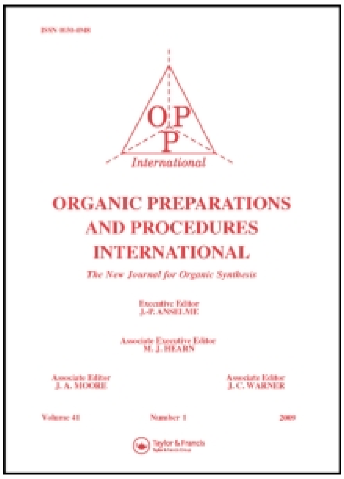

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NEW ROUTES TO 4,5-DISUBSTITUTED FLUORENES

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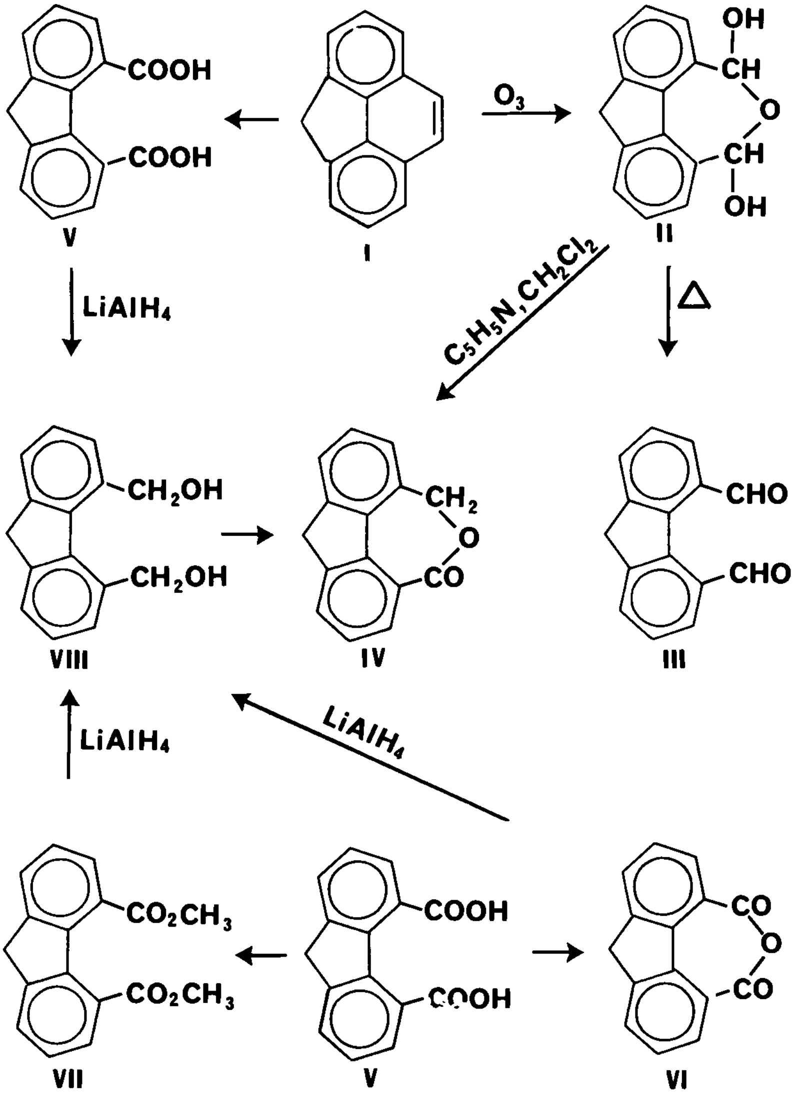
Several routes to 4,5-disubstituted fluorenes are known.[1] These are "tailor made" methods *via* selective substitution of the fluorene skeleton or of a biphenyl system which can in turn undergo a ring closure to the substituted fluorene system. We wish to report new routes for the preparation of 4,5-disubstituted fluorenes based upon the oxidative cleavage of the 9,10 double bond of cyclopenta[def]phenanthrene.

Ozonolysis of cyclopenta[def]phenanthrene (I) in dry dichloromethane at -70°C, followed by reduction with sodium iodide and acetic acid gave fluorene 4,5-dicarboxaldehyde hydrate (II) in 33% yield. The IR spectrum shows an absorption at 3250 cm^{-1}(OH) and no absorptions in the carbonyl region. Upon warming for 15 min. of II in d_7-dimethylformamide at 140°, a new ^1H NMR was observed and it is assigned to fluorene-4,5-dicarboxaldehyde (III). Treatment of II with pyridine in dichloromethane gave the lactone IV, thus supporting the presence of the formyl functions in II and II (vide infra).

It is interesting to note that ozonolysis of phenanthrene under similar conditions, yields the dialdehyde,[2] while ozonolysis of acenaphthene yields the hydrated form of the dialdehyde.[3] We presume that the methylene bridge of the biphenyl system in II forces the two formyl groups into proximity, thus preferring the formation of a stable seven membered hemi-acetal ring as has been observed in the ozonolysis of pyrene,[4] and acenaphthene.[3]

An alternative explanation suggested by a referee is that the methylene bridge deforms the molecule by bending the phenyl rings thus enlarging the distance between the two substituents in the 4,5 positions and providing more room for these substituents.



