

## Chemical and Spectral Behavior of Substituted $\beta$ -Diketones in Concentrated Sulfuric Acid

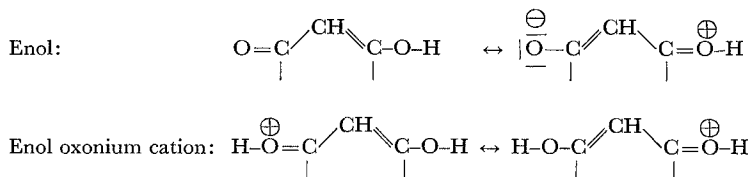
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U.v. spectra of substituted  $\beta$ -diketones, including 1,1-diacetylcyclopropanes, have been determined in concentrated sulfuric acid. Four types of spectral change in course of time were observed. I). Absorption maxima of methyl-, ethyl- and *n*-propyl-acetylacetone remained unchanged for three days, and  $\epsilon_{\max}$  decreased gradually. II). Absorption maximum of isopropylacetylacetone shifted to shorter wave length region with a slight increase of  $\epsilon_{\max}$  in 20 hrs. After this period,  $\lambda_{\max}$  remained unchanged and  $\epsilon_{\max}$  decreased gradually. III). The spectra of propenyl- and allyl-acetylacetone and 1,1-diacetyl-2-methylcyclopropane were identical even when the measurements were made just after the solutions were prepared, and were identical with those of 3-acetyl-2,5-dimethyl-4,5-dihydrofuran. IV). Absorption maxima of ( $\beta$ -acetoxyethyl)-acetylacetone and 1,1-diacetylcyclopropane shifted to longer wave length region gradually and approached to  $\lambda_{\max}$  of 3-acetyl-2-methyl-4,5-dihydrofuran, and only slight decrease of  $\epsilon_{\max}$  were observed. These spectral changes show a slow deacetylation (type I), de-isopropylation with subsequent decomposition (type II), and fast (type III) and slow dihydrofuran formation (type IV) respectively.

Many papers have been published on the ultraviolet absorption spectra of  $\beta$ -diketones concerning their keto-enol equilibria<sup>1)</sup>. Recently Yoffe and co-workers reported the u. v. spectra of  $\alpha$ -substituted  $\beta$ -diketones in organic solvents<sup>2)</sup>. In a previous paper, the present authors also reported those of the  $\beta$ -diketones substituted with chloromercuri-alkyls and -aralkyls and of the non-enolizable  $\beta$ -diketones including 1,1-diacetylcyclopropanes as the special case<sup>3)</sup>. As a part of the study on the basicity of  $\beta$ -diketone, Eistert and co-workers reported that  $\lambda_{\max}$  of oxonium ions which were formed from  $\beta$ -diketones by protonation in concentrated sulfuric acid shifted to longer wave lengths as compared with those of unprotonated enols in organic solvents. This is because of the lower excitation energy due to the more symmetrical resonance hybrid forms of the oxonium ions than those of the corresponding enols<sup>4)</sup>.



In order to investigate the effects of strong acid on the the absorption spectra and chemical behavior of  $\alpha$ -substituted  $\beta$ -diketones including 1,1-diacetylcyclopropanes, u. v. spectra of these compounds have been determined in concentrated sulfuric acid.

All of the discussion described below is concerned with the oxonium ions formed by protonation on carbonyl oxygen, if not mentioned otherwise, because  $\beta$ -diketones

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in concentrated sulfuric acid exist in this form according to Eistert's conclusion.

U. v. spectra of most of the  $\beta$ -diketones studied here changed in both  $\lambda_{\max}$  and  $\epsilon_{\max}$  in course of time after the sulfuric acid solutions were prepared for the spectral measurements. Four types of spectral change were observed.

Type I. Values of  $\lambda_{\max}$  of methyl- (**II**), ethyl- (**III**) and *n*-propyl-acetylacetone (**IV**) remained unchanged even after 60 hrs., and  $\epsilon_{\max}$  decreased gradually.

