

NOVEL FRIEDEL - CRAFTS REACTIONS OF SOME ARENES

SHASHI B. MAHATO^{a*}, NIRUP B. MANDAL^b, ANIL K. PAL^b and SWAPAN K. MAITRA^b

^aIndian Institute of Chemical Biology,
Jadavpur, Calcutta - 700032, India

^bPublic Health & Drugs Laboratory,
Calcutta - 700015, India

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Abstract - The novel secondary Friedel-Crafts acylation products of the arenes, dimethyl resorcinol, *m*-xylene, *m*-methylanisole and *m*-chlorotoluene using dichloroacetylchloride and anhydrous AlCl₃ are described. The formation of the unexpected products has been shown to depend on the nucleophilicity of the arene and the electrophilicity of the acyl carbonyl of the initially formed acylated product. Higher molar proportion of the arene and sometimes elevated temperature are necessary for generation of the products. The reaction pathway has been shown to be influenced by the formation of the possible complex of AlCl₃ and dichloroacetylchloride with the groups adjacent to the dichloroacetyl function, especially at higher temperature. Dimethylresorcinol yields the unique products 4, 5, 6, 7 and 9 and *m*-xylene, *m*-methylanisole and *m*-chlorotoluene furnish 10, 13 and 15 respectively. Electronic factors responsible for generation of the products and rationalisation of their formation are discussed.

Friedel-Crafts reaction encompasses the preparation of diverse types of compounds by alkylation, acylation, cycliacylation and other miscellaneous types of reactions under catalytic effect of Lewis acids-type acidic halides or proton acids^{1,2}. In Friedel-Crafts acylation reaction the effect of the use of excess of acylating reagent on naphthalene derivatives has been studied by Gore *et al*³⁻⁵. In a recent communication⁶ we reported for the first time in the long history of Friedel-Crafts acylation of arenes that when excess amounts of substrates like anisole and phenetole are used interesting polynuclear compounds are formed as secondary reaction products. Subsequently Roberts and his co-workers⁷ also met with somewhat similar novelties with mesitylene. The initial encouraging results prompted us to test the generality of this synthetic method. Our choice of next targets was guided by the assumption that formation of the unexpected products depends on the nucleophilicity of the substrate and electrophilicity of the acylcarbonyl group of the initially formed acylated product. In the present study dimethylresorcinol, *m*-methylanisole, *m*-xylene, *m*-chlorotoluene and *m*-dichlorobenzene which possess varying degrees of nucleophilicity were used as substrates. It was, indeed, observed that greater is the nucleophilicity of the substrate larger is the probability of generation of novel polybenzenoid compounds. Application of elevated temperature was found to be obligatory to induce dichloroacylation and subsequent secondary reactions for substrates with lower nucleophilicity. Among the substrates used, dimethylresorcinol with the greatest degree of nucleophilicity, yielded products of considerable interest. The other substrates have also yielded interesting products except *m*-dichlorobenzene which furnished only the normal dichloroacylated product. This paper reports the various conditions for the generation of the novel polyaryl compounds and rationalisation of the formation of these secondary reaction products.

RESULTS AND DISCUSSION

The reaction was carried out with 1-2 mole of anhydrous AlCl₃, one mole of dichloroacetylchloride and varying amounts of the substrates. The temperature of the reaction was 0-10°C for dimethyl resorcinol

