, 5483 (1958), reported that only starting material was obtained when Thorpe's original procedure was used on adiponitrile (*cf.* ref. 12).

(14) N. R. Easton, H. D. Reiff, G. Svarnas, and B. V. Fish, *J. Am. Chem. Soc.*, **74**, 260 (1952); N. R. Easton and S. J. Nelson, *J. Am. Chem. Soc.*, **75**, 640 (1953).

tassium was used instead of sodium. The reaction proceeded smoothly protected only from atmospheric moisture to give a 77% yield of the desired product VII in a high degree of purity. Use of an inert atmosphere did not improve the yield. Stauffer and Fancher[4d] using the method of Horning and co-workers[15] prepared VII from II in 80% yield by use of sodium-potassium sand (equivalent quantity) in hot toluene under nitrogen.

In connection with this cyclization reaction of II, the recent results of Thompson[13] merit some comment. He found that the homogeneous reaction of adiponitrile with a catalytic quantity of potassium *t*-butoxide in *t*-butyl alcohol produced a 76% yield of dimeric enaminonitrile XII rather than monomeric 1-amino-2-cyanocyclopentene. Ebullioscopic molecular weight determinations for VII gave the following values: 278, 268 (in benzene); 279, 296 (in methyl ethyl ketone). The calculated molecular weight for $C_{19}H_{16}N_2$ monomer is 272. These molecular weight results indicate that VII is a monomer rather than a dimer. This conclusion is corroborated by the infrared spectrum for VII[16] which shows only one band in the C≡N stretching region for a conjugated nitrile (2169 cm.$^{-1}$) while XII shows two bands in this region, one for a conjugated (2180 cm.$^{-1}$) and one for an unconjugated (2240 cm.$^{-1}$) C≡N group.[13] The absence of dimer in the present reaction can be explained in terms of the insolubility of the monomer VII in *t*-butyl alcohol. As the cyclization reaction proceeds, increasingly more product VII is precipitated from solution so that no further reaction to produce dimer can occur.[17]

The hydrolysis of the enaminonitrile VII to the spiro ketone V presented some difficulty. The use of sulfuric acid in various dilutions or a sulfuric-acetic acid mixture gave only a water-soluble product which yielded a reddish oil (probably a sulfonic acid) upon evaporation of the water.[18] Likewise, the use of a hydrochloric-acetic acid mixture gave a low-melting solid which showed only a weak absorption for the carbonyl group in the infrared spectrum. Basic hydrolysis with potassium hydroxide in diethylene glycol afforded none of the desired product.

Other workers have reported difficulty in hydrolyzing other cyclic enaminonitriles or ketonitriles to ketones. Thus Frank and McPherson[5b] reported the unsuccessful hydrolysis of a cyclic six-membered ketonitrile with 10% aqueous sodium hydroxide, or 37% and 50% sulfuric acid solutions. Hydrolysis was accomplished in low yield by means of 10% aqueous sulfuric acid. Using various concentrations of sulfuric acid, two groups of workers[19] failed to hydrolyze 6-imino-5-cyano-1,2,3,4-dibenz-1,3-cycloheptadiene *via* the intermediate iminocarboxylic acid to the corresponding ketone. One successful procedure[19b] involved treatment of the enaminonitrile with concentrated sulfuric acid at room temperature for twenty-four hours followed by steam distillation in dilute sulfuric acid. It appears that an aromatic sulfonic acid, probably formed during the concentrated sulfuric acid treatment, is being hydrolyzed to the parent aromatic hydrocarbon by steam distillation. Horning and co-workers[15,20] hydrolyzed their cyclic enaminonitriles *via* the indirect route: enaminonitrile → ketonitrile → keto ester (or enol ether[4d]) → ketone. Likewise Stauffer and Fancher[4d] followed this same sequence to hydrolyze the enaminonitrile VII to the ketone V in about 48% overall yield. The direct conversion of the enaminonitrile VII to the ketone V has been effected in this study by means of an acetic-phosphoric acid mixture in 88% yield (60% yield of analytically pure material). Thus, it appears that sulfuric acid should be avoided in hydrolysis whenever an extended reflux period is necessary and sulfonation is a possible side reaction.[21] An acetic-phosphoric acid mixture is therefore the reagent of choice in these cases.[22] The conversion of the enaminonitrile VII to the ketone V constitutes the proof of structure for VII in conjunction with the aforesaid molecular weight and infrared spectral data which established VII as a monomer.

The reaction of the enaminonitrile VII with hot polyphosphoric acid led to the ketoamide VIII in excellent yield. Although other workers[14,23] have obtained cyclic ketoamides from cyclic enaminonitriles as by-products in attempted hydrolysis to the ketone, this conversion represents the first example of a clean-cut reaction leading to a single product in high yield. It appears that the vinylamino group is hydrolyzed to the ketone in the

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(15) E. C. Horning, M. G. Horning, and E. J. Platt, *J. Am. Chem. Soc*, **69**, 2929 (1947).

(16) S. Baldwin, *J. Org. Chem.*, **26**, 3288 (1961).

(17) One must assume a small but finite solubility of VII in *t*-butyl alcohol (actually a saturated solution). However, the potassium *t*-butoxide in solution probably converts this all to the anionic form and no free VII remains in solution. Thus dimer formation is prevented (*cf.* ref. 13).

(18) Sulfonation of the aromatic nucleus can readily occur with cold concentrated sulfuric acid or hot dilute sulfuric acid. *Cf.* (a) A. L. Green and D. H. Hey, *J. Chem. Soc.*, 4306 (1954); (b) C. K. Bradsher, E. D. Little, and D. J. Beavers, *J. Am. Chem. Soc.*, **78**, 2153 (1956); (c) C. K. Bradsher and D. J. Beavers, *J. Org. Chem.*, **21**, 1067 (1956).

