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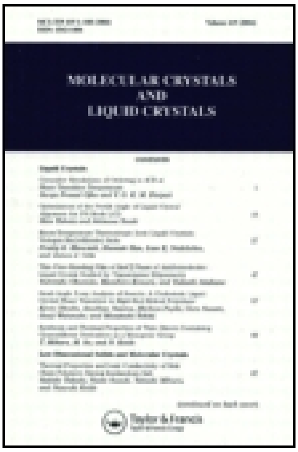

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Friedel-Crafts Reaction of Toluene with Oxalyl Chloride

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FRIEDEL-CRAFTS REACTION OF TOLUENE WITH OXALYL CHLORIDE

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Abstract By the Friedel-Crafts reaction of toluene with oxalyl chloride, three kinds of fluorene derivatives (**c**, **d**, **e**), naphthalene derivative **f**, fluorenone derivative **g**, were obtained in addition to 4,4'-dimethyl benzophenone **b**.. In the compounds (**c**, **d**, **e**, **f**, **g**), **c** shows thermochromism above 135°C in solution, while **e** emits phosphorescence and **f** exhibits fluorescence at room temperature in the solid states.

INTRODUCTION

During preparation of 4,4'-dimethyl benzil **a**, by Friedel-Crafts reaction of toluene with oxalyl chloride, we have found that the benzil derivative **a** further reacts with toluene to give fluorene derivatives catalyzed by anhydrous aluminum chloride. H.A.Fahim reported that the Friedel-Crafts reaction of toluene (1.3 mol) with oxalyl chloride (1 mol) in CS2 affords 4,4'-dimethyl benzophenone **a** in 55% yield and 4-toluic acid in 33% yield.[1] On the other hand, we obtained 4,4'-dimethylbenzil **a**, 4,4'-dimethylbenzophenone **b**, and other three compounds **c**, **d**, and **f**. This report describes preparation, structure and properties of the products.

PREPARATION

The experiment was carried out as follows. Oxalyl chloride (0.05 mol) was dropped to a mixture of toluene (0.5 mol) and anhydrous aluminum chloride (0.35 mol) below 10°C, with stirring. After dropping, the reaction mixture was maintained at 40°C for 1 hr with stirring, then decomposed with ice-water. Products were extracted with chloroform then purified. Structures of the products **a**,**b**,**e**, and **g** were confirmed by direct comparison with an authentic sample or by data writen in litrature. Structure of compounds **c**, **d**, and **f** were determined by Elemental analyses, Mass, IR, PMR, CMR, and UV-VSL spectral

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measurements, while **c** was determined by X-ray analysis. Structure of **f** was also confirmed by X-ray analysis. These data are shown as below.

Compound **c**

Elemental Analysis:
Formula $C_{46}H_{38}O_2$, Calcd(%), C, 88.70; H, 6.16 ; Found(%) : C, 88.41, H , 6.47
Mass : M^+ 311
IR $\nu_{c=o}$, 1690(s-m), 1656(s) cm^{-1}
PMR ($CDCl_3$), ppm, 220 MHz,
δ 7.95(d,1H), 7.36(s,1H), 7.29(s,1H), 7.07(s,1H), 7.01(d,1H), 6.90, 6.76(A_2B_2,4H), 6.36(d,1H), 5.28(d,1H), 2.41(s,3H), 2.18(s,3H), 2.15(s,3H).
UV-VRL (in $CHCl_3$) , nm.
λ_{max} 248(ε=59 100), 262(sh), 302(sh), 314(11 800)
Crystal data
$C_{46}H_{38}O_2$, M, 622.81, orthorhombic, Pca 2_1, a=12.016Å, b=15.915Å, c=17.965Å, V=3435.5Å^3, Z=4, R=0.075 with 2174 reflections, room temperature

