

Since the acidity dependence slope differs from unity, Ia is not a true Hammett base and therefore the intercept does not represent a thermodynamic pK_a . However, relative pK_a 's may easily be obtained for a series of cyclohexadienones. While our protonation data for Ib is not so complete as Ia's it is possible to estimate its " pK_a " as -2.1 . Thus, introduction of two methyl groups in conjugation with the electrophilic center increases the basicity by a factor of 20. Assuming that the effect of the methyl groups is cumulative it is possible to estimate ρ^+ for this protonation reaction.¹⁵ This estimated ρ^+ value of -2.1 reinforces our earlier conclusion from nmr data concerning the pronounced delocalization of charge to the 3,5 positions in these cyclohexadienyl cations.

In so far as protonated IIa is a good model for the first intermediate in the dienone-phenol rearrangement, our results provide experimental evidence supporting the electrophilic character of this reaction. The dramatic deshielding of the 3,5 protons in protonated Ia indicates that a substantial fraction of the positive charge is localized at these positions and provides the driving force for the subsequent 1,2-alkyl or aryl shift. The pronounced effect of methyl substitution on the basicity of this cyclohexadienone ($\rho^+ = -2.1$) confirms these conclusions regarding the distribution of charge in protonated Ia.

We are continuing these and related studies to more fully define the mechanistic details of the dienone-phenol and related rearrangements.

Experimental Section

Melting points (oil bath) and boiling points were uncorrected. Ir spectra and uv spectra were taken on Perkin-Elmer 21 and Cary 15 spectrophotometers. Nmr results were obtained with a Varian A-60A spectrometer with a probe temperature of 35° . Elemental analyses were performed by our analytical division.

4-Dichloromethyl-4-methylcyclohexa-2,5-dienone (Ia).—To 500 ml of water containing 25 g of NaOH was added 100 g of *p*-cresol (0.93 mol, Aldrich Chemical Co.). The flask was equipped with a reflux condenser with a nitrogen inlet and heated on a steam bath. When the temperature of the reaction mixture reached 70° , 125 ml of $CHCl_3$ (186 g, 2.33 mol) was added dropwise with efficient stirring. The mixture was allowed to stir at 75° for 12 hr. After cooling, the reaction mixture was extracted with 250 ml of $CHCl_3$. The $CHCl_3$ extract was washed twice with 100 ml of 10% NaOH and once with water. Drying ($MgSO_4$, 2 hr) and concentration afforded 20.5 g of a dark brown oil, which solidified after standing overnight. Distillation (short path) afforded a slightly yellow oil which solidified [12.6 g, 7.8% yield, bp 87° (0.3 mm)]. Two recrystallizations from pentane afforded 7.84 g of analytically pure Ia: mp 52.5° (lit.⁶ mp $53-55^\circ$); ir (CCl_4) 1670 cm^{-1} ($C=O$).

Anal. Calcd for $C_8H_8Cl_2O$: C, 50.2; H, 4.3; Cl, 37.2. Found: C, 50.1; H, 4.3; Cl, 37.2.

4-Dichloromethyl-3,4,5-trimethylcyclohexa-2,5-dienone (Ib).—This material was prepared in the same way as Ia except for the following modifications. The crude product (25 g; mp $96-100^\circ$; 87% pure by Cl analysis; 18% yield) was dissolved in a small volume of acetone. Water was added to the cloud point followed by a few milliliters of dilute NaOH. The mixture was allowed to stand in an ice bath, and the precipitated solid was collected by filtration. This material was vacuum sublimed at $75-80^\circ$ (0.2 mm) three times to afford an analytically pure product: mp $106-107^\circ$; ir (KBr) 1670 cm^{-1} ($C=O$).

(15) (a) This estimate was arrived at in the following way. We assumed that the appropriate σ^+ value was σ_{para}^+ .^{15b} This choice was based on the fact that transmission of electronic effects from the 3 position to the carbonyl group *via* resonance is possible. Thus, $\rho^+ = 1.3/2(-0.31) = -2.1$. It is interesting to compare this value with that reported for the protonation of acetophenones, $\rho^+ = -2.2$ [R. Stewart and K. Yates, *J. Amer. Chem. Soc.*, **80**, 6355 (1958)]. (b) H. C. Brown and Y. Okamoto, *ibid.*, **80**, 4979 (1958).

Anal. Calcd for $C_{10}H_{12}Cl_2O$: C, 55.2; H, 5.5; Cl, 32.4. Found: C, 55.1; H, 5.1; Cl, 32.3.

