TABLE VI

MAIN CHARACTERISTIC BANDS IN MICRONS OF SOME AROMATIC HYDROCARBONS

Toluene				Pentane					
o-n-Propyl-	*m-n*-Propyl-	*p-n*-Propyl-[a]	*p-t*-Amyl-	3-*o*-Tolyl-	3-*m*-Tolyl-	3-*p*-Tolyl-	*p-n*-Propylcumene	1-Phenyl-1-ethylcyclohexane	1-Ethylindan
8.88	8.52	7.21	7.61	7.56	8.57	7.61	7.20	7.36	7.69
9.17	9.06	7.50	8.06	7.70	8.70	8.03	7.30	8.30	7.91
9.39	9.61	8.92	8.33	8.00	9.36	8.23	7.42	9.23	8.32
9.71	11.10	9.59	8.52	9.11	9.62	8.39	7.75	9.71	8.61
10.12	11.33	9.75	8.90	9.22	11.20	8.75	8.26	10.02	9.19
10.68	11.45	12.45	9.41	9.70	11.36	9.00	8.93	11.37	9.78
13.47	12.83	13.35	9.52	10.33	12.81	9.63	9.35	11.70	10.73
	13.02		9.76	10.64	12.98	9.80	9.49	12.34	13.16
			9.88	10.90	14.24	10.96	9.77	13.27	13.33
			12.28	11.27		11.27	11.89		13.51
			12.88	13.28		12.27	12.39		
			13.82	13.76			14.18		

[a] The synthesis of the compound is described by H. Pines, D. R. Strehlau and V. N. Ipatieff, THIS JOURNAL, 71, 3534 (1949).

spectral analysis. In the following cases, where infrared spectra were not available, it was necessary to synthesize the compounds which were expected to be formed in the ethylation reaction. The infrared spectra of the synthetic aromatic hydrocarbons are given in Table VI.

The infrared spectra of *n*-propyl-, isopropyl- and *sec*-butylbenzene were catalogued by the American Petroleum Institute.[14]

The spectra of 3-phenylpentane, *t*-amylbenzene and 3-methyl-3-phenylpentane were reported previously.[15]

Acknowledgment.—The authors wish to thank Mr. Ed Baclawski of U. O. P., Riverside, Ill., for the infrared spectral analyses.

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[15] H. Pines, W. D. Huntsman and V. N. Ipatieff, THIS JOURNAL, **73**, 4343 (1951); **75**, 2311 (1953).

RIVERSIDE, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Absorption Spectra of Halogenated Cyclopentenones[1]

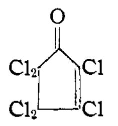
BY E. T. MCBEE, D. K. SMITH AND H. E. UNGNADE

RECEIVED AUGUST 2, 1954

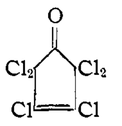
Infrared and ultraviolet absorption spectra have been determined for a series of chlorocyclopentenones. The spectral characteristics of the compounds are in agreement with the conjugated structure for 2,3,4-trichloro-2-cyclopentenone, 2,3,-4,4,5-pentachloro-2-cyclopentenone and the lower melting isomer of hexachlorocyclopentenone. The higher melting isomer of hexachlorocyclopentenone is not conjugated.

Introduction

The structures of the two isomeric hexachlorocyclopentenones I and II have been investigated extensively[2,3,4] and although both chemical[2,4] and physical methods[5] have been applied to this problem, the structural assignments have been tentative. On purely chemical evidence, the lower melting isomer (m.p. 28°) was assigned the conjugated structure I and the higher melting isomer (m.p. 88°) the unconjugated structure II.[4]

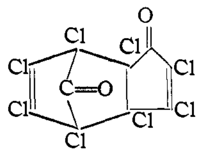


I

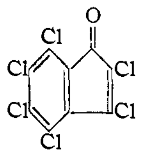


II

The structures of the related 2,3,4,4,5-pentachloro-2-cyclopentenone (III)[3] and 2,3,4-trichloro-2-cyclopentenone (IV)[6] are subject to similar uncertainties, while the diketone V[3,4] can be regarded as structurally certain because of its method of formation by dehydrohalogenation of III and its conversion to perchloroindone (VI) by thermal degradation.



