

large peaks at m/e 309, 105, and 77. *Anal.* Calcd for $C_{30}H_{22}O_2$: C, 86.93; H, 5.35. Found: C, 86.87; H, 5.36.

Attempted Acetonization of 2.—An attempt was made to acetonize the diol in order to assign the *meso* or *dl* structures of the acetonide by nmr.¹⁷ Compound 2 (50 mg) was dissolved in 40 cc of acetone, and 0.5 g of anhydrous cupric sulfate was added. The mixture was refluxed for 4 days. Compound 2 was recovered unchanged.

Preparation of Product at Second Wave.—Electrolyses on the second wave in the borate buffer were attempted. The electrolysis solution was neutralized with hydrochloric acid, precipitating a white, amorphous solid, probably a boric acid ester, which was difficult to characterize.

In a typical electrolysis on the second wave in the carbonate buffer, the precipitated electrolysis product accounted for 83% of the starting material. It was a mixture of materials (mp 145–150°) which showed no significant carbonyl but much hydroxyl absorption in the infrared. The mass spectrum revealed significant amounts of dimeric products. The mixture was very soluble in all common solvents save water, cyclohexane, and alkanes. Separation and characterization of the mixture was complicated by its extreme sensitivity to heat, acids, and dehydrating agents. Of the possible two-electron products the isomers of 1,2,4,5-tetraphenyl-1,2,4,5-cyclohexanetetrol (5) seem most likely on the basis of the above evidence. Although the formation of 1,2-diphenyl-1,2-cyclopropanediol (4) cannot be excluded by either the infrared or mass spectral data, it seems quite unlikely since a sample of the pinacol 2 from the reduction at the first wave is reduced polarographically with an $E_{1/2}$ value identical with that of the second wave of the substrate 1 (*vide infra*). This, combined with the absence of carbonyl absorption in the infrared, further indicates that the expected monomeric reduction product, the ketol 3, is not formed, contrary to earlier assumptions.^{2,3}

Preparation of Product at Third Wave.—The procedure was identical with that used for electrolysis at the first wave except that 0.1 M tetramethylammonium hydroxide (50% ethanol-water) was used as supporting electrolyte and the control potential was -2.0 v *vs.* sce (aqueous). The electrolysis of 2.07 g of 1 was complete in 20 hr.

The electrolysis solution was separated from the mercury cathode, neutralized with hydrochloric acid, and evaporated to half its initial volume. Upon cooling a viscous, yellow oil and

some white, crystalline material separated. Most of the yellow oil was physically separated from the white material which weighed 0.98 g after drying. Recrystallization from benzene-Skellysolve B produced 0.49 g of racemic 6, mp 129–130° (lit.¹⁰ 130°, mmp 129–130°).

The filtrate from the electrolysis solution was extracted three times with ether, the extracts were dried, and the ether was evaporated leaving a colorless oil which crystallized after a few hours producing 0.70 g of solid, mp 85–90°. Recrystallization from benzene-Skellysolve B yielded 0.46 g of material, mp 105–107°. Fractional recrystallizations to constant melting point yielded a first fraction with mp 108°. The melting point of the *meso* form of 6 has been reported as 108–109°. This was verified by preparation of authentic samples of the two isomers of 6 by sodium borohydride reduction of 1.¹⁰ The infrared spectra were identical with those of the electrolytic products.

Electrochemistry of Intermediates and Related Compounds.—The product of the first wave (2) was electroactive at the potential of the second wave of 1, *i.e.*, the second wave is due to the further reduction of the product of the first wave. The half-wave potential of 2 was -1.355 v *vs.* sce (aqueous) at pH 4.2 compared to -1.35 v for the second wave of 1. In the carbonate buffer the half-wave potential of 2 was -1.590 v *vs.* sce (aqueous) compared to -1.61 v for the second wave of 1 (Table I). No wave corresponding to the third wave (-1.85 v) was seen with 2.

When 2 was generated in solution by electrolysis at the first wave in the borate buffer (Table II), the electrolysis solution had a polarographic wave at -1.62 v, very close to the half-wave potential of the second wave of 1 in this medium. Again the third wave was absent.

