of I, where a concentration of 2 × 10^{-3} sufficed. The 95% alcohol and isoöctane were both spectroscopic grade.

Methyl Vinyl Ketone.—This was obtained as an 85% aqueous solution from the du Pont Co. This solution was saturated with potassium carbonate, causing the formation of two layers. The lower aqueous layer was separated and the upper layer was dried over sodium sulfate. The dried ketone was fractionated under reduced pressure.

Methyl Alkyl Ketones and Methyl Cyclopropyl Ketone.—The samples used were all Eastman Kodak Co. White Label products and were fractionated through a 10-plate packed column at atmospheric pressure.

Methyl Cyclobutyl Ketone.—A sample prepared in a 55% yield in a manner analogous to the cyclopentyl and cyclohexyl homologs, was given to us by Dr. W. D. Huntsman of this Laboratory. The material had been fractionated through a 100-plate column.

Methyl Cyclopentyl Ketone.—A solution of 29 g. of cyclopentanecarboxylic acid[12] and 46 g. of acetic acid in 22 g. of acetone was dripped slowly through a Pyrex tube which was heated to 380° in an electric furnace and which contained a manganous carbonate catalyst[13,14] at such a rate that the entire addition took approximately three hours. The light brown condensate was collected, the acetone removed by distillation, and the remaining solution was washed with sodium bicarbonate solution. The resulting homogeneous solution was then extracted several times with ether. The combined ether washings were dried and the ether then removed, leaving a light yellow liquid. Distillation of the residual liquid gave the main fraction, b.p. 60–68° at 20 mm., which weighed 8 g. This was fractionated through a 70-plate column giving 5 g. of a clear fragrant liquid.

Methyl Cyclohexyl Ketone.—A solution was prepared containing 184 g. of distilled cyclohexanecarboxylic acid (Eastman Kodak Co. white label), 222 g. of acetic acid and 128 g. of acetone. This solution was treated in a manner similar to the cyclopentyl homolog. The resultant main fraction boiled at 67.8–71.6° at 13 mm., and weighed 54 g. This was fractionated through a 10-plate column.

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[12] A. S. Hussey, THIS JOURNAL, **73**, 1364 (1951).

[13] J. P. Wibaut, *et al.*, *Rec. trav. chim.*, **58**, 362 (1939).

[14] N. Zelinsky and E. Rjachina, *Ber.*, **57B**, 1932 (1924).

EVANSTON, ILLINOIS

RECEIVED MAY 21, 1951

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Ultraviolet Absorption Spectra of Alicyclic Compounds. III. Phenyl Cycloalkyl and Styryl Cycloalkyl Ketones[1]

BY RAYMOND P. MARIELLA AND RICHARD R. RAUBE

The ultraviolet absorption spectra of phenyl propenyl, cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl ketones were measured in alcohol and isoöctane solutions and compared with benzaldehyde and acetophenone. Similarly, the spectra of styryl vinyl, cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl ketones were measured in alcohol and isoöctane solutions and compared with those of styryl *n*-propyl, *i*-propyl and *i*-butyl ketones and cinnamaldehyde. Because of the strong phenyl ketone and styryl ketone resonance, the contributions of the alicyclic rings are damped out. In these series, a shift to longer wave lengths is noted as the polarity of the solvent is increased.

In continuing our spectroscopic investigations[2] of alicyclic systems, some phenyl alicyclic ketones (Table I) and derivatives (Table II) were prepared, and the ultraviolet absorption spectra (Table III) of the former were measured in isoöctane and alcohol solutions (Fig. 1). In this way, benzaldehyde (I) and acetophenone (II) were compared with phenyl propenyl (III), cyclopropyl (IV), cyclobutyl (V), cyclopentyl (VI) and cyclohexyl (VII) ketones.

TABLE I

Phenyl ketone	B.p.,[a] °C.	Mm.	n^{25}_D	d^{25}_4	R_f	R_c[b,c]	Exalt.
I Hydrogen	72.2	16	1.5433	1.0402	32.17	35.55	0.43
II Methyl	65.0–65.5	3.0–3.4	1.5318	1.0235	36.36	36.36	0.00
III Propenyl	98.6–98.9	3.9–4.0	1.5586	1.0201	46.24	45.13	1.11
IV Cyclopropyl	102.0–102.1	7	1.5514	1.0523	44.35	43.40	0.95
V Cyclobutyl	114.4–114.5	7	1.5452	1.0437	48.53	48.02	.51
VI Cyclopentyl	118.6–118.8	5	1.5424	1.0403	52.74	52.63	.11
VII Cyclohexyl	53.8–55.0[d]	...	....	....	...	...	...

[a] Uncorrected. [b] Atomic refractions taken from Glasstone, "Textbook of Physical Chemistry," 2nd Ed., D. Van Nostrand Co., New York, N. Y., 1946, p. 530. [c] The value for the phenyl-carbonyl exaltation was obtained from the difference in calculated and found molecular refractions of acetophenone and included in all other calculated refractions to give an exaltation for the alkyl group alone. This, of course, assumes no exaltation for the methyl group. [d] Melting point. Analysis for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 83.08; H, 8.61.