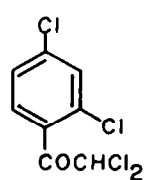
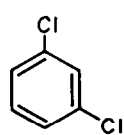
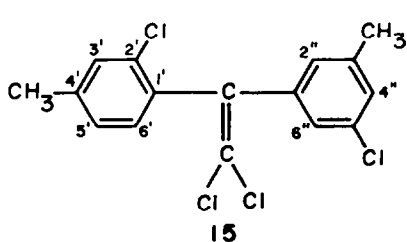
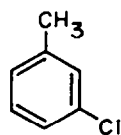
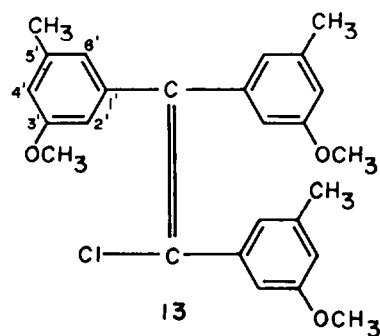
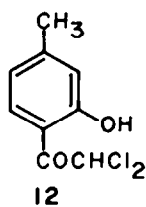
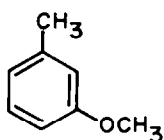
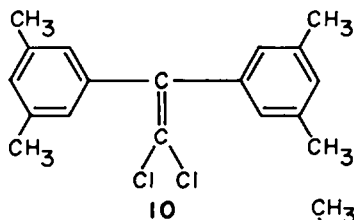
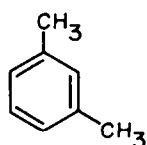
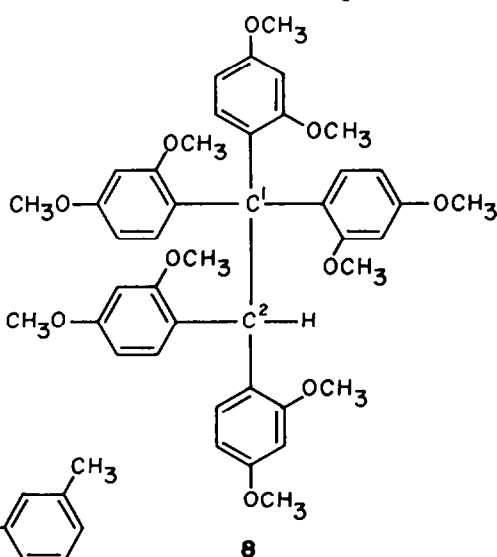
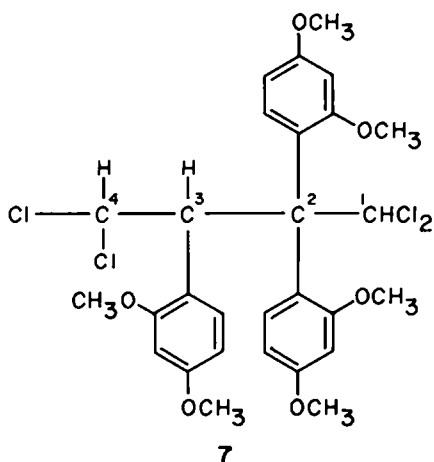
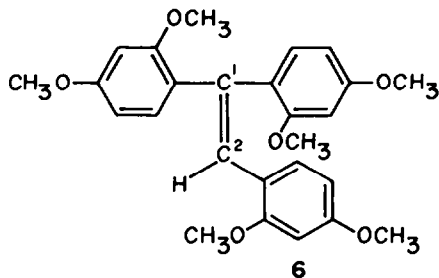
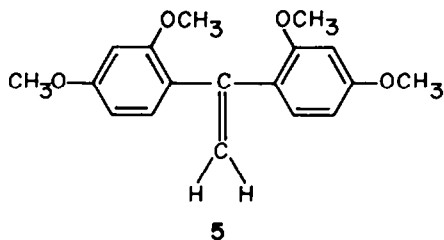
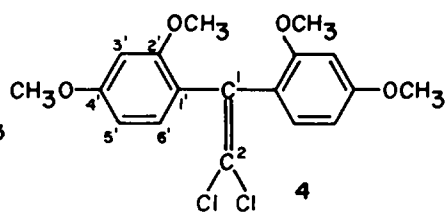
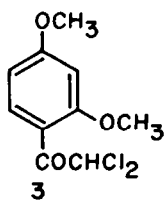
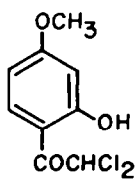
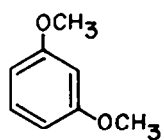
Table. Arenes and their Friedel-Crafts reaction products

