

Absorption Spectra of 1,1-Diacylcyclopropanes and β -Diketones Substituted with Alkyls and Aralkyls Containing Chloromercuri Group

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Ultra-violet and infrared absorption spectra of β -diketones substituted with β -chloromercuriethyl, β -chloromercuri- α -methylethyl and β -chloromercuri- α -phenylethyl groups were determined and compared with those of the corresponding compounds without chloromercuri group. U. v. absorptions of the mercury compounds showed a common peak at 240 m μ . Except this point, no remarkable difference was observed in between u. v. absorptions of substituted β -diketones with and without chloromercuri group. The infrared spectra of the compounds substituted with chloromercuri group were almost identical with those of the corresponding compounds without this substituent, except in the case of (β -chloromercuriethyl) acetylacetone, in the wave number region of 4000-700 cm⁻¹. (β -Chloromercuriethyl)acetylacetone showed a broad and strong peak with a maximum at 1580 cm⁻¹ and no appreciable absorption at 1700 cm⁻¹ region due to carbonyl group. As a special type of substituted β -diketone, u. v. and i. r. spectra of 1,1-diacylcyclopropanes were determined. From these data, it is concluded that the cyclopropane ring and the two carbonyl groups attached to the same ring carbon do not form a cross conjugated system, but one conjugated system as a whole.

INTRODUCTION

In the authors' laboratory, β -diketones substituted with alkyls and aralkyls containing chloromercuri group have been prepared by the reaction of oxymercurials derived from olefins with β -diketones. Demercuration of these mercurials with base gave 1,1-diacylcyclopropanes which are also special types of substituted β -diketone¹⁾. It is desirable to compare the ultra-violet and infrared absorption spectra of these new types of compounds with those of usual substituted β -diketones.

Although many papers dealing with the spectral data of the usual β -diketones have been published already and discussed in many textbooks, only few data are available for ultra-violet absorption in the wave length range shorter than 200 m μ . Therefore, these spectra of typical substituted β -diketones have been determined, reexamined and shown in Table 1 together with those of the new compounds mentioned above.

β -Diketone derivatives show two major absorption bands at about 193-210 and 270-300 m μ . In the literature published so far, the discussions have been limited to those of the latter band. On the ultra-violet absorption of monoketone in the wave length range shorter than 200 m μ , McMurry²⁾ and Holdsworth *et al.*³⁾ reported that the absorption at 192-197 m μ is due to $n \rightarrow \sigma^*$ transition, and the maxima shift to longer wave lengths slightly as the substituents are changed from hydrogen to

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Table 1. Ultra-violet absorption of β -diketone.^a

	$\lambda_{\max}$ m μ	log ϵ	Solvent
CH ₃ COCH ₂ COCH ₃	193.5 272	2.93 3.99	Hexane
	202 274	2.76 3.98	Ethanol
CH ₃ COCHCOCH ₃ CH ₃	192.5 194.5 290	3.03 3.09 3.48	Hexane
	204–205.5 286–290	2.77–2.85 3.48–3.53	Ethanol
CH ₃ CH ₃ COCCOCH ₃ CH ₃	190 192.5 195 $\pm$ 1 202–6 (sh) 292 $\pm$ 1	Ca. 3.0 3.00 3.18–3.30 2.9 $\pm$ 0.1 2.43	Hexane
	207.5 290	2.83 2.45	Ethanol
CH ₃ COCHCOCH ₃ CH ₂ CH ₃	192.3 193.8 291 $\pm$ 1	2.60 2.56 2.64	Hexane
	205.5 292	2.90 3.36	Ethanol
CH ₃ COCHCOCH ₃ CH ₂ CH ₂ CH ₃	193 291–292	3.48 3.48–3.51	Hexane
	204 294	2.85 3.34	Ethanol
CH ₃ COCHCOCH ₃ CH ₃ CHCH ₃	192.5 194.5 298	3.14 3.07 2.34	Hexane
	207.7 $\pm$ 1 298	3.00 2.37	Ethanol
C ₆ H ₅ COCHCOCH ₃ ^b CH ₃	228 309	3.65 4.09	Enol form in ethanol
	247 284 310	4.06 3.18 2.30	Keto form in ethanol
C ₆ H ₅ COCHCOCH ₃ C ₆ H ₅ CHCH ₃	190 192.5 194 202–204 (sh) 250	Ca. 4.0 4.29 Ca. 4.0 3.76	Hexane
HgCl ₂	236	2.43	Chloroform
CH ₃ CH ₂ HgCl	240	2.68	Chloroform
CH ₃ COCH ₂ CH ₂ CH ₂ HgCl	240 283	1.82 1.64	Chloroform
p-MeOC ₆ H ₄ CH ₂ CH ₂ HgCl	240.5 279 (sh)	>3.0	Chloroform
CH ₃ COCHCOCH ₃ CH ₂ CH ₂ HgCl	240 293	3.40 3.84	Chloroform
CH ₃ COCHCOCH ₃ CH ₃ CHCH ₂ HgCl	238–240 296	2.03 2.30	Chloroform
CH ₃ COCHCOCH ₃ C ₆ H ₅ CHCH ₂ HgCl	240.5 296	2.76 2.31	Chloroform
CH ₃ COCHCOCH ₃ C ₆ H ₅ CHCH ₂ HgI	241.5 304 (sh)	2.51	Chloroform
CH ₃ COCHCOCH ₃ C ₆ H ₅ CHCH ₂ HgOAc	241 294 (sh)	3.08 2.48	Chloroform