(19) (a) T. Sakan and M. Nakazaki, *J. Inst. Polytech., Osaka City Univ.*, **1**, No. 2, 23 (1950) [*Chem. Abstr.*, **46**, 5036 (1952)]; (b) C. W. Muth, W. Sung, and Z. B. Papanastassiou, *J. Am. Chem. Soc.*, **77**, 3393 (1955).

(20) E. C. Horning, M. G. Horning, and E. J. Platt, *J. Am. Chem. Soc.*, **70**, 2072 (1948); **72**, 2731 (1950); E. C. Horning and A. F. Finelli, *J. Am. Chem. Soc.*, **73**, 3741 (1951).

(21) This precaution applies to reactive aromatic (ref. 18 and 19) and olefinic (ref. 5b) systems.

(22) It has been noted that K. Mislow and F. A. McGinn, *J. Am. Chem. Soc.*, **80**, 6036 (1958), have also used the acetic-phosphoric acid mixture to hydrolyze a cyclic seven-membered enaminonitrile to the corresponding ketone.

(23) M. S. Newman and W. L. Mosby, *J. Am. Chem. Soc.*, **73**, 3738 (1951).

acid medium[24] while the nitrile group is converted to the amide.[25]

The reaction of polyphosphoric acid on the diacid IX resulted in the interesting diketo spirane XI in fair yield. This spirane was previously produced by the cyclization of the diacid chloride of IX with stannic chloride in unspecified yield.[26] The action of liquid hydrogen fluoride on the diacid IX or diester IIIb resulted only in unchanged starting material and hydrolysis to diacid IX respectively.

In the first attempt to convert the diacid IX *via* the diacid chloride in the conventional manner[27] to the diamide X, a compound (m.p. 227–228°) was obtained which was readily soluble in hot ethanol and gave the correct elemental analysis for the desired diamide X. The preparation of the diamide X directly from the dinitrile II with hot polyphosphoric acid[25a] resulted in a compound (m.p. 258–260°) which was insoluble in hot ethanol as well as in most common organic solvents (hot or cold) but also gave the correct elemental analysis for the diamide X. Subsequent attempts to produce the low-melting form of X by the conventional procedure[27] resulted only in the high-melting form. Finally, boron trifluoride–diacetic acid complex[28] was used to convert the dinitrile II to the diamide X to determine whether this procedure would yield the low-melting form of X. Again, only the high-melting form of X was obtained. The identical nature of all the high melting forms was confirmed by undepressed mixture melting points and identical infrared spectra.

Samples of high-melting X from each of the three different preparations as well as the low-melting form gave a positive ferric hydroxamate test for primary amides.[29] A sample of high-melting X prepared by the boron trifluoride method was hydrolyzed to the acid IX by potassium hydroxide in propylene glycol with the evolution of ammonia. Unfortunately, only enough low-melting X was available for an elemental analysis, an infrared spectral determination, and an x-ray diffraction curve. The infrared spectrum of low-melting X differed in some respects from that of high-melting X (see discussion of spectral data below). The x-ray diffraction curves for the two compounds contained many points of similarity but were definitely not identical. On this basis, it appears that X can exist in dimorphic forms.

The infrared and ultraviolet spectral data for the enaminonitrile VII and related compounds are discussed in the following paper.[16] The spectral data for the β-keto ester IVa indicate that it is totally enolic and chelated. Thus, its infrared spectrum (5% chloroform) exhibits bands at 1658 and 1618 cm.$^{-1}$, assigned to chelated conjugated C=O and conjugated C=C respectively, while no bands appear in the normal ester C=O and ketone C=O regions.[30] Other workers have likewise reported the occurrence of totally enolic β-keto esters,[30,31a–f] but only one other example in a spirocyclic ring system has been observed.[31e]

Since IVa contains the fluorene chromophore and the enolic β-keto ester chromophore, which both absorb strongly in the same region of the spectrum, it is necessary to subtract the spectrum of VI from that of IVa to obtain the value for the enolic β-keto ester.[32]

The ultraviolet subtraction spectrum (IVa–VI) gives: $\lambda_{\max}^{95\%\ C_2H_5OH}$ 255.5 mμ (ϵ 8400); $\lambda_{\max}^{95\%\ C_2H_5OH/0.1N\ HCl}$ 255 mμ (ϵ 8800); $\lambda_{\max}^{95\%\ C_2H_5OH/0.1N\ KOH}$ 286 mμ (ϵ 12,100), 304 mμ (ϵ 6400.) These values agree reasonably well with those previously reported for totally enolic chelated β-keto esters.[31a,c–e] In addition the substantial bathochromic shift (*ca.* 31 mμ) which occurs in basic solution is typical of enolizable β-keto esters[31a,e] and cyclic β-diketones.[33] At present, no reasonable explanation can be offered for the additional band at 304 mμ in basic solution.

The infrared and ultraviolet spectra for the spiroketoamide VIII indicate that it too is entirely in the enolized state. Thus for VIII (mineral oil mull)

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(24) R. A. Benkeser, R. F. Lambert, P. W. Ryan, and D. G. Stoffey, *J. Am. Chem. Soc.*, **80**, 6573 (1958).

(25) (a) H. R. Snyder and C. T. Elston, *J. Am. Chem. Soc.*, **76**, 3039 (1954); (b) C. R. Hauser and C. J. Eby, *J. Am. Chem. Soc.*, **79**, 725 (1957).

(26) (a) K. Hoffmann and E. Tagmann, *Helv. Chim. Acta*, **32**, 1470 (1949); (b) CIBA Ltd., Swiss Pat. **276,141** [*Chem. Abstr.*, **47**, 7546 (1953)]; (c) CIBA Ltd., British Pat. **666,713** [*Chem. Abstr.*, **47**, 7546 (1953)].

