The ester was quantitatively hydrolyzed to p-nitrophenylacetic acid,[7] m. p. 153.4–154.6°, by heating for twenty minutes with concentrated hydrochloric acid.

Summary

A new modification of the Wolff rearrangement of α-diazomethylketones involving a homogeneous reaction medium is described. This involves treating an α-diazoketone in an alcohol with a solution of silver benzoate in triethylamine. The necessity for a hydrogen alpha to both the carbonyl and the diazo group, for silver ion, and for the base, triethylamine, are demonstrated. A possible mechanism involving ionic and free radical intermediates is presented.

COLUMBUS, OHIO RECEIVED JUNE 12, 1950

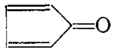
[7] G. R. Robertson, "Organic Syntheses," Coll. Vol. I, p. 406, 1941.

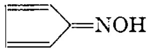
[COMMUNICATION NO. 1343 FROM THE KODAK RESEARCH LABORATORIES]

Dimerization of Cyclopentadienones

BY C. F. H. ALLEN AND J. A. VANALLAN

Cyclopentadienone (I) is unknown. Its oxime (II)[1,2] and tetrachloro-substitution product (III) occur only as dimers (type of IV).[3,4,5] Attempts to prepare 2,3,4-trichloro-5-methyl-[6] and 2,3,5-trichloro-4-methyl-,[7] and 3,5-dichloro-2,4-dimethyl-[8] derivatives result in dimeric forms, analogous to IV, only. The same is true of most aryl derivatives, including the acid (V).[9] Only the monomeric 2,3,4,5-tetraphenylcyclopentadienone (VI) is known.[10]


I



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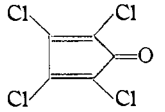

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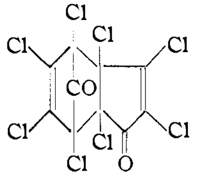

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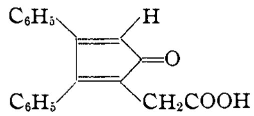

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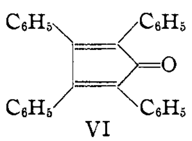
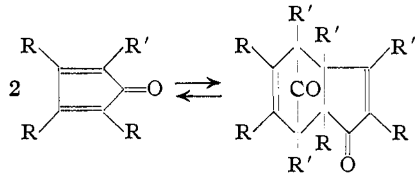
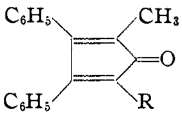


VI

The dimeric products (VII) from 2,5-dimethyl-3,4-diphenyl-[11] and 2,3,5-triphenylcyclopentadienone[12] dissociate readily in solution, while the 2-methyl-3,4-diphenyl derivative, at 200°, gives two products with maleic anhydride, one of which is derived from the monomeric form (VIII), thus showing that there is some dissociation at the elevated temperature of the reaction.[13] The purpose of the work described in this paper was to determine the limits of the reaction of dimerization of cyclopentadienones.



VIII VII



IX

2-Methyl-5-n-propyl-3,4-diphenylcyclopentadienone (IX, R = n-C_3H_7) is a white substance but its solutions are a brilliant red; molecular weight determinations in benzene show that it is a reversible dimer. If the propyl group is replaced by phenyl, a monomeric substance (IX, R = C_6H_5) only results. The 2,5-diethyl-, 2,5-di-n-propyl-, and 2,5-di-n-hexyl-3,4-diphenylcyclopentadienones (VIII, R = C_6H_5, R' = alkyl) are also monomeric. They are bright red solids and give red solutions. It appears, then, that the diethyl compound is the limiting member of the series.

For convenience in consideration, the cyclopentadienones can be arranged in three groups (Table I), between each of which there is a sharp line of demarcation. The first group consists of those that are known only in the dimeric form; they are colorless in solution regardless of the temperature, show the expected molecular weight, and do not react by addition to dienophiles in benzene solution. Members of the second group are colorless solids which give colored solutions, the intensity increasing to a maximum as the temperature is

[1] Thiele, *Ber.*, **33**, 669 (1900).

[2] Alder and Stein, *Ann.*, **496**, 205 (1932).

[3] Zincke and Fuchs, *Ber.*, **26**, 515 (1893).

[4] Zincke, *Ann.*, **367**, 1 (1909).

[5] Zincke and Pfaffendorf, *ibid.*, **394**, 7 (1912).

[6] Bergmann and Francke, *ibid.*, **296**, 167 (1897).

[7] Prentzell, *ibid.*, **296**, 189 (1897).

