Aminolysis of 3. Preparation of Sulfones 5.—A mixture of 0.03 mol of **3** and 0.15 mol of an arylamine was heated for 12 hr under a nitrogen atmosphere at 130–160°. The reaction product was washed with consecutive portions of 10% hydrochloric acid and water. The washed material was dissolved in 100 ml of 95% ethanol; the solution was charcoaled and condensed to one-half volume. The product was filtered off and recrystallized from an appropriate solvent.

The individual sulfones prepared by this method are listed in Table II.

3,3′-Sulfonyldipropionanilide (5, Ar = C_6H_5).—A solution consisting of 9.9 g (0.05 mol) of 3,3′-sulfonyldipropionic acid,[27] 75 ml of thionyl chloride, and 100 ml of chloroform was refluxed for 48 hr. The solvent and excess thionyl chloride were removed by distillation and the residue was dissolved in 150 ml of methylene chloride. This solution was added dropwise to a stirred solution of 18.6 g (0.2 mol) of aniline in 150 ml of methylene chloride. Stirring at room temperature was continued for 2 hr after complete addition. The solid was filtered off and extracted several times with hot water. The water-insoluble material was recrystallized from ethanol: yield 7.4 g (41%), mp 246–247°.

The reaction product was identical (melting point, mixture melting point, and ir spectrum) with the material obtained from the aminolysis of 1,2-oxathiolan-5-one 2-oxide **3** with aniline.

(27) H. S. Schultz, H. B. Freyermuth, and S. R. Buc, *J. Org. Chem.*, **28**, 1140 (1963).

Registry No.—**1**, 10408-21-6; **2**, 19955-27-2; **3**, 19955-28-3; **4**, 927-42-4.

Preparation and Reactions of Diazo Ketones. V.[1] Normal and Abnormal Products from Thermal Wolff Rearrangement of 9-Phenylfluorene-9-carbonyldiazomethane

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As one test of the role of steric factors in leading to abnormal thermal Wolff rearrangement of the diazomethyl ketone **1** from triphenylacetic acid, diazomethyl ketone **5** was prepared from 9-phenylfluorene-9-carboxylic acid (**4a**). Thermal Wolff rearrangement of **5** in 1-hexanol and N-ethylmorpholine gave 50–55% of normal product **6** as well as 35–40% of abnormal product **7**. Decarboxylation of acid **7a** gave 1-methyl-9-phenylfluorene (**9**), which was synthesized from 1-methyl-9-fluorenone (**11**). Nmr spectra for these compounds provide confirmatory proof of structures. The formation of considerable normal product **6** in the 9-phenylfluorene example **5**, compared with none in the triphenylmethane case **1**, supports the view that steric factors are important in impeding normal rearrangement of the latter.

Some years ago in this laboratory, as a result of our interest in using the Arndt–Eistert synthesis of homologous acids in certain synthetic sequences, we undertook a series of investigations aimed at widening the scope of the method, improving the reliability of the experimental procedures, and throwing further light on the mechanisms of the reactions. Wilds and Meader[1a] reported solutions for two of the problems involved, the first concerning the preparation of diazo ketones from acid chlorides and higher diazohydrocarbons,[2,3] and the second an improved and more general method for rearranging diazo ketones to derivatives of the homologous acids.

With these problems clarified, we turned to a study of the synthetic and mechanistic consequences of increasing the steric requirement of the acid chloride on the formation of the diazo ketone, and also on the Wolff rearrangement of the latter. It was known that mesitoyl chloride failed to give a diazo ketone with diazomethane.[4,5] This diazo ketone prepared in another way, however, underwent normal rearrangement to the higher acid, as did 2,4,6-triisopropylbenzoyldiazomethane.[6] Consequently it is clear that the steric requirements of the two steps in the Arndt–Eistert sequence are quite different.

Significant results were obtained by Van Den Berghe[5] in the series *n*-butyryl, isobutyryl, and trimethylacetyl chloride with diazomethane and diazoethane, reflecting the increasing steric requirements, two aspects of which of which should be mentioned here. Reaction of trimethylacetyl chloride and diazomethane proceeded slowly but normally, under the proper conditions, to the diazo ketone (70% yield). With certain diazomethane solutions, however, trace impurities that had little or no effect with *n*- or isobutyryl chloride altered the course of reaction with trimethylacetyl chloride, giving chloromethyl *t*-butyl ketone (50–60% yield), even with an excess of diazomethane present.[7–9] Reaction of *diazoethane* with trimethylacetyl chloride gave several abnormal products instead of the diazo ketone, the latter being present at most only in small amounts.[5]

For rearrangement of these and other potentially sterically hindered diazo ketones, it was essential to

(1) For convenience in reference, we are now assigning to our earlier papers in the series Preparation and Reactions of Diazo Ketones the following numbers: (a) I, A. L. Wilds and A. L. Meader, Jr., *J. Org. Chem.*, **13**, 763 (1948); (b) II, C. E. Blades and A. L. Wilds, *ibid.*, **21**, 1013 (1956); (c) III, A. L. Wilds, J. Van Den Berghe, C. H. Winestock, R. L. von Trebra, and N. F. Woolsey, *J. Amer. Chem. Soc.*, **84**, 1503 (1962); (d) IV, A. L. Wilds, N. F. Woolsey, J. Van Den Berghe, and C. H. Winestock, *Tetrahedron Lett.*, 4841 (1965).