(27) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *Systematic Identification of Organic Compounds*, 4th ed., Wiley, New York, 1956, p. 200.

(28) C. R. Hauser and D. S. Hoffenberg, *J. Org. Chem.*, **20**, 1448 (1955).

(29) S. Soloway and A. Lipschitz, *Anal. Chem.*, **24**, 898 (1952).

(30) N. J. Leonard, H. S. Gutowsky, W. J. Middleton, and E. M. Peterson, *J. Am. Chem. Soc.*, **74**, 4070 (1952).

(31) (a) J. B. Brown, H. B. Henbest, and E. R. H. Jones, *J. Chem. Soc.*, 3634 (1950); (b) E. Wenkert and T. E. Stevens, *J. Am. Chem. Soc.*, **78**, 5627 (1956); (c) S. P. Findlay, *J. Org. Chem.*, **22**, 1385 (1957); **23**, 391 (1958); (d) O. L. Chapman and J. Meinwald, *J. Org. Chem.*, **23**, 162 (1958); (e) F. M. Dean, T. Francis, and K. Manunapichu, *J. Chem. Soc.*, 4551 (1958); (f) G. B. Kline, *J. Am. Chem. Soc.*, **81**, 2251 (1959); (g) In ref. 31e, an alternative formulation, wherein the hydrogen atom migrates to the ester carbonyl group rather than the keto group, has been proposed for conjugated chelated esters such as IVa. For a discussion as to the plausibility of such a structure *cf.* E. Wenkert and B. G. Jackson, *J. Am. Chem. Soc.*, **81**, 5601 (1959), footnote 13.

(32) It was assumed *a priori* that there is little or no interaction between these two chromophores since they are separated by at least one insulating methylene group. The spectrum of the hydrocarbon VI, however, differs somewhat from that of fluorene itself both in $\lambda_{\max}$ and $\epsilon_{\max}$ values (see Experimental). Thus, the spirocyclohexane ring does exert some steric effect on the fluorene chromophore. Therefore, the spectrum of VI rather than that of fluorene itself was used to obtain the subtraction spectrum because VI more nearly simulates the conformation of IVa.

(33) E. R. Blout, V. W. Eager, and D. C. Silverman, *J. Am. Chem. Soc.*, **68**, 566 (1946).

no band appears in the normal ketone C=O region, while bands appear at 3425 and 3185 cm.$^{-1}$ (NH stretching), 1664 cm.$^{-1}$ (chelated conjugated C=O or amide I band), 1637 cm.$^{-1}$ (NH_2 deformation or amide II band), and 1582 cm.$^{-1}$ (C=C stretching). For the analogous β-ketoamides *N,N'*-*p*-phenylenebisacetoacetamide,[34a] *N,N'*-*p*-bisphenylenebisacetoacetamide,[34b] and *N,N'*-bisacetoacetyltoluene-2,6-diamine,[34c] there are bands at 1721–1715 cm.$^{-1}$ (presumably due to the normal ketone C=O stretching), 1664–1645 cm.$^{-1}$ (amide I band), and 1567–1536 cm.$^{-1}$ (amide II band). It seems therefore that there is little or no lowering of the amide C=O frequency through conjugation or chelation. This contrasts with the abnormal lowering of the ester C=O band in chelated conjugated esters described above.

While the infrared spectrum for VIII indicate that it is totally enolic, it remains for the ultraviolet difference spectrum (VIII–VI) to show that it is conjugated chelated as well. Thus the ultraviolet difference spectrum (VIII–VI) parallels that of the difference spectrum for the β-keto ester (IVb–VI): $\lambda_{\max}^{95\%\ C_2H_5OH}$ 255 mμ (ε 8600); $\lambda_{\max}^{95\%\ C_2H_5OH/0.1N\ HCl}$ 254 mμ (ε 8900). In addition, a dilute solution of VIII in 95% ethanol produced a bluish-purple color with ethanolic ferric chloride indicative of an enol. This appears to be the first reported example of a totally enolic β-ketoamide.

The infrared spectrum of the high-melting diamide X (mineral oil mull) showed bands at 3448, 3226, 3106 cm.$^{-1}$ (NH stretching), 1672 cm.$^{-1}$ (amide I band), and 1631 cm.$^{-1}$ (amide II band). The low-melting form of the diamide X (mineral oil mull) had the following bands: 3460, 3300, 3155 cm.$^{-1}$ (NH stretching), 1672 cm.$^{-1}$ (amide I band), and 1626 cm.$^{-1}$ (amide II band). In addition, the low-melting form had sharp but relatively weak bands at 1704 and 1610 cm.$^{-1}$ The remainder of the two spectra was essentially the same. It has been noted that the infrared spectrum of that polymorphic form which has a lesser degree of crystalline order and lower stability usually exhibits a greater number of absorption bands.[35] On this basis the observed lower melting point, increased solubility, and greater number of absorption bands in the infrared spectrum all indicate a lesser degree of crystallinity for the low-melting polymorph of X and are consistent with its apparent instability relative to the high-melting polymorph.

