Further Examination of the Actions of Bases and of Zinc and Acids on *trans*-2,3-Dibenzoylspiro(cyclopropane-1,9′-fluorene)

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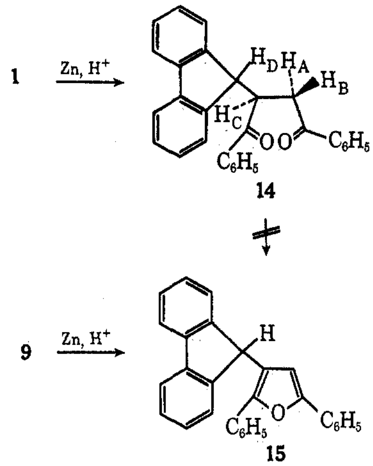
9-Diazofluorene reacts with *trans*-dibenzoylethylene to give *trans*-2,3-dibenzoylspiro(cyclopropane-1,9′-fluorene) (**1**)[2] in quantitative yield. Cyclopropane **1** was reported to undergo various transformations which were not understood and which led to crystalline products of unknown structures.[2] Of special interest is the reaction of **1** with hot excess methanolic potassium hydroxide (Scheme I) to form a red potassium salt, tentatively designated as the dipotassium derivative of dienolate **3**, which upon treatment with methanolic hydrogen chloride gave a yellow compound melting at 195°.[2] This product, unlike **1**, was oxidized by potassium permanganate in acetone and yielded an inner azine readily on treatment with hydrazine hydrate.[2] Finally reduction of **1**, as well as the at 195° melting material, with zinc and acetic acid gave a derivative melting at 209°.[2]

Although the initial workers[2] did not designate a specific structure for the product melting at 195°, *Chemical Abstracts* has assigned it as *cis*-1,2-dibenzoylspiro(cyclopropane-1,9′-fluorene) (**4**).[3] Mechanistically such an isomerization could be rationalized on the basis of kinetic control in which **2**, the monoenolate base of **1**, accepts a proton from the least hindered side. The properties of the isomeride as a *cis*-spirocyclopropane of structure **4** are inconsistent, however, with its color and its rapid oxidation by neutral permanganate.[2] Since in the present authors' opinion, conversions of **1** to **3** and to **4** were probably unlikely because of the expected susceptibility of **2** to ring opening,[4] the actions of base on **1** were investigated further in some detail. A study has also been made of the reduction of **1** and its related derivatives with zinc and acetic acid.

Reaction of **1** with methanolic potassium hydroxide as previously described yields a pink potassium salt from the blood-red alkaline solution. The dry salt was unstable and could not be adequately characterized directly. When **1** was reacted with hot methanolic potassium hydroxide followed by treatment with hydrogen chloride, as far as possible according to the conditions reported previously,[2,5] a pale yellow product, $C_{30}H_{22}O_2$[6] (44% yield), mp 112–123°, was found. Although the reaction sequence has been repeated many times under these conditions, thus far we have not encountered any compound melting at 195°. Surprisingly the compound obtained contained a methoxy group,[7a] it did not show carbonyl absorption, it did not react with hydrazine, and its ultraviolet absorption was quite different from that of **1**.[7b] The product has been identified as 2,5-diphenyl-3-(9′-fluorenyl)-furan (**9**) upon oxidation and by synthesis. In accordance with the properties of furans,[8] **9** was readily converted by nitric acid–acetic acid to 1,2-dibenzoyl-1-(9′-methoxy-9′-fluorenyl)ethylene (**10**) in 85% yield.[9] Diketone **10** was also obtained from **9** by ozonolysis and also by oxidation with potassium permanganate in acetone.

Formation of **9** from **1** can be rationalized on the basis of opening of the conjugate base **2** to delocalized ion **5** which on treatment with methanolic hydrogen chloride could undergo protonation to **6** and subsequently give **9** by a sequence of steps involving highly stabilized cation **8**. Synthesis and proof of structure of **9** were indeed achieved on the basis of the rationalization involving **8** as an intermediate. Reaction of fluorenone (**11**) with the Grignard reagent **12** from 3-bromo-2,5-diphenylfuran[10] resulted in 2,5-diphenyl-3-(9′-hydroxy-9′-fluorenyl)furan[11] (**13**, 17% yield) upon hydrolysis; solution of **13** in methanolic hydrogen chloride gave **9** (88% yield) identical with that derived from **1**.

