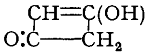
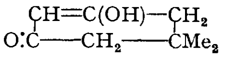
190. " *Dimedone* " *and its Monoethyl Ether.*

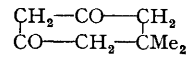
By A. A. Hukins and R. J. W. Le Fèvre.

Chemical evidence shows that ordinary " dimedone " reacts readily as the mono-enol (II), the structure of which is taken as a model for the formula (I) previously proposed for diketen. The moment of dimedone, in benzene solution, is *less* (3·5 as against 3·8 D.) than that of its ethyl ether. This is the reverse of the order commonly found for monohydric alcohols, phenols, etc., and the corresponding R·OEt derivatives, but resembles the situation found for salicylaldehyde, quinol, and the carboxylic acids. The infra-red spectra in carbon tetrachloride of dimedone and ethyl acetoacetate are roughly similar between 2·6 and 3·0 μ and indicate the presence of hydroxyl groups. Under the conditions of measurement, dimedone is unlikely to be entirely diketonic. The observed moments are explicable if the monoenolic hydroxyl group lies in the plane containing the ethylenic double bond.

Angus, Leckie, Le Fèvre, Le Fèvre, and Wassermann (*J.*, 1935, 1751), finding the dipole moment of dimeric keten to be $3{\cdot}1_5$ D. (in benzene) or $3{\cdot}3_0$ D. (in carbon tetrachloride), concluded that, of the then extant formulæ, (I) appeared most nearly correct. Later, others were advanced by Hurd *et al.* (*J. Amer. Chem. Soc.*, 1936, **58**, 962; 1939, **61**, 3355; 1940, **62**, 1147, 1941, **63**, 2174) and Boese (*Ind. Eng. Chem.*, 1940, **32**, 16), which, as Oesper and Smyth (*J. Amer. Chem. Soc.*, 1942, **64**, 768) noted, also required moments near the experimentally observed value. These formulæ differ from (I) by having no hydroxyl groups. Whiffen and Thompson (*J.*, 1946, 1005)


$$\begin{array}{l}\mathrm{CH{=}C(OH)}\\ \mathrm{O{:}C{-\!-}CH_2}\end{array}$$
(I.)


$$\begin{array}{l}\mathrm{CH{=}C(OH){-}CH_2}\\ \mathrm{O{:}C{-\!-}CH_2{-\!-}CMe_2}\end{array}$$
(II.)


$$\begin{array}{l}\mathrm{CH_2{-}CO{-\!-}CH_2}\\ \mathrm{CO{-\!-}CH_2{-}CMe_2}\end{array}$$
(III.)

have more recently reported that the infra-red and Raman spectra of dimeric keten do not show the usual indications of associated or unassociated hydroxyl.

The present measurements were initiated following discussions on the above evidence with Dr. A. Wassermann. He pointed out that, on the basis of (I), dimeric keten would be distinguished from the common β-diketones in that, unless unusual distortions of intervalency angles are supposed, (I) cannot develop an internal O . . . H . . . O bridge, so that the absence of *certain* spectral features characteristic of ordinary enols might therefore be expected. For this reason it seemed of interest to examine another molecule having the same stereochemical limitation as (I).

Dimedone appeared suitable. The summary of its chemistry in Beilstein's " Handbuch " (VII, 599; VII*, 313; VIII, 6) revealed a readiness to undergo reactions as a mono-enol (II), an inspection of models of which confirmed the difficulty of bringing the hydroxylic hydrogen into adequate proximity to the ketonic oxygen.

We give below new data for (*a*) the dipole moment of dimedone and of its monoethyl ether, and (*b*) its infra-red spectrum. For comparison, the spectra of ethyl acetoacetate, salicylaldehyde, phenol, and *p*-cresol are included.

Dipole-moment Determinations.—Dimedone and its monoethyl ether were prepared by the methods cited in Beilstein (*op. cit.*). The apparatus, technique, and symbols used have been described before (cf. *J.*, 1948, 1949). Measurements are relative to benzene, for which $\varepsilon^{25°}_{1000\text{ kc.}} = 2{\cdot}2725$ and $d^{25°}_{4°} = 0{\cdot}87378$.