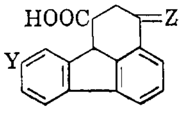
TABLE I

ULTRAVIOLET DATA FOR 1-TETRALONE AND ANALOGS THEREOF

Compound	$\lambda_{\max}$ mμ ($\epsilon_{\max}$)	Solvent
1-Tetralone	248.5 (12,200), 291.5 (1780)	95% C_2H_5OH
XIII	257 (25,120), 328 (5750)	95% C_2H_5OH
XIV	260 (28,840), 273 (19,950), 327 (8320)	Dioxane
XI	225 (16,500), 254 (21,600), 264 (21,800), 336 (5360)	95% C_2H_5OH

It is impossible to construct a model of the diketo spirane XI with Stuart-Briegleb scale models because of the failure to close completely the carbonyl-containing rings. The spirocyclic ring system tends toward perpendicularity while the fluorene portion is planar. The resulting strain within these rings might be expected to force the carbonyl groups out of the plane of the fluorene ring. That this is not the case is indicated by the infrared spectrum of XI (mineral oil mull) which shows a strong band at 1675 cm.$^{-1}$ characteristic of a conjugated or aromatic C=O. For example, the C=O frequency in 1-tetralone is 1681 cm.$^{-1}$ (pure liquid).[36] Thus the carbonyl groups and the fluorene ring in XI must be coplanar to accommodate the resonance between them while the carbonyl-containing rings are only at about a 30° angle to each other.

The ultraviolet spectrum of XI resembles that of 3-keto-1,2,3,10b-tetrahdyrofluoranthene-1-carboxylic acid (XIII),[37a] the 9-bromo analog of XIII (XIV),[38] and 1-tetralone.[37b] The data are summarized in Table I. The ultraviolet spectrum of XV,[37c] the non-ketonic analog of XIII, resembles that of fluorene[37d] rather than that of XIII. Therefore, if the carbonyl groups were not conjugated with the fluorene ring in XI, then its spectrum should also resemble that of XV and fluorene rather than that of XIII, XIV, and 1-tetralone. These ultraviolet data support the view that the carbonyl groups in XI are coplanar with the fluorene ring.



XIII. Z = O, Y = H
XIV. Z = O, Y = Br
XV. Z = H_2, Y = H

EXPERIMENTAL[39]

9,9-Fluorenedipropionitrile (II). This compound was prepared by the published procedure[3b,7] in essentially the same yield (72%), m.p. 120–121°, after two recrystallizations from ethanol (reported m.p. 121°).[3b,7] $\bar{\nu}_{\max}$: 2247 cm.$^{-1}$ (unconjugated nitrile).[40]

During the course of this investigation, it was found that the versatile cyanoethylation catalyst, a 40% aqueous solution of benzyltrimethylammonium hydroxide, is no longer generally available either from the Rohm and Haas Company, Philadelphia, Pa., under the trade name of Triton B,

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[34] Sadtler Infrared Spectra Collection (a) No. 7165; (b) No. 7166; (c) No. 7167. All these spectra were determined as potassium bromide pellets.

[35] M. E. Taylor and T. L. Fletcher, *J. Am. Chem. Soc.*, **80**, 2246 (1958).

[36] W. M. Schubert and W. A. Sweeney, *J. Am. Chem. Soc.*, **77**, 4172 (1955).

[37] R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, Wiley, New York, 1951 (a) No. 327; (b) No. 59; (c) No. 317; (d) No. 311.

[38] A. Weizmann, *J. Org. Chem.*, **16**, 185 (1951).

or from the Commercial Solvents Corporation, Terre Haute, Ind. The latter company as well as the Matheson, Coleman, and Bell Company, Norwood, Ohio, supply an approximately 60% aqueous solution of benzyltrimethylammonium chloride from which an approximately 40% aqueous solution of the hydroxide may be conveniently prepared as follows[41]:

To 17.5 ml. (18.7 g., 0.06 mole of anhydrous salt based on a 60% solution with sp. gr. at 20°/20° of 1.07) of benzyltrimethylammonium chloride solution and 7.5 ml. of water contained in a 50 ml. Erlenmeyer flask is added 7.65 g. (0.033 mole) of silver oxide. The resulting slurry is stirred magnetically for 15 min. and then filtered through a medium-porosity sintered-glass funnel. The filtrate thus obtained (about 25 ml.) is an approximately 40% solution of the free base (*p*H 11 as determined by *p*H Hydrion paper) with a pale yellow color and definite amine odor. If larger quantities are made, it is best to store the remaining hydroxide solution in a polyethylene bottle or paraffin-lined glass bottle in a refrigerator.[42] The hydroxide thus prepared has been successfully used in the above reaction as well as in other cyanoethylations in this laboratory.

Dimethyl 9,9-fluorenedipropionate (IIIa). A. Dry hydrogen chloride was passed into a well stirred suspension of 27.2 g. (0.1 mole) of II in 275 ml. of methanol. The mixture became very hot with noticeable reflux during the first 30 min. After about 1.5 hr., a light yellow solution resulted with a white solid separating 0.5 hr. later. During the next hour, the mixture cooled to room temperature. It was then immersed in an ice-bath and the hydrogen chloride addition rate was increased. When the mixture became saturated, it was heated under reflux on the steam bath for 3 hr., the methanol was distilled, and the white solid was dissolved in 200 ml. of ethylene dichloride. The solution was washed with 50 ml. of water, three 50-ml. portions of 5% sodium bicarbonate solution, with 50 ml. of water and dried over magnesium sulfate. The solvent was flash-distilled, the last traces under reduced pressure with a water pump. Upon cooling, the viscous yellow residue solidified and was recrystallized from 50 ml. of methanol to give 26.2 g. (78%) of product, m.p. 78–79°. An additional 2.5 g. was obtained upon cooling the filtrate in the refrigerator, m.p. 77–79°, total yield 85%. Using a water separator, Bruson obtained a 50% yield of IIIa by heating 9,9-fluorenedipropionic acid (IX) and methanol in toluene with sulfuric acid (m.p. 81–82°).[43] As the product of the present investigation was prepared by a different method and possessed a somewhat lower m.p., the substance was analyzed after three recrystallizations from methanol, m.p. 78–79°. $\bar{\nu}_{max}$: 1724 cm.$^{-1}$ (ester carbonyl).