[8] Francke, *ibid.*, **296**, 209 (1897).

[9] Japp and Murray, *J. Chem. Soc.*, **71**, 149 (1897). The "oxime," m. p. 122–123°, which the authors were unable to identify, is, therefore, the dihydroxylamine salt of the dimer, $C_{38}H_{34}N_2O_8$. Calcd.: C, 70.7; H, 5.1; N, 4.4. Found: C, 69.8; H, 5.6; N, 4.1.

[10] Allen, *Chem. Rev.*, **37**, 209 (1945).

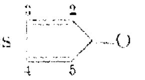
[11] Allen and VanAllan, THIS JOURNAL, **64**, 1260 (1942).

[12] Ziegler and Schnell, *Ann.*, **445**, 276 (1925).

[13] Allen and VanAllan, *J. Org. Chem.*, **10**, 333 (1945).

TABLE 1

SUBSTITUTED CYCLOPENTADIENONES



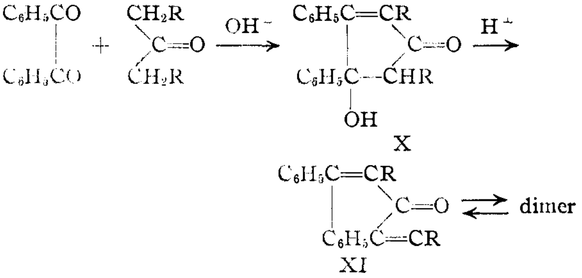
2	3	4	5	Ref.
		Non-dissociating Dimers		
H	H	H	H	1, 2, (oxime)
Cl	Cl	Cl	CH_3	6
Cl	Cl	CH_3	Cl	7
CH_3	Cl	CH_3	Cl	8
Cl	Cl	Cl	Cl	3, 4, 5
H	C_6H_5	C_6H_5	H	15
H	C_6H_5	C_6H_5	CH_3	13
H	C_6H_5	C_6H_5	n-C_5H_{11}	13
H	C_6H_5	C_6H_5	n-$C_{10}H_{21}$	
H	C_6H_5	C_6H_5	CH_2COOH	9
H	C_6H_5	C_6H_5	C_6H_5	
		Dissociating Dimers		
CH_3	C_6H_5	C_6H_5	CH_3	11
CH_3	C_6H_5	C_6H_5	n-C_3H_7	
C_6H_5	C_6H_5	H	C_6H_5	12
		Monomers only		
CH_3	C_6H_5	C_6H_5	C_6H_5	
C_2H_5	C_6H_5	C_6H_5	C_2H_5	
C_6H_{13}	C_6H_5	C_6H_5	C_6H_{13}	
C_6H_5	C_6H_5	C_6H_5	C_6H_5	10

increased; the molecular weights are intermediate between that of a monomer and a dimer, and they add to dienophiles in benzene solution. The third group comprises colored, monomeric compounds that give bright red solutions regardless of the temperature, and which add to dienophiles in benzene solution.

The following conclusions regarding alkylated and arylated cyclopentadienones may be drawn from the available facts. Any cyclopentadienone having fewer than three substituents will exist only as a non-dissociating dimer. In no instance does a trisubstituted cyclopentadienone exist in the monomeric state. If there are three substituents, the dienones will exist as the non-dissociating dimer except in the extreme case, in which there are two aryl groups next to the carbonyl group. When all four positions of the dienones are substituted, a dissociable dimer results when the substituents in the 2- and 5-positions are methyl and an alkyl; otherwise, the substance is a monomer.

The preparation of these dimers consists in condensing benzils and acetones in the presence of alkali, according to the outline.(14)

In nearly all previously studied examples of this condensation, the cyclopentenolone (X) is formed, and dehydrated in a subsequent reaction, using acetic anhydride and a trace of mineral acid. In these instances, a molar equivalent of alkali is necessary to get the highest yield of hydroxyketone (X). Very curiously, it has been observed that with ketones which give the monomeric dienones, only a small amount of alkali is needed.



