constant for $Z_1Z_2Z_3C^{-}$[31] cannot be extended to include cyanodinitromethane. This correlation predicts that nitroform and cyanodinitromethane should have about the same pK values,[31] while Table I shows that their pK values differ by more than 6!

Summary

The effect of changing Z on the equilibrium constant, K, for the dissociation of the carbinol $Z(NO_2)_2CCH_2OH$ according to eq. 1 can be rationalized in terms of changes in the stability of the carbanion $Z(NO_2)_2C^-$ produced by dissociation of the carbinol. (i) The increase in K when CH_3 is replaced by Cl or Br is due to a change in the electrostatic energy of the carbanion. (ii) The increase in K when CH_3 is replaced by NO_2 or CN is much greater than the change in the electrostatic energy of the carbanion predicts. (iii) Effect ii may be due to the extra resonance stabilization of $(NO_2)_3C^-$ by the third nitro group and of $NC(NO_2)_2C^-$ by the cyano group. The third nitro group may contribute less extra resonance stabilization than the cyano group because O–O repulsion makes the carbanion $(NO_2)_3C^-$ deviate sufficiently from coplanarity to make K for Z = NO_2 much less than for Z = CN.

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[31] V. I. Slovetskii, A. A. Fainzil'berg, and S. S. Novikov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 989 (1962). The proposed equation is pK = 12.64 − 2.6 × (inductive constant for $Z_1Z_2Z_3C$). The inductive constant is to be evaluated as Taft's σ^*-value for $Z_1Z_2Z_3C$ or, when this is not available, as $\sum_i (\sigma^* \text{ for } Z_iCH_2)$. For $(NO_2)_3C$, σ^* has been experimentally evaluated as 4.54 [J. Hine and W. C. Bailey, *J. Org. Chem.*, **26**, 2098 (1961)]; the inductive constant for $NC(NO_2)_2C$ can be estimated as 4.10 by the second method, using σ^*-values for $NCCH_2$ and O_2NCH_2 given by Taft (R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 592, 618).

The Reactions of 2,3-Dichloro-1,4-naphthoquinone with Alkali Metal Cyanides

G. A. REYNOLDS AND J. A. VANALLAN

Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

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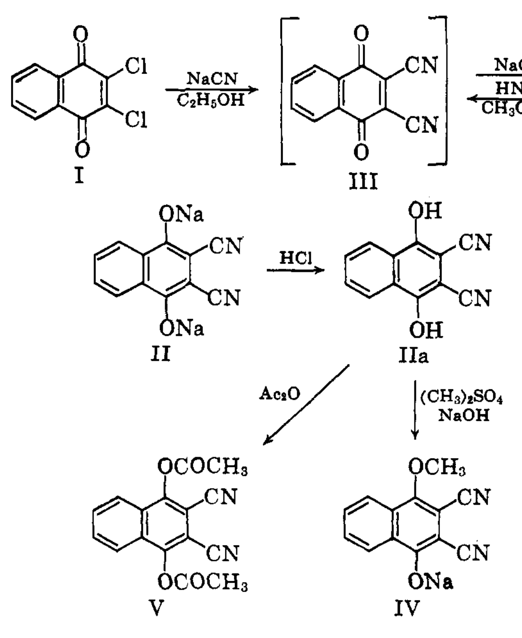
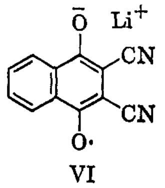
The product obtained by the reaction of 2,3-dichloro-1,4-naphthoquinone with alkali metal cyanides is shown to be the alkali metal salt of 2,3-dicyano-1,4-naphthalenediol. The probable course of the reaction is investigated.