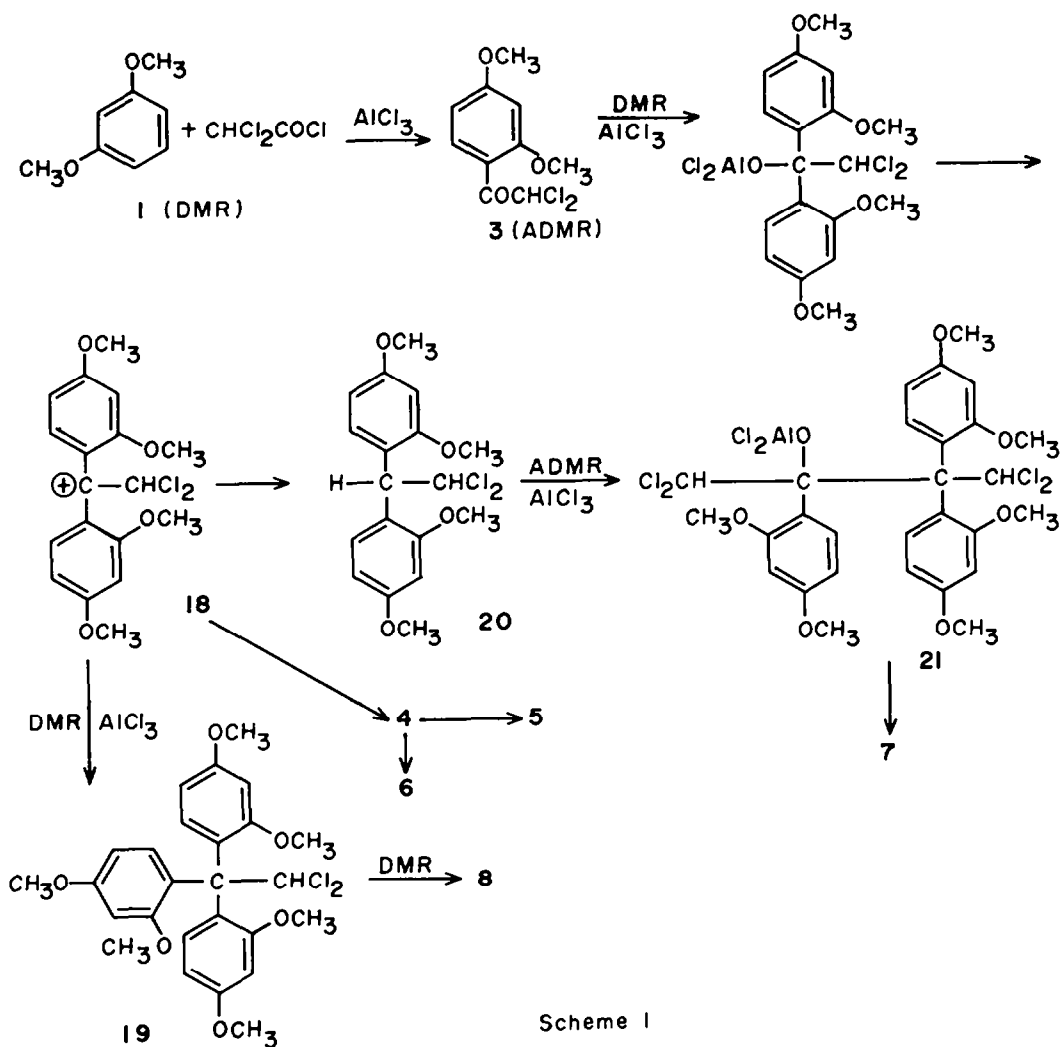
Arenes	Molar proportion (temp °C)	Products	Yield %	
Dimethyl resorcinol (1)	1 (0 - 10)	2-Hydroxy-4-methoxy- ω,ω -dichloroacetophenone (2), 2,4-Dimethoxy- ω,ω -dichloroacetophenone (3).	9 46	
	2 (0 - 10)	2,2-Dichloro-1, 1-bis (2',4'-dimethoxyphenyl) ethylene (4), 1,1,4,4-Tetrachloro-2,2,3-tris (2',4'-dimethoxyphenyl) butane (7).	5 42.5 10	
	3 (0 - 10)	2, 4, 7.	3 36.5 24	
	4 (0 - 10)	4, 7, 1,1-Bis (2',4'-dimethoxyphenyl) ethylene (5), 1,1,2-Tris (2',4'-dimethoxyphenyl) ethylene (6), 1,1,1,2,2-Pentakis (2',4'-dimethoxyphenyl) ethane (8).	22 26.5 14.7 12.4 10.5	
	5 or 6 (0 - 10)	4, 6, 7, 5, 8.	12 17 20 14 11	
	2 (70 - 80)	Complex mixture, the product 2 could be isolated.	6	
	2 or higher (120)	2,2-Dichloro-1, 1-bis(3',5'-dimethylphenyl) ethylene (10).	26	
	1 or higher (below 30)	<i>o</i> -Substituted dimeric product <i>o</i> -Acyated <i>m</i> -xylene.	Trace 12	
	<i>m</i> -Methyl anisole (11)	1 (80)	2-Hydroxy-4-methyl- ω,ω -dichloroacetophenone (12).	30
		2 or higher (80)	2-Chloro-1,1,2-tris (3'-methyl, 5'-methoxyphenyl) ethylene (13).	23.1
<i>m</i> -Chloro toluene (14)	2 or higher (110 - 115)	2,2-Dichloro-1,1(2'-chloro-4'-methylphenyl, 3''-methyl-5''-chlorophenyl)ethylene (15).	16.3	
<i>m</i> -Dichloro benzene (16)	1 or higher (30 - 80)	2,4-Dichloro- ω,ω -dichloroacetophenone (17).	39.5	