A study was then made of reduction of spirocyclopropane **1** and of methoxyfuran **9** with zinc and acetic acid. In principle, **1** (eq 1) and **9** (eq 2) could yield the same product, 2,5-diphenyl-3-(9′-fluorenyl)furan (**15**). Such a result would be in accordance with the previous report[2] that **1** and the unidentified product derived therefrom, mp 195°, yield a derivative, mp 209°, upon reduction. Upon reaction of **1** with zinc–acetic acid–hydrochloric acid, a product, mp 212°, was



(1) **14**

(2) **15**

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[2] L. Horner and E. Lingnau, *Justus Liebigs Ann. Chem.*, **591**, 21 (1955).

[3] *Chem. Abstr.*, **50**, 1695*g* (1956).

[4] R. Breslow, J. Brown, and J. J. Gajewski, *J. Amer. Chem. Soc.*, **89**, 4383 (1967), however, have reported base-catalyzed methyne hydrogen exchange in *cis*-2,3-diphenyl-*trans*-1-benzoylcyclopropane without ring opening.

[5] "*Die blut rote losung wird filtriert, und es wird solange ein trockner HCl-Gas Strom hindurchgeleitet, bis die Farbe in Gelb umgeschlagen ist. Die heisse losung wird from Kalium Chlorid abfiltriert.*"[2]

[6] The molecular formulas of **1**, **4**, **6**, and **13** are $C_{29}H_{20}O_2$, respectively.

[7] (a) The methoxy group was indicated by nuclear magnetic resonance ($CDCl_3$) at δ 2.84 (s, $-OCH_3$); (b) the ultraviolet properties of **9** (λ_{max} EtOH) are 224 mμ (ε 34,150), 229 (33,490), 286 (25,360), 301 (25,250), and 310 (shoulder, 24,160).

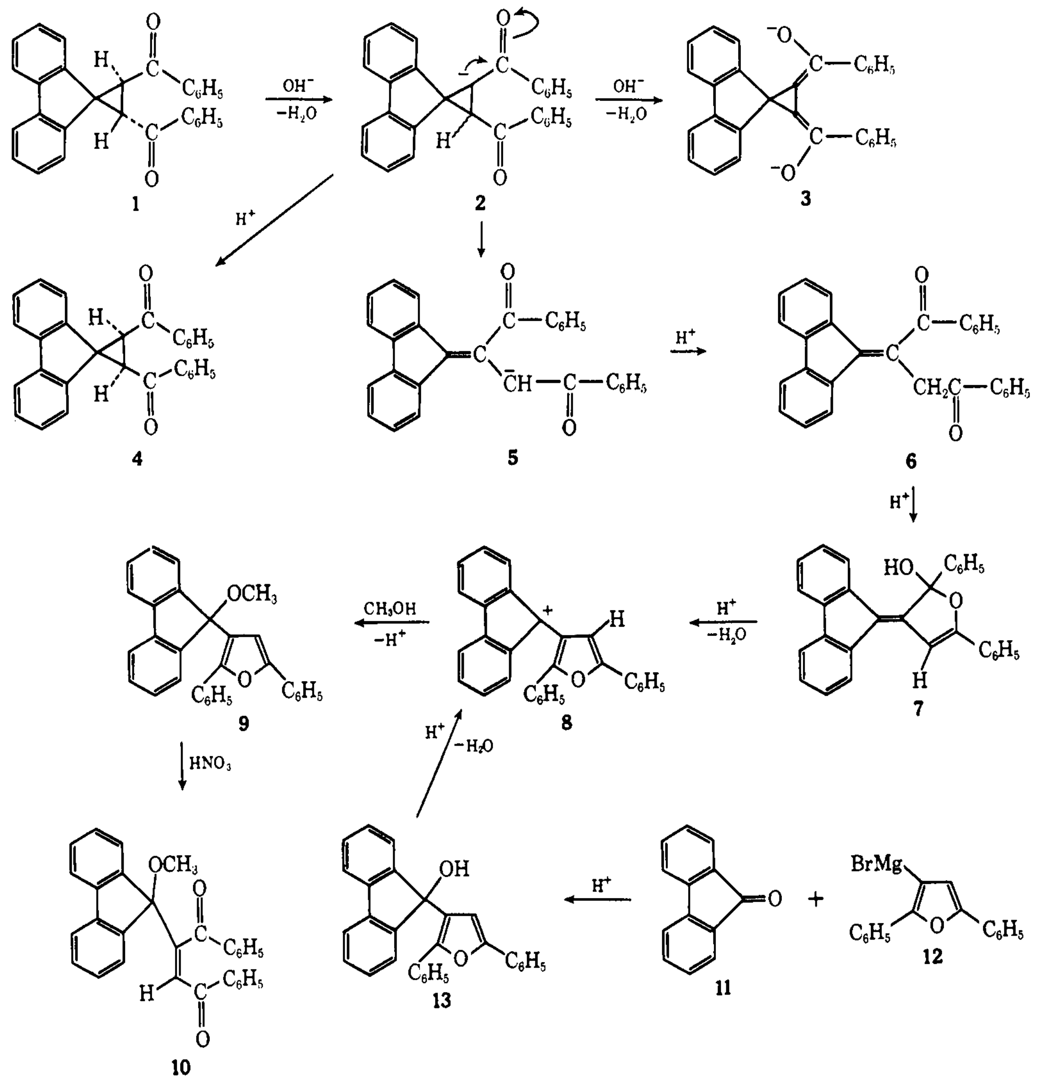
[8] A. P. Dunlop and F. N. Peters, "The Furans," Reinhold, New York, N. Y., 1953, p 47.