The reactions of 2,3-dichloro-1,4-naphthoquinone (I) with nucleophilic reagents are well documented, and it seemed unusual that the reaction of I with alkali metal cyanides had not been reported previously. We found that a mixture of I and sodium or potassium cyanide in ethanol, acetonitrile, or dimethylformamide gave a water-soluble product which was found to be the sodium or potassium salt of 2,3-dicyano-1,4-naphthalenediol (II). The initial product formed from I and the cyanide was probably 2,3-dicyano-1,4-naphthoquinone (III) which was then reduced by cyanide to II. This was demonstrated by preparing the quinone III by oxidation of IIa with nitric acid and treating III with aqueous sodium cyanide, which resulted in the immediate solution of III to form the water-soluble II. The nature of this reduction by means of the cyanide ion was not investigated, and it is not known whether this reduction proceeds through an ion radical similar to that formed from tetracyanoethylene with sodium cyanide.[1] The quinone III was reduced to IIa by sodium dithionite. Lithium iodide with III in acetonitrile solution yielded a green monolithium salt which is probably the ion radical VI since an aqueous solution shows a weak e.p.r. absorption. It has been shown[2] that certain quinones can form stable, free-radical salts. The susceptibility of the quinone III to reduction suggested that it might be a useful dehydrogenation agent, but no naphthalene was formed after a benzene solution of tetralin and III had



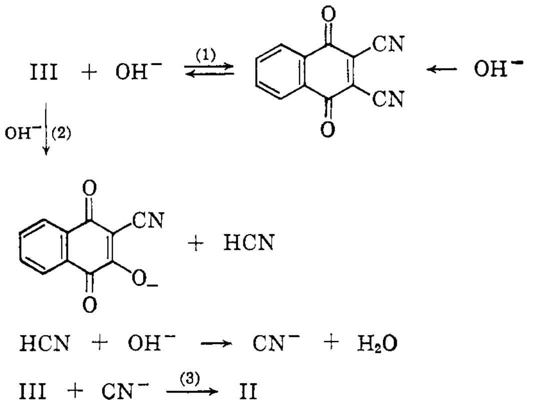


VI

[1] O. Webster, W. Mohler, and R. E. Benson, *J. Am. Chem. Soc.*, **84**, 3678 (1962).

[2] H. Kainer, D. Bijl, and A. C. Rose-Innes, *Nature*, **178**, 1462 (1956); K. Ley and E. Muller, *Angew. Chem.*, **70**, 469 (1958).

been refluxed for 7 hr. The current–voltage curve[3] for III was determined in a supporting electrolyte of 0.1 *M* sodium acetate–acetic acid in a solvent of 1:1 acetonitrile–water using the dropping mercury electrode and saturated calomel reference electrode. The sample gave an oxidation wave at $E_{1/2}$ + 0.10 v. and a reduction wave at $E_{1/2}$ −0.35 v. Compound III was found to be a strong acid by titration in pyridine with 0.1 *N* tetra-*n*-butylammonium hydroxide as the titrant.[3] The first titratable group had a half neutralization potential of −20 and a second h.n.p. at −490 mv. and the ratio of the end points was roughly 1:2.[4] In order to investigate the nature of this double end point, a sample of the quinone III was treated with aqueous sodium hydroxide to give a clear yellow solution. Acidification of the solution resulted in the evolution of hydrogen cyanide and the precipitation of 2,3-dicyano-1,4-naphthalenediol (IIa). The mother liquors were worked up to yield the water-soluble 2-cyano-3-hydroxy-1,4-naphthoquinone (VII). The following series of reactions outline a possible explanation of the titration results.



Equation 1 shows the quinone acting as a strong π-acid. The π-acid character of III was demonstrated by its ability to form yellow, orange, red, and green solutions in benzene, xylene, mesitylene, and anthracene, respectively. Equation 2 illustrates that 2 equiv. of base are required for the displacement of a cyano group by hydroxide, and eq. 3 is a competing reaction which accounts for the formation of II.

The hydroquinone IIa was methylated by means of dimethyl sulfate in a basic medium to yield the sodium salt of 2,3-dicyano-4-methoxy-1-naphthol (IV). Acetylation of IIa by means of acetic anhydride and a catalytic amount of sulfuric acid gave 1,4-diacetoxy-2,3-dicyanonaphthalene (V). The ultraviolet absorption data for the compounds that were prepared are collected in Table I.