Nmr Spectra.—The spectra of the neutral dienones were obtained in a straightforward fashion in $CDCl_3$ containing TMS.

The spectra of the protonated dienones were obtained from solutions containing 16% (wt/wt) of dienone with added tetramethylammonium ion. These spectra were recorded within 1 hr of sample preparation.

Uv Spectra.—Aliquots of aqueous stock solutions containing the dienone were added to chilled H_2SO_4 solutions of the desired strength in volumetric flasks. The flasks were made up to the mark with precooled acid and, in most cases, spectra were recorded with a few hours of mixing. Acid concentrations were determined by titration with standard base.

Registry No.—Ia, 6611-78-5; Ib, 5682-84-8.

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Facile Alkylation of Phenylacetonitrile in Dimethyl Sulfoxide

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The alkylation of α -carbon atoms of nitriles is a very valuable synthetic method for the preparation of sterically hindered nitriles and their derivatives.^{1,2} Normally, the reaction is carried out by treating the nitrile with a strongly basic reagent, such as a metal amide, hydride, or alcoholate, followed by addition of the appropriate alkyl or aryl halide. However, the published methods for synthesizing α -alkylated nitriles are, in general, characterized by poor selectivities and/or cumbersome preparative procedures.

Jarousse³ has alkylated phenylacetonitrile with benzyl chloride and ethyl chloride by using an aqueous solution of sodium hydroxide as the base and in presence of benzyltriethylammonium chloride as the catalyst. In absence of the catalyst, no reaction occurred. This reaction has been studied in detail by Makosza and Serafinowa.⁴

We have now found that nitriles containing sufficiently activated methylene groups, such as phenylacetonitrile, can be conveniently alkylated in excellent yields and selectivities by using aqueous sodium hydroxide as the condensing agent and dimethyl sulfoxide as the reaction solvent. Our results and the reaction conditions are summarized in Table I.

No reaction occurred when alkylation of adiponitrile was attempted. Apparently, a methylene group activated only by a nitrile function is insufficiently acidic to react with the NaOH-DMSO system.

Because of the ease and simplicity with which these preparations can be carried out, and because of the low price of the reagents used, the described procedure

(1) A. C. Cope, H. L. Holmes, and H. O. House, *Org. Reactions*, **9**, 107 (1957).

(2) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, p 184.

(3) J. Jarousse, *C. R. Acad. Sci., Paris*, **232**, 1424 (1951).

(4) M. Makosza and B. Serafinowa, *Rocz. Chem.*, **39**, 1805 (1965).

TABLE I
ALKYLATION OF PHENYLACETONITRILE WITH ALKYL HALIDES AND 50% AQUEOUS SODIUM HYDROXIDE
IN DIMETHYL SULFOXIDE

$$\text{C}_6\text{H}_5\text{CH}_2\text{CN} \xrightarrow[\text{(NaOH)}]{+\text{RX}} \text{C}_6\text{H}_5\text{CH(R)CN} \xrightarrow[\text{(NaOH)}]{+\text{RX}} \text{C}_6\text{H}_5\text{CR}_2\text{CN}$$

Alkyl halide RX	RX, mol equiv	NaOH, mol equiv	Reaction temp, °C	Yield, % ^a		
				I	II	III
				Unalkylated I	Monoalkylated II	Dialkylated III
CH ₃ Cl	Excess	4.0	45	0	0	93
CH ₃ Br	1.5	5.0	30	0	79	8
<i>n</i> -C ₃ H ₇ Br	1.5	5.0	30	0	75	13
<i>n</i> -C ₄ H ₉ Cl	1.0	4.0	26	5	62	8
C ₆ H ₅ CH ₂ Cl	3.0	4.0	52	0	0	96 ^b

^a Unless otherwise indicated, all yields were determined by quantitative glpc of the benzene extracts. ^b Product isolated.

promises to be of particular utility whenever the preparation of α -substituted phenylacetonitriles is desired.

Experimental Section

All reagents were the commercially available products (technical grade), used without purification. A typical alkylation reaction is described in the following example.