Anal. Calcd. for $C_{21}H_{22}O_4$: C, 74.53; H, 6.55. Found: C, 74.78; H, 6.64.

B. In another run a slightly different procedure was used. Thus dry hydrogen chloride was passed directly through an empty safety trap into 125 ml. of methanol in a 300-ml. three necked flask with stirring for about 5 hr. The increase in weight then amounted to about 60 g.[44] Then 5.45 g. (0.02 mole) of II was added and the solution refluxed with stirring overnight. A white solid separated about 30 min. after initial reflux and more solid appeared after the reaction mixture cooled to room temperature. Then the solution was poured into 100 ml. of water. The resulting granular solid was collected by suction filtration, washed well with water, and air-dried to give 5.91 g. (87%) of IIIa, m.p. 80–81°. The melting point of a 1:1 mixture of this compound with authentic IIIa prepared in Method A above was 79–80°, while their infrared spectra were identical. The uncrystallized material is pure enough to be used in subsequent reactions.

C. *Alternative preparation of* IIIa. 9,9-Fluorenedipropionic acid (IX) was prepared by hydrolysis of the dinitrile II by Bruson's procedure.[7] Thus from 27.2 g. (0.1 mole) of II was obtained 29.9 g. of crude diacid IX, m.p. 270–272°. After recrystallization from ethanol, 24.6 g. (80%) of pure product remained, m.p. 274–275°, N. E. 156 (calcd. 155) (reported[7] m.p. 273–274°). $\bar{\nu}_{max}$ (mineral oil mull): 1712 cm.$^{-1}$ (carboxylic acid carbonyl). Compound IX (15.5 g., 0.05 mole) was esterified by the method of Clinton and Laskowski[8] to give 14.0 g. (83%) of IIIa, m.p. 78–79°. The m.p. of a mixture of this ester with authentic IIIa prepared above was 78–79° and their infrared spectra were identical.

Diethyl 9,9-fluorenedipropionate (IIIb). A mixture of 27.2 g. (0.1 mole) of II, 73.6 g. (1.6 moles, 97 ml.) of ethanol, and 39.2 g. (0.4 mole, 22.5 ml.) of concd. sulfuric acid was heated in an oil bath at 130° for 12 hr. When the mixture cooled to room temperature, a solid crystalline mass resulted. Recrystallization of this material from ethanol gave 30.7 g. (84%) of IIIb, m.p. 104–105°. Bruson obtained a 91% yield of this ester from IX by the method described above (m.p. 102–103°).[43] The substance was analyzed after three recrystallizations from ethanol, m.p. 104.5-105.5°. $\bar{\nu}_{max}$ 1724 cm.$^{-1}$ (ester carbonyl).

Anal. Calcd. for $C_{23}H_{26}O_4$: C, 75.38; H, 7.15. Found: C, 75.23; H, 7.36.

9,9-Fluorenedipropionamide (X) A. *From the diacid* IX.[45] The diamide was prepared from the diacid IX by the usual method.[27] The crude product from one run was crystallized from 95% ethanol to give m.p. 227-228°. X-ray data[39]: 7.74–0.4, 4.97–0.4, 4.75–1.0, 4.70–0.6, 4.37–0.5, 4.23–0.8, 3.51–0.5.

Anal. Calcd. for $C_{19}H_{20}O_2N_2$: C, 74.00; H, 6.54. Found: C, 74.05; H, 6.26.

Subsequent experiments by the identical procedure gave only high-melting diamide (see Methods B and C below), m.p. 258–260°.

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(39) All melting points were taken in Pyrex glass capillaries in a modified Hershberg apparatus with Anschütz total-immersion thermometers and on a Fisher-Johns apparatus with calibrated thermometer. Microanalyses were performed by Mrs. K. Kelly and Mr. D. Wilson of UCLA, by Oakwold Laboratory, and by Schwartzkopf Laboratory. The molecular weight determinations were performed by the Clark Microanalytical Laboratory. Infrared spectra were determined at UCLA by Mr. George Moore on a Beckman Model IR-2T Spectrometer and by the author at AFRD on a Perkin-Elmer Model 21 Spectrophotometer. These spectra were determined as approximately 10% solutions in chloroform unless otherwise noted. Ultraviolet spectra were determined on Cary Model 14 and Cary Model 11MS Spectrophotometers in 95% ethanol (distilled). All λ_{max} values are reported in mμ followed by ϵ_{max} values in parentheses. The x-ray powder diffraction curves were determined on a North American Philips X-ray Diffraction Apparatus operated at 35,000 volts and 15 milliamperes with a scanning rate of 1° per minute and a CuK_α radiation source. The interplanar spacings (Å) and relative intensities are given for the six most intense lines, 1.0 being the strongest.

(40) R. E. Kitson and N. E. Griffith, *Anal. Chem.*, **24**, 343 (1952).

(41) N. Collie and S. B. Schryver, *J. Chem. Soc.*, **57**, 778 (1890).

(42) A 60–70% aqueous solution of benzyltrimethylammonium hydroxide has recently been prepared in larger quantities by this same general procedure with the substitution of a basic ion exchange resin for the silver oxide. *Cf.* J. Stuchlik, M. Tichy, and V. Prochazka, *Chem. Listy*, **50**, 662 (1956) [*Chem. Abstr.*, **50**, 8497 (1956)].

(43) H. A. Bruson, U. S. Pat. **2,339,373** (1944); *cf. Chem. Abstr.*, **38**, 3664 (1944).

(44) According to W. Gerard and E. Macklen, *J. Appl. Chem.* (*London*), 241 (1956), 125 ml. of methanol at 27.6° should absorb about 80 g. of dry hydrogen chloride gas.