TABLE I

Compd.	Solvent	Absorption, mμ × 10^{-3}
IIa	CH_3CN	240(87); 261(15.5); 280(6.8); 330 (10.3); 346 (14.4); 363 (15.5)
IIa	CH_3OH	238 (80); 260 (14.0); 278 (5.0); ~335 (5.5); 351 (8.3); 367 (9.6); ~395 (4.3)
III	CH_3CN	267 (14.0); 277 (12.2); 369 (1.6)
III	CH_3OH	250 (12.0); 254 (16.0); 282 (11.8); 335 (1.7)
IV	CH_3CN	240 (6.5); 272 (14.0); 282 (13.0); 338 (8.6); 355 (11.8); 395 (12.9); 412 (14.5)
V	CH_3CN	246(81.0); 285(4.4); 296(4.8); 309(3.9); 333(3.5); 349(5.0)
VI	H_2O	226 (31.0); 267 (13.5); ~347 (3.2); ~372 (4.6); 390 (5.3); 447 (2.6); ~470(2.4); ~530(0.9); 680(1.1); and still considerable absorption at 800
VII	CH_3CN	247 (12.0); 253 (12.9); 279 (15.0); 287 (14.3); 340(2.3)

Experimental

2,3-Dicyano-1,4-naphthalenediol (IIa).—To a suspension of 4.5 g. of I in 75 ml. of ethanol was added a solution of 6 g. of potassium cyanide in 25 ml. of water. After a short time a clear brown solution resulted. The solution was stirred for 1 hr. and filtered to remove a small amount of undissolved I, and the filtrate was acidified with 25 ml. of concentrated hydrochloric acid to yield, after recrystallization from aqueous ethanol, 3.5 g. of the hydroquinone IIa. The melting point was difficult to determine since the material became very dark around 300°. The infrared spectrum showed strong absorption at 3.1 and 4.5 μ typical of hydroxy and cyano groups.

Anal. Calcd. for $C_{12}H_6N_2O_2$: C, 68.5; H, 2.9; N, 13.3. Found: C, 68.5; H, 3.0; N, 13.5.

2,3-Dicyano-1,4-naphthoquinone (III).—A suspension of 5 g. of IIa in 100 ml. of acetic acid was heated on the steam bath and stirred, and 15 ml. of 30% aqueous nitric acid was added in portions over a 1-hr. period. The clear solution was diluted with water and chilled to yield 3.8 g. of III, m.p. 274–275° (from toluene). The quinone III absorbed strongly at 6.95 μ but did not absorb in the nitrile group region. The failure of nitriles to absorb in the 4.5-μ region, however, has been reported many times.

Anal. Calcd. for $C_{12}H_4N_2O_2$: C, 69.2; H, 1.9; N, 13.4. Found: C, 69.3; H, 2.1; N, 13.4.

A solution of 1 g. of III in 25 ml. of chloroform was shaken with a solution of 1 g. of sodium dithionite in 10 ml. of water, and the white solid that separated was collected and washed with water. The product was the diol IIa as shown by the infrared absorption spectrum.

Treatment of III with Potassium Cyanide.—A solution of 0.5 g. of potassium cyanide in 5 ml. of water was added to 1 g. of the quinone III which was suspended in 20 ml. of ethanol. The quinone dissolved immediately. The solution was stirred for 5 min. and acidified with hydrochloric acid; the solid was collected (1 g.). The product was the diol IIa as shown by the infrared absorption spectrum.

Sodium Salt of 2,3-Dicyano-4-methoxy-1-naphthol (IV).—To a suspension of 5 g. of IIa in 50 ml. of water was added 5 ml. of dimethyl sulfate in portions, along with enough aqueous sodium hydroxide to keep the reaction mixture strongly basic. The hydroquinone IIa dissolved. After the reaction mixture had been stirred for 0.5 hr., another solid began to separate. The solid was collected, washed well with water, and recrystallized from aqueous alcohol, to yield 4.1 g. of product which melted at about 280°.

