to give a green material which decomposed at ~375°: ir 3410 (O—H), 1750 (C—O), 1205, 1150, and 1120 cm⁻¹ (C—O).

Registry No.—I, 25557-77-1; II, 25894-27-3; III, 25894-28-4; IV, 25894-29-5; V, 25894-30-8; VI, 25894-31-9; VII, 25894-32-0; VIII, 25894-33-1.

Cyclohexadienyl Cations. II. Evidence for a Protonated Cyclohexadienone during the Dienone–Phenol Rearrangement[1,2]

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In an earlier paper[1] we suggested that the oxygen-protonated cyclohexadienone formed from 4-dichloromethyl-4-methylcyclohexadienone (2) in concentrated acid could be considered a good model for the first intermediate in the dienone–phenol rearrangement.[4] The structure of this ion as well as its equilibrium acidity dependence in concentrated acid solution was firmly established.[1,5] While this suggestion seemed entirely reasonable, it lacked force because of the demonstrated reluctance of 2 to undergo the dienone–phenol rearrangement. Thus, even at 60° in 80% sulfuric acid, 2 rearranges only slowly (half-life ~ 24 hr) to afford a mixture of two rather unusual products.[6]

In this paper, we would like to report the results of a similar investigation on a closely related system, 4,4-dimethylcyclohexadienone (1). This substrate does undergo the dienone–phenol rearrangement rapidly at 25° in 70% perchloric acid to form a single major product, 3,4-dimethylphenol, in >90% yield. Thus, we reasoned that the detection of a protonated cyclohexadienone during the isomerization of this substrate would not suffer from the deficiencies noted above for 2.

Results and Discussion

1 was prepared in a straightforward manner by condensation of the pyrrolidine enamine of isobutyralde-

hyde with methyl vinyl ketone.[7,8] The resulting 4,4-dimethylcyclohexenone was oxidized to the corresponding dienone using 2,3 dichloro-5,6-dicyanobenzoquinone in refluxing carbon tetrachloride.

The uv spectrum of 1 in water is characteristic of a $\Delta^{2,5}$-cyclohexadienone.[9] However, in concentrated sulfuric or perchloric acid solution the spectrum is completely different and nearly identical with that produced by dissolving 2 in concentrated sulfuric acid. These results are summarized in Table I.

TABLE I

ULTRAVIOLET SPECTRAL PROPERTIES OF NEUTRAL AND PROTONATED CYCLOHEXADIENONES

Dienone	Solvent	λ_{max} (nm)	Log ϵ
1	H₂O	235	4.17
2ᵃ	H₂O	238	4.15
1	71.0% HClO₄	260, 295	4.12, 3.57
2ᵃ	90.5% H₂SO₄	262, 294	4.12, 3.56

ᵃ Data from ref 1.

The long wavelength band of the species formed by protonation of 1 can be used to monitor its concentration as a function of acid concentration. The results of such an investigation for solutions of 1 in both sulfuric and perchloric acids are reported in Tables II and III.

TABLE II

EQUILIBRIUM PROTONATION DATA FOR 1 IN HClO₄ AT 25.3°

Absorbanceᵃ	Wt % of HClO₄	[DH⁺]/[D]ᵇ	$-H_0$ᶜ
0.215	41.03	0.157	2.26
0.355	44.35	0.292	2.81
0.573	47.61	0.576	3.18
0.812	50.50	1.076	3.55
1.058	53.55	2.07	4.00
1.200	56.44	3.26	4.47
1.395	59.03	8.08	5.02
1.605	64.16		6.26
1.538	68.83		7.45
1.542	70.95		8.01

ᵃ At 295 nm, concentration 4.12 × 10⁻⁴ M, cell path 1 cm. ᵇ Ratio of concentrations of protonated [DH⁺] to neutral [D] species. ᶜ H_0 values from K. Yates and H. Wai, *Can. J. Chem.*, **43**, 2131 (1965).