(2) (a) Because of the higher reactivity of diazoethane (*vs.* diazomethane), it was found that lower temperatures (−20°) and limited amounts of diazohydrocarbon were necessary to avoid further reaction of the diazo ketone and diazoethane with loss of N_2 to form a mixed azine.[1a,2b,c,3] (b) A. L. Meader, Jr., Ph.D. Thesis, University of Wisconsin, 1947. (c) G. Baddeley, G. Holt, and J. Kenner, *Nature*, **163**, 766 (1949).

(3) P. Yates, D. G. Farnum, and D. W. Wiley, *Chem. Ind.* (London), 69 (1958).

(4) (a) W. E. Bachmann and J. C. Sheehan, unpublished work cited by W. E. Bachmann and W. S. Struve, *Org. Reactions*, **1**, 38 (1942). (b) This failure of mesitoyl chloride to react was confirmed by Van Den Berghe with diazomethane and diazoethane, 90–98% of the acid chloride being recovered. For details see ref 5.

(5) J. Van Den Berghe, Ph.D. Thesis, University of Wisconsin, 1952.

(6) R. C. Fuson, L. J. Armstrong, and W. J. Shenk, Jr., *J. Amer. Chem. Soc.*, **66**, 964 (1944).

(7) Distilled ethereal diazomethane prepared from N-methyl-N-nitrosourethan contained an impurity in trace amounts leading to the chloromethyl ketone. This impurity was removed by treatment with sodium ribbon and redistillation (see Experimental Section for procedure, also ref 5). The significance of these and related findings to the mechanism of diazo ketone and chloromethyl ketone formation has been discussed in theses.[5,8,9]

(8) C. E. Hummel, Ph.D. Thesis, University of Wisconsin, 1956; *Dissertation Abstr.*, **16**, 2305 (1956).

(9) N. F. Woolsey, Ph.D. Thesis, University of Wisconsin, 1961; *Dissertation Abstr.*, **22**, 3000 (1962).

use a reliable test method to get meaningful comparative results. Fortunately, the Wilds–Meader procedure[1a] for thermal Wolff rearrangement in homogeneous solution, heating the diazo ketone at 150–180° with a high-boiling alcohol and tertiary amine, provided such a test, giving reproducible results with a wide variety of diazo ketones; it avoided the occasional unreliability of the classical heterogeneous silver oxide and related catalyzed methods,[10] and the known structural limitations of the homogeneous silver salt–methanol–triethylamine procedure.[11] For examples closely related to the present series, normal rearrangement products were obtained from diphenylacetyldiazomethane and trimethylacetyldiazomethane.[5]

With triphenylacetyldiazomethane (**1**), however, the rearrangement took an abnormal course. After heating the diazo ketone with 1-hexanol and N-ethylmorpholine, two products were obtained, one the ester of the isomeric acid **2**, in which the acetic acid moiety is in the *ortho* position of one ring, and the other a related but dimeric ester, resulting from addition of one ring in the intermediate to that of the second monomer unit (Chart I).[1c,d] None of the normal product could be isolated from these *thermal* Wolff rearrangements under a variety of conditions.[12]

In this abnormal rearrangement, evidently the π-bond system of one aromatic ring, instead of the triphenylmethyl carbon, is providing the electrons for bonding to the diazo carbon (as N_2 is lost). *A priori*, this could be attributed either to an electronic effect (decreased electron availability on the triphenylmethyl carbon) or to a steric effect. The observations that diphenylacetyldiazomethane[5] and triphenylacetyl azide[8] underwent normal rearrangement in the thermal Wolff and Curtius processes, respectively, suggested (but did not establish) that the steric factor was important here.

As a further test of this steric factor, we looked at the synthesis and rearrangement of 9-phenylfluorene-9-carbonyldiazomethane (**5**), in which coplanarity of two rings reduces the steric impedance about the triaryl and carbonyl carbons without major change in the electronic environment. 9-Phenylfluorene-9-carboxylic acid (**4a**)[13] was prepared by metalation and carbonation of 9-phenylfluorene (**3a**).[14] The diazo ketone **5** resulted in good yield by reaction of the acid chloride with diazomethane.

When the diazo ketone **5** was heated with 1-hexanol and N-ethylmorpholine and the product hydrolyzed, two different acids of formula $C_{21}H_{16}O_2$ could be isolated, in approximately a 3:2 ratio. The former (mp 230°) was shown to be the normal rearrangement product, 9-phenylfluorene-9-acetic acid (**6a**), by comparison with an authentic sample prepared by fusion of 9-phenyl-9-fluorenol (**3b**) with malonic acid.[15,16] The two methyl esters also were identical.

The isomeric acid (mp 189°), by analogy to the triphenylacetyl series, could be the abnormal rearrangement product with the acetic acid function in the 1 position of the fluorene ring (**7a**), or the *ortho* position of the 9-phenyl group (**8**). Decarboxylation of the acid gave a hydrocarbon (mp 148–153°) which was shown to be 1-methyl-9-phenylfluorene (**9**) and not 9-*o*-tolylfluorene (**12**). Since both of these hydrocarbons were unknown,[17] authentic samples were prepared of each. By reaction of 1-methyl-9-fluorenone (**11**)[18] with phenyl Grignard reagent and reduction of the resulting carbinol (**10**) with zinc dust and acid, 1-methyl-9-phenylfluorene (**9**, mp 153–153.5°) was obtained. Reaction of *o*-tolyl Grignard reagent with 9-fluorenone, and reduction of the carbinol with zinc, gave authentic 9-*o*-tolylfluorene (**12**, mp 92.5–93.5°),[17] which was clearly different from the decarboxylation product. Infrared and nmr comparisons confirmed that the abnormal rearrangement product is the 1-acetic acid derivative **7**.