but higher for other substrates (see Experimental). No solvent was used as all the substrates employed in the study were liquids.

The structures of all the isolated products were supported by MS, ^1H NMR and elemental analysis. Infra red spectroscopy was used for screening the normal dichloroacylated products which exhibit strong carbonyl absorption.

The MS of 4 showed $\text{M}^+ + 4$ ion at m/z 372 (10% of M^+ ion peak) and $\text{M}^+ + 2$ ion at m/z 370 (65% of M^+ ion peak). The intensities of $\text{M}^+ + 4$ and $\text{M}^+ + 2$ ion peaks are characteristics of the presence of two chlorine atoms in the molecule⁸. The other fragment ion peaks and the ^1H NMR signals of 4 were compatible with its structure. The MS of 7 displayed the $\text{M}^+ + 6$ ion peak at m/z 608 (14% of M^+ ion peak), $\text{M}^+ + 4$ ion peak at 606 (64% of M^+ ion peak) and $\text{M}^+ + 2$ ion peak at 604 (131% of M^+ ion peak). The intensities of these ion peaks are consistent with the presence of four chlorine atoms⁸ in 7. The ^1H NMR spectrum of 7 showed besides other signals the characteristic peaks at δ 5.16 (d, 1H, $J=8$ Hz), 6.68 (d, 1H, $J=8$ Hz) and 7.41 (s, 1H) attributable to C3-H, C4-H and Cl-H respectively. The compound 8 exhibited besides the





Scheme 1

molecular ion peak at m/z 710, two other discernible peaks at m/z 423 and 287 assignable to the fragment ions arising out of the cleavage at C-1-C-2 bond. The ^1H NMR signals of **8** satisfactorily supported its structure.

It is evident that for dimethylresorcinol all the products obtained are *ortho/para* oriented even under strenuous conditions. However, at higher temperature demethylation of the *o*-methoxyl group takes place leading to culmination of the reaction. The failure of the *o*-oriented product **12** of **11** and an analogous product **2** of dimethylresorcinol to undergo further reactions to yield secondary reaction products may be attributed to hydrogen bonding between the *o*-hydroxyl and the acyl carbonyl rendering the latter coplanar with the aromatic ring and consequently the positive charge on the carbonyl carbon is dissipated by conjugation with the ring.

It is noteworthy that although the methyl group is mainly *ortho/para* directing, the *m*-oriented product **10** was preponderant when *m*-xylene was used as substrate at 120°C presumably because of the strenuous conditions of the reaction. The same theory may be invoked to explain the predominant formation of the *m*-oriented product **13** from *m*-methylanisole. It has been stated for Friedel-Crafts alkylation reactions that the more vigorous the conditions with respect to the activity of the catalyst or the alkylating agent (reaction time and the temperature, relative amount of catalyst, absence of solvent, etc.), the greater is the tendency toward the formation of the *meta* derivatives⁹. In the present study of dichloroacylation it

has been observed for the first time that substrate concentration as well as temperature played significant role to induce *meta* orientation. The substrate, *m*-chlorotoluene at 110–115°C, furnished the very interesting product 15 which is a combination of *o*- and *m*-substitution to chloro and methyl groups respectively. Thus under strenuous conditions the preferred orientation for substrates containing methyl group is *meta*. However the products of dimethyl resorcinol are all *o*-oriented. Even at higher temperature and substrate concentration the *o*-oriented demethylated product 2 is predominantly formed and no *m*-substituted product could be detected. This anomalous behaviour may be ascribed to the formation of the possible complex of AlCl₃ and dichloroacetylchloride with adjacent methoxy and chloro groups but not methyl especially at higher temperature which influences the reaction pathway.