Anal. Calcd. for $C_{13}H_7N_2NaO_2$ (246): C, 63.4; H, 2.9; N, 11.4; Na, 9.4. Found: C, 63.9; H, 3.2; N, 11.4; Na, 9.4.

1,4-Diacetoxy-2,3-dicyanonaphthalene (V).—A mixture of 3 g. of 2,3-dicyano-1,4-naphthalenediol, 12 ml. of acetic anhydride, and 3 drops of sulfuric acid was heated until solution took place. On cooling the product separated. Recrystallization from acetic anhydride gave 2.5 g. of white crystals, m.p. 228°. A mass spectrogram shows the parent peak at 294.

Anal. Calcd. for $C_{16}H_{10}N_2O_4$ (294): C, 65.4; H, 3.4; N, 9.5. Found: C, 65.7; H, 3.5; N, 9.4.

Lithium Salt of 2,3-Dicyano-1,4-naphthoquinone (VI).—To a solution of 2 g. of III in 50 ml. of acetonitrile was added 1.4 g. of lithium iodide in 50 ml. of acetonitrile. A green solid separated at once and was collected and washed with acetonitrile. The water-soluble product did not melt below 400° and showed a strong nitrile absorption but no carbonyl absorption in the infrared.

Anal. Calcd. for $C_{12}H_4LiN_2O_2$: C, 67.0; H, 1.9; N, 13.0. Found: C, 66.7; H, 2.2; N, 13.0.

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(3) This determination was run by D. G. Bush, of these laboratories.

(4) The h.n.p. of hydrochloric acid is +30, of phenol −650, and of benzoic acid −300 mv.

Treatment of III with Sodium Hydroxide.—III (1.3 g.) was added to a stirred solution of 1 g. of sodium hydroxide in 25 ml. of water. The quinone dissolved immediately, and the resulting clear yellow solution was acidified with concentrated hydrochloric acid to give hydrogen cyanide (identified by benzidine acetate–copper acetate test paper) and a solid (0.39 g.). The solid was recrystallized from alcohol–water to yield 0.3 g. of IIa identified by infrared and analysis. The mother liquors were evaporated to dryness and the residue was extracted with 25 ml. of hot ethanol. The extract was evaporated to dryness and the residue (0.59 g.) was recrystallized from a mixture of ethanol and petroleum (b.p. 35–60°) to give 0.45 g. of 2-cyano-3-hydroxy-1,4-naphthoquinone (VII), m.p. 198–199°. The infrared spectrum showed strong absorption at 2.8 and 4.4 μ for the hydroxy and cyano groups, and at 5.9 and 6.0 μ for the carbonyl groups.

Anal. Calcd. for $C_{11}H_5NO_3$: C, 66.2; H, 2.5; N, 7.0. Found: C, 66.0; H, 2.5; N, 7.3.

Quantitative Studies in Stereoselective Addition Reactions by Isotope Dilution. Additions of Organometallic Reagents Leading to 2,3-Dicyclohexyl-2,3-butanediol. A Strong Halide Effect[1]

JACK H. STOCKER

Department of Chemistry, Louisiana State University in New Orleans, New Orleans, Louisiana 70122