(45) With Lt. Mutsuo Kuramoto, USAF. The m.p.'s reported in these experiments were determined with a Kofler Micro Hotstage and uncalibrated thermometer.

B. *From the dinitrile* II.[45] One gram of the dinitrile II and 40 g. of polyphosphoric acid[46] contained in an Erlenmeyer flask was heated for 5 min. with stirring in a Wood's metal bath preset at 150°. The yellow solution was poured onto cracked ice, the resulting white solid collected by suction filtration and air-dried to give 1.16 g. of material, m.p. 237–257°. This material was insoluble in acetone, 95% ethanol, benzene, chloroform, ether, ethyl acetate, tetrahydrofuran, *n*-hexane, nitromethane, 5% aqueous sodium bicarbonate, and 10% aqueous sodium hydroxide. It was soluble in hot glacial acetic acid, hot concentrated hydrochloric acid[47] and dimethylformamide. Crystallization from the following solvents gave the corresponding m.p.: dimethylformamide-water (small needles) 257–259°; acetic acid–water (small needles) 256–258°; concentrated hydrochloric acid–water (small needles) 256.5–260°. The last material was submitted for analysis. X-ray data:[39] 8.19–0.9, 7.78–0.9, 6.42–0.6, 4.73–1.0, 4.27–0.7, 4.23–0.8.

Anal. Calcd. for $C_{19}H_{20}O_2N_2$: C, 74.00; H, 6.54; N, 9.09; O, 10.38. Found: C, 74.13; H, 6.70; N, 9.11; O, 10.18.

The melting point of a 1:1 mixture of this material with high-melting diamide prepared in Method A above was not depressed. Likewise their infrared spectra were identical.

C. *From the dinitrile* II. The method of Hauser and Hoffenberg[23] was followed with boron trifluoride–diacetic acid complex.[48] Thus, 3.00 g. (0.011 mole) of II was dissolved in a mixture of 24 ml. $BF_3.2CH_3COOH$ and 4 ml. (0.22 mole) of water. The resulting bluish-green solution became warm and was heated in an oil bath at 120° for 10 min. After the dark green solution was allowed to stand overnight, it was then neutralized with 100 ml. of aqueous 6*N* sodium hydroxide. The solid which separated was collected by suction filtration, washed well with water, and air-dried, m.p. 255–257°, yield practically quantitative. The m.p. of a 1:1 mixture of this material with high-melting X prepared in Methods A and B was not depressed. Likewise, all their infrared spectra were identical. The x-ray data showed that the interplanar spacings for this material were identical to those for the material prepared in Method B. All these high-melting diamides gave a positive ferric hydroxamate test for primary amides by the procedure of Soloway and Lipschitz.[29] To characterize X further, 0.3 g. (1 mmole) of X, 8 ml. of 1*N* potassium hydroxide in propylene glycol, and 0.1 ml. water was refluxed for 24 hr. During this time, there was a slow but steady evolution of ammonia (identified by odor and blue color reaction to moistened pink litmus paper). The solution was poured onto a mixture of cracked ice and concentrated hydrochloric acid. The resultant white solid was collected by suction filtration, washed well with water and air-dried, m.p. 269–273°. The m.p. of a 1:1 mixture of this compound with authentic IX prepared above was not depressed.

Spiro[cyclohexane-1,9'-fluoren]-4-one (V). A. In a system protected from moisture a fine sand was prepared from 1.2 g. (0.05 g.-atom) of clean sodium and 0.2 g. (0.0005 g.-atom) of clean potassium in 100 ml. of purified xylene (distilled from sodium). With the xylene boiling vigorously, 18.3 g. (0.05 mole) of IIIb dissolved in 200 ml. of purified xylene was added over 12 hr. The color changed from light yellow to dark yellow to reddish brown over this period. After the mixture cooled to room temperature, 10 ml. of absolute ethanol was added dropwise with stirring, then 50 g. of crushed ice, and finally 20 ml. of 3*N* hydrochloric acid. The mixture was filtered from an amorphous powdery material appearing at the interface of the two layers. This substance, probably polymeric in nature, was discarded. The aqueous layer was extracted with three 50-ml. portions of xylene and the extracts combined with the original xylene layer. A few drops of the xylene solution in ethanol gave a characteristic purple color with ethanolic ferric chloride. The xylene was evaporated in a current of air on a steam bath leaving a dark-yellow gummy residue. The latter was boiled for 5 hr. in 100 ml. of acetic acid, 50 ml. of hydrochloric acid, and 10 ml. of water. After the mixture cooled to room temperature, it was neutralized with 20% sodium hydroxide and extracted with three 100-ml. portions of ether. The combined extracts were washed with three 100-ml. portions of water, 100 ml. of 5% acetic acid, 100 ml. of 5% sodium carbonate, and with water. After the solution was dried over magnesium sulfate and the ether was evaporated, 2.9 g. (23%) of yellowish-white solid separated, m.p. 205–209°. For analysis, a sample was sublimed at 130° (0.1 mm.), m.p. 208–209°. $\bar{\nu}_{max}$: 1709 cm.$^{-1}$ (C=O in a six-membered ring).[49] $\lambda_{max}^{95\%\ C_2H_5OH}$ 221.5 (infl.) (14,900); 228.5 (6020); 268 (17,000); 290 (5620); 301 (8040).

Anal. Calcd. for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found: C, 87.34; H, 6.26.

By the method outlined above, from 16.9 g. (0.05 mole) of IIIa was obtained 2.3 g. (18%) of V, m.p. 202–207°. The substance was recrystallized five times from ethanol, m.p. 208–209°. A 1:1 mixture of this compound with authentic V melted at 208–209°.