TABLE III

EQUILIBRIUM PROTONATION DATA FOR 1 IN H₂SO₄ AT 25.3°

Absorbanceᵃ	Wt % of H₂SO₄	[DH⁺]/[D]ᵇ	$-H_0$ᶜ
0.149	36.28	0.102	2.15
0.276	42.10	0.200	2.57
0.445	46.57	0.383	3.01
0.668	51.75	0.712	3.56
0.842	54.34	1.100	3.84
1.188	60.07	2.83	4.46
1.402	65.02	6.82	5.09
1.633	94.70		9.79
1.583	94.70		9.79

ᵃ At 295 nm, concentration 4.12 × 10⁻⁴ M, cell path 1 cm. ᵇ Ratio of concentrations of protonated [DH⁺] to neutral [D] species. ᶜ H_0 values from M. J. Jorgenson and D. R. Hartter, *J. Amer. Chem. Soc.*, **85**, 878 (1963).

(1) Part I: V. P. Vitullo, *J. Org. Chem.*, **34**, 224 (1969).

(2) Presented in part at the 157th National Meeting of the American Chemical Society, April 1969, Minneapolis, Minn., Abstract ORGN 163.

(3) Address all correspondence to Department of Chemistry, University of Maryland, Baltimore, Md. 21228.

(4) For a discussion of possible mechanisms of the dienone–phenol rearrangement, see A. J. Waring, *Advan. Alicycl. Chem.*, **1**, 207 (1966), and references contained therein.

(5) E. C. Friedrich, *J. Org. Chem.*, **33**, 412 (1968).

(6) T. G. Miller, *ibid.*, **27**, 1549 (1962).

(7) E. Benzing, *Angew. Chem.*, **71**, 521 (1959).

(8) G. A. Smith, B. J. L. Hiff, W. H. Powers, III, and D. Caine, *J. Org. Chem.*, **32**, 2851 (1967).

(9) Reference 4, p 188.

A conventional indicator plot of these data (Figure 1) was linear and adequately represented by eq 1.

$$\log\,[DH^+]/[D] = (0.62 \pm 0.02)\,[(-3.66 \pm 0.13) - H_0] \quad (1)$$

The slope and intercept of this type of plot completely characterizes the acidity dependence of any equilibrium protonation reaction.[10] E.g., if upon protonation two substrates produce conjugate acids of very similar structure (with regard to charge distribution and solvation), their indicator slopes should be essentially identical. In general, the intercepts of these plots will vary considerably from substrate to substrate and will reflect the intrinsic basicity of a particular substrate.

The slope observed in this work for 1 is identical with that reported[1] for the equilibrium protonation of 2 in sulfuric acid (0.62). This adds confirmatory evidence that very similar species, namely protonated cyclohexadienones, are produced from 1 and 2 in concentrated acid solution. The intercepts, on the other hand, are quite different, −3.66 for 1 and −5.52 for 2. This difference corresponds to a difference in basicity of about a factor of 70, with 1 being the stronger base. This is consistent with the well-known electron-withdrawing tendency of a $CHCl_2$ group (σ^* 1.94)[11] relative to a methyl (σ^* 0.00). Thus, inductive withdrawal of electron density by a $CHCl_2$ group from the protonated form of 2 reduces the basicity of the parent cyclohexadienone.

We believe that the results detailed in this report provide conclusive evidence for the existence of a cyclohexadienyl cation during the isomerization of 1 to 3,4-dimethylphenol. Furthermore, it seems intuitively reasonable that this species is an intermediate which lies directly on the reaction path.

Experimental Section

1-Pyrrolidino-2-methylpropene.[7]—In a 250-ml round-bottom flask equipped with a Dean–Stark separator, dropping funnel, and a magnetic stirring bar was placed 83.6 ml (71.1 g, 1.0 mol) of pyrrolidine. The flask was cooled in an ice bath and 109 ml (86.5 g, 1.2 mol) of isobutyraldehyde was added with stirring. After the addition was complete, the mixture was heated at reflux for 6 hr. A total of 19.5 ml (108%) of water was collected. A further 22 ml of aldehyde was then collected and the residue distilled under reduced pressure. A middle cut had the following properties: 67.6 g (54.2%); bp 63–65° (28 mm) [lit.[7] 70–71° (38 mm)].