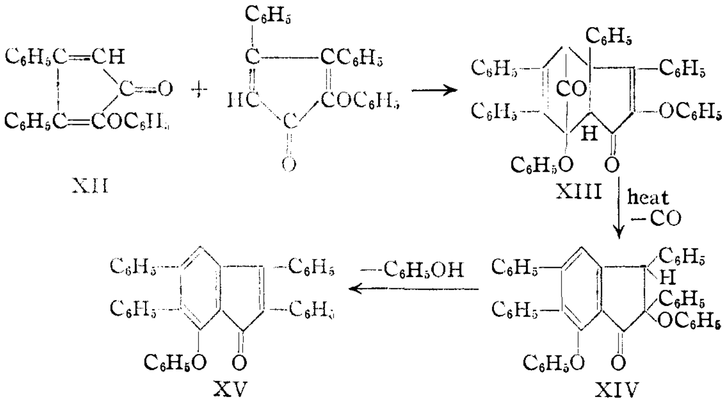
X

XI

Another unusual feature is the failure of these monomeric dienones to dimerize, although they do enter into other diene syntheses.(10) This behavior must likewise be of a steric nature, for not only does the chlorinated series dimerize, but so does the phenoxy derivative (XII → XIII). This is of further interest because the phenoxy group is a ring substituent in the adduct formed by a diene synthesis. The indenone was assigned the structure (XV) by analogy with 2,3,5,6-tetraphenylindenone(15); the intermediate products were not isolated.

Experimental

General Procedure for Cyclopentadienones (VIII).—One-tenth mole of benzil and 0.2 mole of the ketone to be condensed are added to 250 ml. of 0.5% absolute alcoholic potassium hydroxide. The reaction mixture is allowed to stand at room temperature until all the benzil has reacted (about 48 hours). This point is determined by adding a test sample to water; the characteristic crystals of benzil are easily recognized. The mixture is poured into 500 ml. of water, and the precipitated cyclopentenolone (X) is separated by filtration; it may be purified by recrystallization. The 2,5-diethylcyclopentenolone was previously known.(16)



XII

XIII

XIV

XV

3,4-Diphenyl-2,5-di-n-propylcyclopenten-4-ol-2-one was recrystallized from ligroin; m. p. 80°.

Anal. Calcd. for $C_{23}H_{26}O_2$: C, 82.8; H, 7.8. Found: C, 82.7; H, 8.0.

The crude product, after drying in the air, is mixed with 40 ml. of acetic anhydride, and a drop of sulfuric acid is added. The temperature rises 10–15° and the solution

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(14) Japp and Burton, *J. Chem. Soc.*, **51**, 420 (1887).

(15) Allen and Spanagel, This Journal, **55**, 3773 (1933).

(16) Japp and Meldrum, *J. Chem. Soc.*, **79**, 1041 (1901).

TABLE II

PROPERTIES OF 3,4-DIPHENYLCYCLOPENTADIENONES (VIII, R = C_6H_5)

R_1	R_2	M. p., °C.	Yield, %	Empir. form.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Mol. wt., Calcd.	Mol. wt., Found
CH_3	n-C_3H_7	138[a]	57	$C_{42}H_{40}O_2$	87.5	87.4	6.9	6.9	576	326[d] 356[e]
CH_3	C_6H_5	196[b]	68	$C_{24}H_{18}O$	89.4	89.7	5.6	5.5	322	315[d]
C_2H_5	C_2H_6	103[c]	70	$C_{21}H_{20}O$	87.4	87.6	6.9	7.0	288	282[d]
n-C_3H_7	n-C_3H_7	80[c]	84	$C_{22}H_{24}O$	87.4	88.0	7.6	7.5	316	305[d]
n-C_6H_{13}	n-C_6H_{13}	B. p. 251–255° (4 mm.)	34	$C_{29}H_{36}O$	87.0	86.8	9.0	8.8	400	375[d]

[a] From acetic acid. [b] From butyl alcohol. [c] From ethyl alcohol. [d] In boiling benzene (white solid dimer is 56% dissociated in red solution). [e] In boiling carbon tetrachloride (see ref. 10).

becomes a bright red. After an hour, the dienone is precipitated by water and recrystallized from an appropriate solvent, as a bright red solid. Their properties are collected in Table II.

Cyclopentenolones having long aliphatic chains are purified in a slightly different manner. The crude product (*e.g.*, 2-decyl-3,4-diphenylcyclopentenol-4-one[17]) was taken up in benzene, washed, dried and the solvent removed. The residual oil was distilled; the desired material (23.3 g., 83.5%) is in the fraction, b. p. 200–222° (mostly at 218–220°) at less than 1 mm. It was crystallized from 50 ml. of petroleum ether; the yield was 15 g., m. p. 56–58°, unchanged by further recrystallization.

Anal. Calcd. for $C_{27}H_{34}O_2$: C, 83.1; H, 8.8. Found: C, 83.2; H, 8.7.