V



VI

Inasmuch as conjugated ketones, such as I, have characteristic absorption in the ultraviolet[7] and in the infrared,[8] the absorption spectra of the chlorocyclopentenones I–V have been determined for the purpose of structure identification.

Experimental[9]

Materials and Methods.—Hexachloro-2-cyclopentenone (I), prepared by the action of sulfuric acid on octachlorocy-

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[1] Abstracted from a portion of a thesis submitted by Delmont K. Smith to the Graduate School of Purdue University in partial fulfillment of the requirements for the Ph.D. degree.

[2] T. Zincke and F. Küster, *Ber.*, **22**, 486 (1899); **23**, 820, 2200 (1890); **26**, 2104 (1893).

[3] T. Zincke and K. H. Meyer, *Ann.*, **367**, 1 (1909).

[4] J. S. Newcomer and E. T. McBee, THIS JOURNAL, **71**, 946 (1949).

[5] H. Van Brederode, H. Gerding and H. J. Prins, *Rec. trav. chim.*, **65**, 174 (1946).

[6] R. K. Meyers, Ph.D. Thesis, Purdue University, 1950.

[7] A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy," Edward Arnold, London, 1954, p. 90.

[8] J. F. Grove and H. A. Willis, *J. Chem. Soc.*, 486 (1942).

[9] All temperatures are uncorrected.

clopentene,[4] melted at 27–28°. This compound was isomerized thermally[10] to hexachloro-3-cyclopentenone (II), m.p. 87.5–88.5°.[11] Octachlorocyclopentene (VII), obtained from the Hooker Electrochemical Co., melted at 37–38°. The reduction of hexachloro-2-cyclopentenone (I) with stannous chloride and hydrochloric acid in acetic acid[3] gave 2,3,4,4,5-pentachloro-2-cyclopentenone (III), m.p. 82–83°. The 2,3,4-trichloro-2-cyclopentenone (IV), prepared according to Meyers[6] by the action of sulfuric acid on 1,2,3,4-tetrachlorocyclopentadiene, boiled at 84–85° (1.5 mm.), n^{20}_{D} 1.5567, m.p. 27–28°. Octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene-1,8-dione (V), m.p. 165–166°, was prepared from 2,3,4,4,5-pentachloro-2-cyclopentenone (III) by dehydrochlorination by means of sodium acetate in acetic acid[3] and 5-bromomethyl-1,2,3,4-tetrachlorobicyclo[2.2.1]-2-heptene-7-one (VIII) was prepared from 5-bromomethyl-7,7-dimethoxy-1,2,3,4-tetrachlorobicyclo[2.2.1]-2-heptene as described by McBee and Diveley,[12] m.p. 109–110°.

Absorption Spectra.—Ultraviolet absorption spectra were determined in 1-cm. silica cells at 25° with a model DU Beckman spectrophotometer. The solvents were 95% ethanol and spectroscopically pure hexane. The experimental data are given in Figs. 1–3. The infrared absorption spectra were determined in chloroform in sealed capillary cells with a Perkin–Elmer model 21 spectrometer (Table I).[13]