The mechanism of formation of compound 4 is evidently the same as proposed for the analogous products of anisole and phenetole⁶. It is produced by the reaction of the initially formed dichloroacetyldimethylresorcinol with a second mole of dimethylresorcinol through the formation of the carbonium ion 18 (Scheme 1). The process of hydrogenolysis is assumed to be involved in the formation of 5 from 4. That compound 4 is the precursor of 5 is supported by the observation that the yield of 5 increased when 4 was added in the reaction of dimethylresorcinol, dichloroacetylchloride and anhydrous AlCl₃. The trimeric product 6 may reasonably be presumed to have been formed via alkylation of one mole of dimethylresorcinol by compound 4 *cum* hydrogenolysis.

The reasonable precursor of the tetrachloro compound 7 may be the dichloro derivative 20 whose formation from carbonium ion 18 is assumed as the analogous products of anisole and phenetole have been isolated and characterised⁶. The dichloroacetyldimethylresorcinol may undergo nucleophilic attack by the product 20 leading to the formation of the compound 7 through the intermediate 21. The mechanism of formation of 8 from the carbonium ion 8 is envisaged as shown in Scheme 1. The formation of the intermediate 19 is assumed which by alkylation of 2 mols of dimethylresorcinol generates 8.

The results obtained so far strongly suggest the high potential of the method for the preparation of novel polyaryl compounds using substrates of varied nucleophilicity at different reaction temperatures.

EXPERIMENTAL

All melting points are uncorrected. IR spectra were recorded in nujol mull on a Shimadzu IR-435 instrument. ¹H NMR spectra were recorded in CDCl₃ on JEOL FT-100 NMR spectrometer operating at 99.6 MHz. All ¹H shifts are reported relative to Me₄Si. Mass spectra were obtained on Hitachi Model RMU - 6 L and MS 50 - A.E.I. mass spectrometers at 70 eV by the direct insertion method.

Reaction of resorcinoldimethylether with dichloroacetylchloride :

General Procedure: Varying amounts (1,2,3,4,5 and 6 molar proportion) of resorcinol dimethylether (1) was condensed with a fixed (1 molar ratio) amount of dichloroacetylchloride at 0–10°C and sometimes at room temperature in the presence of 1–2 molar proportion of anhydrous AlCl₃ and the reaction mixture was left for 24 h. The product was decomposed with an ice-HCl mixture and then taken up with ether. The ether solution was washed free from acid and dried under reduced pressure, and the residue was subjected to column chromatography over silica gel followed by crystallization.

Thus 1 molar proportion of 1 gave rise to 2 and 3 while 2 molar ratio of 1 generated 2, 4 and 7; when 3 molar proportion of 1 was used, the same products 2, 4 and 7 were obtained in varying yields. Employment of 4 molar ratio of 1 furnished besides 4 and 7 three other products viz. 5, 6 and 8. On the other hand 5 or 6 molar proportion of 1 gave rise to the same products, 4, 5, 6, 7 and 8 although in different yields.

2-Hydroxy-4-methoxy-ω,ω-dichloroacetophenone (2) and 2,4-dimethoxy-ω,ω-dichloroacetophenone (3).

Proportion of reactants: Resorcinol dimethylether 13.81 g (0.1 mol), dichloro acetyl chloride, 14.73 g (0.1 mol), AlCl₃, 13.35 g (0.1 mol). The products 2 and 3 were eluted with petroleum ether and crystallized from MeOH, yield 2.1 g (9%) and 11.45 g (46%), mp 86°C and 110–112°C respectively.

2,2-Dichloro-1,1-bis(2',4'-dimethoxy phenyl) ethylene (4).

Proportion of reactants : Resorcinol dimethylether (27.6 g) (0.2 mol), dichloroacetylchloride 14.73 g (0.1 mol), anhydrous AlCl₃ 26.7 g (0.2 mol). The compound 4 was eluted with petroleum ether : benzene (85:15), crystallized from MeOH, mp 126°C, yield 15.63 g (42.5%); IR 1605, 1574, 1500, 1414, 1303, 1209, 1153, 1117, 1034, 985, 933, 834, 798 cm⁻¹, MS, *m/z*372 (M⁺ + 4, intensity 10% of M⁺ ion peak), 370 (M⁺ + 2,

intensity 65% of M^+ ion peak), 368 (M^+), 307, 295, 151, 121; 1H NMR δ 3.78 (s, 12H, 4 x OCH_3), 6.42 (d, 2H, $J=2$ Hz, 3' - H), 6.46 (dd, 2H, $J=2$, 8 Hz, 5' - H) and 7.16 (d, 2H, $J=8$ Hz, 6' - H). (Found: C, 58.49; H, 4.89. $C_{18}H_{18}Cl_2O_4$ requires: C, 58.55; H, 4.91%).

