[Contribution from the Research Laboratories, Eastman Kodak Company]

THE STRUCTURE OF CERTAIN SUBSTITUTED DIPHENYLCYCLOPENTENONES[1]

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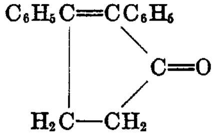
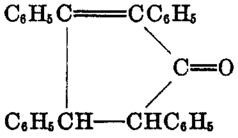
A considerable number of diphenylcyclopentenones have been described in the literature (1–12), but conclusive proof of their structures has not always been possible, owing to the ambiguous nature of the chemical reactions employed for that purpose. Until very recently, no use has been made of such physical properties as light absorption; the instances described in a previous paper (12) are now extended, advantage having been taken of the specimens available from earlier work.

It has been noted (12, 13) in the ultraviolet absorption spectra of two arylated cyclopentenones, of which the structures (I, II) are not in doubt, that a peak at


I


II

300 ± 5 mμ appears to be characteristic of the group $C_6H_5\overset{|}{C}{=}C(C_6H_5)\overset{|}{C}{=}O$. Four of the diphenylated ketones have such an absorption (Table I); this is at variance with these structures as previously written. Accordingly, the necessary modifications have been made, and new structures assigned. For comparison, both isomeric formulations (III–VI) are shown herewith, the old ones in each instance being on the lower line and lettered "a."

The group $C_6H_5\overset{|}{C}{=}CR{-}\overset{|}{C}{=}O$ (when R is not aryl) shows a main absorption peak at 285 ± 5 mμ. Two (VII; a, $R = H$; b, $R = CH_3$) of the cyclopentenones have this property. Finally, there are three that have an unconjugated unsaturated system, the ultraviolet absorption peak of which (255 ± 5 mμ) is near that of dimethylstilbene (Table I). They are of the type of VIII (where $R = Cl$, OCH_3, or $OCOCH_3$), and are the same as those originally established by the chemical evidence. The infrared bands (at 5.70 and 5.75 mμ) are those of an unconjugated carbonyl group in a five-membered ring, and afford an independent confirmation of the conclusions drawn from these structures.

Acceptance of these new structures makes necessary some revision in the interpretation of their chemical behavior, as well as a reconciliation with the data from which conclusions concerning the old structures were drawn.

"Vorländer's ketol" (III), which results when dibenzalacetone is treated with concentrated sulfuric acid and acetic anhydride (3), was represented as shown

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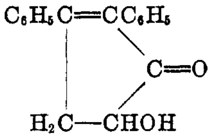
TABLE I

ULTRAVIOLET ABSORPTION DATA

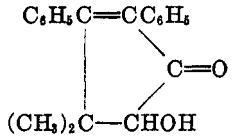
No.	λ_{max}, mμ	log ε	Solvent	m.p., °C[a]
I[b]	295	4.09	Dioxane	109
II[c]	299	4.13	Dioxane	162
III	303	4.63	Dioxane	176
IV	303	4.70	Dioxane	158
V[d]	299	4.45	Ethanol	142
VI	300	4.67	Ethanol	88
VII[e]	285	4.68	Methanol	96
VIII[f]	252	4.42	Acetonitrile	137
IX	258	4.33	Methanol	144
X[g]	234	3.93	Methanol	205
	283	3.26		
XI	252	4.07	Methanol	133
XII	283	4.51	Acetonitrile	120

[a] Given for aid in identification. [b] Ref. 12. [c] Ref. 13. [d] Ref. 10. [e] R = CH_3. [f] R = $OCOCH_3$. [g] R = *o*-toluidine.