The product from the dehydration of 2, 1,4-dibenzoyl-2,3-diphenyl-1,3-butadiene, was very easily reduced in a quasi-reversible process as shown by cyclic voltammetry in 0.1 M perchloric acid in 95% ethanol [$E_{p/2} = -0.1$ v *vs.* sce (aqueous)]. This behavior is consonant with that of other conjugated diones.^{3a} Thus if 2, which is initially formed during electrolysis on the first wave in 0.2 M hydrochloric acid (Table II), dehydrates to the above product, the product would be reduced at the control potential (-1.0 v) and would enhance the current during electrolysis, in accord with experimental observations.

Registry No.—1, 120-46-7; 2, 10562-14-8; 6, 5355-61-3; 1,4-dibenzoyl-2,3-diphenyl-1,3-butadiene, 10562-16-0.

(18) H. E. Zimmerman and J. English, *J. Am. Chem. Soc.*, **76**, 2285 (1954).

(17) (a) F. I. Carroll, *J. Org. Chem.*, **31**, 366 (1966); (b) F. Johnson, A. A. Carlson, and N. A. Starkovsky, *ibid.*, **31**, 1327 (1966).

The Keto-Enol Equilibrium in 1,3-Cyclohexanediones

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The ultraviolet and nmr spectra of dimedone (I) and 1,3-cyclohexanedione (II) were measured in different solvents at various concentrations. In cyclohexane and chloroform solutions, at very high dilutions, the keto forms of I and II exist in equilibrium with the respective monomeric enol forms. With gradual increase of the concentrations, the dimeric enol form becomes dominant, and at still higher concentrations higher degrees of association of the enol form are observed. The proton and ¹⁷O nmr measurements of dimedone (I) at room temperature point to a fast intermolecular hydrogen transfer in the enol form, and to a rapid interconversion of the two conformers Ia and Ib. Lowering of the temperature results in slower interconversion of the two conformers. The activation energy for this process was calculated to be 4.1 ± 0.5 kcal/mole.

The high degree of enolization of acyclic β -diketones has been attributed,¹ among other factors, to stabilization of the enol form by internal hydrogen bonding, hence also the strong solvent dependence of the keto-enol equilibria in these compounds. In the enols of 1,3-cyclohexanediones such internal hydrogen bonding is sterically impossible; nevertheless, these diketones are predominantly enolic. In solvents serving as hy-

drogen acceptors for hydrogen bonds "nucleophilic" solvents, the enol forms may be stabilized by hydrogen bonding with the solvent.² In solvents incapable of accepting hydrogens, the comparatively high enol content was explained by assuming a dimeric enol form held together by hydrogen bonds.² Recently, however, a monomeric enol form was postulated as

(1) G. S. Hammond in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp 445–454; B. Eistert and W. Reiss, *Chem. Ber.*, **87**, 92, 108 (1954); B. Eistert and F. Geiss, *Tetrahedron*, **7**, 1 (1959).

(2) R. S. Rasmussen, D. D. Tunnicliff, and R. R. Brattain, *J. Am. Chem. Soc.*, **71**, 1068 (1949); K. Kodera, *Yakugaku Zasshi*, **80**, 1267 (1960). Cf. K. Nakanishi, "Infrared Absorption Spectroscopy," Holden Day, Inc., San Francisco, Calif., 1962, pp 65–70; C. Tamm and R. Albrecht, *Helv. Chim. Acta*, **43**, 768 (1960).

existing in equilibrium with the keto form and the dimeric enol.³

The present study is concerned with the investigation of the ultraviolet and nmr spectra of dimedone (I) and 1,3-cyclohexanedione (II). The results may throw some light on the problem of the keto-enol equilibrium of 1,3-cyclohexanediones and the molecular association of their enolic forms.

Ultraviolet measurements of I and II were determined in various solvents at different concentration ranges. The measurements were limited by both the solubilities of the compounds and the transparencies of the solvents. In nucleophilic solvents, the λ_{\max} of I and II appeared at a wavelength comparable with those shown by the ethyl enol ether of dimedone (III), and were independent of concentration (Table I).