4,4-Dimethylcyclohexenone.[8]—In a 500-ml round-bottom flask equipped with a condenser, dropping funnel, and a nitrogen inlet tube was placed 52 ml (45 g, 0.36 mol) of 1-pyrrolidino-2-methylpropene. The system was flushed with nitrogen and cooled in an ice bath. At this point, 29.3 ml (25.2 g, 0.36 mol) of methyl vinyl ketone was added dropwise over a period of 0.5 hr. The mixture was allowed to stir under nitrogen for 24 hr. A 350-ml portion of 15% HCl was then added and the mixture allowed to stir for an additional 24 hr. The dark brown reaction mixture was heated on a steam bath for 45 min and allowed to cool. The organic phase was separated from the aqueous layer which was saturated with NaCl and extracted with three 100-ml portions of ether. The ether solution was combined with the organic layer and dried over Na_2SO_4. Removal of the ether afforded 28.3 g (64%) of impure product. Distillation under reduced pressure furnished 18.2 g (41%) of slightly yellow 4,4-dimethylcyclohexenone, bp 89–90° (28 mm) [lit.[8] 81–84° (21 mm)], exhibiting concordant nmr and ir spectra.

4,4-Dimethylcyclohexadienone (1).—In a 500-ml round-bottom flask equipped with an overhead stirring motor, a nitrogen
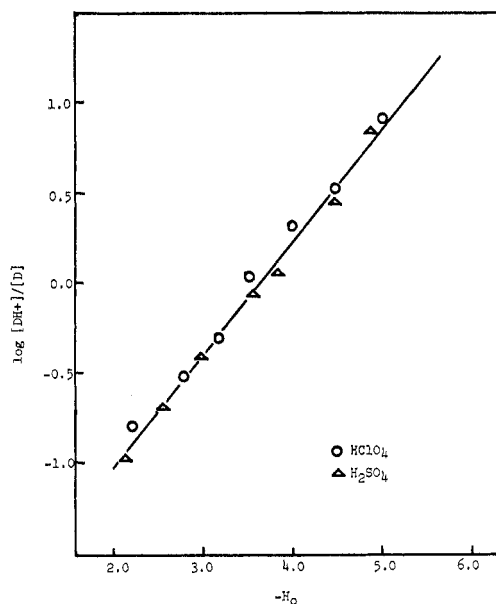
(10) E. M. Arnett, Progr. Phys. Org. Chem., 1, 223 (1963).
(11) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 222.

Figure 1.—Plot of log $[DH^+]/[D]$ vs. $-H_0$ for the protonation of 4,4-dimethylcyclohexadienone in $HClO_4$ and H_2SO_4.

inlet tube, and a condenser was placed 200 ml of CCl_4. To this was added 25 g (0.11 mol) of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) and 7.5 ml (7.0 g, 0.058 mol) of 4,4-dimethylcyclohexenone in 25 ml of CCl_4. The reaction mixture was allowed to reflux on a steam bath with vigorous stirring for 24 hr, cooled to room temperature, and filtered. A 100-ml portion of ether was added and the solution was washed with two 100-ml portions of 10% KOH solution, dried over Na_2SO_4 and the ether removed on a steam bath. There remained 2.89 g (42%) of impure product which was distilled to afford 1.99 g (30%) of water-white 1: bp 60–61° (3 mm) [lit.[12] 90° (15 mm)]; $\nu_{C=O}$ (CCl_4) 1670 cm^{-1}.

