warming the alcohol with excess 1-naphthyl isocyanate and a drop of pyridine.

Anal. Calcd. for $C_{28}H_{26}O_5N_2$: C, 71.47; H, 5.57; N, 5.96. Found: C, 71.61; H, 5.87; N, 6.09.

The acetate was prepared by warming with acetic anhydride and a small amount of zinc chloride. A 64% yield of 3-acetoxymethyl-3-methoxymethyl-2-butanone, b.p. 56–57° (0.5 mm.), n_D^{25} 1.4318, was obtained.

Anal. Calcd. for $C_9H_{16}O_4$: C, 57.42; H, 8.57; OCH_3, 16.49. Found: C, 57.66; H, 8.54; OCH_3, 15.82.

Molecular weight calcd.: 188. Found: 196.

Reaction of paraformaldehyde with methyl isopropenyl ketone. A mixture of 4299 g. (51 moles) of methyl isopropenyl ketone, 150 g. (5 moles) of paraformaldehyde, and 15 ml. of *N* alcoholic potassium hydroxide was stirred at room temperature for 22 hr. An additional 15 ml. of base was then added. The reaction was allowed to proceed for another 4 hr. until the solution was clear and gave a negative Tollens test. The base was neutralized with 3 ml. of acetic acid and the excess methyl isopropenyl ketone (3853 g.) was removed *in vacuo* to leave an almost colorless liquid residue of 327 g. This was washed 3 times with 200-ml. portions of *n*-hexane. The remaining 267 g. of crude product was dissolved in 500 ml. of water and extracted with 400 ml. of methylene chloride in 2 portions. Evaporation of the methylene chloride yielded 139 g. of product. This was distilled at 60 to 120° at 0.5 mm. on a falling-film still. The 126 g. of colorless product, n_D^{25} 1.4690, was water soluble. This preparation was carried out 6 times with similar results. The refractive index of various fractions from the distillation varied from 1.4600 to 1.4692. A sample redistilled on a falling-film still at 95–100° (0.5 mm.) (n_D^{25} 1.4652) give a hydroxyl number by the acetic anhydride pyridine method[7] of about 90% of the theoretical. This hydroxyl determination is of limited accuracy since the acetate formed is decomposed during titration for unreacted acetic acid. This leads to low values for the hydroxyl number.

Anal. Calcd. for $C_6H_{10}O_2$: C, 63.12; H, 8.83; OC_2H_5, 0.00. Found: C, 59.86; H, 8.61; OC_2H_5, 5.81.

The once-distilled product polymerized at 65° in the presence of methyl amyl ketone peroxide catalyst to give a stiff, colorless polymer, insoluble in acetone, dimethylformamide, and γ-butyrolactone.

AZUSA, CALIF.
AKRON, OHIO

(7) V. C. Mehlenbacher in *Organic Analysis*, Interscience, New York, N. Y., 1953, Vol. I, p. 26.

[CONTRIBUTION FROM THE RADIUM INSTITUTE OF THE UNIVERSITY OF PARIS]

Fluorinated Isatins and Some of Their Heterocyclic Derivatives

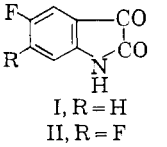
V. Q. YEN, N. P. BUU-HOÏ, AND N. D. XUONG

Received June 3, 1958

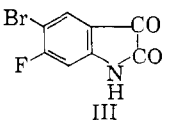
The Sandmeyer isatin synthesis has been applied with success to 4-fluoro-, 3,4-difluoro-, and 4-bromo-3-fluoroaniline, while 2-fluoro- and 2,4-difluoroaniline failed to give the corresponding isatins. The fluorinated isatins thus obtained were used for the synthesis of a large number of fluorine-containing quinolines, acridines, and indophenazines required for testing as potential carcinogens.

Nitrogen heterocyclic compounds containing fluorine have often shown interesting biological activity. Several fluorobenzacridines, for instance, are carcinogenic,[1] and it is known that fluorination enhances the tumor-producing effects of *N,N*-dimethylaminoazobenzene (butter yellow);[2] on the other hand, some 5-fluoropyrimidines have pronounced carcinostatic effects.[3] Thus, it was deemed of interest to investigate fluorinated quinolines, acridines, and other nitrogen heterocycles, few of which have so far been reported in the literature.