Oxidation[5] of I in acetic acid with hydrogen peroxide gave 4,5-fluorene dicarboxylic acid (V). The IR spectrum shows absorptions at 3100 cm^{-1} (OH) and 1700 cm^{-1} (CO) stretching. Treatment of V with acetic anhydride gave the anhydride VI, M.P. 270°, while treatment with diazomethane afforded the diester VII.[6] Reduction of V, VI or VII with lithium aluminum hydride afforded fluorene-4,5-dimethyl alcohol (VIII), m.p.117°. Upon oxidation of VIII with CrO_3 pyridine complex[7] the lactone IV was formed probably via an intramolecular Canizzaro reaction of the intermediate fluorene-4,5-dicarboxaldehyde II. Formation of the lactone IV, m.p. 218° demonstrates the stability of the seven membered ring product.

These results thus provide an easy access to II and V which may serve as useful synthons for a variety of 4,5-disubstituted fluorenes.

EXPERIMENTAL

4,5-Fluorene dicarboxaldehyde hydrate (II).- Into a solution of cyclopenta[def]phenanthrene (5 g, 26 mmole) in dry dichloromethane (400 ml) cooled to -70° with stirring, ozone (Welsbach generator) was bubbled for 3.5 hrs. The resulting solution was flushed with nitrogen (10 min.) followed by the portion-wise addition of sodium iodide (9 g) and acetic acid (250 ml) with stirring. The flask was removed from the cooling bath and left until the temperature became ambient. The resulting brown solution was stirred at room temperature for additional 12 hrs. The mixture was poured on 400 ml of 10% sodium thiosulfate extracted with dichloromethane, and the organic extract washed with 500 ml of 10% sodium thiosulfate, 5% sodium hydrogen carbonate (3 x 100 ml) and 2 x 100 ml of water, dried ($MgSO_4$) and evaporated. The residue was recrystallized from ethyl acetate (80 ml) to afford 2.1 g of II (33%), mp. 141°.

MS. m/e = 222 ($M-H_2O$), 194, 166 (100%), 165.

IR (Nujol): ν_{max} = 3250 (broad), 1380, 1320, 1050, 750 cm^{-1}.

^{1}H NMR ($(CD_3)_2NCDO$): δ = 10.1(s, 2H), 7.1-7.3(m, 6H), 3.87 ppm (s, 2H).

Anal. Calcd for $C_{15}H_{12}O_3$: C, 74.99;H, 5.04; Found: C, 75.25;H, 4.98.

4,5-Fluorene dicarboxylic acid (V).- To a stirred solution of 1.5 g (7.9 mmoles) of I in glacial acetic acid (150 ml) warmed to 85°C a solution of 30% hydrogen peroxide 17 ml (0.56 M) during 1 hr was added dropwise. The solution was heated further for 4 hrs. The solution turned orange and after 2.5 hrs. a white precipitate was observed. The reaction mixture was cooled and the precipitate (800 mg) was filtered. The mother solution was concentrated to 1/3 of its original volume and further 650 mg were obtained. The total amount of V is 1.45 gr (72%): mp. 268°C. Heating of the acid (V), 1 gr in 20 ml of acetic anhydride during 30 min afforded the anhydride VI in quantiative yield, mp. 270°.

M.S. m/e = 254 (M), 236, 210, 166 (100%), 165.

IR (Nujol) ν_{max} = 3100 (broad), 1700, 1430, 1240, 1180, 1155, 890, 750 cm^{-1}.

Anal. Calcd for $C_{15}H_{10}O_4$: C, 70.86;H, 3.96; Found: C, 70.42; H,4.03.

4,5-Fluorene dimethylcarboxylate (VII).- Diazomethane: prepared from 23 g (67 mmoles) of EXR 101 (Aldrich) in 60 ml of sodium hydroxide solution (30%), and 100 ml of ethyl ether. The diazomethane was distilled with the ether into a flask which was cooled to 0°. In another flask equipped with a magnetic stirrer and a dropping funnel were introduced 4 g (16 mmoles) of V with 100 ml of dry ether. The etheral solution of the diazomethane was added during 1 hr. with stirring and left overnight. The excess of diazomethane was decomposed by acetic acid and the etheral solution was washed with 100 ml of water, dried ($MgSO_4$) and evaporated. The residue was recrystallized from ethanol affording 4.3 g (95%), mp. 134°.

IR (Nujol) ν_{max} = 1720, 1600, 1380, 1320, 1200, 1130, 1090, 990, 920, 820, 750 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.1-7.3(m, 6H), 3.8(s, 2H), 3.5 ppm (s, 6H).

Anal. Calcd for $C_{17}H_{14}O_4$: C, 72.34;H, 4.94; Found: C, 72.30;H, 5.00.

4,5-Fluorene dihydroxymethyl (VIII).- Into a three-necked flask equipped with a magnetic stirrer, dropping funnel were introduced 200 ml of dry ether and 3.2 g of $LiAlH_4$. The diester VII (4 g, 14 mmoles) in 80 ml of dry ether was added dropwise with stirring. The rate of addition was such that the ether boiled gently. Then the solution was boiled for another 2 hr., cooled and the excess of $LiAlH_4$ was decomposed with ethyl acetate. The solution was acidified with 80 ml of H_2SO_4 10%, washed with 100 ml of water, 100 ml of sodium bicarbonate (sat. solution), and dried ($MgSO_4$). The etheral solution was evaporated and the residue was crystallized from benzene to yield 2.4 gr of VIII (76%) mp. 117°. Reduction of V (1.25 g, 5 mmoles) in 200 ml of THF was added and worked up under the same conditions afforded VIII (45%).

IR (Nujol): $_{max}$ = 3350 (broad), 1380, 1320, 1050, 750 cm^{-1}.

Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.65;H, 6.19; Found: C, 79.20;H, 6.00.

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