The nmr spectrum of the normal rearrangement product, as the methyl ester **6b**, showed, in addition to the expected 13 aryl hydrogens, singlets at δ 3.44 (CH_2) and 3.28 (OCH_3). The spectrum of the ester of the abnormal acid (**7b**) showed signals for only 12 aryl hydrogens, and a new singlet at δ 5.12 (triarylmethyl H), in addition to singlets at 3.53 (OCH_3) and 3.39 (CH_2).

The chemical shift for the methylene signal of the normal ester **6b** is upfield by 0.26 ppm compared with that for methyl β,β,β-triphenylpropionate (**13**, δ 3.70), reflecting the altered geometry of the three aryl rings in **6b**. Comparing the abnormal ester **7b** with the corresponding ester **2** (R = CH_3) in the triphenyl series, which showed a 14 aryl hydrogen multiplet, and singlets at δ 5.81 (triarylmethyl H) and 3.56 ($W_{h/2}$ 0.6 Hz, 5 H, CH_2 and OCH_3), the methylene signal of the former was shifted 0.17 ppm upfield, and the triarylmethyl hydrogen 0.69 ppm upfield. The triarylmethyl hydrogens showed typical line broadening ($W_{h/2}$ = 2.0 Hz), due to long-range coupling with the aryl hydrogens,[19] as did the methylene hydrogens of the fluorene derivative **7b** ($W_{h/2}$ = 1.4 Hz), but not of the triphenyl derivative **2**, as noted above.

It is not surprising that the chemical shifts of these triarylmethyl hydrogens vary widely. Because of their close proximity to three rings which can give either strong deshielding or shielding,[20] depending upon the geometry, their chemical shifts will be sensitive to structural changes affecting these rings. While this

(10) It is well known that even in the hands of experts an occasional silver oxide or related catalyzed Wolff rearrangement may fail to go, or give lowered yields, owing to unrecognized differences in the heterogeneous catalyst, and other factors.

(11) See M. S. Newman and P. F. Beal, *J. Amer. Chem. Soc.*, **72**, 5162 (1950).

(12) Wolff rearrangement by the photochemical method did give the normal rearrangement products both from diazo ketones **1** and **5**; for a preliminary discussion of this and related results, see ref 1c and 1d.

(13) H. Gilman, W. J. Meikle, and J. W. Morton, *J. Amer. Chem. Soc.*, **74**, 6282 (1952).

(14) F. Ullmann and R. von Wurstemberger, *Ber.*, **37**, 73 (1904).

(15) The comparable reaction of triphenylcarbinol with malonic acid was reported by L. Hellerman, *J. Amer. Chem. Soc.*, **49**, 1735 (1927).

(16) A study, after this part of our work was completed, of the reaction of triarylcarbinols including 9-phenyl-9-fluorenol with malonic acid has been reported by S. Patai and S. Dayagi, *J. Chem. Soc.*, 716 (1962), and following papers. For certain discrepancies with our results on the preparation of the acid **6a**, see Experimental Section.

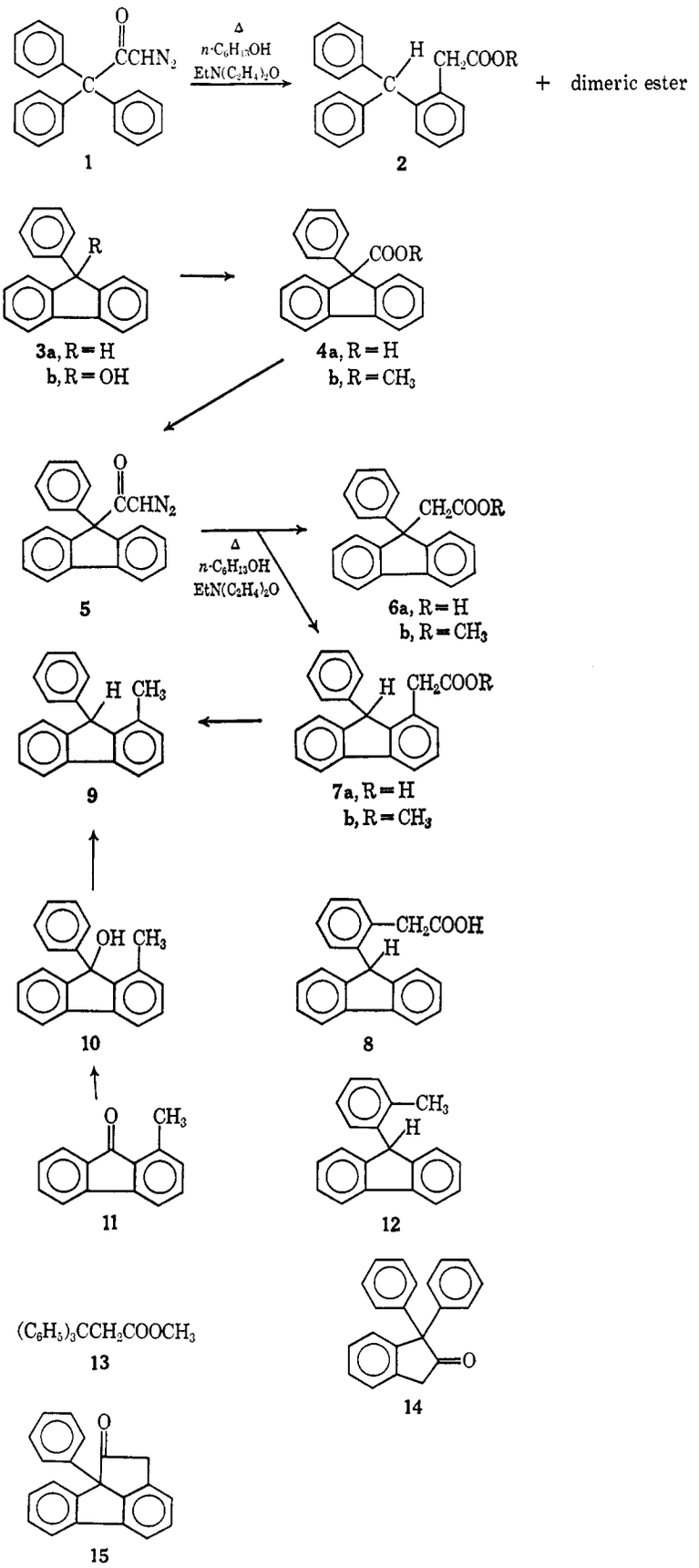
(17) The reported preparation of 9-*o*-tolylfluorene with mp 133° by R. Weiss and E. Knapp [*Monatsh. Chem.*, **61**, 61 (1932)] apparently is incorrect; further details on this compound and the temperature dependence of its nmr spectrum will be reported by N. F. Woolsey and S. Stepenske.

