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Note on the Synthesis of Di-[ω-phenyl-polyene]-diketones

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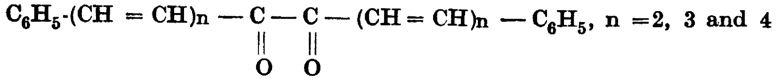
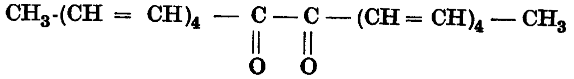
In 3 papers from 1945 and 1946 Karrer and his collaborators[1] have described the preparation and the properties of some polyene-α-diketones *viz.*

I



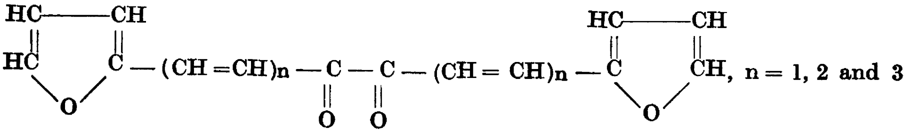
$$C_6H_5\text{-}(CH=CH)n-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-(CH=CH)n-C_6H_5,\ n=2,\ 3 \text{ and } 4$$

II



$$CH_3\text{-}(CH=CH)_4-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-(CH=CH)_4-CH_3$$

III



In the autumn of 1940 Sörensen [2] put forward the hypothesis that »visual purple» was the endiol-protein-komplex of β-carotene, in which the two central hydrogen atoms were substituted with hydroxyl. The free dihydroxy-β-carotene would rearrange to the ketolform which was postulated to be the »visual yellow». The enolization had to be carried out through a specific protein, stabilizing the endiol through complex salt formation quite in analogy with the reversible passage:

astaxanthin + protein ⇄ ovoverdin

of the lobsteregg chromoproteid, the main difference being the different positions of the ketol-grouping.

In astaxanthin two such ketolgroupings symmetrically frame the polyene system, whilst in »visual yellow» only one occupies the central carbon atoms of the β-carotene-skeleton. This difference is, however, important, as in »visual yellow» the ketol grouping interrupts the conjugation and so reduces the U. V.-Spectrum to that of vitamin-A-aldehyde whereas the enolization to the endiol-grouping in »visual purple» re-establishes the conjugated carotenoid spectrum.

With the intention of synthesizing model substances for this theory, Samuelsen carried out the synthesis of some of the diketones of Karrers first series (I). Samuelsen gave a lecture about his synthesis of the ω-diphenyl-polyene-diketones with $n = 1$, 2 and 3 at the meeting of Norsk Kjemisk Selskap, Trondhjems Avdeling on April 29th 1941. Of course, no information about our work could reach professor Karrer.

The synthesis of the simplest of these diketones, 1.6-diphenyl-hexadiene-1,5-dione-3,4 or »cinnamil» which was not prepared by Karrer and Cochand[1] is described in the experimental part. Otherwise we confine ourselves to a tabular comparison of the m. p. stated by Karrer and Samuelsen in 1941. Oxaal in 1946, without knowledge of the Swiss publications, repeated and to some extent improved the procedure of Samuelsen.

n	Yield diketone			M. p.* diketone			M. p. quinoxaline	
	P. K.	E. S.	Fr. O.	P. K.	E. S.	Fr. O.	P. K.	E. S.
1	— %	8.5 %	10.5 %	—	165—166	166	—	194°
2	25 »	45 »	57 »	188.5—189	190—191	191—192	202—203	201°
3	17 »	15 »	—	197	200—201	—	162—163	—
4	5.6 »	—	—	201—202	—	—	—	—

The agreement in m. p. of the diketones and their quinoxalines is quite good. Samuelsen used the piperidonium acetate catalysator of Kuhn, Badstübner and Grundmann[3] which seems to give yields superior to piperidine alone which Karrer has employed. Oxaal has tried to raise the yield of »cinnamil» to that of diphenyl-decatetraene-dione, but could only improve the original yield by a few percent. Probably the reason for these bad yields is some side reaction between »cinnamil» and piperidoniumacetate. All the diphenyl-polyene-diketones give dark reaction products when heated in alcoholic solution with the catalysator; we have, however, got no crystallizing reaction product. Whereas diphenyl-decatetraenedione crystallizes very readily from the reaction medium and so in part escapes further destruction, »cinnamil» only crystallizes on dilution and cooling and therefore is all the time hazardized through side reactions.

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* All m.p. are uncorrected.

EXPERIMENT

Cinnamil = 1,6-diphenyl-hexadiene-1,5-dione-3,4

To 0.4 mole benzaldehyde (42.5 g) and 0.1 mole diacetyl (8.6 g) diluted with 40 ml 57 per cent ethanol was given 0.02 mole glacial acetic acid and 0.02 mole piperidine. The mixture was heated to 81—83° C for 2 hours and cooled down through addition of 100 ml of ethanol. Immediately 1.5 g cinnamil separated; concentration of the mother liquor and cooling gave further 1.25 g pure cinnamil. Yield 10.5 per cent calculated on diacetyl. M. p. 166 uncorr, 169 corr.

21.3 mg gave 10,1 mg H_2O, 64.3 mg CO_2.

$C_{18}H_{14}O_2$ (262.3)	Calc.	C	82.41	H	5.38
	Found	»	82.33	»	5.31

Cinnamil mostly crystallizes in dense needles 3—5 mm long with sawtoothed edge, once however it occured in very fine, flexible, hairy crystals of some cm length. As the morphological difference was very great we were surprised that both preparations proved to be cinnamil: analysis, m. p. and Debye-Scherrer diagrams proved the identity of the two samples. Later on we learned that diphenyl-decatetraene-dione too, which ordinarily crystallizes in six-sided plates through the action of alcali is contaminated with small amounts of some other substance which cause diphenyl-decatetraene-dione to crystallise in long, thin needles. Obviously the crystal habitus of some of the polyenediketones are very sensible to impurities which are formed in alcaline medium.

2,3-Di[β-phenyl-vinyl]-quinoxaline

To 0.52 g cinnamil and 0.22 g *o*-phenylenediamine in 35 ml benzene was added a few drops glacial acetic acid and the mixture heated under reflux for 15 min. 2/3 of the solvent was distilled off and replaced with an equal amount petrol ether. 2.3-di-[β-phenyl-vinyl]-quinoxaline crystallises in slightly yellow needles, m. p. 194° uncorr.

15.9 resp. 28.6 mg gave 49.8; 91.15 mg CO_2 and 7.7; 15.1 mg H_2O.
N(Kjeldahl) 5.6 resp. 6.3 mg used 3.36; 3.76 ml 0.01 *N* H_2SO_4.

$C_{24}H_{18}N_2$ (334.4)	Calc.	C	86.18	H	5.43	N	8.38
	Found		85.42, 86.92	»	5.42, 5.57	»	8.40, 8.35

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2. Lecture given Nov. 8, 1940 in N. K. S. Trondhjems Avdeling, *cf. Tids. Kjemi Bergvesen* 20 (1940) 178.
3. Kuhn, R., Badstübner, W., and Grundmann, Ch. *Ber.* 69 (1936) 98.

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