500° can be used for the production of the 2,3-diacid, no 2,6-diacid being formed.

The temperature-sensitive production of potassium naphthalene-2,3-dicarboxylate was completely unexpected. Although small amounts of phthalic and isophthalic acid are sometimes found in terephthalic acid production by the Henkel process,[4] *ortho* dibasic acids are not the major products formed from potassium salts. We know of no example wherein the nature of the major product formed is temperature dependent as is found here for the disproportionation of potassium 2-naphthoate.

Experimental

Cadmium carbonate, cadmium iodide, anhydrous potassium carbonate, and anhydrous sodium carbonate were reagent grade and were obtained from Matheson Coleman and Bell. 1-Naphthoic and 2-naphthoic acids were also obtained from Matheson Coleman and Bell. The sodium and potassium naphthoates were prepared by allowing stoichiometric amounts of the naphthoic acid and alkali metal carbonate to react in water. The aqueous solutions were evaporated and the salts were dried at 180° under vacuum.

Authentic samples of naphthalene-2,3-dicarboxylic acid and naphthalene-2,6-dicarboxylic acid were prepared by aqueous sodium dichromate oxidations of 2,3- and 2,6-dimethylnaphthalene (Aldrich Chemical Co.) by published procedures.[5]

For the Henkel reactions a thermostatically controlled high-pressure glass-lined autoclave was used. The carefully dried reactants were placed in the autoclave and the air in the system was purged with carbon dioxide. At this point the autoclave was kept cooler than the cylinder of carbon dioxide and some carbon dioxide was allowed to condense in the autoclave. Then the autoclave was vented periodically, as necessary, while being heated to the desired temperature. In this manner the final pressure on the autoclave could be more or less controlled. For those experiments using mixtures of nitrogen and carbon dioxide as the gas under pressure, we can only estimate that approximately 50:50 mixtures were used.

At the end of the reaction time, the autoclave was cooled and vented. The contents were dissolved in hot water and filtered to remove naphthalene and insoluble cadmium salts. The acids were precipitated by adding hydrochloric acid. The insoluble acids were filtered, vacuum dried, and weighed. They were then extracted with ether. Both 1-naphthoic acid and 2-naphthoic acid are readily soluble in ether, whereas the 2,6-diacid is completely insoluble and the 2,3-diacid has a very low solubility. In this way the desired product acids were easily separated from the unreacted starting acids. Infrared analysis readily distinguished between the 2,3-diacid and the 2,6-diacid. In addition, the 2,6-diacid was further characterized by conversion to its dimethyl ester and this was compared with an authentic sample by mixture melting point, 185–186° (lit.[6] m.p. 186°). The 2,3-diacid was also further characterized by conversion to the dimethyl ester; this was compared to an authentic sample by mixture melting point, 46–48° (lit.[6] m.p. 47°). In addition, the 2,3-diacid was converted to the cyclic anhydride by sublimation as was readily shown by the expected change in the infrared spectrum.

Recovered water-soluble acids and ether-soluble acids proved to be largely mixtures which were not further puirfied. Since they were largely mixtures, per cent conversion data are impossible to tabulate.

---

(4) M. Kraus, K. Kochloefl, L. Beranek, V. Bazant, and F. Šorm, *Chem. Ind.* (London), 1160 (1961).

(5) (a) L. Friedman, University Microfilms, LC Card No. mic 60-1181; *Dissertation Abstr.*, **20**, 3953 (1960); (b) J. Yamashita, K. Kurashima, and S. Kato, *Yuki Gosei Kagaku Kyokai Shi*, **20**, 277 (1962); *Chem. Abstr.*, **57**, 16512 (1962); (c) L. Friedman, D. L. Fishel, and H. Shechter, Abstracts, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964, p. 25U; Preprints, Division of Petroleum Chemistry, Sept. 1964, Vol. 9, No. 4, p. D-87.

(6) E. F. Bradbrook and R. P. Linstead, *J. Chem. Soc.*, 1739 (1936).