(18) W. C. Lothrop and P. A. Goodwin, *J. Amer. Chem. Soc.*, **65**, 363 (1943).

(19) See J. A. Elvidge and R. G. Foster, *J. Chem. Soc.*, 592 (1963); E. Lustig and E. P. Ragelis, *J. Org. Chem.*, **32**, 1398 (1967), and references cited by them.

(20) See N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964; H. Suhr, "Anwendungen der kernmagnetischen Resonanz in der organischen Chemie," Springer-Verlag, Berlin, 1965, pp 33–36.

CHART I



signal for triphenylmethane comes at δ 5.44,[21] it is shifted to 5.03 for 9-phenylfluorene (**3a**), and 4.97 for 1-methyl-9-phenylfluorene (**9**). This signal for the ester **2** (R = CH_3) is shifted downfield 0.37 ppm from triphenylmethane, for the ester **7b** only 0.09 ppm downfield from 9-phenylfluorene.

The ester methoxy hydrogens for the triaryl substituted esters **6b** and **13** (δ 3.28 and 3.35) are clearly

(21) H. O. House and V. Kramar, *J. Org. Chem.*, **27**, 4146 (1962), and unpublished results of N. F. Woolsey.

shielded by the aryl rings, while those for esters **7b** and **2** (δ 3.53 and 3.56) come in the normal range for methyl esters.

The nmr spectrum of the decarboxylation product of **7a**, 1-methyl-9-phenylfluorene (**9**), showed in addition to the triarylmethyl hydrogen a singlet for the aryl methyl at δ 2.04, as did the authentic sample of **9** (δ 2.03, 3 H); the corresponding carbinol **10** had this aryl methyl signal at δ 2.08, each showing the usual aryl broadening. The nmr spectrum of 9-*o*-tolylfluorene (**12**) is quite different from those of the 1-methyl isomer **9** and the decarboxylation product of the acid **7a**.[17]

The thermal Wolff rearrangement of 9-phenylfluorene-9-carbonyldiazomethane (**5**) and isolation of products were carried out in several ways in an effort to find other abnormal products, or possible intermediates in the formation of the 1-acetic ester **7**. Chromatography of the products before hydrolysis led to small fractions with infrared spectra suggestive of a hydroxy ketone and a diketone, but no pure compounds could be isolated, except for a trace of 9-phenylfluorene. None of ketone **15** corresponding to direct cyclization of the diazocarbon at the 1 position could be found, and attempts to prepare this ketone by treatment of the diazo ketone **5** with boron trifluoride in ether were unsuccessful, although that procedure gave the indanone **14** in high yield from the diazo ketone **1**.[8]

Determination of the relative amounts of the normal and abnormal acids formed by rearrangement in the 9-phenylfluorene series was difficult, owing to problems of separation. Of the methods examined the best results were obtained by partition chromatography of the acids, the estimated yield of abnormal acid **7a** being about 35–40%, and of normal acid **6a** about 50–55%.

Isolation of 50–55% of the normal homologous product from Wolff rearrangement in the 9-phenylfluorene series **5** supports the contention that steric factors play an important part in preventing normal rearrangement of the more hindered diazo ketone **1** in the triphenylacetyl series. Normal rearrangement of other highly hindered diazo ketones mentioned previously, particularly trimethylacetyldiazomethane, occurs since no other lower energy path for reaction is available. The diazo ketones **1** and **5**, however, have sterically accessible π-electron clouds available in the aryl rings to compete with the electrons of the normally rearranging group.

Electronic as well as steric factors must play a part in favoring reaction at the more electron-rich 1 position of the fluorene ring to give **7**, instead of any significant amount of reaction in the 9-phenyl ring leading to **8**. Molecular models also indicate a preference for the diazo group to lie above the fluorene ring system and away from the phenyl ring. Additionally the greater entropy of activation for reaction in the more freely rotating phenyl ring should also contribute to the observed preference for **7**.

A few examples of other abnormal Wolff rearrangements have now been reported, involving silver-catalyzed procedures.[22] In two cases[22a,b] the products included acids isomeric with those expected, one being formed from a sterically hindered diazo ketone with a β,γ π-bond system (double bond) as for the thermal Wolff cases.