Spectra of Substituted Cyclopropanes & β -Diketones

$\text{C}_6\text{H}_5\text{CH}_2\text{HgBr}$	$\begin{cases} 240 \text{ (sh)} \\ 257 \end{cases}$	4.25	Chloroform
$\text{C}_6\text{H}_5\text{COCH}_2\text{CH}_2\text{CH}_2\text{HgCl}$	$\begin{cases} 240 \text{ (sh)} \\ 245.5 \end{cases}$	4.13	Chloroform
$\text{C}_6\text{H}_5\text{COCHCOCH}_3$ $\text{CH}_2\text{CH}_2\text{HgCl}$	$\begin{cases} 240 \text{ (sh)} \\ 252 \end{cases}$	4.23	Chloroform
$\text{C}_6\text{H}_5\text{COCHCOCH}_3$ $\text{C}_6\text{H}_5\text{CHCH}_2\text{HgCl}$	$\begin{cases} 240 \text{ (sh)} \\ 255 \end{cases}$	4.19	Chloroform
$\text{C}_6\text{H}_5\text{COCHCO}_2\text{C}_2\text{H}_5$ $\text{C}_6\text{H}_5\text{CHCH}_2\text{HgCl}$	$\begin{cases} 240 \text{ (sh)} \\ 252 \end{cases}$	3.21	Chloroform

^a Absorption maxima due to benzenoid structure are not listed.

^b R. A. Morton, A. Hassan and T. C. Calloway, *J. Chem. Soc.*, 1934, 883.

methyl, ethyl and isopropyl group. The absorption of β -diketone in the shorter wave lengths listed in Table 1 appears to be assigned to the same $n \rightarrow \sigma^*$ transition. In hexane solvent, the maxima are observed at about $193 \text{ m}\mu$, and no systematic shift cannot be recognized by the change of the substituents. In ethanol solvent, however, the same tendency in the absorption maximum shift as in the case of monoketone is observed. The red shift in the more polar ethanol is also in accord with the general tendency in $n \rightarrow \sigma^*$ transition.

The absorption at longer wave lengths is considered to be related to the α, β -unsaturated carbonyl system of enol form of β -diketone. In connection with keto-enol equilibria, this problem has been discussed in many books⁴⁾. On the shift of ultra-violet absorption maxima in α, β -unsaturated carbonyl system, it is well known that Woodward's rule is applicable successfully. However, no relationship between the structure of the substituents and the shift of absorption maxima in β -diketone system has been discussed so far. Recently, Closson and Haug reported that a linear relationship is observed in between Taft's σ^* and the transition energy calculated from the wave length of the absorption maximum by equation $E = h\nu =$

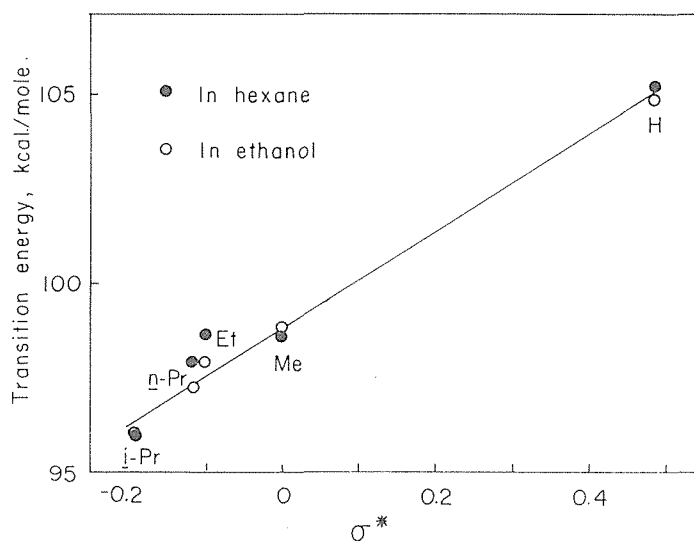


Fig. 1. Relationship between transition energy and σ^* .