Type II. In the case of isopropyl-acetylacetone (**V**),  $\lambda_{\max}$  (307  $m\mu$ ) shifted to a shorter wave length (288  $m\mu$ ) after 20 hrs., while  $\epsilon_{\max}$  increased slightly. After this period,  $\lambda_{\max}$  remained unchanged and  $\epsilon_{\max}$  decreased gradually. The value of  $\lambda_{\max}$  288  $m\mu$  is the same with that of acetylacetone.

Type III. The spectra of propenyl- (**IX**), allyl-acetylacetone (**X**) and 1,1-diacetyl-2-methylcyclopropane (**XII**) showed absorption maxima at the same wave length of 312  $m\mu$ . As is mentioned later, these  $\lambda_{\max}$  cannot be assigned to those of the starting compounds. It seems likely that these diketones form a same product in sulfuric acid rapidly.

Type IV. The spectra of ( $\beta$ -acetoxyethyl)-acetylacetone (**VIII**) and 1,1-diacetylcyclopropane (**XI**) changed gradually in both  $\lambda_{\max}$  and  $\epsilon_{\max}$ , and approached to those of 3-acetyl-2-methyl-4,5-dihydrofuran.

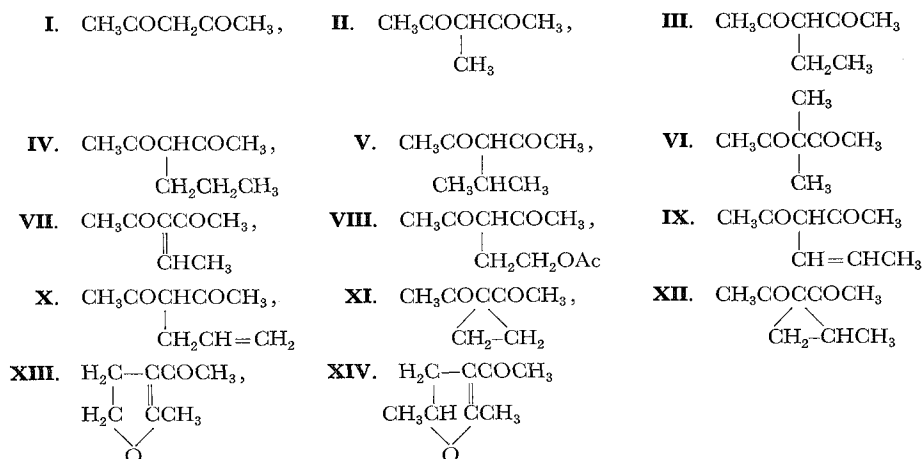
Data obtained are listed in Table 1.

Table 1. U. v. absorption spectra of substituted  $\beta$ -diketones and dihydrofurans in concentrated sulfuric acid.

Time <sup>a)</sup>	5-8 min.		20 hrs.		40-50 hrs.		60 hrs.	
	$\lambda_{\max}$	$\log \epsilon$	$\lambda_{\max}$	$\log \epsilon$	$\lambda_{\max}$	$\log \epsilon$	$\lambda_{\max}$	$\log \epsilon$
<b>I</b>	288	4.18						
<b>II</b>	306	4.10						
<b>III</b>	307	4.15	307	3.83	307	3.55		
<b>IV</b>	308	4.18						
<b>V</b>	307	3.64	288	3.75	288	3.64	288	3.38
<b>VI</b>	303	3.06			303	1.54		
	85% acid							
	305	3.16	305	3.15	305	3.15		
	65% acid							
	305	2.86	305	2.71			305	2.49
	55% acid							
	303	2.40	303	2.24			303	1.90
<b>VII</b>	252	3.92						
	298	3.52						
<b>VIII</b>	297	4.16	308	4.10			312	4.08
<b>IX</b>	313	4.16						
<b>X</b>	313	4.20						
<b>XI</b>	299	4.25	303	4.19	309	4.10	313	4.06
<b>XII</b>	313	4.13					(150 hrs.)	
<b>XIII</b>	312	4.13						
<b>XIV</b>	311	4.19						

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Table 1. (continued)



a) Time interval between the preparation of the solution and the spectral measurement.