At the present time, the structural features which may result in abnormal Wolff rearrangement to an *acid derivative* seem to be twofold: (1) significant steric hindrance at the carbonyl or α carbon of the α'-diazo ketone, and (2) a π-bond system (aryl or double bond) at the β,γ position (suitably arranged for cyclization), which not only allows reaction in the γ position but also cleavage α to the carbonyl group. It may prove possible to enhance the reactivity at the γ position, relative to the α position, sufficiently to get abnormal products when steric hindrance is not so significant as with the present examples. Abnormal reaction (cyclization) may also be observed with certain hindered diazo ketones having the π-bond system at the γ,δ position, although in these cases acid derivatives would not be expected unless some other structural feature facilitated cleavage α to the carbonyl group.

For obtaining the normal rearrangement product, the thermal conditions of Wilds and Meader, as now modified,[1a,23] probably represent the procedure of greatest reliability and highest yield for most diazomethyl ketones, except for those with a high degree of steric hindrance, or leading to highly strained products, or sensitive to the higher temperatures. In these cases the photolytic conditions are preferable. For diazoethyl or higher diazo ketones, the thermal procedure seems to be superior to the photolytic method, which leads to appreciable amounts of unsaturated ketone.

Experimental Section

Melting points are corrected, determined with a Hershberg apparatus unless otherwise indicated; micro melting points were taken with a calibrated microscope hot stage. Uv spectra were run in 95% ethanol on a Cary Model 11 instrument and molecular extinction coefficients (ϵ) are reported. Ir spectra were run using a Baird Model B or a Perkin-Elmer Infracord (i) instrument. Nmr spectra were run at 60 MHz in deuteriochloroform with tetramethylsilane as internal standard using a Varian A-60A or A-60 instrument.

Preparation of Diazomethane.—For making diazo ketones from hindered acid chlorides,[5] diazomethane was prepared from N-methyl-N-nitrosourethan as described previously for diazoethane,[1a] by adding the nitrosourethan solution during 10 min while heating with an oil bath at 65°, then redistilled in the same apparatus while adding ether. The solution was dried with sodium ribbon at 0° for 1–2 hr, decanted and distilled once more as before. Diazomethane was determined by the benzoic acid method;[1a] over-all yields usually ranged from 60 to 75% when an electrically heated oil bath was used for heating during all distillations. Diazomethane for making methyl esters was prepared from N-methyl-N-nitrosourea without distillation.[24]

Determination of Diazo Nitrogen in Diazo Ketones.[25,26]—A solution of the diazo ketone (usually 30–50 mg) in 5 ml of tetraethylene glycol dimethyl ether (tetraglyme) was placed in the reaction flask of a special apparatus. The flask, magnetically

(22) (a) G. Eglinton, J. C. Nevenzel, M. S. Newman, and A. I. Scott, *Chem. Ind.* (London), 686 (1953); *J. Amer. Chem. Soc.*, **78**, 2331 (1956); see ref 1c, footnote 7; (b) A. Small, *J. Amer. Chem. Soc.*, **86**, 2091 (1964); (c) H. O. House, S. G. Boots, and V. K. Jones, *J. Org. Chem.*, **30**, 2519 (1965); (d) E. Wenkert, B. L. Mylari, and L. L. Davis, *J. Amer. Chem. Soc.*, **90**, 3870 (1968).

(23) Currently we prefer to use 1-hexanol or 1-octanol as the high-boiling alcohol and N-ethylmorpholine, γ-collidine or isoquinoline as the tertiary amine. It is not advisable to use benzyl alcohol as in the original procedure, since on standing traces of acid form and can interfere with the rearrangement reaction in sensitive cases. For compounds containing groups sensitive to alkaline hydrolysis of the resulting ester, we use triethanolamine as alcohol and amine,[1a] and hydrolyze the entire product with acid (see Experimental Section).

(24) F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p 165.

(25) This procedure was modified from earlier ones developed by Van Den Berghe[5] and Kraihanzel.[26]

(26) C. F. Kraihanzel, M.S. Thesis, University of Wisconsin, 1959.

stirred, was attached to a small, pressure equalizing dropping funnel with stopcock closure at the top and attached to a manometer and 10-ml gas buret, both filled with mercury (the total internal volume was about 75 ml of which 25 ml of the reaction flask was in a water bath). A freshly prepared mixture of 2.5 ml of 1:1 sulfuric acid–water solution and 2.5 ml of tetraglyme was placed in the dropping funnel, the mixture in the reaction flask was stirred and allowed to equilibrate in the water bath at room temperature for 30 min (room temperature controlled ±2°; bath ±0.1°), then the acid mixture was added to the reaction flask. Another 30 min was allowed for nitrogen evolution and reequilibration. The volume was corrected for any change in room or bath temperature; results were accurate to ±2% with 0.2-mmol samples.

9-Phenylfluorene-9-carboxylic Acid (4a).[13]—9-Phenyl-9-fluorenol (**3b**) was prepared from 9-fluorenone by the procedure of Ullmann and von Wurstemberger,[14] mp 110–111° (from 60–68° petroleum ether). Reduction with zinc dust and acetic and hydrochloric acids gave 94% 9-phenylfluorene **3a**:[14] mp 146.5–147.5°; nmr δ 7.67–7.83 (2 H, m, 4 and 5 aryl H), 6.95–7.55 (11 H, m, remaining aryl H), 5.03 (1 H, s, $W_{h/2}$ = 2.2 Hz, triarylmethyl H).