Obvious intermediates for the synthesis of such heterocycles were fluorinated isatins, which, unlike the chloro and bromo analogs, had hitherto scarcely been investigated. The Sandmeyer isatin synthesis[4] consisting of the condensation of primary arylamines with chloral and hydroxylamine to the corresponding isonitrosoacetanilides, and subsequent cyclization of the latter, was now applied with success to 4-fluoro-, 3,4-difluoro-, and 4-bromo-3-fluoroaniline, which gave, respectively, 5-fluoro- (I). 5,6-difluoro- (II), and 5-bromo-6-fluoroisatin (III). Although the Sandmeyer isatin synthesis with 3-substituted anilines generally leads to mixtures of 4- and 6-substituted isatins, a single compound was obtained in the cyclization of 3,4-difluoro- and 4-bromo-3-fluoroaniline, and the isatins formed were assigned the formulas II and III on grounds of their high melting points and the deactivating influence of the halogen atom on position 4. It is interesting to note that with 2-fluoro- and 2,4-difluoroaniline, the corresponding isonitrosoacetanilides were readily obtained, but failed to give the expected isatins on cyclization



I, R = H
II, R = F



III

with sulfuric acid. Roe and Teague[5] mentioned the α-chloride of 5-fluoroisatin as an intermediate

(1) F. Zajdela and N. P. Buu-Hoï, *Acta Unio Intern. contra Cancrum*, 11, 736 (1955).

(2) *Cf.* H. W. Rumsfeld, W. L. Miller, and C. A. Baumann, *Cancer Research*, 11, 814 (1951).

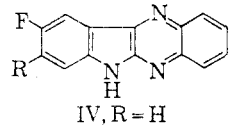
(3) W. Bollag, *Schweiz. med. Wochschr.*, 87, 817 (1957); C. Heidelberger *et al.*, *Cancer Research*, 18, 305 (1958); *Nature*, 179, 663 (1957).

(4) T. Sandmeyer, *Helv. chim. Acta*, 2, 237 (1919).

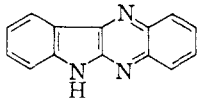
(5) A. Roe and C. E. Teague, *J. Am. Chem. Soc.*, 71, 4019 (1949).

used in an attempt to synthesize 5,5'-difluoroindigo by Baeyer's method,[6] but the properties of 5-fluoroisatin itself were not reported.

The Marchlewski condensation[7] of the above fluorinated isatins with *o*-phenylenediamine readily yielded 9-fluoro- (IV), 8,9-difluoro-(V), and 8-fluoro-9-bromo-indophenazine (VI) (according to the recommended nomenclature, indophenazines are termed 6-indolo[2,3-*b*]quinolines). In the quinoline series, the Pfitzinger reaction[8] of 5-fluoroisatin with acetone, acetophenone, and *p*-

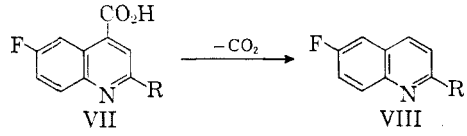


IV, R = H
V, R = F



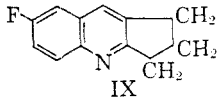
VI

fluoroacetophenone afforded the 2-substituted 6-fluorocinchoninic acids (VII), thermal decarboxylation of which led to the corresponding 6-fluoro-

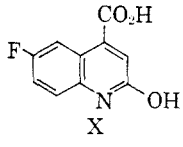


VII VIII

quinolines (VIII). The same sequence of reactions, performed with cyclopentanone, gave 6-fluoro-2,3-trimethylenequinoline (IX) (according to the new nomenclature, 2,3-trimethylenequinoline is to be termed 2,3-dihydro-1-cyclopenta[*b*]quinoline); another quinoline synthesis involved a Camps' reaction[9] with 1-acetyl-5-fluoroisatin, which yielded 6-fluoro-2-hydroxycinchoninic acid (X). In the acridine group, a route to mono- and difluoroacridines was provided by the Pfitzinger-Borsche condensation[10] of 5-fluoro-, 5,6-difluoro-, and 5-

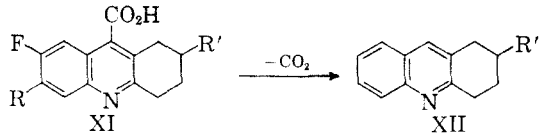


IX



X

bromo-6-fluoroisatin with cyclohexanone and 4-methylcyclohexanone, to give the corresponding 1,2,3,4-tetrahydroacridine-9-carboxylic acid (XI), whose thermal decarboxylation furnished the corresponding fluoroacridine bases (XII).