1,1-Bis (2',4' - dimethoxyphenyl) ethylene (5).

Proportion of reactants: Resorcinol dimethyl ether 55.2 g (0.4 mol), dichloro acetyl chloride 14.73 g (0.1 mol) and anhydrous $AlCl_3$ 27.6 g (0.2 mol). The product 5 was eluted with petroleum ether: benzene (65:35) and crystallized from MeOH, mp 120-121°C, yield 4.43g (14.7%); IR 1612, 1581, 1501, 1307, 1262, 1209, 1158, 1134, 1098, 1069, 1042 and 882 cm^{-1} , MS, m/z 300 (M^+), 275, 257, 241, 213, 198, 185; 1H NMR δ 3.68, 3.76 (each s, 12 H, 4 x OCH_3), 5.48 (s, 2H, 2-H), 6.36 (d, 2H, $J=8$ Hz, 3'-H), 6.48 (dd, 2H, $J=2$, 8 Hz, 5'-H), 7.53 (d, 2H, $J=8$ Hz, 6'-H). (Found: C, 71.87; H, 6.77. $C_{18}H_{20}O_4$ requires: C, 71.98; H, 6.71%).

1,1,2 - Tris (2', 4' - dimethoxyphenyl ethylene (6).

Proportion of reactants: Resorcinol dimethylether 55.2 g (0.4 mol), dichloroacetylchloride 14.73 g (0.1 mol), anhydrous $AlCl_3$ 27.6g (0.2 mol). The product 6 was eluted with petroleum ether: benzene (70:30) and crystallized from MeOH, mp 145-146°C, yield 5.44g (12.4%); IR 1608, 1584, 1500, 1417, 1348, 1307, 1260, 1206, 1171, 1128, 1038, 938, and 827 cm^{-1} , MS, m/z 421 ($M^+ - CH_3$), 406, 390, 286, 271, 255, 151, 121; 1H NMR δ 3.64, 3.72 (each s, 18H, 6 x OCH_3), 6.08 (s, 1H, 2-H), 6.28 (dd, 3H, $J=2$, 8 Hz, 5' - H), 6.40 (d, 3H, $J=2$ Hz, 3'-H), 6.60 (d, 3H, $J=8$ Hz, 6'-H). (Found: C, 70.70; H, 6.61. $C_{28}H_{28}O_6$ requires: C, 70.74; H, 6.65%).

1,1,4,4 - Tetrachloro 2,2,3 - tris (2', 4' - dimethoxyphenyl) butane (7).

Proportion of reactants: Resorcinol dimethylether 55.2g (0.4 mol), dichloroacetylchloride 14.73g (0.1 mol), $AlCl_3$ 27.6g (0.2 mol). The compound 7 was eluted with petroleum ether: benzene (75:25) and crystallized from MeOH, yield 15g (26.5%), mp 178-179°C, IR 1605, 1580, 1502, 1308, 1211, 1158, 1128, 1034, 920 and 826 cm^{-1} , MS, m/z 608 ($M^+ + 6$, intensity 14% of M^+ ion peak), 606 ($M^+ + 4$, intensity 64% of M^+ ion peak), 602 (M^+), 521, 519, 383, 381, 370, 368; 1H NMR δ 3.68, 3.69, 3.72, 3.73, 3.76 (each s, 18H, 6 x OCH_3), 5.16 (d, 1H, $J=8$ Hz, 3-H), 6.36 (d, 3H, $J=2$ Hz, 3'-H), 6.44 (dd, 3H, $J=2$, 8 Hz, 5' - H), 6.68 (d, 1H, $J=8$ Hz, 4-H), 7.16 (d, 3H, $J=8$ Hz, 6'-H) and 7.41 (s, 1H, 1-H). (Found: C, 55.59; H, 5.08. $C_{28}H_{30}Cl_4O_6$ requires: C, 55.65; H, 5.00%).

