

SYNTHESIS OF 1,1-DIARYLCYCLOPENTANETETRONE HYDRATES

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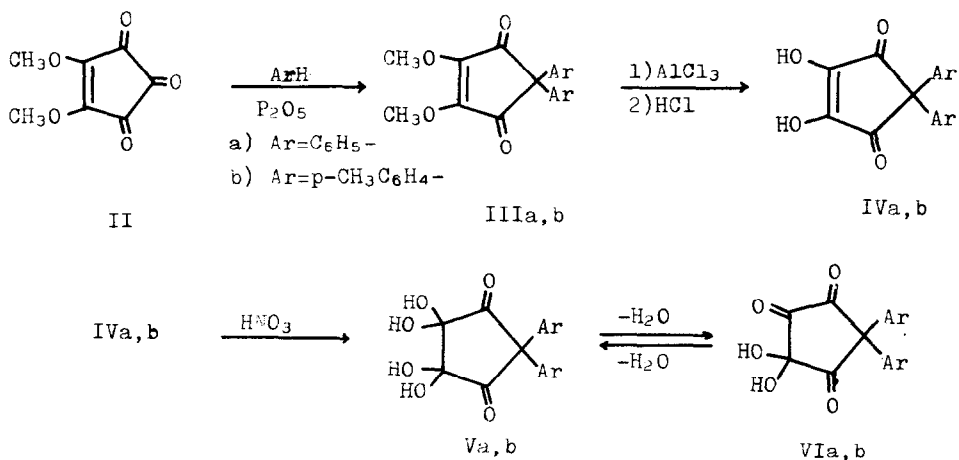
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Five membered cyclic vic-tetraketone I is expected to show interesting properties on account of its unique arrangement of functional groups.

This paper describes the synthesis of its hydrated forms: 1,1-diaryl-cyclopentanetetrone hydrates.

Dimethylcroconate II¹⁾ was heated in refluxing benzene (or toluene) in the presence of phosphorus pentoxide for 15 hours. It condensed with two equiv. of benzene (or toluene) at its central one of the vic-tricarbonyls to give 1,2-dimethoxy-4,4-diphenylcyclopentene-3,5-dione IIIa (4,4-di-p-tolyl, IIIb) in 13 % yield.



1) The compound was prepared by a modification of the procedure reported by R. Malakovski and S. Prebendovski (Ber., 71, 2241 (1938))

IIIa (mp 126.5-127°C) had two carbonyl bands at 1750 (vw) and 1680 (s) cm^{-1} , and a conjugated C=C band at 1637 cm^{-1} . In the ultraviolet, IIIa showed a broad absorption band of λ_{max} 297 μ ($\log \epsilon=3.86$) in ethanol.

IIIa was hydrolyzed with hydrochloric acid after complex formation with aluminum chloride, to give 4,4-diaryl-1,2-dihydroxycyclopentene-3,5-dione IV (70%) (IVa melted at 188°C and IVb at 212°C). IV was a dibasic acid (acidity constants of IVb was $\text{pk}_1=3.55$ and $\text{pk}_2=9.82$ in 50% ethanol by potentiometric titration), and showed $\nu_{\text{C=O}}$ near 1650 cm^{-1} , which is similar to a carbonyl absorption band of p-quinone. IVa was readily oxidized with nitric acid at room temperature, giving 1,1-diphenylcyclopentanetetrone dihydrate Va ($\text{C}_{17}\text{H}_{10}\text{O}_4 \cdot 2\text{H}_2\text{O}$, 95%, decomp. pt 134-7°C with foaming) as white crystals. (By analogy, IVb gave 1,1-di-p-tolylcyclopentanetetrone trihydrate Vb; $\text{C}_{19}\text{H}_{14}\text{O}_4 \cdot 3\text{H}_2\text{O}$, decomp. pt 94-96°C). IR spectra of V showed $\nu_{\text{C=O}}$ near 1790 (vw) and 1750 (s) cm^{-1} . Two equiv. of water molecules contained in V is probably combined to the central pair of the vic-tetracarboxyls to form two gem-diols in vicinal position. (One more molecule of water in Vb (trihydrate) is not combined to carbonyl group as the infrared spectral properties of Vb were quite similar to those of Va).