XI XII

In the indigo group, Roe and Teague's observation that reduction of 5-fluoroisatin α-chloride with zinc resulted mainly in 5,5'-difluoroindirubine was confirmed, except that the amount which was formed in this reaction was more substantial than indicated.

EXPERIMENTAL

Preparation of 5-fluoroisatin (I). A solution of 90 g. of chloral hydrate and 1300 g. of crystallized sodium sulfate in 1200 ml. of water was mixed with a solution of 55.5 g. of *p*-fluoroaniline and 110 g. of hydroxylamine hydrochloride in 800 ml. of water and 43 ml. of hydrochloric acid, and the mixture refluxed for 2 min. After cooling, the precipitate of *p-fluoroisonitrosoacetanilide* was collected and washed with water. Yield: 88 g. of a product crystallizing from water in fine colorless needles, m.p. 160° (a by-product, colorless needles, m.p. 302° from acetic acid, was obtained).

Anal. Calcd. for $C_8H_7FN_2O_2$: C, 52.7; H, 3.9; N, 15.4. Found: C, 52.5; H, 3.9; N, 15.5.

This isonitroso compound (87 g.) was added portionwise and with stirring, to 360 ml. of sulfuric acid, the temperature being kept between 60 and 70°, then raised to 80° for 20 min. On cooling, the reaction-product was poured on crushed ice, and the yellow precipitate of crude *5-fluoroisatin* was collected, and purified by dissolution in aqueous sodium hydroxide and subsequent acidification. Recrystallization from aqueous acetic acid yielded 44 g. of brick red needles, m.p. 227°.

Anal. Calcd. for $C_8H_4FNO_2$: C, 58.2; H, 2.4. Found: C, 58.1; H, 2.7.

The *oxime* crystallized from ethanol in yellowish needles, m.p. 275°.

Anal. Calcd. for $C_8H_5FN_2O_2$ N, 15.6. Found: N, 15.6.

9-Fluoroindophenazine (IV). A solution of 2.5 g. of the 5-fluoroisatin and 1.6 g. of *o*-phenylenediamine in 10 ml. of acetic acid was refluxed for 15 min., and the precipitate obtained on cooling was recrystallized from acetic acid, yielding 2.5 g. of fine yellow needles, m.p. 302°; orange-red halochromy with sulfuric acid.

Anal. Calcd. for $C_{14}H_8FN_3$: C, 70.9; H, 3.4; N, 17.7. Found: C, 70.9; H, 3.5; N, 17.5.

6-Acetyl-9-fluoroindophenazine was obtained by refluxing for 15 min. a solution of 0.5 g. of the foregoing compound in 10 ml. of acetic anhydride; the precipitate formed after cooling crystallized from acetic acid in colorless needles (0.4 g.), m.p. 201°, giving an orange halochromism with sulfuric acid.

Anal. Calcd. for $C_{16}H_{10}FN_3O$: C, 68.8; H, 3.6; N, 15.1. Found: C, 69.0; H, 3.7; N, 14.8.

5-Fluoroisatin α-chloride. Prepared from 5.5 g. of 5-fluoroisatin and 7 g. of phosphorus pentachloride in 22 ml. of anhydrous benzene, this compound crystallized from benzene in brick red needles (3.5 g.), melting with decomposition around 201°. This compound was obtained by Roe and Teague,[5] but was not purified.

Anal. Calcd. for C_8H_3ClFNO: Cl, 19.3. Found: Cl, 19.6.