To 0.11 mol of *n*-butyllithium in ether was added a solution of 22.6 g (0.093 mol) of 9-phenylfluorene (mp 148–150°) in benzene, keeping the temperature below 10°. After stirring 1.5 hr at 25° the mixture was poured onto an excess of solid carbon dioxide and allowed to stand overnight. By isolation of the acidic fraction (95%) and recrystallization from benzene and petroleum ether (90–100°) 20.8 g (78%) of acid **4a** was obtained, mp 193.5–195°,[13] with additional material in the filtrates. Another crystalline form, mp 200–202.5°, also was obtained: mmp 194–196°; ir (i, $CHCl_3$) 5.85 (s, acid CO), 6.35, 6.69, 6.89 (w, m, ms, aryl rings), 7.14 (m), 8.93 (ms), 9.69 (w), 14.4 μ (s).

Anal. Calcd for $C_{20}H_{14}O_2$: C, 83.90; H, 4.92. Found: C, 84.14; H, 4.93.

The **methyl ester 4b** was prepared with diazomethane and recrystallized from methanol: mp 164–165°; ir (i, $CHCl_3$) 5.75 (s, ester CO), 6.25, 6.69, 6.89, 6.97 (w, m, ms, ms, aryl rings), 8.18 (s), 8.54 (m), 9.80 (ms), 14.4 (ms); nmr δ 7.00–7.80 (13 H, m, aryl H), 3.74 μ (3 H, s, $W_{h/2}$ = 0.6 Hz, OCH_3).

Anal. Calcd for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37. Found: C, 83.66; H, 5.25.

9-Phenylfluorene-9-carbonyldiazomethane (5).—A solution of 5.0 g of 9-phenylfluorene-9-carboxylic acid (**4a**) in 11.5 ml of pure thionyl chloride was refluxed for 9 hr, then concentrated under reduced pressure at 25°, followed by addition and similar evaporation of two to four 25-ml portions of dry benzene to ensure complete removal of thionyl chloride (odor); the crude acid chloride was used, 5.2 g (95%), mp 87–90°, Cl 11.70% (calcd 11.63%).

A solution of 5.2 g (17 mmol) of acid chloride in 50 ml of ether and 50 ml of benzene (both anhydrous) was added over 30 min at 0° to a stirred solution of 96 mmol of sodium-dried diazomethane in 315 ml of ether. While stirring for 30 min more at 0° the yellow diazo ketone precipitated. After removal of excess diazomethane and some of the solvent under reduced pressure at 0°, 4.1 g of pale yellow diazo ketone **5** was obtained, mp 153.5–154.5° (diazo N_2 97%). A second crop of 0.75 g from benzene–petroleum ether made a total of 92%. Recrystallization of the first crop from benzene–petroleum ether raised the melting point to 159–160° (diazo N_2 99%).

Rearrangement of 9-Phenylfluorene-9-carbonyldiazomethane (5).—A mixture of 1.10 g of the diazo ketone **5** (mp 155.5–156.5°), 5 ml of 1-hexanol and 5 ml of N-ethylmorpholine (each solvent redistilled) was placed in the reaction flask, attached through a reflux condenser to a large gas buret. The flask was then immersed in an oil bath preheated to 175–180°, and heated at that temperature for 15–25 min (N_2 evolution 93% of theory, over in 6 min). After dissolving in ether and washing with dilute acid (1:2 HCl), the solvent and 1-hexanol were removed, finally by azeotropic distillation with xylene and benzene. The residue in benzene–petroleum ether (1:5) was chromatographed on 100 g of alumina (Woelm), collecting 30-ml fractions. After a small amount (14 mg) of 9-phenylfluorene in fractions 13–15, eluted with 1:1 benzene–petroleum ether, the next major fractions (35–42, eluted with 15:1 benzene–petroleum ether) contained a green oil (0.63 g) having an ir spectrum closely resembling that of *n*-hexyl 9-phenylfluorene-9-acetate (see below). Hydrolysis with 7 g of potassium hydroxide in 13 ml of 50% methanol at reflux for 5 hr gave, after dilution, ether extraction and acidification, 0.44 g of pale green solid, mp 200–220°, a mixture containing mainly the normal acid **6a**.[27] Fractions 43–73 (0.11 g, eluted with ether and then chloroform) of hydrolysis gave 0.09 g of an acid mixture. Fraction 76, eluted with 10:1 chloroform–acetone, gave 15 mg of an oil, ir ($CHCl_3$) 5.80 (s, CO), 6.00 (ms, conjugated CO), 6.23, 6.69, 6.88 μ (w, m, s, aryl rings), which suggested a diketone, although no solid quinoxaline derivative could be obtained. Fractions 77–78 (44 mg) and 79 (28 mg) [ir ($CHCl_3$) 2.75, 2.90 (w, w, OH), 5.85 (ms, CO), 6.10 (ms, conjugated CO), 6.25 (shoulder), 6.70, 6.89 μ] were suggestive of a ketol. Further elution with chloroform–acetone mixtures and acetone alone gave in fractions 80–91 a total of 108 mg (after evaporation of acetone condensation products), of which 4 mg was solid, micro mp 134–141°. Fraction 91 (32 mg), which appeared from the ir spectrum to contain a ketol, was acetylated with acetic anhydride (ir 5.72, acetate CO) but still could not be crystallized.

Since a previous run had shown that part of the product was converted into the salt and held on the adsorbent, the alumina was digested with 5% potassium hydroxide for 30 min on the steam bath, filtered, acidified with dilute hydrochloric acid until all the aluminum hydroxide was in solution, then extracted with ethyl acetate. The resulting product was recrystallized twice from ethyl acetate–petroleum ether and from chloroform–petroleum ether to give 0.13 g of solid, mainly the abnormal acid **7a**, micro mp 175–177°. Treatment with diazomethane and recrystallization from dilute methanol gave the abnormal methyl ester **7b**, mp 97–100° (mixture melting point not depressed).