An attempted cyclization of IIIa with sodium hydride in benzene[50] resulted in recovery of starting material and some hydrolysis to the diacid IX, m.p. 274–275°, which showed no depression on a mixture m.p. determination with authentic IX.

The *oxime* was prepared by refluxing 1.0 g. of V, and 1.0 g. of hydroxylamine hydrochloride in 5 ml. of ethanol, and 5 ml. of pyridine for 2 hr. The solvents were evaporated in a stream of air, the last traces being removed under reduced pressure. The solid was triturated and digested in hot water, filtered with suction, washed well with water, and air-dried. The crude product crystallized from ethyl acetate in needles, m.p. 221–222°.

Anal. Calcd. for $C_{18}H_{17}ON$: C, 82.10; H, 6.51; N, 5.32. Found: C, 82.32; H, 6.29; N, 5.03.

The yellow *2,4-dinitrophenylhydrazone* was produced by the method of Johnson.[51] It was insoluble in hot benzene, ethanol, and acetic acid. For the analytical sample, it was triturated and digested in boiling benzene, filtered with suction, and washed well with hot benzene., m.p. 273–275°.

Anal. Calcd. for $C_{24}H_{20}O_4N_4$: C, 67.28; H, 4.71; N, 13.08. Found: C, 67.27, H, 4.74; N, 13.09.

The *semicarbazone* was prepared by refluxing for 5 hr. 0.25 g. of V, and 0.25 g. of semicarbazide hydrochloride in 3 ml. of ethanol to which 0.3 ml. of pyridine had been added. The mixture was poured into 25 ml. of water and digested on the steam bath for 1 hr. The product was filtered with suction, washed well with water, and air-dried. The crude product crystallized from acetic acid in glistening plates, m.p. 227–228°.

Anal. Calcd. for $C_{19}H_{19}ON_3$: C, 74.73; H, 6.27; N, 13.76. Found: C, 74.83; H, 6.41; N, 14.08.

B.[45] The published procedure[52] was modified as follows: To 3.1 g. (0.01 mole) of diacid IX was added 18.6 g. of acetic anhydride and the mixture was heated at 100° for 24 hr. The solution was evaporated at 100° under reduced pressure and another 18.6 g. of acetic anhydride was added to the remaining gelatinous mass. The previous procedure of heating and evaporating was repeated. The remaining gray-

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(46) We are indebted to the Victor Chemical Company and the Virginia-Carolina Chemical Company for generous samples of polyphosphoric acid.

(47) See E. E. Magat, *J. Am. Chem. Soc.*, **73**, 1367 (1951), who reported that in general amides are soluble in concentrated hydrochloric acid.

(48) We are indebted to the General Chemical Division, Allied Chemical and Dye Corporation, for a sample of this material.

(49) L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, 2nd Ed., Methuen & Co., Ltd., London, 1958, p. 147.

(50) J. F. Tinker, *J. Org. Chem.*, **16**, 1417 (1951).

(51) G. D. Johnson, *J. Am. Chem. Soc.*, **73**, 5888 (1951).

(52) A. Horeaux, *Compt. rend.*, **228**, 2039 (1949).

ish-white gelatinous mass was pyrolyzed at 250° (0.3 mm.) for 1 hr. The solid which had sublimed was scraped from the distilling head and both the reaction flask and head were rinsed with ethanol. The sublimed material and ethanol washings were combined, the entire mixture heated to dissolve as much as possible, and the resulting solution filtered from the insoluble material. The volume was reduced to 250 ml. and the solution was chilled to give 1.25 g. of a white solid, m.p. 195–210°. This solid gave a positive 2,4-dinitrophenylhydrazine test. The volume was further reduced to 30 ml. to give 0.28 g. of crystals, m.p. 189–203°. The first crop was sublimed at 170° (0.15 mm.) to give 1.19 g. (48%) of solid, m.p. 205–207°. The m.p. of a 1:1 mixture of this compound with authentic spiro ketone prepared in Method A was 205–206°.

C.[45] In a 100-ml. round bottom flask equipped with an air condenser were placed 5 g. (0.0161 mole) of diacid IX and 1 g. (0.00317 mole) of powdered barium hydroxide octahydrate. The mixture was heated at 295–300° for 24 hr. After about 2 hr. needles had sublimed on the side of the flask. There was a black residue remaining at the bottom of the flask and some of the sublimed needles appeared to have decomposed. The needles were recrystallized from absolute ethanol to give 0.1 g. (2.5%) of spiro ketone V, m.p. 207–208°. The m.p. of a mixture of this compound with authentic V prepared in Method A was 206–207°.

3-Carbomethoxyspiro[cyclohexane-1,9′-fluoren]-4-one (IVa). The procedure of Stauffer and Fancher[4d] was followed. A few drops of the washed toluene solution of ester IVa in 95% ethanol gave a deep purple color with one drop of aqueous 10% ferric chloride indicative of the presence of enol. Then 3 g. of crude IVa was crystallized from 10 ml. of methanol and 5 ml. of acetone, m.p. 122.5–123° (reported[4d] m.p. 122–123°). This material was used in the infrared and ultraviolet spectral studies. $\lambda_{max}^{95\%\ C_2H_5OH}$ 228 (8500); 263 (23,000); 289.5 (6600); 301.5 (8600); 221 (infl.) (17,500). $\lambda_{max}^{95\%\ C_2H_5OH/0.1N\ HCl}$ 228 (8600); 263 (23,100); 289.5 (5700); 301.5 (8000); 221 (infl.)(17,200). $\lambda_{max}^{95\%\ C_2H_5OH/0.1N\ KOH}$ 228 (7700); 268 (21,600); 290 (17,600); 301.5 (15,000).