TABLE I
ULTRAVIOLET ABSORPTION SPECTRA OF DIMEDONE (I),
1,3-CYCLOHEXANEDIONE (II), AND DIMEDONE ENOL
ETHYL ETHER (III)

Solvent	Dimedone, $\lambda, m\mu (\epsilon)$	1,3-Cyclohexane- dione, $\lambda, m\mu (\epsilon)$	Dimedone enol ethyl ether, $\lambda, m\mu (\epsilon)$
Cyclohexane	<i>a</i>	<i>b</i>	238 (13,600)
Ethyl ether	243 (14,400)	241.5 (16,300)	240 (15,800)
Acetone	246 (13,000)	244 (15,000)	245.5 (16,500)
Chloroform	<i>a</i>	<i>b</i>	248 (16,800)
Dimethyl sulfoxide	251 (16,500)	250 (16,500)	251.5 (15,500)
Dimethyl- formamide	253 (14,800)	252 (15,500)	253 (16,000)

^a See Table II. ^b See Table III.

In cyclohexane and in chloroform solutions, however, I and II showed a strong concentration dependence of both λ_{\max} and ϵ_{\max} . Thus, in very dilute cyclohexane solution I and II showed a maximum absorption at 236 and 237 $m\mu$, respectively (Tables II and III), similar to that of the enol ether III. Since at these dilutions the λ_{\max} values are independent of concentration, the enol forms appear to be monomeric. At increasing concentration, on the other hand, the absorption maxima of I and II approach the constant wavelengths of 252 and 250.5 $m\mu$, respectively; the

TABLE II
ULTRAVIOLET ABSORPTION SPECTRA AND THE FRACTION OF THE
ENOL FORM DIMEDONE (I) IN CYCLOHEXANE AND CHLOROFORM

Total concn, mole/l. $\times 10^2$	$\lambda, m\mu (\epsilon)$	Fraction of the enol form, α
In Cyclohexane		
0.071	252 (1900)	0.136
0.068	252 (1850)	0.132
0.064	252 (1570)	0.112
0.061	252 (1520)	0.109
0.057	251.5 (1380)	0.098
0.050	251 (1200)	0.086
0.043	249 (865)	0.061
0.035	248 (755)	0.054
0.007	237 (220)	0.016
0.006	237 (220)	0.016
In Chloroform		
3.90	252 (2300)	0.139
1.61	248 (1540)	0.093
0.62	246.5 (727)	0.044

(3) N. Cyr and L. W. Reeves, *Can. J. Chem.*, **46**, 3057 (1965).

TABLE III
ULTRAVIOLET ABSORPTION SPECTRA AND THE FRACTION OF THE
ENOL FORM OF 1,3-CYCLOHEXANEDIONE (II) IN
CYCLOHEXANE AND CHLOROFORM

Total concn, mole/l. $\times 10^2$	$\lambda, m\mu (\epsilon)$	Fraction of the enol form, α
In Cyclohexane		
0.080	250.5 (5720)	0.408
0.074	250.5 (5470)	0.390
0.066	250.5 (5160)	0.369
0.057	250.5 (4700)	0.336
0.053	249.5 (3300)	0.236
0.041	248 (3000)	0.214
0.022	243 (1180)	0.084
0.012	242.5 (1100)	0.078
0.008	240 (900)	0.064
0.004	236 (680)	0.048
0.002	236 (680)	0.048
In Chloroform		
1.87	250.5 (4160)	0.252
0.42	246.5 (2400)	0.145
0.23	246 (1670)	0.010

absorption intensity, however, remains strongly concentration dependent. The enol form responsible for these absorptions seems to be associated in dimeric or other polymeric form. An analogous solvent dependence of the ultraviolet absorption has been previously observed in benzoic acid. For this compound monomeric and dimeric forms were postulated to exist in *n*-hexane at low and high concentrations, respectively.⁴