TABLE II[a,b]

	2,4-Dinitrophenylhydrazone		Nitrogen, %		*p*-Nitrophenylhydrazone		Nitrogen, %	
	Formula	M.p.,[c] °C.	Calcd.	Found	Formula	M.p., °C.	Calcd.	Found
IV	$C_{16}H_{14}N_4O_4$	211–213[d]	17.2	17.2	$C_{16}H_{15}N_3O_2$	130–131	14.9	14.7
V	$C_{17}H_{16}N_4O_4$	172–173	16.4	16.3	$C_{17}H_{17}N_3O_2$	148–149	14.2	14.5
VI	$C_{18}H_{18}N_4O_4$	143–144	15.8	15.5	$C_{18}H_{19}N_3O_2$	121–123	13.6	13.9
VII	$C_{19}H_{20}N_4O_4$	201–202	15.2	15.2	$C_{19}H_{21}N_3O_2$	149	13.0	13.2

[a] Analyses by C. Brauer and J. Sorensen. [b] K. v. Auwers and E. Lammerhist, *Ber.*, **54**, 1011 (1924), report the preparation of a *p*-nitrophenylhydrazone of phenyl propenyl ketone, however, we were unable to prepare any normal derivative of this compound. [c] Uncorrected. [d] C. F. H. Allen and R. Boyer, *Can. J. Research*, **9**, 159 (1933), report a m.p. of 151°.

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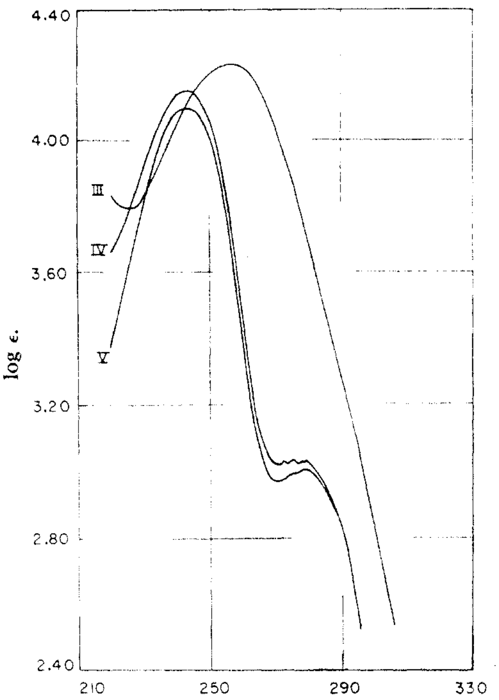
[1] Presented in part before the Fall Meeting of the American Chemical Society, Atlantic City, N. J., September, 1949.

[2] R. P. Mariella and R. R. Raube, THIS JOURNAL, **74**, 518 (1952).



Wave length (mμ).

Fig. 1.—(In alcohol). Spectra of I, II, VI and VII were almost identical to that of V, and are omitted.

The preparation of these compounds is given in Table IV.

TABLE III

MAXIMA

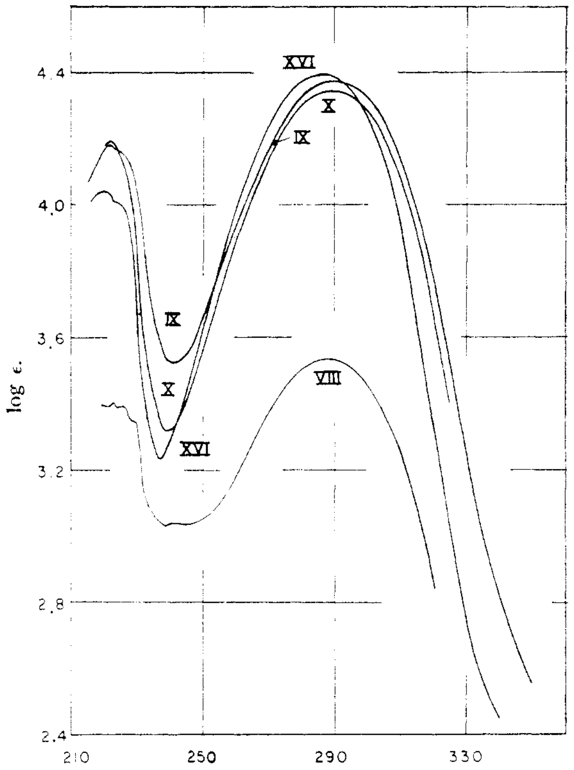
	In alcohol mμ	In alcohol log ε	In isoöctane mμ	In isoöctane log ε
I	246	4.12	241	4.14
	282	3.13	279	3.05
			289	2.98
II	242	4.09	239	4.08
	280	3.02	278	2.93
			286	2.86
III	256	4.24	249	4.25
IV	244	4.15	238	4.15
	272	3.03	278	2.93
	275	3.03	286	2.82
	277	3.03		
	279	3.03		
V	244	4.10	239	4.11
	279	3.01	278	2.94
			287	2.84
VI	243	4.09	238	4.11
	278	3.01	278	2.97
			286	2.88
VII	243	4.08	239	4.08
	274	3.02	273	2.94
	278	3.02	278	2.96
			287	2.85

Also, a series of styryl ketones (Table V), styryl vinyl (VIII), cyclopropyl (IX), cyclobutyl (X), cyclopentyl (XI) and cyclohexyl (XII) ketones were prepared and their ultraviolet absorption spectra (Table VI) in alcohol and isoöctane solutions (Fig. 2) were compared with those of styryl *n*-propyl (XIII), *i*-propyl (XIV), *i*-butyl (XV) ketones and cinnamaldehyde (XVI). Some derivatives are listed in Table VII.