The spectral behavior of type I is similar to that of unsubstituted acetylacetone reported by Eistert. This appears to show the destruction of  $\beta$ -diketo skeleton, probably by deacetylation. An example of time-spectra relation is shown in fig. 1. Since preparative experiments showed that these compounds could be recovered from the solutions in fairly good yields, the spectra of earlier measurements can be assigned to those of the  $\beta$ -diketones.

The change of the spectra of **V** (type II, shown in fig. 2) makes a sharp contrast to that of type I. The shift of  $\lambda_{\text{max}}$  to  $288 \text{ m}\mu$  with a slight increase of  $\epsilon_{\text{max}}$  shows a conversion to a product without losing  $\beta$ -diketo skeleton. Since acetylacetone is the only possible  $\beta$ -diketone which shows absorption maximum at  $288 \text{ m}\mu$ , it can be concluded that dealkylation of **V** to form acetylacetone proceeds first, and then the decomposition of  $\beta$ -diketone follows. Since the more facile splitting of isopropyl group than normal alkyl groups is recognized widely in aromatic compounds, there is no reason why the same tendency cannot be expected in the case of substituted  $\beta$ -diketones.

The spectra of **IX**, **X** and **XII** were identical even when the measurements were made as soon as the solutions were prepared, and it seems likely that these three compounds react rapidly to form the same compound in sulfuric acid. Preparative experiments proved that this is the case. When the sulfuric acid solutions of these compounds were diluted with water half an hour after preparing the solution, and extracted with ether, 3-acetyl-2,5-dimethyl-4,5-dihydrofuran (**XIV**) was obtained in all cases. It is clear that **IX**, **X** and **XII** form **XIV** rapidly in concentrated sulfuric acid and the spectra observed are those of **XIV**. This was reconfirmed by the fact that the spectra of **XIV** which was separated and redissolved were identical with those of **IX**, **X** and **XII** in both  $\lambda_{\text{max}}$  and  $\epsilon_{\text{max}}$ . It appears that **XIV** is formed from **IX** and **X** through protonation to the double bonds leading to a common secondary carbonium ion and subsequent intramolecular O-alkylation. **XII** appears to form the same carbonium ion by ring opening.

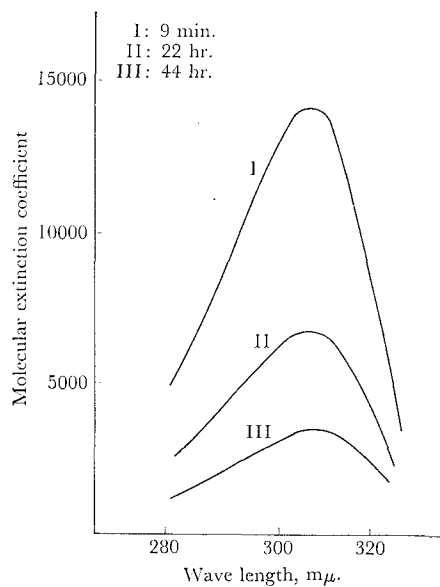


Fig. 1. U. v. spectra of ethylacetylacetone in sulfuric acid.

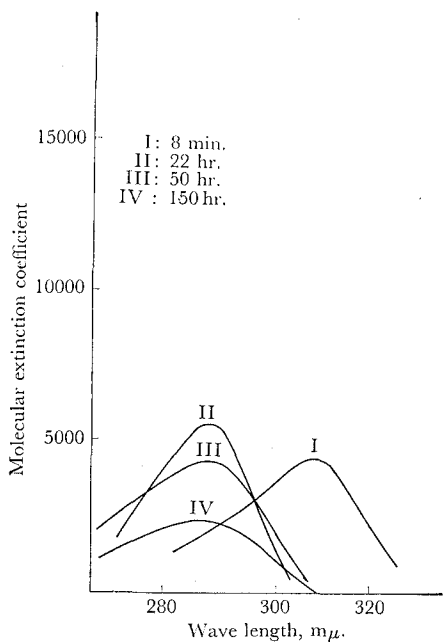


Fig. 2. U. v. spectra of isopropylacetylacetone in sulfuric acid.