The keto-enol equilibrium of I and II may be described by keto \rightleftharpoons enol monomer \rightleftharpoons enol dimer \rightleftharpoons enol polymer. The molar concentration of the enolic form [en] may be calculated from the measured ϵ_{\max} values if the absorption intensity of the pure enol were known. Since at high dilution practically all the enol is monomeric, the ϵ_{\max} value gives directly the enol fraction α , and, hence, the equilibrium constant K_1 (eq 1 below),

$$K_1 = \frac{[\text{en}]}{[\text{ke}]} = \frac{\alpha}{1 - \alpha} \quad (1)$$

[ke] being the molar concentration of the keto form. At high concentrations, on the other hand, the constant λ_{\max} value indicates that the concentration of the enol monomer is negligible, and that the entire enolized fraction is associated in one or more polymeric forms. For an equilibrium in which only one of the associated forms, the polymeric one, is dominant, the equilibrium constant will be given by

$$K_n = \frac{[\text{en}]}{n[\text{ke}]^n} = \frac{\alpha}{n(1 - \alpha)^{n-1}} \quad (2)$$

and the degree of association may be obtained from the slopes of the plot of $\log [\text{en}]$ vs. $\log [\text{ke}]$.

In Tables II and III are presented the ϵ_{\max} values at different concentrations, and the calculated enol fractions (α) based on ϵ 14,000 for the pure enol form in cyclohexane solution.⁵ At high dilutions, only a small fraction of the diketone is enolized. Figure 1 shows the plot of $\log [\text{en}]$ as a function of $\log [\text{ke}]$ for

(4) M. Ito, *J. Mol. Spectry.*, **4**, 144 (1960); W. F. Forbes, A. R. Knight, and D. L. Coffen, *Can. J. Chem.*, **38**, 728 (1960).

(5) This value is taken from the ultraviolet spectrum of the enol ether III in the same solvent.

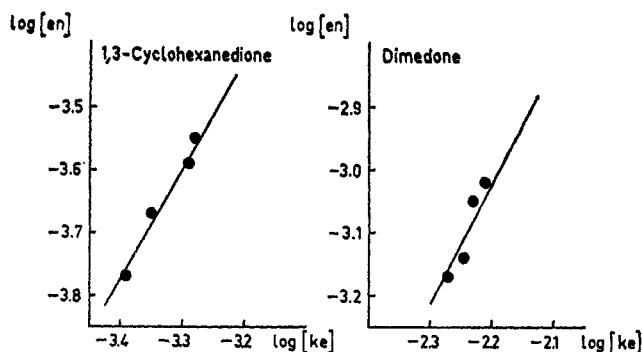


Figure 1.—Log of the molar concentrations of the enol forms of dimedone (I) and 1,3-cyclohexanedione (II) vs. log of the respective keto forms (from ultraviolet measurements).

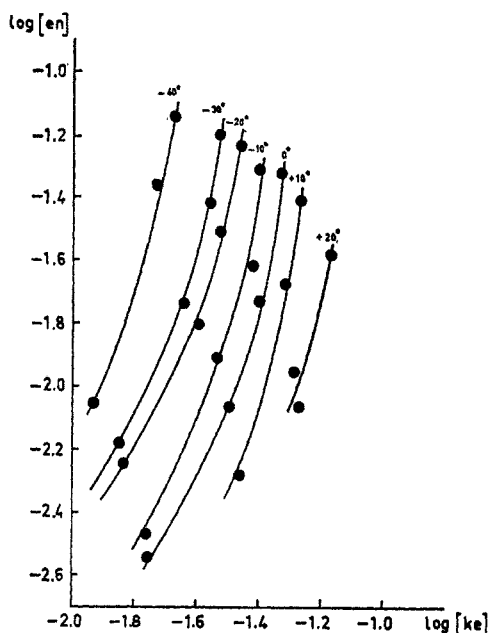


Figure 2.—Log of the molar concentrations of the enol form of dimedone (I) vs. log of the molar concentrations of the keto form (from nmr measurements).