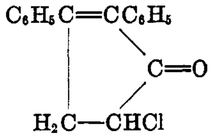
in IIIa by Von Liebig (5) based on degradation by alkali and by oxidizing agents. The same products, *viz.*, desoxybenzoin, benzil, benzoic and oxalic acids, and carbon dioxide, can be readily accounted for by either structure. Von Liebig



III



IV



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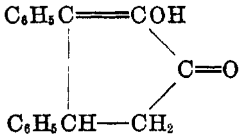
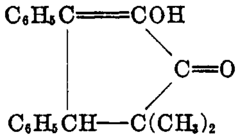
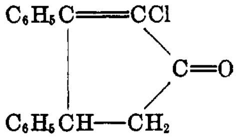


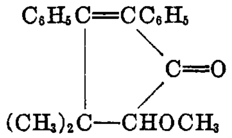
IIIa



IVa



Va



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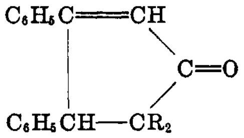
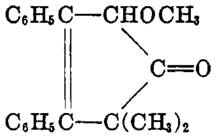


VII



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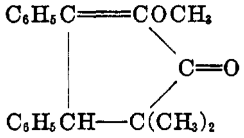
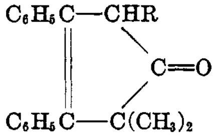
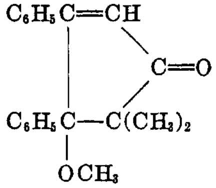


VIa (9)



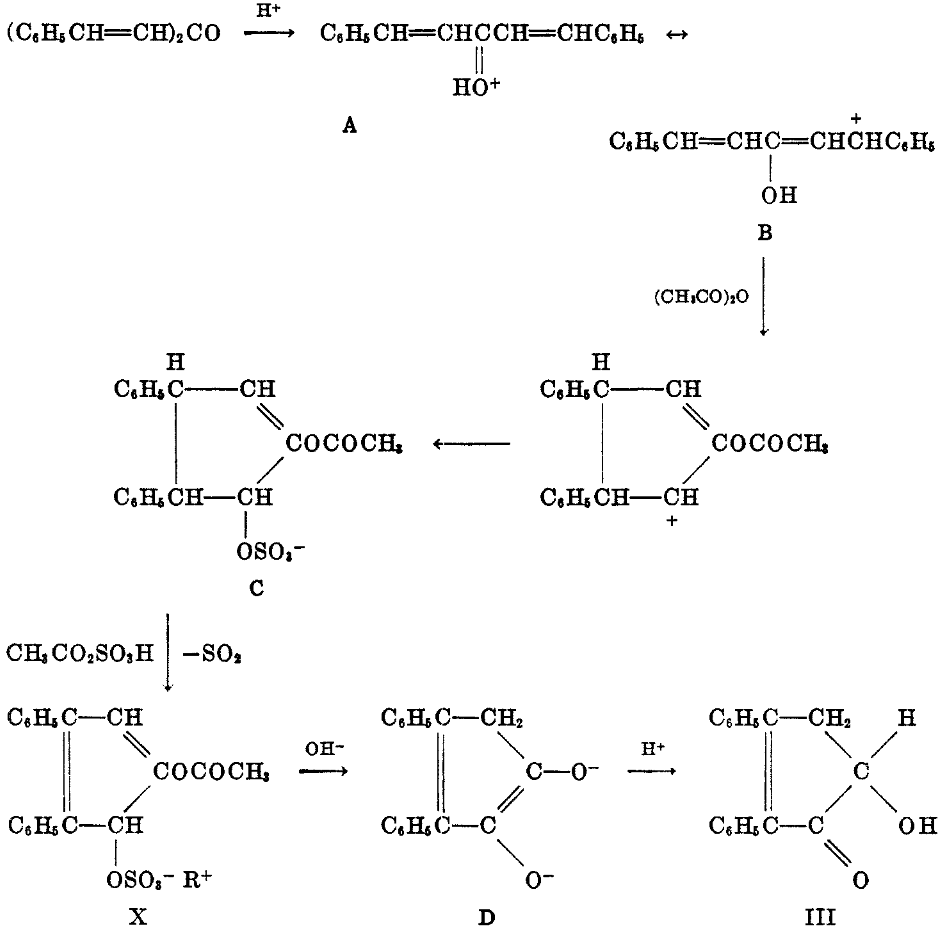
VIII



IXa

found one discrepancy: non-formation of a quinoxaline derivative; the latter would not be expected of the corrected structure, III. It has now been shown that an osazone results when the "ketol" is treated with excess phenylhydrazine; this behavior would be expected of the new structure, but not of the older one. Attention should also be called to the similarity in properties to LaForge and Soloway's α-hydroxyketone (14).

