

Reimer-Tiemann reaction using carbon tetrachloride

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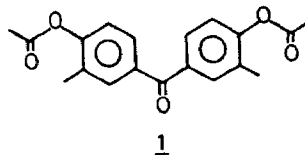
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The title reaction has been carried out on the three isomeric cresols, thymol and 3,4-dimethylphenol, and the phenolic carboxylic acids so obtained have been characterised.

The carboxylation of phenol by carbon tetrachloride under alkaline conditions, was originally reported by Reimer and Tiemann¹. The critical catalytic effect of copper metal on this reaction was reported later². The main disadvantage of this reaction is low selectivity and yield.

Komiyama and Hirai using β -cyclodextrin obtained the *para*-isomer in excellent yield^{3,4}. Later Sasoon and Razintsky found that the orientation of attack of trichloromethyl cation (generated by copper catalyst from carbon tetrachloride) on phenolate was strongly dependent on the concentration of the aqueous sodium hydroxide used, and that selective *para*-carboxylation occurred under very mild conditions and with high isolated yield⁵. Presently we have extended the Sasoon-Razintsky's approach⁵ to *o*-, *m*-, *p*-cresols, thymol and 3,4-dimethylphenol with a view to preparing the corresponding acids not reported earlier by this method (Table 1).

It is found that the carboxyl group enters the free *ortho* position when the *para* position is blocked by a substituent. Normally, in other cases, *para*-selectivity is observed. In the case of *o*-cresol, in addition to the formation of 4-hydroxy-3-methylbenzoic acid, another compound, m.p.240°, could be



obtained which was converted directly to its acetate (Ac₂O/Py), m.p.102° (CH₃CN/pet.ether). This acetate has been assigned the structure 1 on the basis of the following spectral data and mechanistic considerations; CIMS: m/z 344 (M⁺ + 18); IR(nujol): 1750, 1650 cm⁻¹; PMR (acetone-d₆): δ 2.38 (s, 6H), 2.48 (s, 6H), 7.36 (2H, d, J = 8 Hz), 7.78 (2H, dd, J = 8 & 2 Hz), and 7.87 (2H, d, J = 2 Hz). It may be pointed out in this connection that the condensation of xylenols with carbon tetrachloride in the presence of a Lewis acid as a catalyst has been reported⁶ to yield, *inter alia*, the corresponding benzophenones.

The acid obtained from *m*-cresol was found to be identical with an authentic sample of 4-hydroxy-2-methylbenzoic acid⁷. In the case of 3,4-dimethylphenol, the entry of the carboxyl group in one particular *ortho* position of the two available is probably due to the fact that it is sterically less hindered.

Experimental

General procedure for Reimer-Tiemann reaction using CCl₄

In a two necked round bottomed flask equipped with a reflux condenser and a dropping funnel, was prepared a solution of appropriate phenol (0.0648 mole) in 50% aqueous NaOH (30 ml) and copper powder (0.1 g) was added to it. The mixture was heated to 80°C while stirring and CCl₄ (10.2 g, 0.0662

Table 1 —Reimer-Tiemann reaction of various cresols, thymol and 3,4-dimethylphenol with CCl₄

Entry No.	Phenol	Acid obtained			
		Name	m.p. (°C)	lit. ⁸ m.p. (°C)	Yield (%)
1	<i>p</i> -cresol	6-Hydroxy-3-methylbenzoic acid	152		20
2	<i>m</i> -cresol	4-Hydroxy-2-methylbenzoic acid	171	153	16
3	<i>o</i> -cresol	4-Hydroxy-3-methylbenzoic acid	175	177-78	12
4	Thymol	<i>p</i> -Thymotic acid	156	174-75	6
5	3,4-Dimethylphenol	2-Hydroxy-4,5-dimethylbenzoic acid	198	157	199
					43

mole) was added dropwise during a period of one hour. The temperature of the reaction mixture was maintained at 80°, under gentle reflux for another 5 hours. Additional copper powder (0.05 g) was added after every 2 hr. The contents of the flask were cooled, filtered and the dark coloured alkaline filtrate was acidified with HCl. The crude acid was filtered, washed with water and purified chemically using activated charcoal. The purified acid was recrystallised from a suitable solvent.

In the case of *o*-cresol, the reaction mixture on work up as above gave red coloured solid which could not be dissolved completely in sat. NaHCO₃ solution. The red coloured residues (1.4 g), that remained after fixing the acid with colds NaHCO₃, could be dissolved in warm sat. NaHCO₃ solution. The red coloured filtrate, so obtained, on acidification with HCl gave a red solid (1.35 g), m.p. 240°. This was directly converted to acetate I.

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References

- 1 (a) Reimer K & Tiemann F, *Ber dt chem Ges.* 9 (1876) 1285.
(b) Wynberg H, *Chem Rev.* 60 (1960) 169.
- 2 Vollany F J & Lang J, *J Am chem Soc.* 72 (1950) 2301.
- 3 Komiyama M & Hirai H, *Makromol Chem, Rapid Commun.* 2 (1981) 661.
- 4 Komiyama M & Hirai H, *J Am chem Soc.* 106 (1984) 174.
- 5 Sasoon Y & Razintsky M, *J chem Soc, Chem Commun.* (1985) 1134.
- 6 Driver J E & Lai T F, *J chem Soc.* (1958) 3009.
- 7 Kamat V P, *Synthetic and transformation studies of terpenoids and aryl ketones.* Ph D Thesis, University of Bombay, 1984.
- 8 *Dictionary of Organic Compounds*, Vol III (Eyre & Spottiswoode, London), 1965, pp. 1675, 1707, 1815, 1816.