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AROMATIC RING OXIDATION OF ALKYLBENZENES

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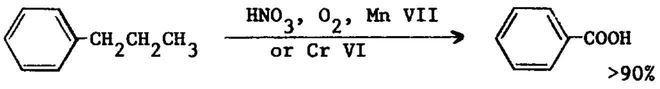
We have observed that 30% aqueous H_2O_2 in TFA (trifluoroacetic acid) causes the nmr singlet of benzene to disappear without the appearance of any new CH absorptions.[1] Since H_2O_2-TFA converts polymethylbenzenes to cyclohexadienones[2] and phenols,[2,3] the concept arose that H_2O_2-TFA might completely oxidize the benzene ring in alkylbenzenes and leave the aliphatic component untouched. This concept was encouraged by observations that small aliphatic alcohols, acids, esters, and amides are inert to H_2O_2-TFA.[4,5]

A one hr reflux with 30% H_2O_2-TFA (8-16 mols H_2O_2 per mol of alkylbenzene) effected complete oxidation of toluene, ethylbenzene, propylbenzene, and isopropylbenzene. The nmr spectra of the reaction mixtures showed that benzoic acid was absent and that only aliphatic hydrogens were present. With toluene, acetic acid was the only product (nmr). With ethylbenzene, 81% of the nmr absorption was due to propionic acid (1.04 t, 2.35 q) and 19% was due to acetic acid (2.00). The mol ratio was 72:28.

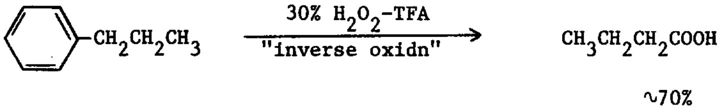
With propylbenzene, 6% of the nmr absorption was due to acetic acid, 74% due to butyric acid (0.83 t, 1.52 m, 2.28 t), 8% due to propionic acid, and 13% was unidentified background in the 1-2 δ region. Butyric acid is the major product. The propionic and acetic acid do not arise via butyric acid.[4,5]

Even isopropylbenzene gave isobutyric acid, although the 1.29 δ doublet accounted for only 32% of the total absorption. Acetic acid accounted for only 3% of the absorption. The remaining unidentified absorption is in the 1.1-3.0 region. Again, benzoic acid was absent.

The oxidations are termed "inverse oxidations" because the aliphatic component of the structure is preserved in contrast to oxidizing agents such as HNO_3, O_2, Mn VII, and Cr VI. These latter agents selectively attack the benzylic hydrogen and form benzoic acid. This contrast is exemplified in eqs 1 and 2.



(1)



(2)

Methoxybenzene (anisole) reacted at 25°. The equilibrium mixture of methanol (3.38) and methyl trifluoroacetate (3.88) accounted for 73% of the band areas. The remaining area was distributed between three narrow bands at 3.02, 3.45, and 3.74.

These above reactions can be applied to the analysis of the alkyl, alkoxy, and other aliphatic components of coal. Excess 30% H_2O_2-TFA converts >20 mesh Pittsburgh Seam or Illinois Number 6 coals[6] to a colorless solution after one hr reflux. The nmr spectrum indicates acetic acid as the only major product. In contrast, HNO_3, O_2, $KMnO_4$, and CrO_3 oxidize the methyl groups with the production of benzene polycarboxylic acids.[7,8]

A series of competition experiments were conducted. Benzene reacted much faster than cyclohexane. Chlorobenzene reacted slower than cyclohexane but did compete. Benzoic acid, nitrobenzene, benzenesulfonic acid, and maleic acid were inert relative to cyclohexane.

CAUTION. Solvent removal from excess H_2O_2-TFA runs can result in explosion. The peroxide must be destroyed with MnO_2 until a KI test is negative before solvent removal.

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References

1. Reaction is complete in several hrs at 25°. Solvent removal leaves a white solid. Presuming it to be oxalic acid dihydrate, the weight indicates a 21% yield. At lower temperatures, benzene has been reported to form low yields of phenol (A. K. Yatsimirskii and I. V. Berezin, Dokl. Akad. Nauk SSSR, **223**, 414 (1975); Chem. Abstr., **83**, 163343 (1975)).
2. H. Hart, Accounts Chem. Res., **4**, 337 (1971).
3. T. Suzuki and S. Naito, Ger. Patent 2,404,114; Chem. Abstr., **81**, 151796 (1974).
4. N. Deno and L. A. Messer, Chem. Comm., 1051 (1976).
5. N. Deno, E. J. Jedziniak, L. A. Messer, M. D. Meyer, S. G. Stroud, and E. S. Tomezsko, submitted to Tetrahedron.
6. We are indebted to Mr. Philip Dolsen of the Coal Research Section, College of Earth and Mineral Science, The Pennsylvania State University, for generously supplying these samples.
7. A. E. Bearse, J. L. Cox, and M. Hillman, "Production of Chemicals by Oxidation of Coal," Battelle Institute, Columbus, Ohio, and references therein, 1975.
8. A recent and complete study is P. D. Salbut and A. Wielpolski, Koks Smola Gaz, **4**, 351 (1969); Chem. Abstr., **73**, 37222 (1969); Rocz. Chem., **44**, 585 (1970); Chem. Abstr., **73** 122220 (1969).