reaction mixture was then poured into 75 ml of water and extracted with 30 ml of ether. The aqueous layer was saturated with sodium chloride and extracted with three 50-ml portions of ether. The combined ethereal extracts were washed with brine and dried over sodium sulfate. Concentration under reduced pressure gave a colorless oil which on distillation yielded 2.11 g (96%) of **5**: bp 86–88° (0.05 mm) [lit.[1] bp 76–77° (0.1 mm)]. The spectral properties of this material were identical with those reported for **5**.[1]

Registry No.—**1**, 17990-00-0; **6** (*cis*), 18019-46-0; **6** (*trans*), 17990-02-2; **7** (*cis*), 17990-01-1; **7** (*trans*), 17990-03-3.

Acknowledgment.—Support of this research by a grant from the National Institutes of Health is gratefully acknowledged. F. N. T. is grateful for an NDEA Fellowship.

Cyclohexadienyl Cations. I. Protonation of Cyclohexadienones

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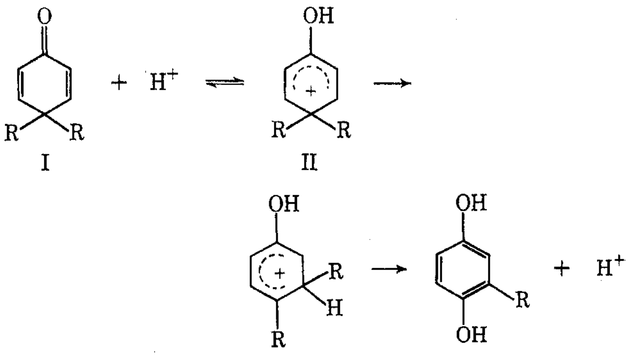
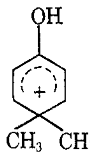
The formation of phenols from cyclohexa-2,5-dienones in the presence of an acid catalyst is a well-known reaction.[2] While many of the mechanistic details of this reaction remain unclear, there appears to be general agreement that the first step involves protonation (or coordination) of the carbonyl oxygen to form a cyclohexadienyl cation.[2b] Whereas the ultimate fate of this first intermediate depends critically on many factors, the second step seems to involve the migration of a group (usually aryl or alkyl) to a neighboring electron-deficient carbon atom.[2b,c] Subsequent expulsion of a proton furnishes the stable phenol product. This sequence is illustrated below for a simple 4,4-disubstituted cyclohexa-2,5-dienone.



It is apparent that both the rate- and product-determining steps (which may be the same) are inextricably related to the basicity of the dienone and the distribution of charge in the first intermediate II.

A few years ago Bloom[3a] and Budzikiewicz[3b] noted that certain cyclohexadienones such as 4-dichloromethyl-4-methylcyclohexa-2,5-dienone formed stable complexes in sulfuric acid. These complexes were formulated as "delocalized ions."[3b]



IIa

We felt that these stable ions[5] would provide excellent models for the first intermediate II in the dienone–phenol rearrangement. Our investigations had a twofold purpose. First, we wished to elucidate as completely as possible the structure and charge distribution of these stable complexes. Nmr spectroscopy seemed admirably suited to this task. Secondly, we wished to evaluate the acidity dependence for this protonation reaction to quantitatively assess the effect of substituents on the basicity of the carbonyl group.

At the time this work was completed, Friedrich[5] reported the nmr and uv spectral properties of several neutral and protonated cyclohexadienones. Friedrich's nmr and uv spectra for neutral and protonated 4-dichloromethyl-4-methylcyclohexa-2,5-dienone are essentially identical with the spectra detailed in the present work.

Results and Discussion

4-Dichloromethyl-4-methylcyclohexa-2,5-dienone (Ia) and 4-dichloromethyl-3,4,5-trimethylcyclohexa-2,5-dienone (Ib) were prepared by the reaction of sodium hydroxide and chloroform with *p*-cresol and 3,4,5-trimethylphenol, respectively.[6] These materials dissolved readily in 90.5% sulfuric acid forming stable solutions.

A complete tabulation of the nmr data for both Ia and Ib in deuteriochloroform and sulfuric acid can be found in Table I.