In another run, the neutral fraction of the rearrangement product was hydrolyzed with 20 ml of 20% potassium hydroxide in 50% methanol at reflux for 4 hr, the acidic fraction isolated (66%) and the neutral fraction rehydrolyzed twice, giving further acidic fractions (25 and 9%). Aliquots of these fractions were carried through partition chromatography on silicic acid (using 9:1 $HCONH_2$–0.5 *N* H_2SO_4 as the stationary phase and 10% CCl_4 in petroleum ether as the mobile phase).[28] From the first hydrolysis product was obtained 13% of oily acid (fractions 1–26), 39% of crystalline acid (fractions 27–38), micro melting points ranging from 173 to 178°, mainly the abnormal acid **7a**, then 3% of oil (fractions 39–40) and 26% of solid (fractions 41–53), micro melting points ranging from 194 to 210°, mainly the normal acid **6a**. Recrystallization of appropriate fractions from dilute methanol gave 28% of the abnormal acid **7a**, mp 184–189°, and 21% of normal acid **6a**, mp 225–228°.

By similar separation, the combined second and third hydrolysis fractions gave mainly the normal acid **6a**, an additional 20–25% being obtained before recrystallization, with micro melting points ranging 185–227°.

In summary, the best estimates for the acids present after hydrolysis of the thermal rearrangement product using 1-hexanol and N-ethylmorpholine are 50–55% of the normal acid **6a**, and 35–40% of the abnormal acid **7a**, of which about two-thirds of each could be obtained in reasonably pure form by recrystallization of the acids or methyl esters. Other methods of separation or estimation of the isomers were less satisfactory.[29]

In other rearrangment runs the diazo ketone **5** was heated with triethanolamine[18a] at 180–185° from 15–20 min; then the entire product was hydrolyzed by heating with dilute hydrochloric acid (1:1) at reflux for 5 hr, giving 75–80% of the crude acid mixture, mp 170–195°, from which the same abnormal acid **7a**, mp 187–190°, methyl ester **7b**, mp 100.5–101°, and the normal acid ester **6b**, mp 91–92°, could be isolated by chromatography of the methyl esters on alumina as described above, including alkaline digestion of the adsorbent to obtain the abnormal acid.

Methyl 9-Phenylfluorene-1-acetate (7b) from Rearrangement of 5.—By recrystallization of the abnormal **methyl ester (7b)** the purest sample was obtained as small, colorless needles or

(27) Further hydrolysis of the neutral fraction gave more of the acid (*cf.* below).

(28) This procedure is a modification of that of P. M. Bhargava and C. Heidelberger, *J. Amer. Chem. Soc.*, **77**, 166 (1955); see also H. G. Cassidy in "Technique of Organic Chemistry," Vol. 5, A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1951, p 291.

(29) At the time this part of the work was completed (1960) good integrated nmr spectra were not possible with our instrumentation, nor was satisfactory resolution of the methyl esters by glpc possible with equipment then available. If future work is done, either of these methods should be satisfactory with the techniques now available. Since the product composition probably varies some with conditions of rearrangement, it does not seem necessary to obtain higher accuracy for present purposes.

rods from dilute methanol: mp 100.6–101.4° (vacuum dried at 80°); mixture melting point with methyl 9-phenylfluorene-9-acetate was depressed to 70–80°; there was evidence of a second crystalline form melting around 84–85°; uv max 269 mμ (ε 17,100), 281.5 (10,000), 292.5 (5170), 304 (7200); shoulders 236, 259, 265, 275; uv min 242, 280, 288, 299; ir ($CHCl_3$) 5.78 (s, ester, CO), 6.23, 6.65, 6.85, 6.94 μ (m, m, ms, ms, aryl rings); ir (CS_2) 5.73 (s), 13.22–13.31 (s), 13.58 (m), 14.34 μ (s); nmr δ 7.65–7.85 (2 H, *m*, 4 and 5 aryl H), 6.90–7.55 (10 H, m, remaining aryl H), 5.12 (1 H, s, $W_{h/2}$ = 2.0 Hz, triarylmethyl H), 3.53 (3 H, s, OCH_3), 3.39 (2 H, s, $W_{h/2}$ = 1.4 Hz, CH_2).

Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 83.96; H, 5.86.

The purest sample of the **abnormal acid 7a**, from partition chromatography and recrystallization from dilute methanol, was obtained as colorless needles, mp 188.5–189.5°.[30]

9-Phenylfluorene-9-acetic Acid (6a). A. From Rearrangement of 5.—Recrystallization of a sample of the normal acid from benzene–petroleum ether (bp 90–100°) and from dilute methanol gave colorless material: mp 227.5–230°; mixture melting point with an authentic sample (see below) was undepressed; uv max 236 (ε 12,800), 267 (14,400), 270 (14,600), 294 (4800), 305 (7100), 278 mμ (sh); uv min 234, 244, 289, 300 mμ.

The **methyl ester (6b)** of the normal acid, prepared with diazomethane and recrystallized from dilute methanol, melted at 91.5–93°; mixture melting point with an authentic sample (see below) was undepressed.

B. From 9-Phenyl-9-fluorenol (3b).—Several runs were made under varying conditions using malonic acid and 9-phenyl-9-fluorenol (**3b**, mp 109.5–110.5°) in equal weights, or three times as much malonic acid, and heating at 160–170° for periods of 0.5–3.5 hr. Although the crude acid was obtained in as high as 97% yield, mp 205–225°, it was not pure; separation from the accompanying impurity was difficult.[16] Recrystallization from benzene–acetic acid gave 50% of solid, mp 227.5–229.5°, which was mainly the desired acid **6a**, while the material in the second and third crops melted below 210°.[31] Purification of the acid was difficult, the best material being obtained by recrystallization both as the methyl ester and the acid, the latter from ethanol, mp 229–230°.