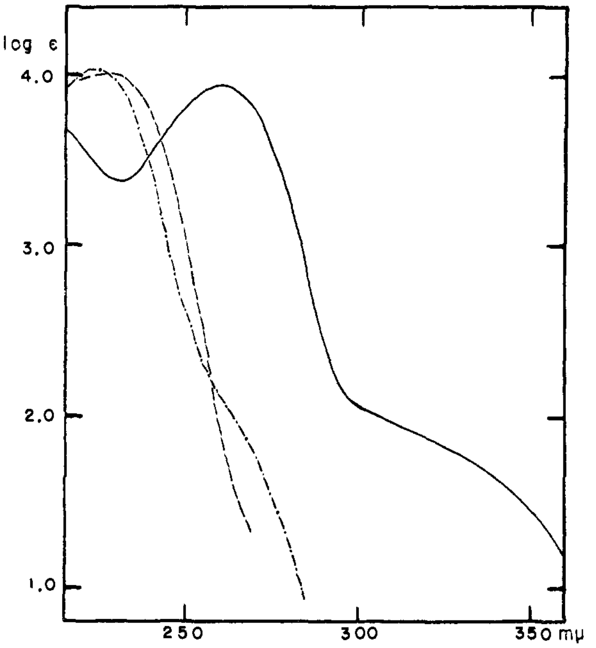

Fig. 1.—Ultraviolet absorption spectra in 95% ethanol: ——, hexachloro-2-cyclopentenone; —·—·—, hexachloro-3-cyclopentenone; -----, octachlorocyclopentene.

Discussion of Results

The ultraviolet absorption spectrum of the lower melting hexachlorocyclopentenone (I) is characteristic of an α,β-unsaturated ketone (Fig. 1). It exhibits a high intensity K-band at 259 mμ due to the conjugated system and an inflection corresponding to the low intensity R-band of the carbonyl grouping.[7,14] The absorption spectrum of I in hexane (Fig. 2) clearly shows both the high intensity K-band and the low intensity R-band. This is in accord with the work of Scheibe[15] who established that non-polar solvents caused the two bands to separate. The lower melting isomer therefore can be assigned structure I.

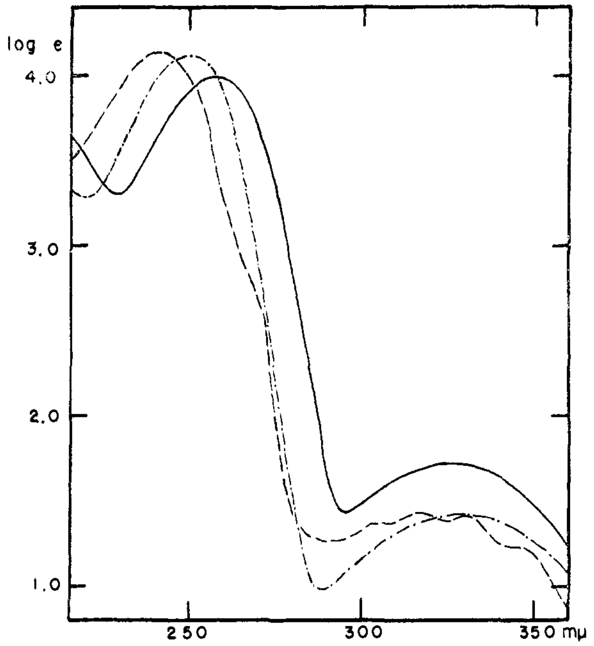

Fig. 2.—Ultraviolet absorption spectra in hexane: ——, hexachloro-2-cyclopentenone; —·—·—, 2,3,4,4,5-pentachloro-2-cyclopentenone; -----, 2,3,4-trichloro-2-cyclopentenone.