Sprio[cyclohexane-1,9′-fluorene] (VI). The modified Wolff-Kishner method[10] was employed. Thus from 2.35 g. (0.00948 mole) of V, 1.33 g. (0.02 mole) of 85% potassium hydroxide, and 1 ml. (0.0175 mole) of 85% hydrazine hydrate in 25 ml. of diethylene glycol was obtained 2.00 g. (90%) of the spirane VI, m.p. 78–79°, recrystallized once from methanol. For analysis, a sample was sublimed at 80° (0.1 mm.), m.p. 79.5–80° (reported[11] m.p. 80.0–80.5°). $\lambda_{max}^{95\%\ C_2H_5OH}$ 228 (5400); 264 (14,600); 267.5 (14,800); 290 (5620); 301 (8880). For fluorene itself: $\lambda_{max}^{95\%\ C_2H_5OH}$ 220 (15,800); 261.5 (19,300); 288.5 (6300); 300 (9600).

Anal. Calcd. for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.51; H, 7.62.

Spiro[Δ^3-cyclohexene-1,9′-fluorene]-3-carbonitrile, 4-amino- (VII). In a 300-ml. flask fitted with a reflux condenser capped by a drying tube, there was placed 13.6 g. (0.05 moles) of II in 150 ml. of *t*-butyl alcohol (distilled from calcium hydride). Clean potassium (0.1 g.) was added and the mixture was heated under reflux for 12 hr. to give 10.5 g. (77%) of VII, m.p. 264–265°. The substance is essentially insoluble in common organic solvents, hot or cold, but is soluble in hot acetic acid or hot 2-ethoxyethanol (Cellosolve). It was analyzed after four recrystallizations from 2-ethoxyethanol with a final methanol washing, m.p. 265–266° (reported[4d] m.p. 264–265°). $\lambda_{max}^{95\%\ C_2H_5OH}$ 221.5 (infl.) (17,800); 229 (9670); 267.5 (27,300); 289 (8000); 301 (8330).

Anal. Calcd. for $C_{19}H_{16}N_2$: C, 83.79; H, 5.92; N, 10.29. Found: C, 83.52; H, 5.88; N, 10.26.

Attempted cyclizations with sodium ethoxide[12] or sodium in dioxane[5e] resulted only in recovery of starting material.

Hydrolysis of VII *to* V. Under a nitrogen atmosphere 1.0 g. (0.00367 mole) of VII was dissolved by heating in a solution of 25 ml. of glacial acetic acid and 1.5 ml. of distilled water contained in a 50-ml. three necked round bottom flask equipped with a glass-encased magnetic stirring bar. The solid dissolved after about 30 min. of gentle refluxing and heating was continued for another 15 min. Then 10 ml. of 85% phosphoric acid was dropwise *via* a pressure-equalized dropping funnel. The solution was then refluxed and stirred magnetically for 16 hr. Upon cooling to room temperature, the light yellow solution was poured onto about 50 g. of crushed ice whereupon a white solid separated. After being filtered with suction, washed with water, and air-dried, the material (0.91 g., 100%) melted at 195–200°. This material was crystallized from 30 ml. of 95% ethanol to give 0.80 g. (88%) of ketone, m.p. 205–212°. This substance was sublimed at 170° (0.1 mm.) to give 0.55 g. (60%) of very pure material, m.p. 211–212°. The melting point of a 1:1 mixture of this compound with authentic V was not depressed while the infrared spectra of the two compounds were identical.

3-Carboxamidospiro[cyclohexane-1,9′-fluoren]-4-one (VIII).[45] The enaminonitrile VII (1 g.) and polyphosphoric acid (20 g.) were heated for 30 min. in an oil bath preset at 100° with occasional manual stirring (glass rod). The yellow-brown solution was poured onto cracked ice. The resulting solid was filtered with suction, washed with water, and air-dried, to give 1.09 g. of yellow-tinged material, m.p. 218–222°. A small sample was sublimed at 220° (0.05 mm.), m.p. 226–229°. The material was insoluble in benzene, chloroform, methanol, acetone, nitromethane, acetic acid, hot concentrated hydrochloric acid, and hot aqueous 10% potassium hydroxide. The analytical sample was prepared by trituration in nitromethane, filtration, and recrystallization from dimethylformamide-nitromethane, m.p. 227–229°. $\lambda_{max}^{95\%\ C_2H_5OH}$ 221 (infl.) (18,000); 228 (9600); 263 (22,400); 289 (5600); 301.5 (8000).

Anal. Calcd. for $C_{19}H_{17}O_2N$: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.34; H, 6.17; N, 4.72.

1,1′-[4,4′-Diketo-1,2,3,4,1′,2′,3′,4′-octahydro-8,8′-binaphthyl]spirane (XI).[45] The diacid IX (5 g.) and 150 g. of polyphosphoric acid were heated and stirred mechanically for 25 min. in a Wood's metal bath preset at 130°. The color of the solution became progressively darker throughout the reaction. The dark brown solution was poured onto 300 g. of cracked ice, the resulting greenish precipitate was filtered with suction, washed well with water, and dissolved in 100 ml. chloroform. This solution was washed with 100 ml. of 5% sodium bicarbonate solution, 100 ml. of water, and 100 ml. of saturated sodium chloride solution. The organic phase was dried over anhydrous magnesium sulfate, filtered, and the solvent evaporated in a stream of nitrogen. The yellow-brown residue was crystallized from ethyl acetate to give 2.06 g. (47%) of XI, m.p. 211–215°. The analytical sample was prepared by sublimation at 185–190° (0.1 mm.) and recrystallization from ethyl acetate, m.p. 214–215° (reported 190–194°[26b,c], 207–208°[26a]).

Anal. Calcd. for $C_{19}H_{14}O_2$: C, 83.20; H, 5.15; O, 11.65. Found: C, 83.23; H, 5.06; O, 11.47.

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