	Dimedone.				Dimedone ethyl ether.			
$100w_1$	0·1480	0·1837	0·1953	0·2486	0·3908	0·9337	1·5138	2·2632
$\varepsilon^{25°}_{1000\text{ kc.}}$	2·2850	2·2905	2·2923	2·2960	2·3095	2·3565	2·4094	2·4757
$d^{25°}_{4°}$	0·87407	0·87419	0·87417	0·87420	0·87412	0·87468	0·87527	0·87602

	M.	Mean $\alpha\varepsilon_2$.	Mean β.	$_\infty P_1$ (c.c.).	$[R_L]_D$ (c.c.).	μ, D.
Dimedone	140	9·46	0·225	286	38	3·46
Dimedone ethyl ether ...	168	9·12	0·109	339·2	47	3·76

The moments of dimedone and of its ethyl ether are related in an unusual manner. Normally, the moments of alcohols and phenols are greater than those of their ethers. Among the hydroxylic compounds resembling dimedone in this respect may be noted salicylaldehyde ($\mu = 2{\cdot}9$ D.) and *o*-methoxybenzaldehyde ($\mu = 4{\cdot}1$ D.) (Curran, *J. Amer. Chem. Soc.*, 1945, **67**, 1835), quinol and its dimethyl ether (Lander and Svirbely, *J. Amer. Chem. Soc.*, 1945, **67**, 332), and the lower fatty acids and esters (cf. *Trans. Faraday Soc.*, 1934, Appendix).

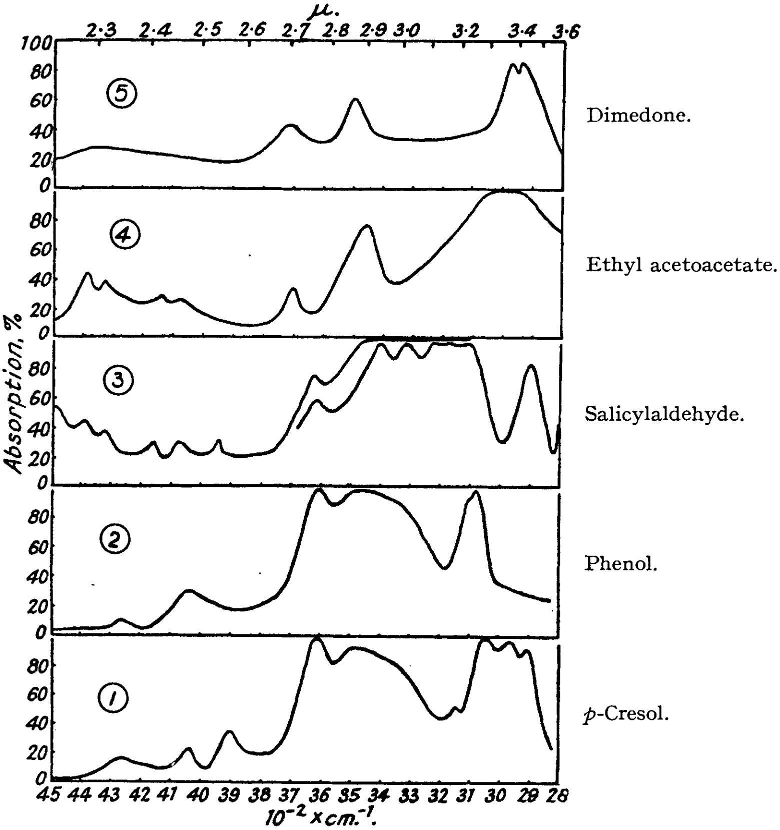
However, there is no extant evidence to suggest that dimedone in dilute benzene solutions is 100% mono-enolised. Since 3 : 3-dimethyl*cyclo*hexanone has $\mu = 2{\cdot}92$ D. (Hassel and Naeshagen, *Z. physikal. Chem.*, 1932, *B*, **19**, 434), dimedone, were it a pure diketone, should, by elementary structural and vectorial considerations, have much the same value. The greater moment now found, *viz.*, 3·5 D., is therefore an *indication* that dissolved dimedone is not entirely in the diketo-form. The mono-enol most probably contains a conjugated system, the effect of which is seen in 3 : 5-dimethyl*cyclo*hex-5-en-1-one ($\mu = 3{\cdot}8$—$4{\cdot}0$ D., compared with 3 : 5-dimethyl*cyclo*hexan-1-one, $\mu = 2{\cdot}9$ D.; Hassel and Naeshagen, *loc. cit.*). Speculation concerning the possible moment of the mono-enol would accordingly be of little use. Nevertheless, that this should be *higher* than μ_{diketo} is plausible, and that it should be *lower* than $\mu_{\text{mono-enol ether}}$ is (see later) understandable.