Product Study.—A 183.0-mg sample of 1 was treated at 25° with 3.0 ml of 72% $HClO_4$. After 30 min (ten half-lives), the mixture was poured onto ice and extracted with three 30-ml portions of ether. The ether solution was dried over Na_2SO_4 and removed on a steam bath leaving 175 mg (96%) of 3,4-dimethylphenol. After one recrystallization from hexane, the slightly purplish product had mp 59–61°. Authentic 3,4-dimethylphenol, recrystallized once from hexane, had mp 62.5–65°.

In a separate experiment 74.9 mg of 1 was treated at room temperature with 1.0 ml of 72% $HClO_4$ for 5–6 half-lives. Workup of the reaction mixture in the way described above afforded 74.8 mg (100%) of an oil. The ir spectrum of the crude product revealed the presence of unreacted dienone and 3,4-dimethylphenol exclusively. Gas chromatographic analysis demonstrated the presence of a single major product which was collected and shown to be 3,4-dimethylphenol by a comparison of its ir with that of authentic material.

The quantitative conversion of 1 to 3,4-dimethylphenol is further substantiated by uv spectroscopy. These results are summarized in Table IV. As can be seen from the results in

TABLE IV
Uv PRODUCT STUDY FOR 1

Substrate	Solvent, %	λ_{max} (nm)	Log ϵ
1[a]	$HClO_4$, 71.0	207, 271	3.07, 3.86
3,4-Dimethylphenol[b]	$HClO_4$, 71.0	207, 271	3.01, 3.81
1[a]	H_2SO_4, 94.7	302	1.49
3,4-Dimethylphenol[b]	H_2SO_4, 94.7	303	1.53

[a] After 10 half-lives at 25.3°. [b] Aldrich Chemical Co., recrystallized from hexane.

Table IV the phenol product is not stable in sulfuric acid but is rapidly sulfonated, presumably to a mixture of sulfonic acids.

(12) F. G. Bordwell and K. Wellman, J. Org. Chem., 28, 1347 (1963).

Equilibrium Protonation Studies.—A wholly aqueous solution of 1 (0.0618 M, 20 μl) was placed in a clean, dry cuvette. To this was added 3.00 ml of an acid solution of the desired strength previously equilibrated at 25.3°. The contents of the cuvette were thoroughly mixed by several rapid inversions and placed in the thermostated cell compartment of the Cary 16 spectrophotometer. The absorbance was monitored as a function of time and the initial absorbance obtained by a back extrapolation to the time of mixing. Acid concentrations were determined by mixing carefully weighed amounts of standardized acid and distilled water.


## Alkylation of 5-Substituted Tetrazoles with α-Chlorocarbonyl Compounds

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As part of a study on the preparation of polyfunctional tetrazoles, we have alkylated 5-substituted tetrazoles with α-chlorocarbonyl compounds to prepare 1- and 2-carbonyl substituted isomers. Substitutions of 5-substituted tetrazoles with α-haloacetates and triethylamine in acetone have recently been reported.[1] 5-Substituted 1-carboalkoxymethyltetrazoles were previously prepared by an indirect method involving ring closure to form the tetrazole ring.[2] The alkylation of tetrazoles with alkyl halides, dialkyl sulfates, and diazomethane also has been reported.[3] Our work[4] has included several chlorocarbonyl compounds other than chloroacetate, and the reactions were conducted in methanolic potassium hydroxide except that with chloroacetic acid, the reactions also were carried out in aqueous sodium hydroxide. The substitution reactions in methanolic potassium hydroxide (eq 1) and in aqueous sodium hydroxide (eq 2) were as follows.