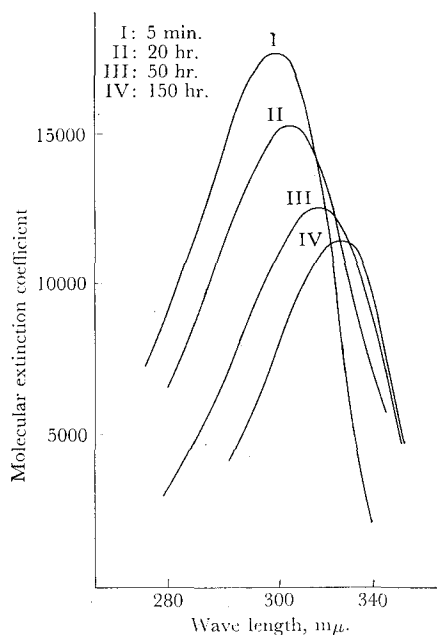
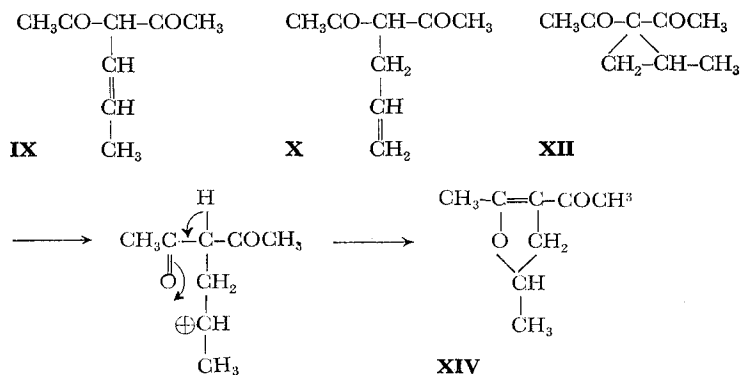
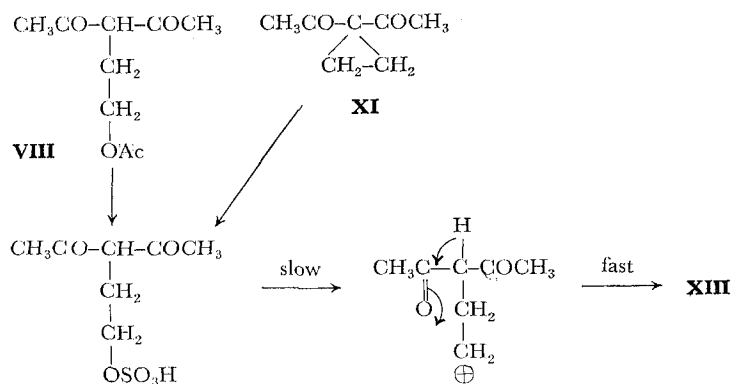


Fig. 3. U. V. spectra of 1,1-diacetylcyclopropane in sulfuric acid.

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Sulfuric acid solutions of **VIII** and **XI** gave 3-acetyl-2-methyl-4,5-dihydrofuran (**XIII**), when diluted with water and extracted with ether, as in the case mentioned above. On the other hand, the spectra of **VIII** and **XI** in the earlier stage of the measurement apparently differed from those of **XIII**. This phenomenon can be explained by the following mechanism. The compounds, **VIII** and **XI** react first to



form the common sulfate, from which carbonium ion is formed and gives **XIII**. In contrast to the case of the formation of **XIV**, the intermediate carbonium ion is primary and its formation is much slower than that of secondary one. Therefore, the rate of formation of **XIII** is much slower and this reflects to the slow spectral change. The spectra observed in the early stage of the measurements can be assigned to those of the sulfate. In the case of preparative experiments, the concentrations are much higher than those of spectral measurements, and it is not surprising that the dihydrofuran was obtained at only 30 minutes after the compounds were dissolved in sulfuric acid.

Dimethyl-acetylacetone (**VI**) is a non-enolizable  $\beta$ -diketone. Therefore, the absorption observed at  $292 \text{ m}\mu$  in hexane<sup>3)</sup> is not due to  $\pi \rightarrow \pi^*$  transition as in the cases of other  $\beta$ -diketones, but to  $n \rightarrow \pi^*$  transition of carbonyl group. Since this transition is "prohibited" one, the value of  $\log \epsilon = 2.43$  is unusually large. The same phenomena were observed in sulfuric acid solutions, and the higher the concentration of sulfuric acid was, the larger the value of  $\log \epsilon$  was. The reason of these

results is not easy to explain and will be studied in future.