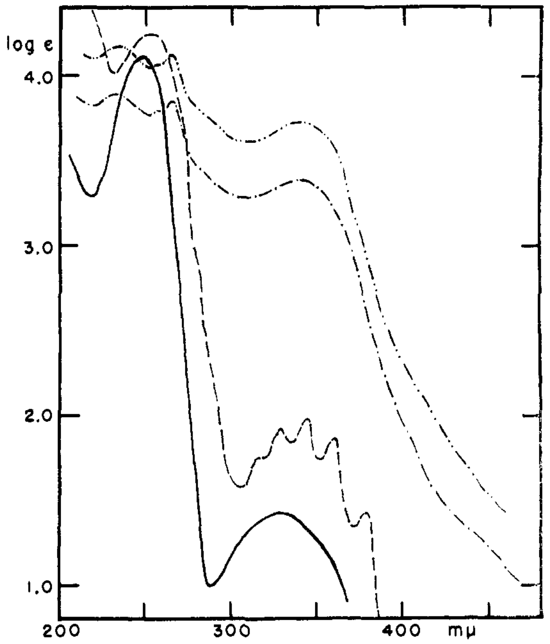

Fig. 3.—Ultraviolet absorption spectra of: ——, 2,3,4,4,5-pentachloro-2-cyclopentenone in hexane; -----, octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene-1,8-dione in hexane; —·—·—, 2,3,4,4,5-pentachloro-2-cyclopentenone in 95% ethanol; —··—··—, octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene-1,8-dione in ethanol with hydrochloric acid.

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(10) H. J. Prins, *Rec. trav. chim.*, **68**, 384 (1949).

(11) J. W. Engelsma and H. Gerding, *ibid.*, **68**, 51 (1949).

(12) E. T. McBee and W. R. Diveley, This Journal, **77**, 493 (1955).

(13) Infrared spectra by H. Susi.

(14) H. L. McMurray, *J. Chem. Phys.*, **9**, 241 (1941).

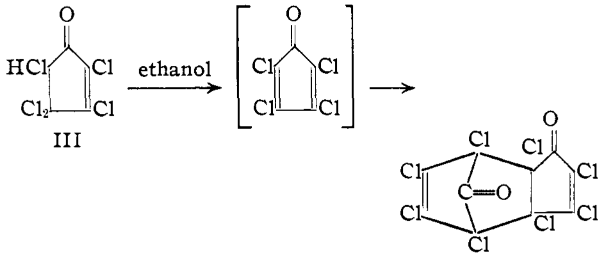
(15) G. Scheibe, *Ber.*, **58**, 586 (1925).

The spectrum of the higher melting isomer II in alcohol has a single absorption band at 223 mμ which is characteristic of the carbon–carbon double bond since it is analogous to the absorption band of octachlorocyclopentene (VII)[16a] in position and intensity. The weak absorption band of the isolated carbonyl group occurs at 318 mμ (log ε 1.19) in hexane, but is absent in ethanol, which is ascribed to solvation. Hence, these spectral data are in agreement with the unconjugated structure, II. Similarly, the spectra of III and IV establish that these compounds are α,β-unsaturated ketones in accord with the previous assignments.

The substitution of halogen causes a bathochromic shift of the primary absorption band of α,β-unsaturated compounds. Thus, Bowden and co-workers[16] found that the maxima of alkyl vinyl ketones undergo a bathochromic shift of 20 mμ for each chlorine substituent on the ethylenic carbons. In the present investigation, a shift of 10 mμ per vinylic chlorine atom is observed for the cyclic ketones. It is especially interesting to note that this also holds for cyclic dienes since four vinylic chlorine atoms in 1,2,3,4-tetrachlorocyclopentadiene (λ_{max} 274 mμ[16a]) shift its absorption band by 39 mμ as compared with cyclopentadiene (λ_{max} 235 mμ).[17] The non-vinylic chlorine atoms in I, III and IV contribute a bathochromic shift of approximately 6 mμ each to the primary absorption bands of these α,β-unsaturated ketones. It is therefore possible to determine the position of the high intensity maxima in conjugated chlorinated compounds.[18–20] Thus, in 2,3,4,4,5-pentachloro-2-cyclopentenone (III), the two vinylic chlorines contribute a shift of 20 mμ to the maximum of cyclopentenone (214 mμ)[20] and the three non-vinylic chlorines an additional 18 mμ to give λ_{max} 252 mμ, which compares favorably with the observed value of 249 mμ. The agreement between calculated and observed values is even better for 2,3,4-trichloro-2-cyclopentenone (IV) (λ_{max} 242 mμ, calcd. 240 mμ) and hexachloro-2-cyclopentenone (I) (λ_{max} 258 mμ, calcd. 258 mμ).