Magnetic Shielding of Alkyl Protons in Hindered Phenols

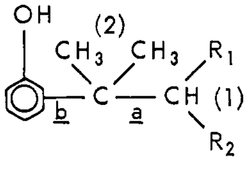
K. C. DEWHIRST AND C. A. REILLY

Shell Development Company, Emeryville, California

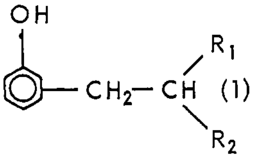
Received February 1, 1965

In a recent paper, Cook and Danyluk[1] have examined the n.m.r. spectra of a series of substituted phenylacetylenes. They found that in general electron-donating substituents increased the shielding of the acetylenic protons and electron-withdrawing groups decreased the shielding, but that *ortho* substitution decreased the shielding irrespective of the substituent group. In the present paper similar observations are reported for a series of alkylphenols.[2]

The n.m.r. data obtained for the (1) and (2) protons of alkylphenols I and II are summarized in Table I.



I



II

As may be seen, the (1) and (2) protons in series I are always less shielded in the *ortho* isomer than in the *para* isomer and the effect appears to increase with increasing alkyl substitution. The nature of an alkyl substituent has little effect on the magnitude of the shift. In series II, however, in which the *gem*-dimethyl groups have been removed, virtually no difference is observed between the shifts of proton (1) in the *ortho* and *para* isomers.

A few measurements were made on compounds Ib and Ie in hexachloroacetone at elevated temperatures. The shifts observed were small and inconclusive. More careful studies on solutions of known concentrations would be required to establish the effect of temperature.

The various conformations of compound I obtained by rotation about bond a are shown in Figure 1. Although rotation about this bond must be rapid owing to the observed single, sharp methyl resonance, the conformations a and b would be expected to become relatively more populated[3,4] as one progresses in the series $R_1 = R_2 = H$ to $R_1 = R_2 = CH_3$. In these conformations (identical when $R_1 = R_2$) the (1) proton is subject to the influence of the ring current[5] of the phenyl group and the local shielding effects of the rest of the molecule. The magnitude of such effects will be a function of the conformation. Thus, it seems probable that Δ_1 is negligible in compound II owing to extremely rapid rotation, and that the magnitude of Δ_1 in compound I

---

(1) C. D. Cook and S. S. Danyluk, *Tetrahedron*, **19**, 177 (1963).

(2) For a specific application of this phenomenon to structural elucidation, see K. C. Dewhirst and F. F. Rust, *J. Org. Chem.*, **28**, 798 (1963).

(3) W. G. Dauben and K. S. Pitzer in "Steric Effects in Organic Chemistry, M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 1.

(4) D. J. Cram, ref. 3, pp. 273, 274.

(5) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy," Pergamon Press Ltd., London, 1959, p. 125.

TABLE I

CHEMICAL SHIFTS[a,b] OF ALKYLPHENOLS

Compd.	R_1	R_2	δ_1	Δ_1	δ_2	Δ_2
Ia	H	H	1.2	0.15	1.2	0.15
Ib	H	CH_3	1.49 ± 0.01	0.26 ± 0.01	1.13 ± 0.01	0.11 ± 0.01
Ic	H	C_6H_5	3.2	0.35	1.3	...
Id	H	$C(CH_3)_3$	1.7	0.28	1.3	0.13
Ie	CH_3	CH_3	1.8	0.75	1.2	0.10
IIa	H	$C(CH_3)_2OH$	1.8	0.01	...	...
IIb	CH_3	CH_3	...	0[c]	...	...

[a] δ_i is the chemical shift in p.p.m. from internal TMS of proton (i) for the *para* isomer. [b] Δ_i is the value of δ_i (*ortho*) − δ_i (*para*). [c] The *para* isomer used here for reference was Ie.

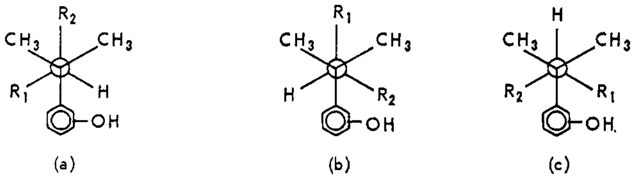


Figure 1.—Conformations of compound I about bond a.