2.859 $\bar{\nu}$ in alkyl ester system⁵³. Analogous plots have been made with the data in Table 1 and illustrated in Figure 1. Although the number of the point is limited, fairly good linear relationship is obtained with data in both hexane and ethanol.

In the case of dimethylacetylacetone, enolization is impossible. Therefore, the absorption with a maximum at 292 $m\mu$ has to be considered to be due to the carbonyl group which is not conjugated with carbon-carbon double bond. The reasons, why the maximum is observed in such a longer wave length region as compared with the usual one (for example, 273 $m\mu$ in acetone) and the intensity is so high, are not yet clear. An example of high intensity of this band of unenolizable β -diketone can be found in the case of 2,2,5,5-tetramethyl-cyclohexa-1,3-dione ($\log \epsilon = 2.4$ at $\lambda_{\max}$ 274 $m\mu$)⁶³.

The ultra-violet spectra of the mercury compounds have been determined in chloroform, because of the low solubilities of these compounds in hexane and ethanol. Accordingly, the spectra in the wave length region shorter than 230 $m\mu$ could not be obtained. Data are listed in Table 1.

With all of the mercurials including those that contain no carbonyl group and are listed in the same table for a convenience of comparison, a common absorption maximum was observed at 240 $m\mu$. Changing the acid radicals attached to mercury, no shift of this band was observed. These facts appear to show that this absorption could be assigned to that of carbon-mercury bond. To conclude this definitely, however, further study is required, because mercuric chloride shows an absorption at 236 $m\mu$ in chloroform. The 240 $m\mu$ band of (β -chloromercuriethyl)acetylacetone disappeared in the other solvents such as methanol, ethanol and isopropanol. Although it was not confirmed that the same phenomena could be observed with the other mercurials because of the low solubilities in the alcohols, this makes it doubtful that this absorption is due to carbon-mercury bond. Another possibility of assignment of this band is that to the metal chelate formation by β -diketone system. It is reported that various metal chelates show absorptions at about this wave length range of 240-260 $m\mu$ ⁷³. However, there has been no report on the chelate compound between mercuric chloride and acetylacetone. Several attempts to prepare this chelate in this laboratory were also unsuccessful. Further, the fact that this absorption can be observed even in the mercurials containing no carbonyl group is difficult to explain. The intensity of this band in the case of ethylmercuric chloride was not increased by the addition of acetylacetone. Thus, at present, it is difficult to determine the origin of this absorption. In the case of (β -chloromercuriethyl) acetylacetone, the intensity of this absorption is much stronger than in the other cases. No reasonable explanation is available.

Except this 240 $m\mu$ absorption, the other absorption maxima of the mercurials were observed at the same wave lengths as in the corresponding β -diketones without chloromercuri group. However, the intensities are stronger in the compounds containing mercury. This enhancement of absorption is observed in the mercurials containing no carbonyl group similarly.

With (β -chloromercuriethyl) acetylacetone, the effects of solvent on the absorption were examined and the data are listed in the following table.

Spectra of Substituted Cyclopropanes & β -Diketones

Solvent	$\lambda_{\max}$	$\log \epsilon$
Acetic acid containing 7.5% water	296	3.76
Methanol	204	3.93
	294	3.31
Ethanol	204	3.30
	293	3.08
Isoprpanol	204	4.12
	294	3.91

No remarkable effect can be recognized except that the intensities in ethanol solvent are considerably weaker than in the other solvents.