The Baeyer reduction of 3 g. of the foregoing chloride (suspended in 40 ml. of acetic acid) with 10 g. of zinc powder, yielded 1.2 g. of a violet mixture, which was resolved by treatment with acetic acid. The insoluble portion consisted of *5,5'-difluoroindigo* (0.15 g.), crystallizing from pyridine in blue needles, which volatilized at high temperature to give off purple vapors. The acetic acid solution gave

(6) A. von Baeyer, *Ber.*, **11**, 1297 (1878); **12**, 457 (1879).

(7) *Cf.* E. Schunck and L. Marchlewski, *Ber.*, **28**, 2528 (1895); **29**, 202 (1896); L. Marchlewski and L. G. Radcliffe, *Ber.*, **34**, 1014 (1901); N.P. Buu-Hoï and H. K. Wei, *Rev. sci.*, **82**, 168, 306, 370 (1944); N. P. Buu-Hoï and D. Guettier, *Bull. soc. chim. France*, **13**, 586 (1946).

(8) *Cf.* W. Pfitzinger, *J. prakt. Chem.*, **56**, 283 (1897); N. P. Buu-Hoï, R. Royer, N. D. Xuong, and P. Jacquignon, *J. Org. Chem.*, **18**, 1209 (1953).

(9) R. Camps, *Arch. Pharm.*, **237**, 659 (1899).

(10) W. Borsche and K. Rottsieper, *Ann.*, **377**, 70 (1910); N. P. Buu-Hoï, T. B. Loc, and N. D. Xuong, *Bull. soc. chim. France*, **2**, 174 (1958).

SUBSTITUTED 1,2,3,4-TETRAHYDROACRIDINES

Substituents[a]		Formula	M.P., °C.	Analyses N Calcd.	Found
7-Fluoro-9-carboxy-	XI; R = R′ = H	$C_{14}H_{12}FNO_2$	326	5.7	5.8
7-Fluoro-	XII; R = R′ = H	$C_{13}H_{12}FN$	71	7.0	7.0
2-Methyl-7-fluoro-9-carboxy-	XI; R = H, R′ = CH_3	$C_{15}H_{14}FNO_2$	319	5.4	5.4
2-Methyl-7-fluoro-	XII; R = H, R′ = CH_3	$C_{14}H_{14}FN$	88	6.5	6.6
6,7-Difluoro-9-carboxy-	XI; R = F, R′ = H	$C_{14}H_{11}F_2NO_2$	336	5.3	5.5
6,7-Difluoro-	XII; R = F, R′ = H	$C_{13}H_{11}F_2N$	70	6.4	6.4
2-Methyl-6,7-difluoro-9-carboxy-	XI; R = F, R′ = CH_3	$C_{15}H_{13}F_2NO_2$	341	5.1	5.3
2-Methyl-6,7-difluoro-	XII; R = F, R′ = CH_3	$C_{14}H_{13}F_2N$	80	6.0	5.8

[a] The acids were prepared as for the other cinchoninic acids, and were recrystallized from ethanol or acetic acid; the bases were recrystallized from methanol.

on concentration, violet needles of *5,5′-difluoroindirubine* (0.5 g.).

N-Acetyl-5-fluoroisatin. A mixture of 2.5 g. of 5-fluoroisatin and 50 ml. of acetic anhydride was refluxed for 15 min., and the precipitate obtained on cooling was collected, washed with ether, and recrystallized from acetic acid. Yield: 2.3 g. of yellow needles, m.p. 149°.

Anal. Calcd. for $C_{10}H_6FNO_3$: C, 58.0; H, 2.9; N, 6.8. Found: C, 58.1; H, 3.1; N, 6.8.

6-Fluoro-2-hydroxycinchoninic acid (X). A solution of 1.5 g. of the foregoing acetyl compound and 1 g. of sodium hydroxide in 30 ml. of water was refluxed for 1 hr., left overnight, then neutralized with dilute hydrochloric acid; after filtration, addition of acid was continued until *p*H 6. The precipitate formed was collected and recrystallized from acetic acid, giving 0.8 g. of yellowish sublimable prisms, which did not melt below 360°.

Anal. Calcd. for $C_{10}H_6FNO_3$: N, 6.8. Found: N, 7.0.