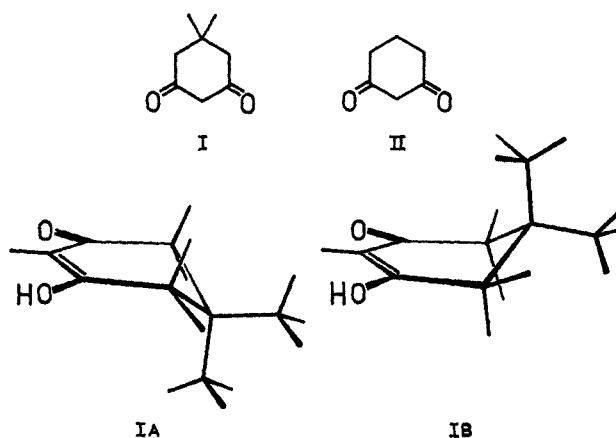
the higher concentration range in which λ_{\max} becomes constant. This plot approximates a straight line whose slope gives roughly $n = 2$, showing that the dominant enolic form is dimeric.

The equilibrium constant calculated from eq 2 substituting $n = 2$ is for dimedone (I) $K_2 = 1.2 \pm 0.1 \times 10^2$ l./mole, and for 1,3-cyclohexanedione (II) $K_2 = 5.2 \pm 0.5 \times 10^2$ l./mole. The measurements in chloroform (Tables II and III) were limited to a narrow concentration range owing to the opaqueness of this solvent (only cells of 0.01-cm thickness could be used), and consequently, no quantitative results could be deduced. Nevertheless, a concentration dependence of both the absorption maxima and their intensities was observed. The λ_{\max} found in chloroform at high concentration is similar to that in cyclohexane, and may also be ascribed to the associated form. Upon dilution the maximum shifts to shorter wavelengths, as the contribution of the monomeric form increases. The low intensity of λ_{\max} at the highest dilutions measured in chloroform points to a small enol monomer/keto ratio, which is *ca.* 0.05 in dimedone and 0.1 in 1,3-cyclohexanedione (the calculations were

based on the assumption that $\epsilon_{\max} = 16,500$ for 100% enol form in chloroform).⁵

In the nmr spectrum, dimedone (I) shows in deuteriochloroform discrete signals of both the enol and the keto forms. The methyl protons appear as singlets at 1.09 for the enol, and 1.04 ppm for the keto form. The four methylene protons also show singlets at 2.25 and 2.51 ppm for the enol and keto forms, respectively. In addition, a singlet of the vinylic proton of the enolic form appears at 5.48 ppm, and singlet of the methylene protons between the carbonyl groups of the keto form appears at 3.33 ppm. The chemical shift of the hydroxylic proton of the enol varies with the concentration.

The fact that in the enolic form of dimedone the two methyl signals coincide, and moreover, that all the four protons of the methylene groups are equivalent, points to a rapid (on the nmr time scale) interconversion of the two conformers IA and IB. The two un-



equivalent methylene groups of enol methyl ether of dimedone (III) give rise to two separate nmr singlets at 2.20 and 2.28 ppm (equidistant from the respective signals in I). In view of this, the equivalence of the two methylene groups in the enol form of dimedone shows that a fast proton transfer takes place, equalizing the environment of the two methylene groups.

Additional evidence for this proton exchange which makes both oxygens in dimedone enol equivalent, is provided by the ¹⁷O nmr spectrum in benzene solution. Two signals were observed, an intense one at -239 ppm (downfield from water as a reference) and a weak one at -538 ppm. The former signal is assigned to both oxygens of the enol, and the latter to the oxygens of the keto tautomer.⁶ The position of the intense signal may be regarded as an average between the chemical shifts of a carbonyl and a hydroxy oxygen, and is similar to that observed in the enolic form of symmetrically substituted β - and α -diketones.⁶

The proton nmr spectrum of dimedone in deuteriochloroform was studied in detail at various concentrations and temperatures. In this solvent the enol/keto ratio was estimated by integration of the methylene signals of the two forms as well as the vinylic proton signal and the signals of the methylene protons between the two carbonyl groups. The results presented in Table IV show that the keto form is increased

(6) M. Gorodetsky, Z. Luz, and Y. Mazur, *J. Am. Chem. Soc.*, **89**, 1183 (1967).