1,1,1,2-Pentakis (2', 4' - dimethoxyphenyl) ethane (8).

Proportion of reactants: Resorcinol dimethylether 55.2g (0.4 mol), dichloroacetylchloride 14.73g (0.1 mol), $AlCl_3$ 27.6g (0.2 mol). Elution of the product 8 was done with petroleum ether: benzene (50:50), and crystallized from MeOH, yield 7.45g (10.5%), mp 195-196°C, IR 1607, 1583, 1500, 1316, 1253, 1201, 1151, 1103, 1034, 940, 831 and 805 cm^{-1} , MS, m/z 710 (M^+), 423, 287, 151, 121; 1H NMR δ 3.58, 3.64, 3.73 (each s, 30H, 10 x OCH_3), 6.0 (s, 1H, 2-H), 6.18 (dd, 5H, $J=2.5$, 8 Hz, 5'-H), 6.32 (d, 5H, $J=2.5$ Hz, 3'-H) and 6.44 (d, 5H, $J=8$ Hz, 6'-H). (Found: C, 70.86; H, 6.56. $C_{42}H_{46}O_{10}$ requires: C, 70.97; H, 6.52%).

Reaction of *m*-xylene with dichloroacetylchloride:

General Procedure: Varying amounts (two or higher molar ratio) of *m*-xylene (9) was condensed with a fixed (1 molar ratio) amount of dichloroacetylchloride at 120°C for 6 h in the presence of 1-2 molar proportion of anhydrous $AlCl_3$ and the reaction mixture was kept for 44 h at room temperature (25°C) and was worked up as usual.

2,2 - Dichloro-1, 1 - bis (3', 5' - dimethylphenyl) ethylene (10).

Proportion of reactants: *m*-xylene 31.8g (0.3 mol), dichloroacetylchloride 14.73g (0.1 mol), $AlCl_3$ 27.6g (0.2 mol). The compound 10 was eluted with petroleum ether and crystallized from ethyl acetate, mp 306°C, yield 7.95g (26%), 1H NMR δ 2.40 (s, 12H, 4 x CH_3), 7.60 (s, 4H, 2' - H, 6' - H), 8.04 (s, 2H, 4' - H); MS, m/z 234 ($M^+ - 2Cl$), 220, 190, 178, 165, 139, 97. (Found: C, 70.91; H, 5.88. $C_{18}H_{14}Cl_2$ requires: C, 70.83; H, 5.94%).

Reaction of 3-methylanisole with dichloroacetylchloride:

General Procedure: Varying amounts (1 or 2 molar proportion) of 3-methylanisole (11) was condensed with a fixed (1 molar ratio) amount of dichloroacetylchloride at 80°C for 2 h in the presence of 1-2 molar proportion of anhydrous $AlCl_3$ and the reaction mixture was kept for 24 h at room temperature (25°C) and worked up as usual. Thus 1 molar ratio of 11 gave rise to 12 while 2 molar ratio of 11 gave 12 and 13.

2 - Hydroxy - 4 - methyl - ω,ω - dichloroacetophenone (12).

Proportion of reactants: 3-methylanisole 12.21g (0.1 mol), dichloroacetylchloride 14.73 g (0.1 mol) and $AlCl_3$ 13.35 g (0.1 mol). The product 12 was eluted with benzene and crystallized from CH_2Cl_2 , mp 125-126°C, yield 6.60g (30%); IR 3402 (hydroxyl), 1671 (carbonyl), 1631, 1556, 1317, 1229, 1174, 1124, 874, 845 and 803 cm^{-1} ; 1H NMR, δ 2.54 (s, 3H, CH_3), 5.64 (s, 1H, $COCHCl_2$), 6.63 (s, 1H, 3-H), 6.76 (d, 1H, $J=8$ Hz, 5' - H), 7.80 (d, 1H, $J=8$ Hz, 6' - H); MS, m/z 222 ($M^+ + 4$), 220 ($M^+ + 2$), 216 (M^+).

2 - Chloro - 1,1,2 - tris (3' - methyl - 5' - methoxyphenyl) ethylene (13).