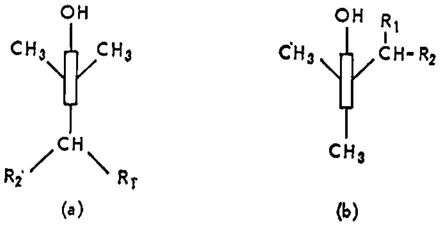
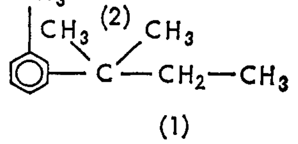


Figure 2.—Conformations of compound I about bond b.

increases with increasing steric crowding owing to increasing conformational preference.

Typical conformations of compound I obtained by rotation about bond b are shown in Figure 2. If these conformations are equally populated in the *ortho* isomer then only the local shielding effects of the hydroxyl group can be responsible for the observed shifts since the ring current is almost certainly the same for the *ortho* and *para* isomers. If the conformations are not equally populated, however, the *effect* of the ring current will be different in the two isomers due to differences in the position of the hydrogen with respect to the plane of the benzene ring.[5]

An attempt was made to determine the relative magnitude of the two effects by measuring the spectrum of compound III, for which the steric situation is similar,[4] but any electric field effect of the OH group will be absent. The *ortho–para* shift for protons (1) of III was found to be 0.18 ± 0.01 p.p.m., *i.e.*, about 70% of that found for the corresponding phenol Ib. The shift of protons (2) was 0.13 ± 0.01, nearly identical with Δ_2 of series I.



III

These observations indicate that an electric field effect of the hydroxyl group as well as ring current effects of the phenyl group (and thus preferred conformations about bond b) are involved.

Although more work is clearly required to elucidate the exact nature of the shifts, the work is presented here for those who may be interested in further investigation.

Experimental

Most of the n.m.r. spectra were recorded at room temperature with a Varian Associates high-resolution spectrometer (V-4300) at 40 Mc.p.s. The chemical shifts were measured in 50% carbon tetrachloride solution relative to tetramethylsilane as internal standard. For the temperature-dependent studies, a Varian A60 spectrometer was used.

Alkylphenols.—These compounds were prepared by the aluminum phenoxide catalyzed alkylation of phenol with the appropriate olefin according to the procedure of Dewhirst and Rust.[2] The only unreported compound is 2-(2-hydroxyphenyl)-2,4,4-trimethylpentane (*ortho*-Id), b.p. 130° (10 mm.), m.p. 40–42°.

Anal. Calcd. for $C_{14}H_{22}O$: C, 81.5; H, 10.8. Found: C, 81.4; H, 10.7.

2-(2-Tolyl)-2-methylbutane (IIIa).—The *para* isomer has already been reported.[6] The *ortho* isomer was prepared by adding 1.7 moles of *t*-amyl chloride to 1.7 moles of *o*-tolylmagnesium bromide in ether. The mixture was hydrolyzed with dilute hydrochloric acid, washed with water, and dried. The isoamylene and ether were distilled off, and the residue was refluxed with sodium in amyl alcohol to remove halogen impurities. The mixture was distilled to give 3 g. (1.1%) of product, b.p. 120–121° (50 mm.), $n^{25}D$ 1.5032.

The infrared spectrum of this material showed strong bands at 728 and 758 cm.$^{-1}$, characteristic of an *ortho* disubstituted benzene, and a doublet at 1358 and 1373 cm.$^{-1}$, characteristic of a *gem*-dimethyl group.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.8; H, 11.2; mol. wt., 162. Found: C, 88.2; H, 11.0; mol. wt., 158.

---

[6] M. J. Schlatter and R. D. Clark, *J. Am. Chem. Soc.* **75**, 361 (1953).

The *ortho–para* Ratio in Electrophilic Aromatic Substitution. Evidence for a Linear Coordination Effect in Nitration of Anisole[1]

PETER KOVACIC AND JOHN J. HILLER, JR.

*Department of Chemistry, Case Institute of Technology,
Cleveland, Ohio 44106*

Received March 23, 1965

The literature contains a goodly number of reports dealing with the cyclic or quasi-ring coordination effect[2]

---

[1] From the Ph.D. Thesis (1965) of J. J. H., presented at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964.

[2] For a review, see ref. 1.