[9] Infrared absorption by **10** (λ_{max}, KBr) occurs at 5.85 (>C=O) and 6.12 μ (>C=O); nuclear magnetic resonance for the methoxy group ($CDCl_3$) is exhibited at δ 2.9 (s, $-OCH_3$).

[10] R. F. Lutz and J. M. Smith, Jr., *J. Amer. Chem. Soc.*, **63**, 1148 (1941).

[11] Alcohol **13** exhibited infrared absorption (λ_{max}, KBr) at 2.87 (OH) and 8.9 μ (CO) and nuclear magnetic resonance ($CDCl_3$) at δ 7.0 (s, furan H).

Scheme I



obtained in 39% yield whose properties are in close agreement with that previously reported.[2] The reduction product, $C_{29}H_{22}O_2$, was assigned the structure 1,2-dibenzoyl-1-(9′-fluorenyl)ethane (**14**) on the basis of its mass spectrum (*m/e* 402), its carbonyl absorption (6.01 μ), and its distinctive ABCD nmr spectrum.[12] In contrast, reduction of **9** gave 2,5-diphenyl-3-(9′-fluorenyl)furan (**15**, $C_{29}H_{20}O$), mp 158–159°, in 20% yield. The structure of **15** was confirmed by its nmr ($CDCl_3$): δ 5.5 (s, 1, 9′-fluorenyl H) and 6.33 (s, 1, furan H). All attempts to effect cyclization of **14** to **15** under vigorous acidic conditions were not fruitful.

Combination of the present and previous observations rules out the possibility that the isomer of **1** found to melt at 195° [2] is **4**. Further, the characterization of **14**, the compound melting at 212° reported in the initial work[1] from reduction of **1**, made **6** an attractive possibility for the 195° melting compound, since this would readily explain the reported zinc–acetic acid transformation to **14**. To our great surprise this belated reasoning led to isolation of the 195° melting substance by minor alteration of the reaction conditions! The blood-red filtrate resulting from **1** and methanolic potassium hydroxide, on saturation with dry hydrogen chloride *in the cold*, precipitated the yellow isomer melting at 195° and characterized as **6**[13] (Scheme I).

The involvement of **6** in the change of **1** to **9** was quickly demonstrated by isolation of **9** on saturation of a hot methanolic solution of **6** with dry hydrogen chloride. Interestingly examination of this reaction mixture by thin layer chromatography showed no unchanged **6**. Finally, as reported earlier, **6** was transformed to **14** by zinc–acetic acid (20% yield).

The study initiated to understand the reported transformations of **1** is now complete.

Experimental Section

General Procedure.—All melting points were taken on a Fisher–Johns melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 137 Infracord spectrometer. Ultraviolet spectra were obtained with a Cary 14 spectrophotometer. A Varian A-60 spectrometer was used for determining the nmr spectra (in $CDCl_3$ solution unless otherwise specified) and the results are expressed in parts per million downfield from internal tetramethylsilane.

Reaction of *trans*-2,3-Dibenzoylspiro(cyclopropane-1,9′-fluorene) (1) with Methanolic Potassium Hydroxide. Isolation of

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[12] The nmr properties of **14** ($CDCl_3$) are δ 2.1 (d of d, J_{AB} = 18, J_{AC} = 3 Hz, A), 3.38 (d of d, J_{AB} = 18, J_{BC} = 10 Hz, B), 4.45 (d, J_{CD} = 3 Hz, D), and 5.1 (d of t, J_{BC} = 10, J_{AC} = 3, J_{DC} = 3 Hz, C).

[13] The ir absorption of **6** (λ_{max} KBr) occurs at 5.91 and 6.02 μ (>C=O); nmr for the $-CH_2C_6H_5$ protons is exhibited at δ_{CDCl_4} 4.81 (s). The data clearly rule out any isomer of **6** in which the double bond is conjugated with both benzoyl groups.