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Compund **d**

Elemental Analysis:
Formula $C_{23}H_{20}O_2$, Calcd(%): C, 84.15 H, 6.10 ; Found(%) : C , 84.26, H , 6.12
Mass : M^+ 328
IR ν_{OH}, 3416(m), $\nu_{C=O}$1659(s) cm^{-1}
PMR ($CDCl_3$), ppm, 60 MHz,
δ 7.52(s,2H), 7.34, 6.85(A_2B_2,4H), 7.08(m,4H), 7.07(s,1H), 5.62(br,1H), 2.42(s,6H), 2.20(s,3H).
UV-VRL (in EtOH) , nm.
λ_{max} 214(ε=63 000), 226(sh), 234(56 000), 242(53 000), 302(sh), 315(9800)

Compound **f**

Elemental Analysis:
Formula $C_{30}H_{24}$, Calcd(%), C, 93.70; H, 6.30; Found(%) : C ,93.60, H , 6.42
Mass : M^+ 384
IR $\nu_{c=o}$, 1690(s-m), 1656(s) cm^{-1}
PMR ($CDCl_3$), ppm, 220 MHz,
δ 8.56(d,4H), 8.47(s,4H), 7.43(d,4H), 2.64(s,12H).
UV-VRL (EtOH) , nm.
λ_{max} 250(sh), 270(sh), 277(ε=29 600), 291(32 300), 303(43 200), 343(9 800), 356(9700), 389(1 600)

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Crystal data of **f**

$C_{30}H_{24}$, M, 384.3, Monoclinic, C2/c, a=30.149(4), Å, b=3.997(2)Å, c=19.878(4)Å, β=122.76298)°, V=2014.5(13)$Å^3$, Z=4, D_x=1.267gcm^{-3}, λ=1.54184Å, μ=5.04 cm^{-1}
R=0.059 with 752 reflections, room temperature

TABLE I shows structure, Mp., and yields of the products. and FIGURE 1 shows stereoscopic view of **c**.

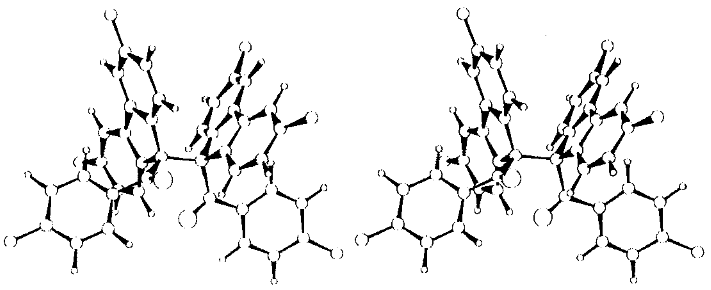

FIGURE 1 Stereoscopic view of **c**

T.Ohwada and K.Shudo reported that diphenylmethanol bearing a carbonyl group such as benzoyl gives fluorene derivative and phenylphenanthrol in the presence of a strong acid like trifluoromethanesulfonic acid.[2] In our reaction, excess amount of toluene and aluminum chloride was used to the quantity of oxalyl chloride. Therefore, it can be considered that initially produced benzil derivative **a** further react with toluene to give **d**-**f** catalyzd by aluminum chloride. Hydrogen chloride resulted in degradation of aluminum chloide in this reaction contributes to form the compounds **d**-**f**. Compound **c** may be formed by oxidation of **e**. Compound **g** also may be formed by oxidation of **d**. Isolation of **d** and **e** suggest us formation of bifluorenyliden **h** but the compound could not be detected.