Pfitzinger reactions with 5-fluoroisatin. A 20% solution of potassium hydroxide (2.5 moles) in ethanol was refluxed for 12 hr. with equimolar amounts of the isatin and the appropriate ketone, the solvent was distilled off in vacuum, and the residue taken up in water; the aqueous solution was extracted with ether and acidified with acetic acid. The cinchoninic acid precipitated was recrystallized.

6-Fluoro-2-phenylcinchoninic acid (VII; R = C_6H_5), prepared with acetophenone, crystallized from ethanol, colorless prisms, m.p. 223°.

Anal. Calcd. for $C_{16}H_{10}FNO_2$: N, 5.3. Found: N, 5.3.

6-Fluoro-2-phenylquinoline (VIII; R = C_6H_5), prepared by heating the above acid over its melting point and distilling the residue in vacuum, crystallized from ethanol in colorless prisms, m.p. 86°; its yellow picrate had m.p. 176°.

Anal. Calcd. for $C_{15}H_{10}FN$: N, 6.3. Found: N, 6.3.

6-Fluoro-2-(4-fluorophenyl)cinchoninic acid (VII; R = C_6H_4F), prepared with *p*-fluoroacetophenone, crystallized from ethanol in colorless prisms, m.p. 251°.

Anal. Calcd. for $C_{16}H_9F_2NO_2$: N, 4.9. Found: N, 5.0.

6-Fluoro-2-(4-fluorophenyl)quinoline (VIII, R = C_6H_4F) crystallized from methanol in colorless needles, m.p. 128°; its yellow picrate had m.p. 172°.

Anal. Calcd. for $C_{15}H_9F_2N$: N, 5.8. Found: N, 5.6.

6-Fluoro-2-methylcinchoninic acid (VII; R = CH_3), prepared with acetone in water, crystallized from water in colorless needles, m.p. 246°.

Anal. Calcd. for $C_{11}H_8FNO_2$: N, 6.8. Found: N, 7.0.

6-Fluoro-2,3-trimethylenecinchoninic acid, prepared from cyclopentanone, crystallized from acetic acid, yellowish needles, m.p. 306°.

Anal. Calcd. for $C_{13}H_{10}FNO_2$: N, 6.1. Found: N, 5.9.

6-Fluoro-2,3-trimethylenequinoline (IX) crystallized from methanol, colorless needles, m.p. 88°; picrate, m.p. 231°.

Anal. Calcd. for $C_{12}H_{10}FN$: N, 7.5. Found: N, 7.7.

5,6-Difluoroisatin (II). The condensation of 20 g. of 3,4-difluoroaniline with 27 g. of chloral hydrate and 37 g. of hydroxylamine hydrochloride, performed as for *p*-fluoroaniline, yielded 29 g. of *3,4-difluoroisonitrosoacetanilide,* crystallizing from water in silky colorless needles, m.p. 156°.

Anal. Calcd. for $C_8H_6F_2N_2O_2$: C, 48.0; H, 3.0; N, 14.0. Found: C, 47.9; H, 3.0; N, 14.2.

Cyclization of 28 g. of this compound with 106 ml. of sulfuric acid afforded 14 g. of *5,6-difluoroisatin,* which was purified by dissolution in aqueous sodium hydroxide and acidification; recrystallization from aqueous acetic acid gave shiny red needles, m.p. 226°.

Anal. Calcd. for $C_8H_3F_2NO_2$: C, 52.5; H, 1.7. Found: C, 52.2; H, 1.8.

8,9-Difluoroindophenazine (V). Condensation of 1.7 g. of the foregoing isatin with 1 g. of *o*-phenylenediamine in 15 ml. of acetic acid yielded 1.5 g. of a compound, crystallizing from acetic acid in yellow, sublimable needles, m.p. 337°, giving orange-yellow coloration with sulfuric acid.

Anal. Calcd. for $C_{14}H_7F_2N_3$: N, 16.5. Found: N, 16.5.

6-Acetyl-8,9-difluoroindophenazine, obtained by acetylation of the foregoing compound with acetic anhydride, crystallized from acetic acid in yellowish needles, m.p. 239°, giving an orange-yellow coloration with sulfuric acid.