Proportion of reactants: 3-methylanisole 24.42 g (0.2 mol), dichloroacetylchloride 14.73 g (0.1 mol), $AlCl_3$ 26.7 g (0.2 mol) and the product 13 was eluted with benzene. It crystallized from CH_2Cl_2 , mp 188-189°C,

yield 9.76g (23.1%). IR 1606, 1574, 1338, 1298, 1262, 1231, 1111, 1030, 964, 904, 858 and 826 cm^{-1} , $^1\text{H NMR}$ δ 2.58 (s, 9H, 3 x CH_3), 3.90 (s, 9H, 3 x OCH_3), 6.56 (s, 3H, 4' - H), 6.78 (s, 3H, 2' - H), 7.70 (s, 3H, 6' - H); MS, m/z 424 ($\text{M}^+ + 2$), 422 (M^+), 387 ($\text{M}^+ - \text{Cl}$), 392, 360. (Found: C, 73.80; H, 6.49. $\text{C}_{26}\text{H}_{27}\text{ClO}_3$ requires: C, 73.84; H, 6.43%).

Reaction of 3-chlorotoluene with dichloroacetylchloride :

General Procedure : Varying amounts (2 and 4 molar proportion) of 3 - chlorotoluene (14) was condensed with a fixed amount (1 molar proportion) of dichloroacetylchloride in the presence of 1-2 molar ratio of anhydrous AlCl_3 . The reaction mixture was heated slowly (60-65°C) for 4 h and then refluxed at a temperature of 110-115°C for 8 h and thereafter kept at room temperature (25°C) for 24 h. The product was decomposed and worked up as usual. Thus 2 molar ratio of 14 gave rise to 15 and the same product was also obtained when the reaction was conducted with 4 molar ratio of 14.

2,2 - Dichloro-1,1 (2' - chloro - 4' - methylphenyl, 3'' - methyl - 5'' - chlorophenyl) ethylene (15).

Proportion of reactants: 3-chlorotoluene 23.3 g (0.2 mol), dichloroacetylchloride 14.73 g (0.1 mol) and anhydrous AlCl_3 26.7 g (0.2 mol). The product 15 was eluted with petroleum ether and crystallized from hexane, mp 227-228°C. Yield 5.63 g (16.3%), IR 1615, 1584, 1321, 1196, 1167, 1033, 989, 917, 788, 765 and 739 cm^{-1} , $^1\text{H NMR}$ δ 2.45 (s, 6H, 2 x CH_3), 7.24 (d, 1H, $J=2$ Hz, 2'' - H), 7.28 (d, 1H, $J=2$ Hz, 6'' - H), 7.72 (brs, 2H, 3' - H, 4'' - H), 7.84 (d, 1H, $J=8$ Hz, 5' - H), 8.26 (d, 2H, $J=8$ Hz, 6' - H); MS, m/z 274 ($\text{M}^+ - 2 \text{Cl}$), 234, 220, 206. (Found: C, 55.47; H, 3.59. $\text{C}_{16}\text{H}_{12}\text{Cl}_2$ requires: C, 55.53; H, 3.50%).

Reaction of m - dichlorobenzene with dichloroacetylchloride :

General Procedure : Varying amounts (2, 3 or 4 molar proportion) of m- dichlorobenzene (16) was condensed with a fixed amount (1 molar ratio) of dichloroacetylchloride in the presence of 1-2 molar ratio of anhydrous AlCl_3 . The reaction mixture was heated slowly (60-65°C) for 4 h and then refluxed at 110-115°C for 8 h. Thereafter the reaction mixture was kept for 24 h at room temperature (25°C). Worked up as usual and thus 2 molar proportion of 16 gave rise to 17 and the same product was also obtained when the reaction was conducted with 3 molar and 4 molar ratio of m- dichlorobenzene (16).

2,4 - Dichloro - ω,ω - dichloroacetophenone (17).

Proportion of reactants: m - dichlorobenzene 29.4g (0.1 mol), dichloroacetylchloride 14.73 g (0.1 mol) and anhydrous AlCl_3 26.7 g (0.2 mol). The product 17 was eluted with petroleum ether and crystallized from MeOH, mp 164°C, yield 10.2 g (39.5%), IR 1697 (carbonyl), 1581, 1551, 1411, 1306, 1264, 1164, 1107, 1050, 913, 870, 844 and 789 cm^{-1} . $^1\text{H NMR}$ δ 7.28 (s, 1H, COCHCl_2), 7.30 (dd, 1H, $J=2, 8$ Hz, 5' - H), 7.52 (d, 1H, $J=2$ Hz, 3' - H), 8.0 (d, 1H, $J=8$ Hz, 6' - H).

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