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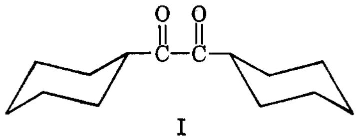
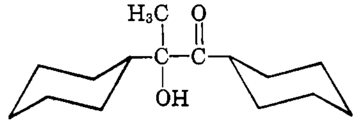
The addition of methyllithium, methylmagnesium chloride, methylmagnesium bromide, and methylmagnesium iodide to 1,2-dicyclohexylethanedione (I) and 1,2-dicyclohexylpropan-2-ol-1-one (II) has been studied by isotope-dilution techniques. The identity of the diastereoisomeric glycols formed was established by nuclear hydrogenation of the established *meso*- and *dl*-racemate phenyl analogs. The following ratios were observed for I and (II), the *meso* form predominating in all cases: methyllithium, 7:1 (8:1); methylmagnesium chloride, 9:1 (7:1); methylmagnesium bromide, 4.5:1 (4:1); and methylmagnesium iodide, 3:1 (3:1). While monoaddition to I appeared rapid, Grignard production of glycol was very slow, particularly in the case of the iodide. The results underscore the need to specify or choose the Grignard halogen in stereoselective synthesis. The addition of cyclohexylmagnesium chloride, cyclohexylmagnesium bromide, and cyclohexylmagnesium iodide to biacetyl produced less than 1.0% of either glycol.

Two general methods are presently used in predicting the course of the stereoselective production of a second, adjacent asymmetric carbon by various addition–reduction techniques. These methods involve conformational control,[2] or a more or less rigid cyclic intermediate.[3] It has recently been suggested[4] that a dipolar model, also involving conformation control, may be invoked usefully. The examination[3] of a "test case," where the first two models would predict opposite results (*i.e.*, the addition of appropriate organolithium reagents to benzil or biacetyl to produce, stereoselectively, the two diastereoisomers of 2,3-diphenyl-2,3-butanediol) gave results in accord with the semirigid model. A subsequent examination employing the related Grignard reagents[5] showed the situation to be considerably more complex. Although the addition of the various methyl organometallic reagents to benzil gave results in accord with the semirigid model, as did the addition of phenyllithium, phenylmagnesium iodide, and diphenylmagnesium to biacetyl, addition to the latter of the chloride or bromide Grignard reagent could best be explained by invoking one of the alternative models. Accordingly, it should be of value to have additional data describing this type of reaction involving other systems. Referring to the earlier work as involving a methyl–phenyl system, the present paper, to be the first of several, offers details of an investigation of the methyl–cyclohexyl system, selected for its freedom from aromatic influences. The correspondence of the methyl group in the two systems should permit some cross comparison of the relative effects of the cyclohexyl and phenyl substituents.

Preparation of the unlabeled I was carried out in 84% over-all yield by way of a standard acyloin-type condensation followed by oxidation with cupric acetate. Contrary to the usual very brief reaction time for the latter step, a reflux time of less than 1 hr. produced inseparable diketone–ketol mixtures. The ketol II was prepared by the inverse addition of limited amounts of methylmagnesium bromide to I.



I



II

The identities of the diastereoisomeric glycols were established conveniently by nuclear hydrogenation of the known phenyl analogs[3] using 5% rhodium-on-alumina catalyst.[6,7] The yields were excellent: 93% for the *meso* and 94% for the *dl* form. These phenyl analogs were available from the stereoselective addition of methyllithium to benzil (*meso*) and phenyllithium to biacetyl (*dl*).[5] This route also proved useful for the preparation of larger amounts of the glycols to be used in the dilution studies. Some of the *meso* form so used

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[1] Presented before the Division of Organic Chemistry at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

[2] "Cram's Rule"; see D. J. Cram and F. A. Abd Elhafez, *J. Am. Chem. Soc.*, **74**, 5829 (1952).

[3] D. J. Cram and K. R. Kopecky, *ibid.*, **81**, 2748 (1959).

[4] D. J. Cram and D. R. Wilson, *ibid.*, **85**, 1245 (1963).

[5] J. H. Stocker, P. Sidisumthorn, B. M. Benjamin, and C. J. Collins, *ibid.*, **82**, 3913 (1960).

[6] Engelhard Industries, Newark, N. J.

[7] A brief communication describing the use of this catalyst to minimize benzyl-type hydrogenolysis in nuclear hydrogenation and including these examples appeared earlier: J. H. Stocker, *J. Org. Chem.*, **27**, 2288 (1962).