Anal. Calcd. for $C_{16}H_{19}F_2N_3O$: C, 64.6; H, 3.1; N, 14.2. Found: C, 66.7; H, 3.1; N, 14.3.

5-Bromo-6-fluoroisatin (III). Condensation of 3 g. of 4-bromo-3-fluoroaniline with 3 g. of chloral hydrate and 4 g. of hydroxylamine hydrochloride yielded 4 g. of *4-bromo-3-fluoroisonitrosoacetanilide,* crystallizing from water in fine yellowish needles, m.p. 194° (decomp.).

Anal. Calcd. for $C_8H_6BrFN_2O_2$: C, 36.8; H, 2.3; N, 10.7. Found: C, 37.0; H, 2.4; N, 10.6.

Cyclization of 3.5 g. of this acetanilide with 16 ml. of sulfuric acid afforded 3 g. of *5-bromo-6-fluoroisatin,* crystallizing from dilute acetic acid in shiny orange prisms, m.p. 252°.

Anal. Calcd. for $C_8H_3BrFNO_2$: N, 5.7. Found: N, 5.9.

Pfitzinger reaction with cyclohexanone gave a cinchoninic acid, decomposing above 305°.

9-Bromo-8-fluoroindophenazine (VI). Condensation of 0.5 g. of the foregoing isatin with 0.22 g. of *o*-phenylenediamine in 18 ml. of acetic acid yielded 0.4 g. of a product crystallizing from pyridine in silky yellow needles, m.p. 297°.

Anal. Calcd. for $C_{14}H_7BrFN_3$: C, 53.2; H, 2.2; N, 13.3. Found: C, 53.4; H, 2.3; N, 13.1.

The *6-acetyl derivative,* prepared in the usual way, crystallized from acetic acid in yellowish prisms, m.p. 251°, giving an orange-yellow coloration with sulfuric acid.

Anal. Calcd. for $C_{16}H_9BrFN_3O$: N, 11.4. Found: N, 11.2.

Behavior of o-fluoroaniline and 2,4-difluoroaniline in the Sandmeyer reaction. (a) Condensation of *o*-fluoroaniline with chloral hydrate and hydroxylamine yielded *o-fluoroisonitrosoacetanilide,* crystallizing from aqueous acetic acid in colorless prisms, m.p. 118°.

Anal. Calcd. for $C_8H_7FN_2O_2$: C, 52.7; H, 3.9; N, 15.4. Found: C, 52.8; H, 4.1; N, 15.5.

On treatment with sulfuric acid, this acetanilide afforded a compound of unknown constitution, crystallizing from

acetic acid in pale yellow needles, m.p. 281° (Found: C, 53.2; H, 3.1; N, 15.4), and none of the expected 7-fluoroisatin.

(b) Condensation of 2,4-difluoroaniline with chloral hydrate and hydroxylamine afforded *2,4-difluoroisonitrosoacetanilide*, crystallizing from acetic acid in colorless needles, m.p. 135°.

Anal. Calcd. for $C_8H_6F_2N_2O_2$: C, 48.0; H, 3.0; N, 14.0. Found: C, 47.7; H, 3.1; N, 14.3.

Sulfuric acid converted this anilide into a product crystallizing from acetic acid in yellow prisms, m.p. 291° (dec.) (Found: C, 47.4; H, 2.5; N, 13.8.)

Acknowledgment. The authors express their gratitude to Dr. G. C. Finger (State Geological Survey, Urbana, Ill.,) for the gift of 2,4- and 3,4-difluoroaniline used in the present research.

PARIS VE, FRANCE

[CONTRIBUTION FROM COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

Hydrogen Peroxide *cis*-Oxidative Cleavage of 2,5-Diarylfurans. Conformations and Reactions of *cis* and *trans* Methyl- and Mesityl-Dimesitoylethylenes[1]

ROBERT E. LUTZ AND CHI-KANG DIEN[2]

Received May 29, 1958

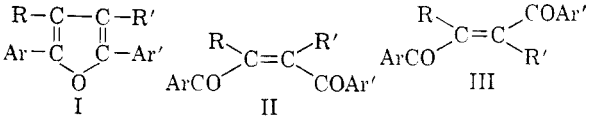
Hydrogen peroxide oxidatively cleaved a series of 2,5-diarylfurans to *cis* unsaturated 1,4-diketones. In three cases 2,2′-bis-(3-furanones) were obtained as by-products stemming from β-oxidation. β-Acetoxydiphenylfuran underwent chiefly α-oxidation to the 2-hydroxy-3-furanone. 2,5-Mesityl groups did not inhibit the *cis*-oxidative cleavage as in the nitric-acetic acid reactions. The mechanism of *cis*-oxidative cleavage is discussed with pertinent comments on ozonation.

