The Synthesis of Naphthalene-2,3-dicarboxylic Acid by the Henkel Process

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A general description of the Henkel reaction can be found in articles by Raecke[1] and Sherwood.[2] Examples of the Henkel reaction are the formation of phthalate salts by the disproportionation of sodium or alkaline earth benzoates or of terephthalate salts by the disproportionation of potassium, rubidium, or cesium benzoates at high temperatures in the presence of certain catalysts. Rearrangements of dicarboxylate salts also occur and the reaction is not confined to the benzene series; other aromatic systems behave similarly. The above-mentioned products are not the sole products but are the major ones.

TABLE I

DISPROPORTIONATION OF NAPHTHOATE SALTS UNDER PRESSURE

Expt. no.	Time, hr.	Temp., °C.	CO_2 pressure, p.s.i.g.	Carboxylate salt used[a]	Weight of salt, g.	Weight of K_2CO_3, g.	Weight of $CdCO_3$, g.	Weight of 2,3-diacid, g.	Weight of 2,6-diacid, g.	% yield
1	3	400	1050	K-2	2.00	0	0	0.0513	0	5.00
2	3	400	2900	K-2	1.99	0	0	0.0662	0	6.45
3	3	400	4700	K-2	2.05	0	0	0.0997	0	9.46
4	3	400	5500	K-2	2.00	0	0	0.269	0	26.1
5	1.75	400	5800	K-2	0.995	0	0	0.108	0	21.1
6	3	400	6050	K-2	2.00	0	0	0.261	0	25.4
7	3	400	8000	K-2	1.98	0	0	0.479	0	47.1
8[b]	3	400	5600	K-2	1.01	0	0	0.0980	0	18.8
9[c]	3	400	5750	K-2	0.946	0	0	0.0896	0	18.4
10[d]	3	400	5550	K-2	1.02	0	0	0.0878	0	16.7
11[e]	3	400	3700	K-2	0.958	0.202	0.0622	0.0986	0	20.0
12	3	350	6000	K-2	0.940	0.180	0.0449	0.0142	0	2.94
13	3	450	6150	K-2	1.02	0.106	0.0613	0	0.361	69.0
14[f]	3	500	3250	K-2	1.17	0.207	0.0403	0	0	0
15[g]	6	400	. . .	K-2	2.00	2.00	0	0	0.390	37.9
16[e]	3	400	3750	Na-2	1.09	0.135	0.0834	0.241	0	39.7
17	2	350	6100	Na-1	1.01	0.448	0.0693	0	0.153	27.2
18	2	400	3500	Na-1	1.00	0.456	0.118	0	0.282	50.6
19	2	450	6200	Na-1	1.02	0.500	0.171	0	0.270	47.5
20	2	400	6000	Na-1/2	1.06/0.980	1.02	0.0569	0	0.514	45.3
						Weight of Na_2CO_3, g.				
21	6	400	5950	Na-2	0.982	0	0	0.134		24.5
22	4	400–500	6000–6500	Na-2	1.58	0.985	0.195	0.244	0	27.7
23	2	450	5900	Na-2	1.04	0.586	0.0649	0.180	0	31.3

[a] K-2 is potassium 2-naphthoate, Na-2 is sodium 2-naphthoate, Na-1 is sodium 1-naphthoate, and Na-1/2 is mixed sodium 1- and 2-naphthoate. [b] Fe_2O_3 (0.020 g.) added. [c] Fe_3O_4 (0.30 g.) added. [d] Fe_2O_3 (0.042 g.) added. [e] N_2 and CO_2. [f] Black, extensive decomposition. [g] CdI_2 catalyst (0.49 g.).

Raecke[1] discussed the Henkel reaction applied to the naphthalene system as did one group of Japanese workers.[3] These papers discuss the synthesis of naphthalene-2,6-dicarboxylic acid by the rearrangement of the potassium salt of naphthalene-1,8-dicarboxylic acid or by the disproportionation of the potassium salts of 1-naphthoic acid and 2-naphthoic acid, using carbon dioxide under pressure and cadmium salts as catalysts.

We have investigated the thermal disproportionation of both sodium and potassium salts of 1-naphthoic acid and 2-naphthoic acid under carbon dioxide pressure both with and without catalysts. The behavior of the salts of the two acids is completely different in the absence of catalysts, and under certain conditions in the presence of catalysts.

The salts of 1-naphthoic acid disproportionate to naphthalene and the salts of naphthalene-2,6-dicarboxylic acid only, with or without catalysts. However, under certain conditions, salts of 2-naphthoic acid disproportionate into naphthalene and the salts of naphthalene-2,3-dicarboxylic acid, none of the 2,6-diacid being formed.

The experiments are summarized in Table I. The yields are calculated on the basis that 2 moles of the starting salt is required to form 1 mole of product. Examination of the data leads to the following conclusions. (1) Only 2-naphthoate salts give the 2,3-diacid, 1-naphthoate salts always give the 2,6-diacid. (2) Increasing the pressure increases the product yield. (3) The pressure of iron oxides does not influence the nature of the product. (4) Cadmium carbonate is effective at increasing the yield of 2,3-diacid. Cadmium halides are effective catalysts but always give the 2,6-diacid.[3] (5) 400° appears to be the optimum temperature for the production of the 2,3-diacid when potassium (or mixtures of potassium and sodium) salts are used; at 350° the yield is much lower, whereas at 450° the 2,6-diacid is produced instead. When *only* sodium salts are present, temperatures as high as

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(1) B. Raecke, *Angew. Chem.*, **70**, 1 (1958).

(2) P. W. Sherwood, *Chem. Ind.* (London), 1096 (1960).

(3) J. Yamashita, K. Enomoto, H. Ebisawa, and S. Kato, *Yuki Gosei Kagaku Kyokai Shi*, **20**, 501 (1962); *Chem. Abstr.*, **58**, 3367 (1963).

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.

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(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

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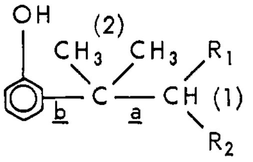
In a recent paper, Cook and Danyluk[1] have examined the n.m.r. spectra of a series of substituted phenylacetylenes. They found that in general electron-donating substituents increased the shielding of the acetylenic protons and electron-withdrawing groups decreased the shielding, but that *ortho* substitution 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.



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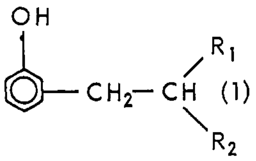

II

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

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(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.