2,5-Diphenyl-3-(9'-methoxy-9'-fluorenyl)furan (9).—To a suspension of 1 (5.0 g, 0.0125 mol) in methanol (125 ml) was added 30% methanolic potassium hydroxide (25 ml), and the red mixture was refluxed for 0.5 hr. The hot solution was filtered and the filtrate was treated with dry hydrogen chloride until it became yellow. The mixture was filtered and the filtrate was cooled. The yellow precipitate was collected, washed free of acid, and dried to give crude **9** (2.754 g), mp 113–120°. Crystallization from methanol gave pure **9** (2.283 g, 44.3% yield), mp 122–123°.

Anal. Calcd for $C_{30}H_{22}O_2$: C, 86.95; H, 5.31; OCH_3, 7.49. Found: C, 86.88; H, 5.19; OCH_3, 7.80.

Oxidation of 2,5-Diphenyl-3-(9'-methoxy-9'-fluorenyl)furan (9) with Nitric Acid.—To a stirred suspension of **9** (0.09 g, 0.00022 mol) in glacial acetic acid (0.5 ml) was added a mixture of nitric acid (concentrated, *d* ~1.42, 0.1 ml) in glacial acetic acid (0.3 ml). The mixture became clear in 0.25 hr. After 0.5 hr a white solid precipitated from solution. Stirring was continued for another 0.5 hr. After excess ice–water had been added, the precipitate was collected, washed free of acid, dried, and crystallized from ethanol to give 1,2-dibenzoyl-1-(9'-methoxy-9'-fluorenyl)ethylene (**10**, 0.079 g, 85%), yellow crystals, mp 159–160°.

Anal. Calcd for $C_{30}H_{22}O_3$: C, 83.72; H, 5.11. Found: C, 83.71; H, 4.97.

Oxidation of 2,5-Diphenyl-3-(9'-methoxy-9'-fluorenyl)furan (9) with Potassium Permanganate.—A solution of **9** (0.2 g, ~0.0005 mol) and potassium permanganate (0.40 g, ~0.0025 mol) in acetone–water–acetic acid (26–3–0.5 ml) was stirred at room temperature for 2 hr. Sodium bisulfite was added and the mixture was made strongly acidic with dilute hydrochloric acid. After most of the acetone had been removed under reduced pressure, the residue was extracted with excess ether, washed with saturated sodium bicarbonate, dried ($MgSO_4$), and evaporated. The residual oil (~0.2 g) on trituration with ether gave **10** (0.1 g, 48% yield), mp 160–161°.

Ozonolysis of 2,5-Diphenyl-3-(9'-methoxy-9'-fluorenyl)furan (9).—A solution of **9** (0.40 g, ~0.001 mol) in methylene chloride was ozonized at 40° for 20 min. The ozonide was reduced with zinc dust and a trace of hydroquinone. The crude product on trituration with ether gave **10** (0.064 g, 15.2% yield), mp 159–161°.

2,5-Diphenyl-3-(9'-hydroxy-9'-fluorenyl)furan (13).—To stirred magnesium turnings (0.15 g, ~0.006 g-atom) and dry ether (20 ml) was added dropwise a solution of 3-bromo-2,5-diphenylfuran (1.5 g, ~0.005 mol) in dry ether (20 ml). A crystal of iodine was added and the stirred suspension was held at 38° for 22 hr. A solution of fluorenone (**11**, 0.9 g, 0.005 mol) in dry ether (20 ml) was then added dropwise and the mixture was heated for another hour. The reaction solution was poured onto crushed ice–dilute sulfuric acid and then extracted with ether. The ethereal extract was washed with water and with saturated sodium bicarbonate, dried ($MgSO_4$), and evaporated. The residue was chromatographed on silica gel. Elution with benzene-hexane gave nearly pure **13** (0.34 g, 17% yield) as a pale yellow solid which was crystallized from hot benzene, mp 163–164°.

Anal. Calcd for $C_{29}H_{20}O_2$: C, 86.97; H, 5.0. Found: C, 87.06; H, 5.1.

Synthesis of 2,5-Diphenyl-3-(9'-methoxy-9'-fluorenyl)furan (9).—A solution of 2,5-diphenyl-3-(9'-hydroxy-9'-fluorenyl)furan (**13**, 0.075 g, ~0.0002 mol) in methanolic hydrochloric acid (7–8 ml) was stored overnight. The filtrate was poured into cold water (100 ml) and the yellow solid was filtered to yield additional **9**, mp 116–117°. The crude products were combined and crystallized from methanol to give pure **9** (0.068 g, 88%), mp 122–123°. This material was identical (analysis, tlc, mixture melting point, ir, and nmr) with **9** as obtained from **1** and methanolic potassium hydroxide.