The K-band maxima of the three conjugated ketones (I, III, IV) undergo hypochromic shifts with increasing chlorine substitution. This is in accord with the small hypochromic effect generally attributed to halogen substituents.[16] The reverse effect occurs in the R-band maxima, where the chlorine substitution causes a hyperchromic effect.

The ketone III gives a bright yellow solution in 95% ethanol and an ultraviolet absorption spectrum quite different from that obtained in hexane (Fig. 3). It has been shown[3] that III is dehydrochlorinated easily to tetrachlorocyclopentadienone, which can be isolated only as the dimer,[21] octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene-1,8-dione (V).



III

V

Since the alcoholic solution of III is strongly acidic, it is likely that III is dehydrochlorinated in ethanol. That V is formed is indicated by the fact that an ethanol solution of V in the presence of a small amount of hydrochloric acid gives a yellow solution with an absorption spectrum identical with that obtained from III in ethanol (Fig. 3). The difference in the intensities of the absorption curves is ascribed to incomplete dehydrochlorination (50%) of III in ethanol at 25°, and the red shift of the spectrum of V from hexane to hydrochloric acid in ethanol to the formation of a halochromic salt.[22]

The structural assignments of the ketones I–V are confirmed by the infrared absorption spectra of the compounds (Table I).

TABLE I

INFRARED ABSORPTION BANDS OF CYCLOPENTENONES IN CHLOROFORM

Compound	ν (C=O), μ	ν (C=C), μ	Compound	ν (C=O), μ	ν (C=C), μ
I	5.75	6.39	V	5.53, 5.81	6.39
II	5.63	6.33	VII	....	6.30
III	5.80	6.37	VIII	5.56	6.39
IV	5.87	6.37			

The carbonyl absorption frequencies for the conjugated cyclopentenones I, III and IV vary from 5.75 to 5.87 μ, which compares with the value of 5.83 μ for the C=O band in unsubstituted conjugated cyclopentenones.[8] The shifts to shorter wave lengths are due to the electron-attracting chlorine substituents.[8] The carbonyl stretching frequency for the unconjugated ketone II occurs at 5.63 μ. This also agrees well with the value of 5.73 μ for the carbonyl band of unconjugated cyclopentenones if the shift due to chlorine is allowed for. The infrared absorption spectrum of V shows two bands in the carbonyl range. The band at 5.81 μ corresponds to the α,β-unsaturated carbonyl grouping and the band at 5.53 μ is due to the bridge carbonyl group. The assignment is confirmed by the C=O absorption band of 5-bromomethyl-1,2,3,4-tetrachlorobicyclo[2.2.1]-2-heptene-7-one (VIII)[11] which occurs at 5.56 μ. The high frequency of this carbonyl band probably is due to strain in the bicyclic ring system.

Acknowledgments.—The authors wish to thank the Hooker Electrochemical Company for financial assistance in this work.

LAFAYETTE, INDIANA

[16a] E. T. McBee, C. W. Roberts and J. D. Idol, Jr., in press.

[16] K. Bowden, E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 948 (1946).

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[18] R. B. Woodward, *ibid.*, **63**, 1123 (1941); **64**, 72 (1942).

[19] A. E. Gillam and E. F. West, *J. Chem. Soc.*, 486 (1942).

[20] R. L. Frank, R. Armstrong, J. Kwiatek and H. A. Price, THIS JOURNAL, **70**, 1379 (1948).

[21] C. F. H. Allen, *Chem. Revs.*, **37**, 209 (1945).

[22] P. Pfeiffer, "Organische Molekülverbindungen," Ferdinand Enke, Stuttgart, 1927, p. 66.