The spectral change of **VI** belongs to type I. The rate of decrease of  $\epsilon$  was the fastest in 95% acid. When the acid concentration was 85%, the rate was the slowest. This suggests that two different mechanisms of the decomposition of **VI** are operative in the concentration ranges of higher and lower than 85% respectively.

Ethylidene-acetylacetone (**VII**) showed two absorption maxima which might be due to cis- and trans- $\alpha,\beta$ -unsaturated carbonyl group. Definite assignment, however, requires further investigation.

From the results mentioned above, it is clear that careful consideration is required to discuss the u.v. spectra of  $\beta$ -diketones in sulfuric acid. For example, the spectra which were obtained with **IX**, **X** and **XII** do not tell anything about the spectra of these diketones themselves. In the cases of **I**, **II**, **III**, **IV**, **V** and **VI**, the spectra obtained are those of the oxonium ions which are formed by protonation on oxygen of carbonyl, if data of early stage of measurements are used. Concerning the effects of alkyl-substituent on the spectra, it can be concluded that alkyl substitutions at  $\alpha$ -carbon of acetylacetone shift the absorption maximum to longer wave length region by  $19 \pm 1$   $m\mu$ . The shifts were independent of the structure of the alkyl group in **I-V**.

Finally, it must be mentioned on the discrepancy between the spectral data of isopropylacetylacetone by Yoffe and co-workers and by ourselves. In hexane solution, Yoffe gave  $\lambda_{\max} = 251$   $m\mu$  and  $\epsilon = 3600$ . According to our experiments,  $\lambda_{\max}$  and  $\epsilon$  were 298  $m\mu$  and 244 respectively. Yoffe's data show that appreciable amount of enol form must exist in hexane solution. Our careful examination by infrared spectroscopy and by n. m. r. in deuteriochloroform solution could not detect the presence of enol form. We believe that our data are correct.

## EXPERIMENTAL

**Material.** Commercial sulfuric acid (analytical grade, 95%) was used for the

Table 2.  $\beta$ -Diketones used for u. v. spectra measurement.

	Boiling point, °C/mmHg		Refractive index (20°)	
<b>II</b>	75- 78/26	reported 86/ 60 <sup>1)</sup>	1.4421	reported 1.4420 <sup>1)</sup>
<b>III</b>	80- 82/20	83- 85/35 <sup>1)</sup>		1.4415 <sup>1)</sup>
<b>IV</b>	93- 95/25	87- 89/17 <sup>1)</sup>		1.4463 <sup>1)</sup>
<b>V</b>	77- 80/19	82- 83/20 <sup>1)</sup>		1.4420 <sup>1)</sup>
<b>VI</b>	79/27	54/8 <sup>1)</sup>	1.4299	1.4311 <sup>1)</sup>
<b>VII</b>	100-112/22	44- 45/0.04 <sup>2)</sup>		1.4608 (25°) <sup>2)</sup>
<b>VIII</b>	113-115/ 5	107-108/ 2.5 <sup>3)</sup>	1.4597	
<b>IX</b>	82- 90/16	82/14 <sup>4)</sup>		1.4875 (25°) <sup>4)</sup>
<b>X</b>	190-225	195-196 <sup>5)</sup>		

<sup>1)</sup> S. T. Yoffe, E. M. Popov, K. V. Vatsuro, E. K. Tulikova and M. T. Kabachink, *Tetrahedron*, **18**, 923 (1962).

<sup>2)</sup> B. D. Wilson, *J. Org. Chem.*, **28**, 314 (1963).

<sup>3)</sup> H. Henecka, *Chem. Ber.*, **81**, 179 (1948).

<sup>4)</sup> M. E. McEntee and A.R. Pinder, *J. Chem. Soc.*, 4419 (1957).