Reduction of *trans*-2,3-Dibenzoylspiro(cyclopropane-1,9'-fluorene) (1) with Zinc–Acetic Acid–Hydrochloric Acid.—A stirred suspension of **1** (0.25 g, 0.0006 mol) and zinc dust (0.25 g, ~0.0035 g-atom) in acetic acid (3 ml) was kept at 75–80° for 0.5 hr. Concentrated hydrochloric acid (3 ml) was added in one lot and heating was continued for an additional hour. The yellow mixture was decanted and diluted with saturated sodium chloride solution (15 ml). The resulting mixture and the zinc residue were extracted with ether. The ether extracts were washed with aqueous sodium carbonate and with saturated sodium chloride, dried ($MgSO_4$), and evaporated. The crude product on crystallization from benzene gave 1,2-dibenzoyl-1-(9'-fluorenyl)ethane (**14**, 0.99 g, 39.4% yield), mp 212–213°.

Anal. Calcd for $C_{29}H_{22}O_2$: C, 86.56; H, 5.47. Found: C, 86.64; H, 5.50.

Reduction of 2,5-Diphenyl-3-(9'-methoxy-9'-fluorenyl)furan (9) with Zinc–Acetic Acid–Hydrochloric Acid.—Under conditions described for **1**, **9** (0.26 g, ~0.0006 mol) was reduced to give 2,5-diphenyl-3-(9'-fluorenyl)furan (**15**, 0.048 g, 20% yield), white crystals, mp 158–159°.

Anal. Calcd for $C_{29}H_{20}O$: C, 90.62; H, 5.21. Found: C, 90.82; H, 5.55.

Reaction of *trans*-2,3-Dibenzoylspiro(cyclopropane-1,9'-fluorene) (1) with Methanolic Potassium Hydroxide Followed by Hydrogen Chloride at 0°. Isolation of 1,2-Dibenzoyl(1-fluorenylidene)ethane (6).—To a suspension of **1** (1.0 g, 0.0025 mol) in absolute methanol (25 ml) was added 30% methanolic potassium hydroxide (5 ml) and the mixture was refluxed for 0.5 hr. The blood-red solution was filtered, cooled in ice, and treated with dry hydrogen chloride until precipitation of yellow **6** was complete. The reaction mixture was filtered, washed free of acid and salt, and dried, and the resulting crude product (0.4 g, mp 195–196°) was crystallized from benzene to give pure **6**, mp 198° (0.382 g, 38.2% yield).

Anal. Calcd for $C_{29}H_{20}O_2$: C, 86.97; H, 5.04. Found: C, 86.84; H, 5.29.

Reduction of 1,2-Dibenzoyl(1-fluorenylidene)ethane (6) with Zinc–Acetic Acid. Isolation of 1,2-Dibenzoyl-1-(9'-fluorenyl)ethane (14).—Under conditions described for **1**, **6** (0.125 g, 0.0003 mol) was reduced to **14** (0.025 g, 20% yield), mp 213–214°. This product was identical (mixture melting points, tlc, ir) with that obtained from **1**.

Transformation of 1,2-Dibenzoyl(1-fluorenylidene)ethane (6) to 2,5-Diphenyl-3-(9'-methoxy-9'-fluorenyl)furan (9).—A suspension of **6** (0.075 g, 0.00018 mol) in absolute methanol (8 ml) was refluxed for 0.25 hr. The hot suspension was saturated with dry hydrogen chloride. The mixture became clear in 2 min. After 0.1 hr excess methanol was removed under reduced pressure and the residue was cooled. The yellow crystals were collected and crystallized from hot methanol to give pure **9**, mp 122–123° (0.030 g, 30.8% yield).

The compound was identical (tlc, mixture melting point, ir) with that prepared from **1**.

Registry No.—**1**, 31684-96-5; **6**, 31684-97-6; **9**, 31684-98-7; **10**, 31684-99-8; **13**, 31685-00-4; **14**, 31685-01-5; **15**, 31685-02-6; zinc, 7440-66-6; nitric acid, 7697-37-2; acetic acid, 64-19-7; hydrochloric acid, 7647-01-0; potassium permanganate, 7722-64-7.

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Solvent Steric Effects. V. Azobis-2-methyl-3-phenyl-2-butane. The Absolute Configuration of Some Derivatives of 2-Methyl-3-phenylbutane[1]

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A stereoselective memory effect has been reported for the coupling of 3-methyl-2-phenyl-2-butyl radical

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