Except for the case of (β -chloromercuriethyl)acetylacetone, no difference in infrared spectra was observed in between the substituted β -diketones with and without chloromercuri group in the wave number range of 4000-700 cm^{-1} . The spectra of (β -chloromercuriethyl)acetylacetone are entirely different from those of corresponding ethylacetylacetone. Absorptions at 1720-1700 cm^{-1} region, due to carbonyl group in the latter, disappeared almost completely and a broad and strong absorption with its maximum at 1580 cm^{-1} appeared in the latter. In Figure 2, the spectra of this mercurial together with those of (β -chloromercuri- α -phenylethyl)-acetylacetone are shown for a convenience of comparison. This unusual absorption was not observed in the cases of the other mercurials. Combined with the characteristic ultra-violet absorption of this compound mentioned in the earlier part of this paper, special type of configuration should be considered for this mercurial.

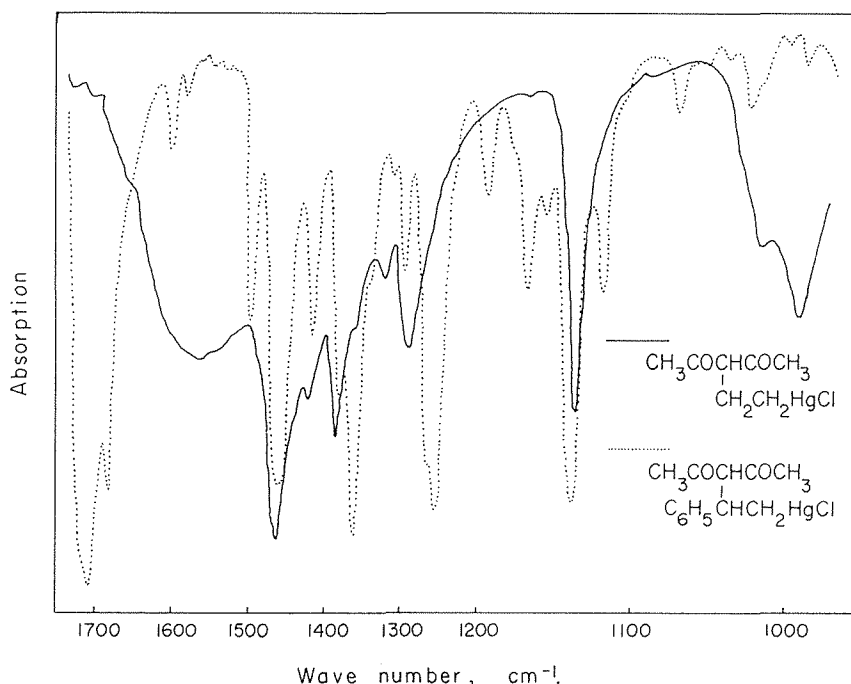


Fig. 2. Infrared spectra of (β -chloromercuriethyl)acetylacetone and its phenyl derivative.

Infrared absorption of metal chelates of β -diketone, for example, in the case of mercuric chloride chelate with benzoylacetone, shows rather sharp three peaks at 1605, 1570 and 1550 cm^{-1} and is entirely different from those mentioned above. Instead, the shape of the peak is similar to that of enol form of β -diketone. It is most likely that this compound exists as enol form and gave such an infrared absorption. Usually, substitution with alkyl group results in the decrease of enol content of acetylacetone, and the absorption at this region in ethylacetylacetone is much weaker than in the case above. It appears, therefore, that substitution of β -position of ethyl group in ethylacetylacetone with chloromercuri group results in a remarkable increase of enol content, although no reasonable explanation for it is available at present.

Data of absorption maxima due to carbonyl group are shown in Table 2.

1,1-Diacetylcyclopropane is a special type of substituted β -diketone, but not form the enol. The spectra of this compound are interesting in connection with the problem on the conjugation of cyclopropane ring with carbonyl group. Ultra-violet spectra were determined and shown in Table 3.

Considerable amounts of evidence to show the conjugation between cyclopropane ring and carbonyl group have been accumulated⁹. 1,1-Diacetylcyclopropane system provides a new material for the problem, because two carbonyl groups are attached to the same ring carbon here.

As is shown in Table 3, the absorption maximum of 1,1-diacetylcyclopropane due to $n \rightarrow \pi^*$ is observed at 285 $\text{m}\mu$ (in hexane) which is shifted to a longer wave length from that of acetylcyclopropane (277 $\text{m}\mu$ in isooctane⁹). The intensity is also much stronger in the diacetyl derivative. This clearly shows that the conjuga-

Table 2. Infrared absorption maxima due to carbonyl group in various substituted β -diketones.

