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SOME PHENOLIC CONSTITUENTS OF COAL SOOT

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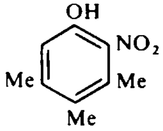
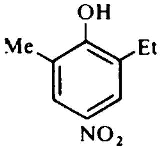
Abstract—Three nitro-phenolic compounds have been isolated from coal soot and identified.

AT THE present time pollution in general is much talked about and we wish to record some of the work done in continuation of that described in[1] and earlier papers. This account describes the isolation of four alkyl substituted nitrophenols from the soot derived from coal fires. This has been obtained from three different sources, a Yorkshire seaside town and two from residential areas in Northumberland. Soot and dust from coke fires have not so far given the compounds here described. The soot is extracted with NaOH, the sludge filtered and the deep reddish-brown filtrate gassed with CO_2 and extracted with ether-benzene to give a tar **A**.

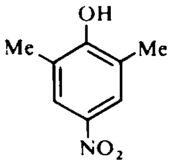
When this is heated with acetic anhydride and pyridine a part **B** is acetylated and a part **C** remains soluble in NaOH. From **B** by hydrolysis and chromatography over alumina three crystalline compounds I, II and III are obtained in that order. Mass spectroscopy, IR spectra and NMR measurements have shown them to be $C_9H_{11}O_3N$, (I), $C_9H_{11}O_3N$, (II) and $C_8H_9O_3N$, (III). The literature,[2,3,4] records the following compounds having mps agreeing with the above but none are available for direct comparison.



I



II



III

From **C** a small amount of a compound has been obtained (mp 143–144°), which mass spectroscopy shows to be $C_8H_9O_5N$ (IV), but it has not been isolated in sufficient amount for NMR measurement.

EXPERIMENTAL

Chromatography has been done with alumina (Brockman) in tubes of 10 mm i.d. and the sublimations in evacuated tubes as described in 1.

Extraction of the soot. 1 kg of dry soot was stirred with hot 1NNaOH (2½ l) and filtered. The filtrate was gassed with CO_2 and extracted three times with ether-benzene. Removal of the solvent left 2·5 g of thick brown tar **A**.

Separation by acetylation. The tar (2·5 g) was heated for 5 hr in the water bath with acetic anhydride (7 ml) and pyridine (7 ml). EtOH was added and the mixture heated in the water bath under reduced pressure to remove solvents. The residue was nearly all soluble in ether and the solution was shaken with excess IN NaOH. From the ether 0·92 g **B** of acetyl derivative was obtained and addition of HCl to the red NaOH solution gave 1·4 g **C** of ether soluble material and 0·2 g of ether insoluble. The 0·92 g in ether (3 ml) was run down a 20 cm column of Al_2O_3 and washed successively with ether 2 ml (× 15) and then with 20% EtOH-ether 2 ml (× 5). The ether eluates gave **D** (0·75 g) and eluates 19, **20** and **21** washed out a sharp brown band **E** (0·04 g). EtOH then took down only a trace of material but when H_2O was run down a deep yellow eluate was obtained of a yellow solid (0·025 g) of an aluminium complex almost all soluble in EtOH but from which no definite compound has been yet obtained.

Hydrolysis of **D** *and* **E**. These were combined and heated for 3 hr in a water bath with MeOH–MeOK. The addition of H_2O gave an alkali insoluble material (0·12 g) and the addition of HCl to the alkaline solution gave a solid (0·52 g) of which 0·02 g was insoluble in ether.

The 0·5 g in ether (3 ml) was dropped down 20 cm of Al_2O_3 and washed successively with ether 2 ml (× 25) and then with 20% EtOH-ether 2 ml (× 10). From eluates **4–9**, 0·125 g of material was obtained and eluates **10–15** gave a crystalline solid (0·035 g) whilst eluates **30–33** gave a crystalline solid (0·08 g). The 0·125 g in ether (2 ml) was dropped down a column of alumina (10 cm) and washed with 1 ml portions of ether. From eluates **11–24** a crystalline material was obtained (m.p. 80–85°) which when sublimed and recrystallised from light petroleum b.p. 40°–50° gave long colourless needles m.p. 96–98° I; ν_{max} 3410, 2920, 1665, 1565, 1495, 1310, 1280, 1213, 1175, 1088, 1019, 920, 879 and 750 cm^{-1}; NMR values τ 2·4 (phenyl), 7·55, 7·72, 7·73 (3-methyl groups) and 4·73 (probably-OH).

The 0·035 g in ether (2 ml) was dropped down alumina (10 cm) washed with ether 1 ml (× 30) and then with 20% EtOH-ether 1 ml (× 10). Eluates **20–30** gave 5 mg which did not crystallise and eluates **31–40** 20 mg of solid m.p. 120° which when sublimed and recrystallised from light petroleum (60–80°) gave colourless plates m.p. 135–136° (II); ν_{max} 3480, 2820, 1588, 1509, 1330, 1285, 1242, 1173, 1100, 1031, 995, 940, 895 and 741 cm^{-1}; NMR values (τ scale) 2·05 (phenyl), 7·7 (methyl), 7·3 and 8·7 (ethyl) and 4·75 (OH).

The 0·08 g crystallised in plates from 10% C_6H_6-light petroleum (60–80°) which when sublimed and recrystallised melted at 169–170°, III. Found: C, 57·77; H, 5·44; N, 8·15. $C_8H_9O_3N$ requires C, 57·5; H, 5·4; N, 8·4%); ν_{max} 3465, 2920, 1590, 1510, 1478, 1331, 1250, 1240, 1180, 1097, 1028, 1003, 940, 898, 742 and 729 cm^{-1}; NMR values (τ) 2·09 (phenyl), 7·69 (6 methyl protons) for 2 symmetrical methyl groups. OH group not observed.

Mass spectroscopy showed I, II and III to have M.Ws of 181, 181 and 167 resp. and fragmentation patterns indicated the presence of CH_3, NO_2 and OH groups in all three. NMR measurements indicate $3CH_3$ and probably an —OH group in a benzene ring in I, of CH_3— and C_2H_5— and probably an OH group in a benzene ring in II and of 2 symmetrically placed CH_3 groups in III but did not show the presence of an --OH group.

The IR spectra of II and III are very similar with the alkyl groups in II and III in virtually identical environments and the spectrum of III is identical with that given in the Sadtler collection.

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