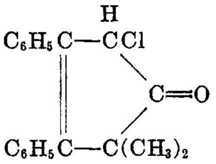
The steps in the formation of the ketol (III) from dibenzalacetone can now be formulated as shown.



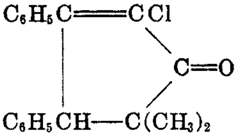
The addition of sulfuric acid to the ketone, suspended in acetic anhydride, gives immediately the bright red color of the oxonium salt (**A**). Its resonance contributor (**B**) then is cyclized, with accompanying acetylation and sulfation (**C**); the latter reacts with acetylsulfuric acid (and loss of sulfur dioxide) to give X, which was isolated as the *o*-toluidine salt (X, $R^+ = o\text{-}CH_3C_6H_4NH_3^+$). The ultraviolet absorption spectrum of this salt has bands at 234 mμ (ε = 8600) and 283 mμ (ε = 1800), the former being close to that of cyclopentadiene (239 mμ) (15); the positions of the substituent groups are assumed to be the same as in the ketol, and are consistent with the reactions. When the salt is treated with aqueous sodium carbonate, it is hydrolyzed to the enediol (**D**), which, on acidification, yields the ketol (III). The enediol is responsible for the color produced when the ketol is treated with ferric chloride (5). The formation of desylacetic acid, on oxidation, probably takes place by way of a 1,2-diketone.

All that has been said about the ketol, III, applies equally well to Gray's dimethyl homolog (IV) (4). As an α-hydroxyketone, it should give an osazone when treated with 2,4-dinitrophenylhydrazine (which, indeed, it does), but no quinoxaline (which it does not).

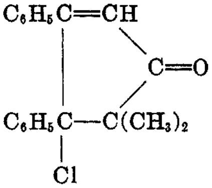
Two chlorides are formed by the action of thionyl chloride (7, 9), on dimethylanhydroacetonebenzil.



XI



XII



XIII

The one first formed has a melting point of 133°, while the second, which also results from the first by the action of alkaline reagents, melts at 120° (B and S 126°). Since the first, from its absorption, belongs to the VIII series, it must have the structure XI, while XII is the second; the isomeric XIII has to be discarded, since it could not be formed by an alkaline treatment of XI.

Acknowledgment. We are indebted to D. W. Stewart, of these Laboratories, for the ultraviolet spectra reported.

EXPERIMENTAL

1-Acetoxy-3,4-diphenyl-5-sulfato-1,3 cyclopentadiene (o-toluidine salt) (X). Equal weights of *o*-toluidine hydrochloride and the potassium salt (16) were heated in a few ml. of dilute hydrochloric acid for several min. The salt has a melting point of 205–206° dec. after crystallization from alcohol.

Anal. Calc'd for $C_{28}H_{25}NO_6S$: C, 65.1; H, 5.2; N, 2.9; S, 6.7.
Found: C, 65.3; H, 5.9; N, 3.0; S, 6.6.

1,2-Diphenyl-1-cyclopentene-3,4-dione bisphenylhydrazone. A mixture of 6 g. of the ketol (III), 200 ml. of alcohol, 8 ml. of phenylhydrazine, and a few drops of acetic acid was refluxed for 4 hours, seeded, and chilled; 8.5 g. of the yellow osazone (one g. more as a second crop), m.p. 152–154°, was obtained (92% yield). The melting point was unchanged after recrystallization from alcohol.

Anal. Calc'd for $C_{29}H_{24}N_4$: C, 81.4; H, 5.5; N, 13.1.
Found: C, 81.1; H, 5.9; N, 13.2.

SUMMARY

The structures of several related substituted diphenylcyclopentenones have been revised to take into account their recently determined ultraviolet absorption spectra.

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Effective with Volume 21, the Journal will use a double column format with a page size approximately 6½″ by 9″. Authors should consider this in connection with graph sizes, and table compositions.