The **methyl ester 6b** was recrystallized from petroleum ether: mp 91.5–92.5°; ir ($CHCl_3$) 5.79 (s), 6.95 μ (s); ir (CS_2) 5.76, 8.38, 8.62–8.72, 13.24, 13.43, 13.60, 14.40; nmr δ 7.65–7.85 (2 H, m, 4 and 5 aryl H), 7.10–7.55 (11 H, m, remaining aryl H), 3.44 (2 H, s, $W_{h/2}$ = 0.8 Hz, CH_2), 3.28 (3 H, s, OCH_3).

Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 84.02; H, 5.74.

The ***n*-hexyl ester** was prepared by refluxing a solution of the acid in *n*-hexanol containing some sulfuric acid. The crude product, after washing and drying, was evaporatively distilled in a sublimation apparatus at 180° (0.1 mm): ir (i, on oil) max 5.81 (s, CO), 6.70, 6.91, 7.85, 8.66, 8.77, 14.43 μ (all m).

Decarboxylation of the Abnormal Acid 7a to 1-Methyl-9-phenylfluorene (9).—A mixture of 82 mg of 9-phenylfluorene-1-acetic acid (**7a**, mp 187–189°), 0.5 g of copper powder and 5 ml of redistilled isoquinoline was heated at 225° for 1 hr and at 235° for 15 min, then cooled, diluted with benzene, filtered and washed with acid and base. The neutral fraction was sublimed twice at 0.02 mm; then the oily solid (19 mg) was chromatographed on 3 g of alumina (Woelm), using petroleum ether. In fractions 2–9 was obtained 13 mg of solid which was recrystallized from dilute ethanol to give 6 mg, micro mp 148–153°. A mixture with authentic 1-methyl-9-phenylfluorene (see below) melted at 150–153°. The infrared spectra of the two samples in KBr were essentially identical. The nmr of a less pure sample, mp 148–152°, showed the methyl signal at δ 2.04 (smaller peaks at δ 1.27 and 1.50 due to a persistent impurity).

1-Methyl-9-fluorenone (11).—2-Acetylamino-2′-methylbenzophenone was prepared in 52% yield by the procedure of Lothrop and Goodwin,[18] and hydrolyzed. The total crude amine from 8.63 g of the acetylamino compound was treated in 700 ml of 50% sulfuric acid at −5° with 2.5 g of sodium nitrite; then after 1 hr at −5°, the solution was heated to 60–70° on the steam bath for 2 hr. Isolation of the product by chromatography as reported[18] and recrystallization from petroleum ether gave 4.30 g, mp 98–100° (lit.[18] mp 98°), and 0.50 g, mp 97–100°, for a total of 73%.

1-Methyl-9-phenyl-9-fluorenol (10).—Following the procedure for 9-phenyl-9-fluorenol,[14] to an excess of phenyl Grignard reagent in ether was added 1-methyl-9-fluorenone in benzene–ether solution. The resulting carbinol (79%, mp 134–136°) was recrystallized from petroleum ether: mp 136.5–137°; ir ($CHCl_3$) max 2.74 (OH), 6.71, 6.90, 8,60, 9.77, 14.34 μ; nmr δ 6.90–7.70 (12 H, m, aryl H), 2.19 (1 H, broad s, OH), 2.08 (3 H, s, $W_{h/2}$ = 1.4 Hz, CH_3).

Anal. Calcd for $C_{20}H_{16}O$: C, 88.20; H, 5.92. Found: C, 88.32; H, 5.83.

1-Methyl-9-phenylfluorene (9).—A solution of 1.20 g of the fluorenol **10** in 16.5 ml of acetic acid and 20 ml of 25% hydrochloric acid was heated at reflux with 1.15 g of zinc dust for 3 hr, then decanted and the zinc washed with hot acetic acid. Cooling the solution gave 0.78 g, mp 152–153.5°, and an additional 0.08 g (total 91%) on dilution and recrystallization. Three recrystallizations from ethanol gave the analytical sample: mp 153–153.5°; ir (KBr) 6.95, 12.51, 13.12–13.35, 13.6 μ; nmr δ 7.55–7.85 (2 H, m, 4 and 5 aryl H), 6.90–7.50 (10 H, m, remaining aryl H), 4.97 (1 H, s, $W_{h/2}$ = 1.7 Hz, triarylmethyl H), 2.03 (3 H, s, $W_{h/2}$ = 1.6 Hz, CH_3).

Anal. Calcd for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found: C, 93.79; H, 6.38.

Registry No.—**4a**, 18554-43-3; **4b**, 18554-44-4; **5**, 18554-45-5; **6a**, 18554-46-6; **6b**, 18554-47-7; ***n*-hexylester of 6a**, 18554-48-8; **7a**, 18554-18-2; **7b**, 18554-49-9; **9**, 18554-50-2; **10**, 18554-51-3.

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(30) There were indications of a second crystalline form melting around 230–240°, and possibly a third at 175–176.5°.

(31) The nmr spectra of these fractions of the acid showed two CH_2 singlet peaks, at δ 3.37, corresponding to the normal acid, and at 3.31, in ratios of 55–60 to 45–40%. The second peak may be due to acid **7a** in this reaction also, as a result of reaction of the intermediate carbonium ion in the 1 position, or the isomeric 3-acetic acid derivative.