<sup>5)</sup> I. P. English, *J. Am. Chem. Soc.*, **68**, 453 (1946).

experiments. Acetylacetone was also a commercial product and used after careful distillation. Substituted  $\beta$ -diketones, **II**, **III**, **VI**, **VII**, **VIII**, **IX** and **X** were prepared by the methods that were reported in the literature and listed in table 2. By hydrogenation of **IX** with platinumblack catalyst, **IV** was prepared. The preparation of **V** (borohydride reduction of 3,3-diacetyl-2-methyl-propylmercuric chloride), **XI** and **XII** was reported in a previous paper. By gas-chromatography, it was confirmed that all these samples except **VII** contained no detectable amounts of impurities. Despite careful distillations, **VII** contained unknown impurity of less than 2%.

**Spectral measurement.** According to usual method, spectra were determined by HITACHI EPS-2U.

**Recovery of  $\beta$ -diketones from sulfuric acid solution.** The experimental procedure is the same as that of isolation of **XIII** that is described below. The yields of recovery were 50, 60, 60 and 20% in the cases of **I**, **IV**, **VI** and **VIII** respectively. By gaschromatography, it was confirmed that the recovered ones were the same with the original samples.

**3-Acetyl-2-methyl-4,5-dihydrofuran (XIII).** 1,1-Diacetyl-cyclopropane (5.0 g.) was dissolved into 20 ml. of sulfuric acid (commercial, analytical grade, 95%). After standing for half an hour, the solution was added with 100 ml. of water, and extracted with 70 ml. of ether five times and then with 70 ml. of benzene three times. The ether- and benzene-extracts were combined together respectively and washed with aqueous saturated sodium bicarbonate. The water layer was neutralized with dilute aqueous sodium hydroxide solution and then extracted with 70 ml. of ether five times and then with 70 ml. of benzene three times. The ether and benzene extracts were combined together respectively and dried with sodium sulfate. Distillation of the ether extract gave 3.0 g. (b.p.  $\sim 103^\circ/25$  mm Hg) and the benzene extract 0.8 g. (b.p.  $\sim 110^\circ/35$  mm Hg) of liquid respectively. Comparing with the authentic sample<sup>9</sup> these liquid products were shown to be **XIII** with unknown impurity of about 2%, by gas-chromatography and infrared absorption. The yield was 78%.

**3-Acetyl-2,5-dimethyl-4,5-dihydrofuran (XIV).** The solution of **XII** (1.7 g.) in 95% sulfuric acid (7 ml.) was worked up as in the case of **XI**. A quantity of 1.2 g. of **XIV** (b.p.  $\sim 95^\circ/13$  mm Hg, 70% yield) was obtained. U.v. and i.r. spectra of this liquid showed the presence of 3-acetyl-2-methyl-dihydrofuran skeleton. The n.m.r. spectra showed signals at  $\tau$  8.62 (doublet), 7.79 (singlet+triplet), 7.67-6.67 (multiplet) and 5.0-4.6 (multiplet) with relative intensities of 3:6:2:1, which can be assigned to protons of 5-methyl, 3-acetyl+2-methyl, methylene (4) and methine (5) respectively.

From sulfuric acid solutions of **IX**, and **X**, the same product was obtained with 34 and 35% yield respectively.

#### REFERENCES

- (1) See, for example, A.E. Gillam and E. Stern, "An Introduction to Electronic Absorption Spectroscopy",

Edward Arnold, London (1960), p. 103 and p. 257.

- (2) S.T. Yoffe, E.M. Popov, K.V. Vatsuro, E.K. Tulikova and M.T. Kabachnik, *Tetrahedron*, **18**, 923 (1962).
- (3) K. Ichikawa, O. Itoh, T. Kawamura and M. Fujiwara, *Bull. Inst. Chem. Res., Kyoto Univ.*, **43**, 213 (1965).
- (4) B. Eistert, E. Merkel and W.Reiss, *Chem. Ber.*, **87**, 1513 (1954).
- (5) K. Ichikawa, S. Uemura and T. Sugita, *Tetrahedron*, **22**, 407 (1966).
- (6) K. Ichikawa, O. Itoh, T. Kawamura, M. Fujiwara and T. Ueno, *J. Org. Chem.*, **31**, 447 (1966).