Table I

Nmr Spectral Data[a] for Ia and Ib in $CDCl_3$ and 90.5% H_2SO_4 at 35°

Dienone	Solvent	2,6 H	3,5 H	4 CH_3	3,5 CH_3	$CHCl_2$
Ia	$CDCl_3$[b]	6.38 (d)[c]	7.00 (d)[c]	1.52		5.87
Ia	H_2SO_4[d]	7.36 (d)[e]	8.33 (d)[e]	1.65		6.20
Ib	$CDCl_3$[b]	6.26		1.55	2.22	6.10
Ib	H_2SO_4[d]	7.14		1.73	2.69	6.32

[a] Varian A-60A spectrometer, reported in parts per million from TMS. [b] Tetramethylsilane internal standard. [c] Doublet, $J = 10$ cps. [d] Tetramethylammonium ion internal standard. [e] Doublet, $J = 9.5$ cps.

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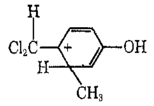
(1) Address all inquiries to the Department of Chemistry, University of Kansas, Lawrence, Kansas 66044.

(2) (a) H. H. Inhoffen, *Progr. Org. Chem.*, **2**, 146 (1953). (b) N. L. Wendler, *Mol. Rearrangements*, **2**, 1028 (1964). (c) A. J. Waring, *Advan. Alicyclic Chem.*, **1**, 207 (1966).

(3) S. M. Bloom, *Tetrahedron Lett.*, **21**, 7 (1959); (b) H. Budzikiewicz *ibid.*, **7**, 12 (1960).

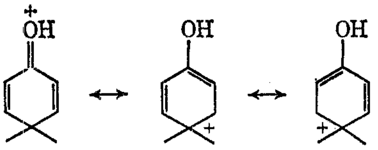
(4) The stability of IIa to rearrangement may reflect the difficulty in forming the next intermediate which would have a partial positive charge adjacent to a $CHCl_2$ group, *e.g.*



(5) E. C. Friedrich, *J. Org. Chem.*, **33**, 413 (1968).

(6) K. Von Auwers and G. Keil, *Ber.*, **35**, 4207 (1902). See also A. J. Waring, *Advan. Alicyclic Chem.*, **1**, 146 (1966), and H. Wynberg, *Chem. Rev.*, **60**, 169 (1960).

In Ia the most predominant change accompanying protonation is the large deshielding observed for the 2,6 and 3,5 protons. In accord with simple MO theory the deshielding observed for the 3,5 protons (1.33 ppm) is larger than for the 2,6 protons (0.98 ppm) reflecting charge delocalization to the 3,5 positions *via* resonance.



Only inductive withdrawal of electron density from the 2,6 positions is possible. These results are very similar to those reported by Olah[7] for *p*-methoxyethylene phenonium ion and by Bourns[8] for carbon-protonated phenol.

It is interesting to note that no charge development at C-4 is possible. Consistent with this notion is the nearly identical chemical shifts observed for the 4-methyl group in Ia and Ib in deuteriochloroform and sulfuric acid. The slight downfield shift observed in these cases is nearly equal to the expected solvent shift.[9]

The nmr results for Ib furnished additional information concerning the distribution of positive charge in these ions. Thus, once again the 2,6 protons were deshielded in sulfuric acid solution (0.88 ppm). Also, the ring methyl groups experienced some deshielding (0.47 ppm) consonant with a partial positive charge at C-3 and C-5.

The extensive delocalization of charge in the protonated forms of Ia and Ib was expected to produce large changes in the electronic spectra of these materials.[10] The uv spectral data presented in Table II confirmed these expectations. It is apparent that major changes in the electronic structure accompany proton addition which are in every way consistent with an extensively delocalized structure for these ions.[10]

TABLE II

UV SPECTRAL DATA[a] FOR Ia IN H_2O AND 90.5% H_2SO_4

Dienone	Solvent	λ_{max}, mμ	ε, l. (mol cm)$^{-1}$
Ia	H_2O	235	14,700
Ia	H_2SO_4	262, 294	13,100, 3600
Ib	H_2O	242	17,300
Ib	H_2SO_4	263, 320	16,600, 6930

[a] Cary Model 15 spectrophotometer, 25°.

It is interesting to note the similarity in the spectrum of Ib in sulfuric acid solution to the carbon-protonated conjugate acid of 3,5-dimethylphenol. In 70% perchloric acid this phenol has λ_{max} at 313 mμ with an ϵ_{max} of 8400 l. (mol cm)$^{-1}$.[11]

The longer wavelength bands present in the conjugate acids of these protonated cyclohexadienones can be used to conveniently monitor their concentration as a function of acid concentration. Such a study has been carried out for Ia and the results are collected in Table III. It can be seen that protonation occurs only in more concentrated acid solutions, requiring the use of an acidity function as a measure of the proton-donating ability of the solvent. We have chosen H_0 since this acidity function has recently been carefully redetermined in sulfuric acid solution.[12] A conventional plot of the equilibrium protonation data for Ia is given in Figure 1.