TABLE IV

THE FRACTION OF THE ENOL FORM OF DIMEDONE (I) FROM THE NMR MEASUREMENTS IN DEUTERIOCHLOROFORM SOLUTION

Total concn, mole/l. $\times 10^2$	Nmr, ppm, at given temp, °C						
	+25°	-10°	0°	-10°	-20°	-30°	-40°
9.40	0.28	0.41	0.5	0.54	0.63	0.69	0.77
6.25	0.18	0.23	0.35	0.39	0.51	0.59	...
4.16	0.05	0.13	0.21	0.30	0.38	0.45	...
2.05	0.05	0.05	0.14	0.17	0.28	0.32	0.43

by both high dilution and increased temperature, whereas at high concentration and lower temperature the enol form is favored.

In Figure 2, $\log [en]$ vs. $\log [ke]$, based on the nmr measurements, is plotted for various concentrations and temperatures. It may be assumed that, in the concentration range measured, all the enol exists in polymeric and not monomeric form (as shown by the ultraviolet measurements), and since the slopes in Figure 2 tend to increase with the concentration, an increasing degree of association of the enol molecule is indicated.

1,3-Cyclohexanedione (II) also shows in the nmr separate peaks due to the enol and keto forms.⁷ Since the signals of six methylene protons common to both forms give a complicated pattern due to vicinal coupling, the enol/keto ratio was calculated by integration of the singlets of the vinylic proton in the enol form and the methylene protons between the two carbonyl groups in the keto form.

In Table V, the enol/keto ratio is given for different concentrations at room temperature, and here also the enol content increases with concentration. The slope of $\log [en]$ vs. $\log [ke]$ (Figure 3) indicates again an increase in the degree of association of the enol form at higher concentrations, although the effect is of smaller amount than in dimedone (I).

TABLE V

THE FRACTION OF THE ENOL FORM OF 1,3-CYCLOHEXANEDIONE (II) FROM THE NMR MEASUREMENTS IN DEUTERIOCHLOROFORM SOLUTION AT ROOM TEMPERATURE

Total concn, mole/l. $\times 10^2$	Fraction of the enol form, α
6.8	0.46
10.3	0.52
15.3	0.65
22.9	0.72
24.0	0.71
34.0	0.76
51.0	0.815
76.8	0.89

The nmr signals of the methyl and methylene protons of dimedone enol broaden with decrease of temperature. The line broadening was observed in deuteriochloroform as well as in acetone and in a mixture of deuteriochloroform-pyridine. On the other hand, the resonance line of the vinyl proton in the enol form and all three signals of the keto form were unaffected by temperature changes. The line width of the enol methylene signal, measured at half its height, increased from 2 to 8.1 cps

(7) For the peak assignment see ref 3.

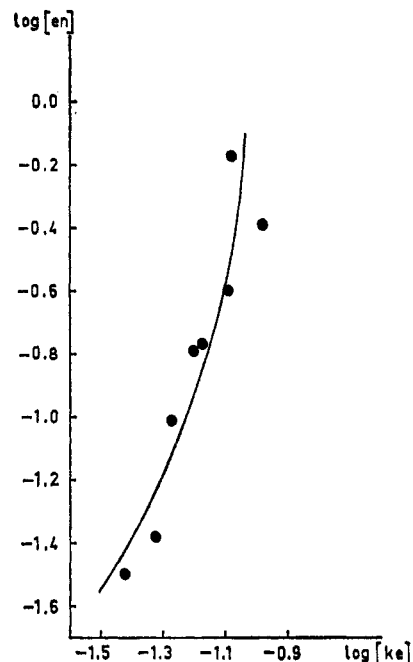


Figure 3.—Log of the molar concentrations of the enol form of 1,3-cyclohexanedione (II) vs. log of the molar concentrations of the keto form (from nmr measurements).