The new *cis* methyl- and mesityl-dimesitoylethylenes were shown to be labile and in this respect unlike *cis*-methyldibenzoylethylene which is the more stable form. They underwent *cis*-acetoxy-addition-furanization. The *cis*- and *trans*-mesityl dimesitoylethylenes were reduced 1,6 to stereoisomeric di-enols which were oxidizable to the *trans* unsaturated diketone; the di-enol from the *cis* isomer furanized readily, that from the *trans* isomer did not.

The stability relationships and the differences in this respect from the phenyl analogs are explained in terms of steric consequences of the differences between the abilities of phenyl and mesityls to conjugate effectively with the unsaturated 1,4-dicarbonyl system. The different courses of the reductions of the *cis*- and *trans*-mesityl dimesitoylethylenes are explained in terms of different conformations with respect to that half of the molecule carrying the α-mesityl group.

The action of hydrogen peroxide on 2,5-diarylfurans was studied for comparisons with nitric-acetic acid and lead tetraacetate oxidations,[3–5] and in the hope that it would bring about *cis*-oxidative cleavage of the sterically more hindered 2,5-dimesitylfurans. Such cleavage would furnish a convenient method of preparing certain *cis* unsaturated 1,4-diketones which would not be easily obtainable otherwise. The latter hope, which proved to be sound, stemmed from earlier work by Clauson-Kaas on the hydrogen peroxide oxidations of simpler furans.[6,7] By this reaction the new *cis*-methyl- and mesityl-dimesitoylethylenes have been obtained, completing two important *cis-trans* pairs, and permitting a comparative study of the effect of configuration on some of the reactions of unsaturated diketone systems.

The hydrogen peroxide oxidations of the series of 2,5-diarylfurans Ia–q utilized a glacial acetic acid—30% aqueous hydrogen peroxide mixture. They are summarized in the formulations I–V and in Table I.[8]



I II III

(a) Ar = Ar′ = C_6H_5, R = R′ = H
(b) Ar = Ar′ = *p*-BrC_6H_4, R = R′ = H
(c) Ar = Ar′ = C_6H_5, R = Cl, R′ = H
(d) Ar = Ar′ = C_6H_5, R = Cl, R′ = $OCOCH_3$
(e) Ar = Ar′ = C_6H_5, R = COC_6H_5, R′ = H
(f) Ar = *p*-BrC_6H_4, Ar′ = C_9H_{11} (mesityl), R = R′ = H
(g) Ar = C_6H_5, Ar′ = C_9H_{11}, R = H, R′ = COC_6H_5
(h) Ar = Ar′ = C_9H_{11}, R = R′ = H
(i) Ar = Ar′ = C_9H_{11}, R = CH_3, R′ = H
(j) Ar = Ar′ = C_9H_{11}, R = R′ = CH_3
(k) Ar = Ar′ = R = C_9H_{11}, R′ = H
(l) Ar = Ar′ = C_9H_{11}, R = C_6H_5, R′ = H
(m) Ar = Ar′ = C_9H_{11}, R = CH_3, R′ = Br
(n) Ar = Ar′ = C_9H_{11}, R = R′ = Br
(o) Ar = Ar′ = C_9H_{11}, R = $OCOCH_3$, R′ = H
(p) Ar = Ar′ = C_9H_{11}, R = $OCOCH_3$, R′ = CH_3
(q) Ar = Ar′ = C_9H_{11}, R = $OCOCH_3$, R′ = C_9H_{11}

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(8) The work here reported was exploratory; although attention was given to yields, extensive study was not made to develop the best preparative conditions.