α,α -Dimethylphenylacetonitrile.—A 500-ml four-necked flask having a gas inlet tube fused to the bottom and equipped with a mechanical stirrer, reflux condenser, two 250-ml dropping funnels (the second one mounted on a side-area adaptor), and a thermowell was charged with 100 ml of dimethyl sulfoxide and methyl chloride was introduced for 15 min. While passage of methyl chloride was continued, to the stirred solution of the gas was added simultaneously 32 g of 50% aqueous sodium hydroxide and 11.7 g of phenylacetonitrile. The reactants were added at such a rate that the temperature of the exothermic reaction was kept between 45 and 50°. After the exothermic reaction had subsided, stirring and introduction of methyl chloride were continued for an additional 60 min. Upon completion of this period, the contents of the reaction flask were diluted with 250 ml of water and the aqueous mixture was extracted with two 100-ml portions of benzene and one 100-ml portion of ether. The combined organic extracts were washed with saturated sodium bicarbonate solution, followed by saturated sodium chloride solution. After drying over anhydrous sodium sulfate, the solvents were evaporated, leaving 14.0 g (93% of theory) of a yellowish oil. Analyses by glpc coupled with a mass spectrograph and by nmr proved this product to be α,α -dimethylphenylacetonitrile.

Registry No.—I, 140-29-4; dimethyl sulfoxide, 67-68-5.

The Dimerization of 2,4-Di-*t*-butyl-6-ethenyl-Quinone Methide. A Possible Diels-Alder Mechanism

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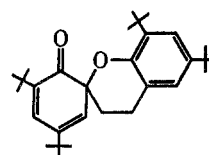
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Work by Waters³ has shown that lead dioxide oxidation of 2,4-di-*t*-butyl-6-methylphenol (1) leads to the ketochroman dimer 2. In connection with our interest in the synthesis of stable relatively simple *o*-quinone

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(3) W. Waters, *J. Chem. Soc.*, 243 (1954).



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methides we have investigated the lead dioxide and alkaline potassium ferricyanide oxidation of the closely related phenol 2,4-di-*t*-butyl-6-ethylphenol (3). Our choice of this phenol was dictated by the results in two areas of investigation. First, lead dioxide or alkaline potassium ferricyanide oxidation of the 2,6-di-*t*-butyl-4-alkyl-substituted phenolic system has shown that the 4-methyl compound leads to 1,2-bis(3,5-di-*t*-butyl-4-hydroxyphenyl)ethane and its oxidation product, 3,5-3',5'-tetra-*t*-butylstilbene-4,4'-quinone,⁴ whereas the 4-ethyl compound⁵ (or more highly substituted analogs) leads to the stable *p*-quinone methide. Second, several reactions have been reported where an *o*-quinone methide was the expected product but where dimeric or more complex compounds were the only isolated products.⁶ In each case the intermediate *o*-quinone methide would possess an unsubstituted methylene group. Therefore, it appeared reasonable that further substitution of the methyl group of 1 might lead to the stable *o*-quinone methide 7.

Oxidation by 3 lead dioxide or alkaline potassium ferricyanide did not result in the isolation of the *o*-quinone methide 7 but instead produced three new compounds—ketochroman dimers, 8 and 9, and an unidentified compound, a trimer based on the starting phenol 3 (see Experimental Section). The structures of 8 and 9 were established by chemical means, molecular weights, and ultraviolet, infrared, and nmr spectroscopy.

Oxidation of 3 produces phenoxy radical 5 as evidenced by the immediate appearance of a deep green color with an absorption maximum at 580 m μ .⁷ The possible fates of this radical are represented in Chart I. Most probably phenoxy radical 5 disproportionates⁸ to phenol 3 and *o*-quinone methide 7, which subsequently reacts with itself *via* a Diels-Alder mech-

(4) C. D. Cook, *J. Org. Chem.*, **18**, 261 (1953).

(5) C. D. Cook and B. E. Norcross, *J. Amer. Chem. Soc.*, **78**, 3797 (1956).

(6) (a) L. Smith and J. Horner, Jr., *ibid.*, **60**, 670 (1938); (b) P. Gardner and H. Sarrafzadeh R., *J. Org. Chem.*, **25**, 641 (1960); (c) S. Cavitt, H. Sarrafzadeh R., and P. Gardner, *ibid.*, **27**, 1211 (1962); (d) A. B. Turner, *Quart. Rev. (London)*, **18**, 347 (1964).

(7) For λ_{max} of other phenoxy radicals, see C. D. Cook, D. A. Kuhn, and P. Fianu, *J. Amer. Chem. Soc.*, **78**, 2002 (1956).

(8) C. D. Cook and B. E. Norcross, *ibid.*, **81**, 1176 (1959).