Infra-red Spectra.—Nearly saturated solutions in carbon tetrachloride of dimedone, ethyl acetoacetate, salicylaldehyde, phenol and *p*-cresol were examined, as described by Anderson, Le Fèvre and Savage (*J.*, 1947, 448). Solvent and solutes were dried and/or redistilled, as appropriate, immediately before use. The plots of absorption against wave-length are reproduced in the figure.

Discussion.—Curves (1) and (2) are in satisfactory agreement with the results of Fox and Martin (*Proc. Roy. Soc.*, 1937, *A*, **162**, 419) and provide " bench marks " for the remaining substances. These authors (*Trans. Faraday Soc.*, 1940, **36**, 897) list the following absorptions to be expected for compounds containing hydroxyl groups : 2·765 μ for monomeric hydroxyl, with a " modification " at 2·776—2·807 μ, 2·865 μ for dimeric hydroxyl, and 2·987—3·006 μ for polymeric hydroxyl. The intramolecular O–H bond in methyl salicylate is prominent at 3·122 μ.

The absorption around the last quoted frequency is intensely shown by our results for salicylaldehyde. It is notably absent with dimedone, as anticipated from our introductory premise (p. 897), and also with ethyl acetoacetate, an observation which is undergoing further investigation.

Bawn (*J.*, 1932, 1189) concluded " that the normal hydroxyl vibration existing in the alcohols is not present in the infra-red spectra of the enolic forms of certain tautomeric compounds ". Ethyl acetoacetate was among the substances examined. He found absorption at 2·9 μ but associated it with the carbonyl group. However, Kohlrausch and Dadieu (*Ber.*, 1930, **63**, 1657; Kohlrausch, " Smekel-Raman Effekt ", Berlin, 1931; *J. Opt. Soc. Amer.*, May, 1931) had previously described the Raman spectrum of ethyl acetoacetate, identified certain shifts with the C═O and C═C linkages, and reported a hydroxyl band at 3380 cm.$^{-1}$ as present although very faint. The last had been undetected by Venkateswaran and Bhagavantam (*Indian J. Physics*, 1930, **5**, 129). For these reasons we have included ethyl acetoacetate as well as dimedone in our figure; both show absorption in the 2·6—3·0 μ region. The weaker band in each case occurs just under 2·70 μ. With dimedone the stronger lies at 2·86—2·87 μ, and with ethyl acetoacetate at 2·89—2·90 μ.



The band at 2·70 μ is somewhat unexpected. Davies (*Trans. Faraday Soc.*, 1940, **36**, 333) reports it also for carbon tetrachloride–chloral hydrate mixtures, but ascribes it to an overtone or combination characteristic of $-CCl_3$. Fox and Martin (*loc. cit.*) note that wet benzyl alcohol absorbs at 2·698 and 2·776 μ, whereas the carefully dried liquid absorbs at the latter wave-length only. It is difficult to be certain that our result is not similarly due to traces of moisture; however, our materials were redistilled immediately before use and the solvent in all five cases had been prepared and stored uniformly. There is no sign of absorption at this point in three of our spectra.