Compound	cm^{-1}	Compound	cm^{-1}
		$\text{CH}_3\text{COCH}_2\text{COCH}_3$	1720 1700 1640—1540 (chelate ring)
		$\text{C}_6\text{H}_5\text{COCH}_2\text{COCH}_3$	1640—1580 (chelate ring)
		$\text{C}_6\text{H}_5\text{COCH}_2\text{CO}_2\text{C}_2\text{H}_5$	1730 1678 1630—1605 weak
$\text{CH}_3\text{COCHCOCH}_3$ $\text{CH}_2\text{CH}_2\text{HgCl}$	Broad and strong peak at 1580	$\text{CH}_3\text{COCHCOCH}_3$ CH_2CH_3	1730 1710 Broad peak at 1600
$\text{CH}_3\text{COCHCOCH}_3$ $\text{CH}_3\text{CHCH}_2\text{HgCl}$	1720 1698	$\text{CH}_3\text{COCHCOCH}_3$ CH_3CHCH_3	1718 1698 1685 (sh)
$\text{CH}_3\text{COCHCOCH}_3$ $\text{C}_6\text{H}_5\text{CHCH}_2\text{HgCl}$	1706 1670	$\text{CH}_3\text{COCHCOCH}_3$ $\text{C}_6\text{H}_5\text{CHCH}_3$	1710 1685
$\text{C}_6\text{H}_5\text{COCHCOCH}_3$ $\text{CH}_2\text{CH}_2\text{HgCl}$	1700 1670		
$\text{C}_6\text{H}_5\text{COCHCOCH}_3$ $\text{C}_6\text{H}_5\text{CHCH}_2\text{HgCl}$	1720 1670	$\text{C}_6\text{H}_5\text{COCHCOCH}_3$ $\text{C}_6\text{H}_5\text{CHCH}_3$	1725 1675
$\text{C}_6\text{H}_5\text{COCHCO}_2\text{C}_2\text{H}_5$ $\text{C}_6\text{H}_5\text{CHCH}_2\text{HgCl}$	1720 1670		

Table 3. Ultra-violet absorption of 1,1-diacetylcyclopropane.

Cyclopropane	$\lambda_{\max}$ m μ	log ϵ	Solvent
1,1-Diacetyl-	216	2.18	Hexane
	285	1.69	
	206	2.21	Ethanol
	275-276	2.34	
	205	>3.2	Water
	276	2.05	
1,1-Diacetyl- 2-methyl-	195 $\pm$ 0.5	3.67	Hexane
	268 $\pm$ 1	2.80	
	203	2.54	Ethanol
	278	2.84	
	190	3.67	Water
	282	2.72	
1-Acetyl- 1-benzoyl-	214	3.67	Hexane
	244	4.09	
	290	3.33	
	306	3.30	
	203.5	3.32	Ethanol
	246	4.03	
	278	2.34	
	304	3.33	

tion is much stronger in the diacyl system than in the mono acyl system. The shift of the maximum due to $n \rightarrow \sigma^*$ from 187.8 (in acetylcyclopropane) to 216 m μ (in diacetylcyclopropane) also supports this conclusion.

According to Calvin's definition¹⁰, 1,1-diacetylcyclopropane belongs to a "cross conjugated system". In this system, the absorption maximum should be observed at the same wave length as that of the independent conjugate system. Therefore, if 1,1-diacetylcyclopropane belongs to this system, the shift mentioned above is difficult to explain. The two carbonyl groups and cyclopropane ring should form one conjugate system as a whole. The molecular structure which is consistent with this conclusion can be attained by the geometrical configuration that the two carbonyl groups exist in the plane perpendicular to that of cyclopropane ring.

Infrared spectra are also consistent with this conclusion. The absorption maximum at 1690 cm⁻¹ in diacetylcyclopropane due to carbonyl is in longer wave length region than 1704 cm⁻¹ in acetylcyclopropane.

The maxima in ultra-violet absorption in 1,1-diacetyl-2-methylcyclopropane are observed in much shorter wave lengths as compared with those of 1,1-diacetylcyclopropane. It appears that the methyl substitution at the other ring carbon inhibit the conjugation by steric effect. Even usual type of conjugation between carbonyl and cyclopropane appears to be lost in this system. This is consistent with the chemical property of this compound that its thermal stability is much less than that of 1,1-diacetylcyclopropane¹.

EXPERIMENTAL

Materials. The preparation of the compounds used is reported in reference 1. Commercial spectro-grade solvents were used without further purification.

Spectral measurements. Ultra-violet spectra were determined by HITACHI EPS-2U. Infrared spectra were obtained by JASCO IR-S.

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