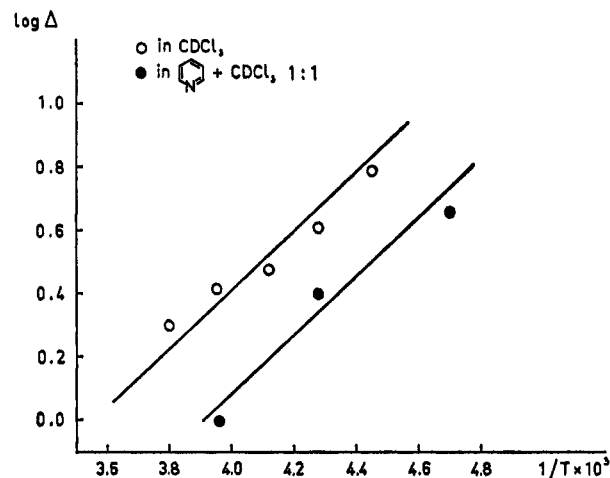


Figure 4.—Plot of the log of the corrected line width of the CH_2 signal in dimedone (I) as a function of the inverse absolute temperature.

in deuteriochloroform when the temperature was lowered gradually from +27 to -50° . In deuteriochloroform-pyridine mixture, the half-width increased from 2.5 to 7.2 cps between +27 and -60° .

The comparatively sharp line, observed at room temperature for the four methylene protons of the enol form of dimedone, is consistent with a rapid inversion of the two conformers IA and IB. Each of the conformers should have shown separate signals of the axial and equatorial protons coupled to each other. The line broadening indicates a progressively slower interconversion of the two conformers. Although the coalescence temperature could not be reached, the energy of activation for this conversion could be estimated roughly from the Arrhenius relation using the line-width measurements at various temperatures.

At temperatures well above the coalescence, the line width (Δ) is in a good approximation, inversely pro-

portional to the rate constant k ,⁸ and the energy of activation ΔH is given by

$$\Delta H = -2.3R \frac{d \log k}{d \left(\frac{1}{T}\right)} = 2.3R \frac{d \log \Delta}{d \left(\frac{1}{T}\right)}$$

The plot of $\log \Delta$ (corrected by subtracting the value of the line width at 27°⁹) vs. $1/T$ gives a straight line (Figure 4) from which the activation energy of the conversion was calculated to be 4.1 ± 0.5 kcal/mole.

The temperature independence of the nmr line widths in the keto tautomer of dimedone points to its higher conformational mobility.¹⁰ The nmr signals of its homolog, the 2,2,5,5-tetramethylcyclohexanedione (at 0.98, 1.28, and 2.59 ppm), were also found to remain sharp when the temperature was decreased to -80° . On the other hand, the comparatively higher energy

(8) S. Alexander, *J. Chem. Phys.*, **37**, 967 (1962); *ibid.*, **38**, 1787 (1963); see also J. E. Anderson and J. M. Lehn, *J. Am. Chem. Soc.*, **89**, 81 (1967).

(9) Since at temperatures above 27° the amount of the enol form was negligible, the values of the line width at 27° were used in the calculations as the natural line widths.

(10) The mobility of cyclohexanone and 2,2'-dimethylcyclohexanone is indicated *inter alia* by the temperature independence of their nmr spectra, down to ca. -80° : R. Perret, *Bull. Soc. Chim. France*, **5**, 753 (1966).

barrier observed in the enolic form of the 1,3-cyclohexanediones may be caused by the rigidity of the three sp^2 -hybridized carbon atoms causing a considerable distortion of the bond angles in the conversion of IA to IB.

Experimental Section

Ultraviolet absorption spectra were measured on a Cary 14 spectrophotometer, using cells of 5-, 1-, 0.1-, and 0.01-cm thickness. The proton nmr measurements were done on a Varian A-60 instrument, and the line-width determination was performed on a Varian HR, 100-Mc instrument. The peak positions are given in parts per million (ppm) downfield from tetramethylsilane as an internal reference. The ¹⁷O nmr spectrum of dimedone was recorded on a V-4200 Varian wide-line spectrometer operating at 8.13 Mc/sec; the derivative of the absorption line was recorded using a 40-cps sweep modulation. The chemical shift was measured relative to H₂¹⁷O as an external standard.