Peaks between 2·8 and 2·9 μ are clearly reconcilable with the presence of hydroxyl—possibly dimeric (cf. Fox and Martin, *loc. cit.*), although carboxylic hydroxyl absorbs at 2·84 μ, the hydroxyl of chloral hydrate at 2·82 μ (Davies, *loc. cit.*), and that of phenol in several solvents at 2·79 and 2·96 μ (Gordy and Nielsen, *J. Chem. Physics*, 1938, **6**, 12). Particularly relevant seem the observations of Buswell, Rodebush, and Whitney (*J. Amer. Chem. Soc.*, 1947, **69**, 770) on certain vinyl alcohols stabilised against enol-keto rearrangement by the steric hindrance of substituent groups. These compounds all showed weak absorption around 2·76 μ (*i.e.*, where monomeric $O-H$ is expected to display itself) and stronger absorption at 2·84 to 2·86 μ. Wulf, Liddel, and Hendricks (*J. Amer. Chem. Soc.*, 1936, **58**, 2287) had earlier found *o*-chlorophenol to absorb at 2·775 and 2·825 μ, while Davies (*loc. cit.*) had similarly reported 2·782 and 2·84 for *o*-bromophenol, and 2·775 and 2·896 for benzoin. These authors explain their results by suggesting that the hydroxyl group can adopt coplanar configurations with respect to its oxygen and the two carbons of the double bond (cf. Pauling, *J. Amer. Chem. Soc.*, 1936, **58**, 94). There are thus two positions for the hydrogen atom. That in which it is more remote from the ethylenic linkage ("*trans*") is identified with the normal frequency 2·76 μ, but this being always the weaker of the two absorptions, the inference is drawn that the *cis*-configuration has, in each case, the lower energy, and, at ordinary temperatures, is therefore the form which predominates.

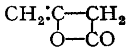
If we may assume that the absorption between 2·86 and 2·87 μ in dimedone corresponds to the longer wave-band for each of the molecules just quoted, a *qualitative* explanation can be provided of our dipole-moment results. The mono-enolic form of dimedone will exist chiefly as "*cis*-enol" in which the $H-O-C$ resultant moment operates to some degree against the $C{=}O$ moment. Ethylation should destroy the factors (? a type of hydrogen-bond formation with $C{=}C$) which stabilise the *cis*-forms, and in many of the infinitude of configurations available to the ethoxy-group during "free" rotation, a resultant $C-O-C$ moment will augment the $C{=}O$ moment.

Dimeric Keten.—When we first read Whiffen and Thompson's paper (*loc. cit*) we suspected that the infra-red spectrum of dimeric keten there reported did not incontrovertibly exclude the participation of (I) in the manner set out by the University College authors (*J.*, 1935, 1751). In particular, we felt that any absorption between the approximate limits 2·9 and 2·7 μ (3440 and 3700 cm.$^{-1}$), even if weak, might be evidence of hydroxyl. Two such bands (at 3370 and 3620 cm.$^{-1}$) *were* listed (Whiffen and Thompson, *loc. cit.*, p. 1007), as "very weak bands . . . much more reasonably interpreted as overtones and combinations". Further, Whiffen and Thompson also noted that the absorptions at 1865 and 1895, and 1685 and 1705 cm.$^{-1}$ varied in relative intensity in different solvents. In the discussion, these frequencies were associated with $C{=}O$ and $C{=}C$ stretching vibrations. Now, Meyer with Kappelmeier (*Ber.*, 1911, **44**, 2718; 1912, **45**, 2852) and Schoeller (*Ber.*, 1920, **53**, 1410) had demonstrated the marked sensitivity to solvents of keto-enol equilibria, and if dimeric keten contained the $\cdot CH_2\cdot CO\cdot$ unit, replacement of chloroform as a medium by carbon tetrachloride, would, by analogy, probably increase the percentage of enol, and thus cause change in the appropriate intensities.

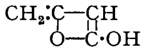
However, in view of the definite absorptions now observed with two authentic keto-enolic substances, we are inclined to concur with Whiffen and Thompson's explanation of the bands at 3370 and 3620 cm.$^{-1}$ and to agree that their work dismisses formula (I).

Since our experiments were concluded, we have had the advantage of perusing the MS. of a recent paper by Dr. A. Wassermann (*J.*, 1948, 1323) on the acidity of dimeric keten. He concludes

(IV.)



$CH_2{:}C-CH_2$, $O-CO$



$CH_2{:}C-CH$, $O-C\cdot OH$

(V.)

that (IV) $\rightleftharpoons$ (V), with the equilibrium normally much in favour of (IV), provides a satisfactory formulation, which is additionally congruent with extant dipole moment as well as spectrographic evidence.

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