Diisobutyl ketone did not condense with benzil under any conditions tried. This appears to be another instance of hindrance to a reaction[18] that is incapable of being forced.

7-Phenoxy-2,3,5,6-tetraphenylindenone (XV).—Benzil and phenoxyacetone were condensed by the usual procedure, and the crude cyclopentenolone after dehydration was at once heated until the thermometer registered 250° at 3 mm. Upon the addition of methanol to the residue, it set to an orange mass of crystals. They were recrystallized from p-cymene, or o-dichlorobenzene, melted at 308°, and gave the characteristic green color with concentrated sulfuric acid.

Anal. Calcd. for $C_{39}H_{26}O_2$: C, 89.2; H, 4.8; RMgX addn., 1.0. Found: C, 89.2; H, 5.0; addn., 1.1.

Summary

Benzil has been condensed with various aliphatic ketones and the resulting cyclopentenolones dehydrated. The cyclopentadienones so formed may remain as such or dimerize. The limits of the reaction have been outlined.

ROCHESTER 4, N. Y.

RECEIVED MAY 5, 1950

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[17] We are indebted to Dr. D. M. Burness, of these Laboratories, for this preparation.

[18] Allen and Rosener, THIS JOURNAL, **49**, 2110 (1927).

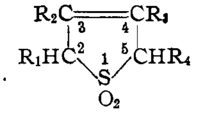
[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY OF WESTERN RESERVE UNIVERSITY]

Thermal Dissociation of Methyldihydrothiophene-1-dioxides[1]

BY OLIVER GRUMMITT, ALAN E. ARDIS AND JEAN FICK

Introduction

To study further[2] the thermal stability of the 2,5-dihydrothiophene-1-dioxide or cyclic sulfone ring system, the rates of the thermal dissociation



to the conjugated diene hydrocarbon and sulfur dioxide[3] of several methyl substituted derivatives have been investigated. The compounds reported here are the cyclic sulfones of butadiene (R_1–R_4 are H), of piperylene (R_1 is CH_3, R_2–R_4 are H), of isoprene (R_2 is CH_3, R_1, R_3, R_4 are H), of 1,3-dimethylbutadiene (R_1 and R_3 are CH_3, R_2 and R_4 are H), and of 2,3-dimethylbutadiene (R_2 and R_3 are CH_3, R_1 and R_4 are H).

Experimental

Preparation of Sulfones.—Butadiene (Ohio Chemical) and sulfur dioxide (Ohio Chemical) in a mole ratio of 1/2 and with the addition of 1% of hydroquinone with respect to the butadiene (to retard polysulfone formation)[4] were allowed to react at 100° for 12 hours in a steel bomb[5] or at room temperature for two–three weeks in pressure bottles. The crude sulfone was purified by three crystallizations from hot (50°) water, using Norit in the first crystallization; yields ranged from 80–85%; m. p. 64.5–65.0°.[3b]

Isoprene sulfone was made at room temperature using a 2/1 sulfur dioxide:isoprene mole ratio, 1% of hydroquinone, in 80% yield, m. p. 63.0–63.5°.[3b] Redistilled Eastman Kodak Co. isoprene was used.

Piperylene sulfone was made from Eastman Kodak Co. piperylene which had been isomerized to the *cis–trans* equilibrium mixture according to Frank, *et al.*,[6] and redistilled at 42–43°. Equimolar quantities of hydrocarbon and sulfur dioxide reacted at 100° to give a 50% yield of the sulfone as an oil. This was purified by distilling unreacted hydrocarbon and sulfur dioxide from the crude product, extracting with water, drying and distilling at 0.1 mm.[2a,7]

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[1] Presented before the Organic Division of the American Chemical Society at Atlantic City, September 20, 1949.

[2] (a) Craig, THIS JOURNAL, **65**, 1006 (1943); (b) Drake, Stowe and Partansky, *ibid.*, **68**, 2521 (1946).

[3] (a) Staudinger, German Patent 506,839; *C. A.*, **25**, 522 (1913); (b) Eigenberger, *J. prakt. Chem.*, [2] **127**, 307 (1930).

[4] Staudinger and Ritzenthaler, *Ber.*, **68B**, 455 (1935).

[5] Hooker, Drake and Stowe, U. S. Patent 2,395,050, Feb. 19, 1946.

[6] Frank, Emmick and Johnson, THIS JOURNAL, **69**, 2313 (1947).

[7] We gratefully acknowledge the assistance of Dr. D. Craig of the B. F. Goodrich Company, Research Center, in this vacuum distillation.