TABLE III

EQUILIBRIUM PROTONATION DATA FOR Ia IN H_2SO_4 AT 25°

Absorbance[a]	Wt % H_2SO_4	$[DH^+]/[D]$	$-H_0{}^b$
0.032	47.38	0.0380	3.15
0.055	52.47	0.0680	3.65
0.082	55.42	0.105	3.95
0.122	58.95	0.165	4.35
0.212	62.60	0.326	4.78
0.365	67.01	0.734	5.35
0.555	70.44	1.80	5.87
0.652	72.96	3.07	6.25

[a] At 294 mμ, concentration 2.36×10^{-4} *M*, cell path 1 cm.
[b] H_0 values from ref 12.

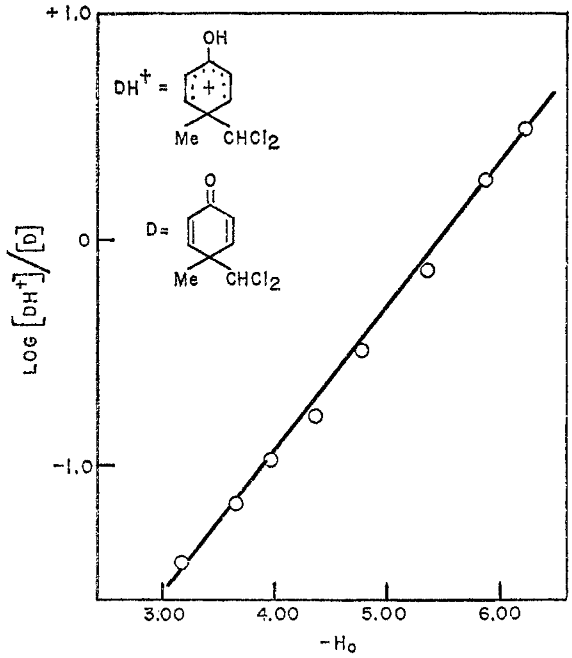


Figure 1.—Plot of log $[DH^+]/[D]$ *vs.* $-H_0$ for the protonation of 4-dichloromethyl-4-methylcyclohexa-2,5-dienone in H_2SO_4.

The results are adequately described by eq 1. While

$$\log [DH^+]/[D] = -0.624\,H_0 - 3.44 \text{ (least squares)} \quad (1)$$

a detailed discussion of the acidity dependence of this reaction is beyond the scope of this work, a few points are worth noting. The slope observed in this work is close to that reported[13] for the protonation of acetophenone in sulfuric acid (0.73) and substantially smaller than the published[14] value of 1.0 for the carbon protonation of 3,5-dimethoxyphenol, even though the conjugate acid of this latter material should have a structure very similar to protonated Ia. We would like to defer further comment on this aspect of our work until the completion of work now in progress.

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(7) G. A. Olah, E. Namanworth, M. B. Comisaraw, and B. Ramsey, *J. Amer. Chem. Soc.*, **89**, 711 (1967).

(8) T. Birchall, A. N. Bourns, R. J. Gillespie, and P. J. Smith, *Can. J. Chem.*, **42**, 1433 (1964).

(9) T. D. J. D'Silva and H. J. Ringold, *Tetrahedron Lett.*, 1505 (1967).

(10) H. H. Perkampus, *Advan. Phys. Org. Chem.*, **4**, 222 (1966).

(11) A. J. Kresge, private communication.

(12) M. J. Jorgenson and D. R. Hartter, *J. Amer. Chem. Soc.*, **85**, 878 (1963).

(13) K. Yates and H. Wai, *Can. J. Chem.*, **43**, 2131 (1965).

(14) W. Schubert and R. H. Quacchia, *J. Amer. Chem. Soc.*, **85**, 1278 (1963); A. J. Kresge, G. Barry, K. Charles, and Y. Chiang, *ibid.*, **84**, 4343 (1962).

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°); 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°; 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° (0.2 mm) three times to afford an analytically pure product: mp 106–107°; ir (KBr) 1670 cm^{-1} (C=O).

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.

Acknowledgment.—The author wishes to thank Professor A. J. Kresge and Drs. J. F. Brennan and D. P. Cords for helpful discussions throughout the course of this work.

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[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).

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.

Jarousse[3] 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).