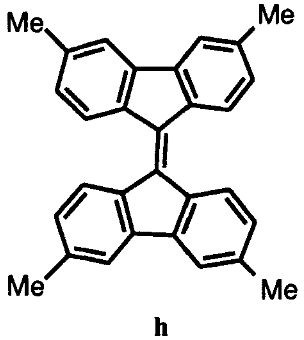

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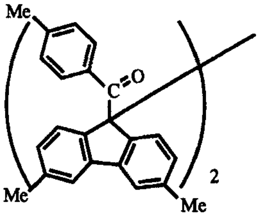
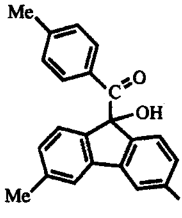
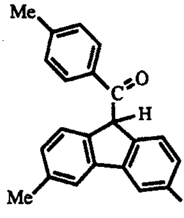
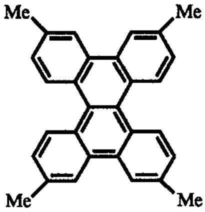
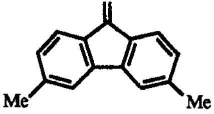
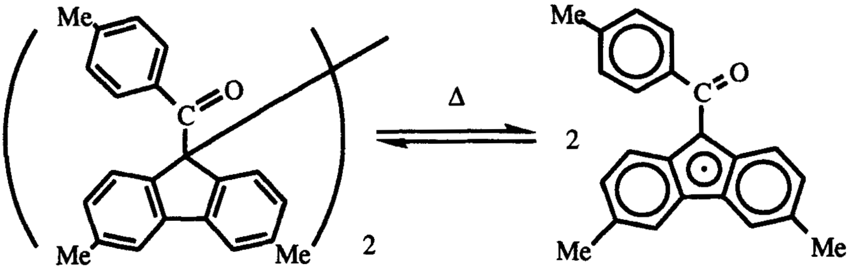
TABLE I Reaction products of Toluene with Oxalyl Chloride, (data in lit.)

		Mp.(°C)		Yield at 40°C (%)	
				1 hr	24 hr
a	4,4'-dimethyl benzil	102-104 (105°C)	light yellow plates	57	--
b	4,4'-dimethyl benzophenone	95 (95°C)	colorless needles	1.6	7.5
c	 9,9'-(4-methylbenzoyl)-9,9'-bis(3,6-dimethylfluorenyl)	241-242	colorless prisms	0.4	8.2
d	 3,6-dimethyl,9-hydroxy,9-(4-methylbenzoyl)fluorene	158-160	colorless prisms	0.8	0.9
e	 3,6-dimethyl,9-(4-methylbenzoyl)fluorene	163-164 (163°C[2])	colorless needles	--	31
f	 tetra(3,3',3'',3'''-tetramethylbenzo)-1,2,3,4,5,6,7,8-naphthalene	239-240	light yellow needles	0.3	0.7
g	 3,6-dimethyl-9-fluorene	118 (118°C[3])	yellow prisms	--	trace

To obtain a better yield of fluorene derivatives we tried elongation of the reaction time up to 24 hr at 40°C. The reaction gave higher yields of products **b** and **c** but lower yield of **f**. Besides these, other two compounds **e** and **g** were resulted. When the benzil derivative **a** was reacted with toluene at 40°C for 24 hr in the presence of aluminum chloride, the reaction gave compounds **c** and **e** as main products and **d**, **f**, and **g** were obtained as minor products. Thus compounds **c-f** were found to be formed by reaction of **a** with toluene catalyzed by aluminum chloride. On elevation of reaction temperature up to 100°C, the reaction gave higher yields of products **c-g**, but on 24°C, the reaction gave higher yields of **f** and lower yield of **c**.

PROPERTIES OF PRODUCTS c-f

c showed thermochromic property.above 135°C in naphthalene. That is, above 135°C, colorless solutionof **c** turned to reddish purple and the color deepened with further heating until bioling. On cooling, the color reverted to original one reversibly. **e** showed esr signal (g=2.0031) above 135°C in naphthalene and the signal intensity increased with elevation of temperature and weakened with decrease of the temperature. Thus the thermochromism of **e** is due to radical dissociation of the dimer on heating as shown in SCHEME 1.



SCHEME 1

e emits phosphorescence at room temperature in the solid states, E_X:344, E_M,max :431(weak), 555, 602, 689 nm, and life timewas 785 msec, while crystal **f** exhibits fluorescence at room temperature, E_X : 392, E_M, max: 422,453(sh) nm. Intensity of the fluorescence in the solid state is stronger (1.4 times) than that of anthracene.

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