$$\text{1 and 2 isomers} \quad (1)$$
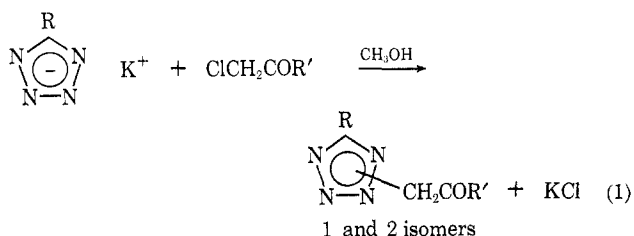
$R = NH_2;\ R' = OH,\ OCH_3,\ OC_2H_5,\ CH_3,\ C_6H_5,\ NH_2$ and
$R = CH_3,\ CF_3,\ C_6H_5,\ p\text{-}NO_2C_6H_5;\ R' = OCH_3$

$$\text{1 and 2 isomers} \quad (2)$$
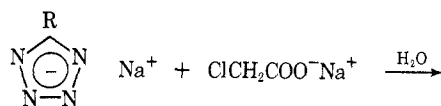
$R = NH_2,\ CH_3,\ CF_3,\ C_6H_5$
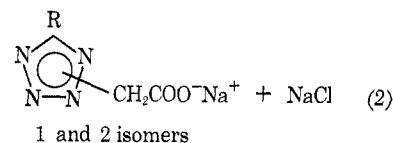
The reaction of potassium 5-aminotetrazolate with α-chlorocarbonyl compounds (eq 1) in methyl alcohol gave mostly 1-substituted products and minor products substituted in the 2 position. The yield of 2-substituted isomer varied from 0 to ca. 21% (Table I). The chlorocarbonyl compounds evidently exerted some influence in directing substitution on the tetrazole ring in addition to the strong inductive effect of the 5-substituent group. Substitution on the 1- and 2-ring positions of different tetrazoles with chloroacetate in methyl alcohol or chloroacetic acid in water clearly demonstrated the inductive effect of the 5 substituents. Electron-donating groups favored 1 substitution and electron-withdrawing groups favored 2 substitution. This inductive effect also was demonstrated in the work reported by Raap[1] and in prior work[3] on the alkylation of 5-substituted tetrazoles. In the reactions with chlorocarbonyl compounds in methanolic potassium hydroxide or in aqueous sodium hydroxide, neutralization of the strong base by formation of the salts of the tetrazoles and of chloroacetic acid prevented hydrolysis of the chlorocarbonyl compounds. With chloroacetic acid 2 mol of base per mol of tetrazole were required to give an appreciable yield of substitution product. Apparently, substitution on the ring occurred only in reaction with the tetrazolate anion which formed after all or most of the chloroacetic acid was converted to salt. Decreased yields were obtained with excess base owing to hydrolytic reaction with chloroacetic acid or ester.

The 1- and 2-carbomethoxymethyl-5-aminotetrazole isomers were readily acetylated with acetic anhydride to stable diacetyl derivatives (Table I). The acetylated 2-substituted isomer could be distilled at low pressure at 180–190° without decomposition. 1-Acetonyl-5-aminotetrazole also was acetylated to a diacetyl derivative, but it was hydrolyzed rapidly in boiling water to monoacetyl derivative.

The strong acidity (see Table II) of 1- and 2-carboxymethyl-5-aminotetrazole and of 2-carboxymethyl-5-trifluoromethyltetrazole manifests the strong electron-withdrawing effect of the tetrazole ring.[5] Rapid hydrolysis of the tetrazolyl acetate esters in cold aqueous alkali also demonstrated the same electron-withdrawing effect. This is in accord with the known fact that strong electron-withdrawing groups substituted in the α position of acetates greatly accelerate hydrolysis.[5] The 5-substituent group apparently has only a weak

(1) R. Raap and J. Howard, *Can. J. Chem.*, **47**, 813 (1969).

(2) C. R. Jacobson and E. D. Amstutz, *J. Org. Chem.*, **21**, 311 (1956).

(3) Robert C. Elderfield, "Heterocyclic Compounds," Vol. 8, Frederick R. Benson, Ed., Wiley, New York, N. Y., 1961, Chapter 1. Section on alkylation of tetrazoles and references there.

(4) F. Einberg, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, p ORGN, 173.

(5) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehard and Winston, New York, N. Y., 1959.