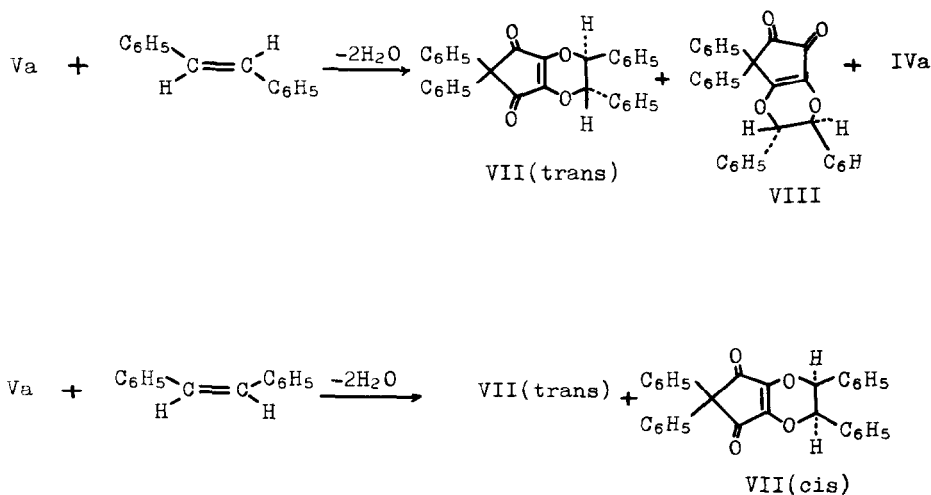
The retention of five membered ring and existence of the potential vic-tetra-ketone structure in V were confirmed by:

- 1) Reaction of Vb with triphenylphosphine gave the endiol IVb (81.5%) and triphenylphosphine oxide (79%).
- 2) Condensation of Vb with o-phenylenediamine gave the corresponding bis-quinoxaline derivative.

Vb turned to a dark solid by holding at 57°C (lower temperature than its decomp. pt) in vacuo (3/100 mmHg) for 28 hours. The result of the elemental analysis of this solid showed that at least two of the three attached water molecules could be removed, but the last one could hardly be removed without decomposition. Azeotropic dehydration of Va (with toluene) could also remove one of the two attached water molecules (measured by Karl Fisher method). From the resulting solution, which showed $\nu_{\text{C=O}}$ at 1755-1760 cm^{-1} , ν_{OH} at 3400 cm^{-1} and λ_{max} (in toluene) at 556 μ ($\epsilon=12.5$), dihydrate Va was readily recovered as a white crystalline precipitate by shaking it with small amount of water. These data are consistent

with the existence of the tetraketone monohydrate VI in the solution.

The results interesting enough to note were obtained when V was reacted with olefins. When Va was heated in chlorobenzene under reflux in the presence of trans stilbene, two 1,4-adducts: VII(trans)²⁾ and VIII, were obtained along with small amount of endiol IVa. VII(trans) had a molecular formula of C₃₁H₂₂O₄ (mp 224-5°C). It showed in the infrared $\nu_{C=O}$ at 1690 cm⁻¹ and λ_{max} (in ethanol) at 298 m μ (log ϵ =3.91) in the ultraviolet, which resemble to the spectral properties of III in these regions. In nmr, it exhibited a singlet at 5.0 τ (2H) along with a multiplet (2.7-3.2 τ) due to aromatic protons. From these data, the structure of VII(trans) was confirmed as the 1,4-adduct of the tetraketone and stilbene: the centered carbonyl groups of the former reacting as a heterodiene combined with the olefinic double bond of the latter as a dienophile.



2) This compound is so named because this is a main reaction product of Va with trans stilbene and probably has the stereochemical structure depicted in the scheme.

VIII (mp 246-7°C) had the same molecular formula as VII(trans) and its ir spectrum showed $\nu_{C=O}$ at 1760 and 1710 cm^{-1} , which resembles to carbonyl absorption bands of 1,5-diphenyl-5-hydroxycyclopentene-3,4-dione. In nmr, it exhibited two doublets (4.75 and 5.10 τ , $J=8$ cps), which are assignable to the signals due to two protons on p-dioxene ring. VIII is, therefore, another 1,4-adduct of the tetra-ketone produced by a reaction occurred on the sidely positioned pair carbonyls.

1,4-Addition of Va with Stilbene

	mol. ratio of stilbene/Va	reaction temp.	reaction time	products %			
				VII(trans)	VII(cis)	VIII	IVa
1)	1.67(trans)	131°C	7 hr	68	0	4.7	8
2)	1.67(cis)	131°C	5 hr	10.4	4.1	-	27
3)	10(trans)	131°C	7 hr	82	0	6	1.9
4)	10(trans)	131°C	5 hr	47	11	(2.4)*	7.5

Chlorobenzene was used as a solvent and the reactions were carried out under nitrogen atmosphere. * cis and trans mixture.

When this addition was carried out using cis stilbene as a dienophile, two adducts: VII(cis) (mp 181.5-182.5°C, $\nu_{C=O}$ 1690 cm^{-1} , $\nu_{C=C}$ 1650 cm^{-1} , a singlet due to p-dioxene protons 4.4 τ)³⁾ and VII(trans), were obtained and stilbene recovered from the reaction mixture contained approximately 13 % of trans isomer in the experiment shown in 2) in the table. As stilbene and reaction products are stable stable in this reaction condition respectively, this reaction seems to be inherently accompanied by the isomerization of cis stilbene. Further investigation of th this reaction including mechanisms will be published elsewhere.

 3) For the discussion on nmr of p-dioxene, see; (a) G. Pfundt and S. Farid, Tetrahedron, 22, 2237 (1966). (b) Y.L. Chow and T.C. Joseph, Chem. Comm., 604 (1968)