The commercially available samples of dimedone and 1,3-cyclohexanedione were purified by repeated crystallization. The solvents used were spectroscopic grade; the chloroform was ethanol free.

Registry No.—I, 126-81-6; II, 504-02-9; III, 13019-14-2.

The Trichloromethylation Reaction. Ring-Chain Tautomerism. II¹

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Several anhydrides have been subjected to the trichloromethylation reaction using sodium trichloroacetate in dimethoxyethane solution. The trichloromethylation products exist in either of two tautomeric forms, the keto acid or the lactol. If the trichloroacetyl and carboxyl groups are held in fixed coplanarity, the stability of the lactol tautomer is quite high and the compound crystallizes in that form. If the groups are not held coplanar, then the keto acid tautomer is isolated. In solution the compounds are in tautomeric equilibrium and the presence of two tautomeric forms may be detected spectroscopically. The yields of the trichloromethylation products are generally quite good, but, in cases where side reactions are particularly significant, low yields result. Sodium trichloroacetate reacts with aldehydes to give trichloromethylcarbinols, with acetyl chloride to give 1,1,1-trichloro-2-propanone, and with methyl iodide to give 1,1,1-trichloroethane. Sodium tribromoacetate may be used to introduce the tribromomethyl group, reaction occurring with both anhydrides and aldehydes. The use of sodium trifluoroacetate has not been successful. The decomposition of sodium trichloro- and tribromoacetate is strongly accelerated by the presence of the anhydride. The possibility that the trihalomethylation reaction involves a participation by the trihaloacetate ion is suggested.

The decomposition of sodium trichloroacetate in the presence of anhydrides is a useful synthetic method for introducing the trichloromethyl group into organic compounds.² A variety of anhydrides readily undergoes the addition reaction to produce trichloromethyl ketones, keto acids, and lactols in high purity, often in excellent yield. The reaction is quite rapid; in certain cases yields of >70% are realized after only 30 min in refluxing dimethoxyethane. Occasionally, lower yields (10–50%) result, and the product may be accompanied by considerable amounts of tarry material. This is due in part to the abstraction of hydrogen or chlorine from the primary product by the trichloromethyl anion, to give an anion which may undergo further reactions. Abstraction reactions of this type are well known^{3,4} and

often lead to complex condensation products. The isolation of appreciable amounts of dichloroprotonanemonin from the trichloromethylation of succinic anhydride is one instance in which a side reaction product was actually identified.⁵

We have now investigated the trichloromethylation of several additional anhydrides and have extended the general scope of the reaction to include aldehydes, an acid chloride, and an alkyl iodide. The use of sodium tribromo- and trifluoroacetate in the trihalomethylation reaction has also been explored.

Reaction of sodium trichloroacetate with the appropriate anhydride provided reasonably good yields of trichloromethylation products 1–4. Reaction with chlorendic anhydride produced a considerable amount of tar, from which the amorphous trichloromethyl lactol 5 was sublimed. This compound was difficult to purify and a satisfactory analysis was obtained on the methyl ester 6.

(1) Taken in part from the Ph.D. dissertation of J. C. Sharp, West Virginia University, Oct 1966, and the M.S. theses of K. E. Atkins and D. E. Battin, Kanawha Valley Graduate Center of West Virginia University, 1965.

(2) A. Winston, J. P. M. Bederka, W. G. Isner, P. C. Juliano, and J. C. Sharp, *J. Org. Chem.*, **30**, 2784 (1965).

(3) W. M. Wagner, H. Kloosterziel, and A. F. Bickel, *Rec. Trav. Chim.*, **81**, 925 (1962).

(4) W. M. Wagner, H. Kloosterziel, and A. F. Bickel, *ibid.*, **81**, 933 (1962).

(5) A. Winston and J. C. Sharp, *J. Am. Chem. Soc.*, **88**, 4196 (1966).