TABLE IV

R	RCOOH Rgt., g.	RCOOH Prod., g.	RCOOH %	RCOCl Rgt., g.	RCOCl Prod., g.	RCOCl %	$RCOC_6H_5$ Rgt., g.	$RCOC_6H_5$ Prod., g.	$RCOC_6H_5$ %
Propenyl	...	...	...	...	...	[a]	59	57	68
Cyclopropyl	116	55	64[c]	55	44	71	43	45[b]	73
Cyclobutyl	500	187	75[d]	187	167	76	75	87	87
Cyclopentyl	134	85	75[e]	50	55	95	53	55	79
Cyclohexyl	...	...	..[a]	75	72	84	72	79	86

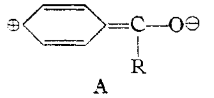
[a] Samples were obtained from the Eastman Kodak Company and were fractionated. [b] Reaction mixture must be kept at room temperature or below to prevent formation of γ-phenylbutyrophenone. [c] Prepared from the reaction of γ-chlorobutyronitrile with sodium hydroxide and subsequent hydrolysis to the acid. See C. M. McClosky and G. H. Coleman, *Org. Syntheses*, **24**, 36 (1944). [d] Prepared by the saponification of ethyl 1,1-cyclobutanedicarboxylate and decarboxylation of the resulting diacid at 170°. See J. R. Fischer, Thesis, California Institute of Technology, 1941. [e] A. S. Hussey, THIS JOURNAL, **73**, 1364 (1951).



Wave length (mμ).

Fig. 2.—(In alcohol). Spectra of XI–XV are almost identical to that of X and are omitted.

In the phenyl ketone series, contributions from such forms as A are so great that the cross-conjugation effects of the various R groups are damped out, with the exception of the case where R is propenyl, in which case form B is important.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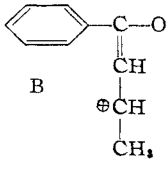
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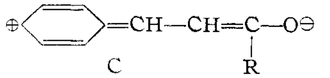
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TABLE V

$C_6H_5CH{=}CHCOR$

	R	B.p., °C.	Mm.	Yield, %	d^{20}_4	n^{20}_4	MR[a] Calcd.	MR[a] Found	Exaltation
VIII	Vinyl	83.0–84.8	0.5	5	1.0172[g]	1.4673[g]	42.51	43.18	0.67
IX	Cyclopropyl[b]	139.4[c]	3.7	67	1.0509[d]	1.6073[d]	51.36	56.62	5.26
X	Cyclobutyl[e]	171.4–171.9[f]	10	59	1.0391[d]	1.5752[d]	55.98	59.25	3.27
XI	Cyclopentyl	166.5–166.9	8	37	1.0331[g]	1.5836[g]	60.60	64.84	4.24
XII	Cyclohexyl[h]	56.0–56.5[i]	..	35	.....	.....	...	...	..
XIII	*n*-Propyl	112.1–112.2[j]	1	68	0.9943	1.5693	53.56	57.43	3.87
XIV	*i*-Propyl	108.8–109.0[k]	0.7	91	0.9864	1.5683	53.56	57.82	4.26
XV	*i*-Butyl	113.0–114.0[l]	1	53	0.9714	1.5580	58.18	62.48	4.30
XVI	Hydrogen[m]	85.8	1.1	..	1.0510	1.6207	43.71	44.21	0.50

[a] Using the atomic refractions of Glasstone, "Textbook of Physical Chemistry," 2nd ed., D. Van Nostrand Co., Inc., New York, N. Y., 1946, p. 530. [b] Calcd. for $C_{12}H_{12}O$: C, 83.68; H, 47.03. Found: C, 83.64; H, 7.21. [c] M.p. 51.3–51.7°. [d] Measurements made on supercooled liquid. [e] Calcd. for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.95; H, 7.77. [f] M.p. 60–62°. [g] Values at 25°. [h] Calcd. for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.24; H, 8.50. [i] M.p. [j] B.p. also determined as 147.6–148.2° at 9 mm. [k] B.p. also determined as 103.0–104.0° at 0.5 mm. and 131.6–132.4° at 6 mm. [l] B.p. also determined as 134.2–134.6° at 4 mm., and 120.6° at 2.6 mm. [m] Eastman Kodak Co. product was distilled through a 10 plate column.

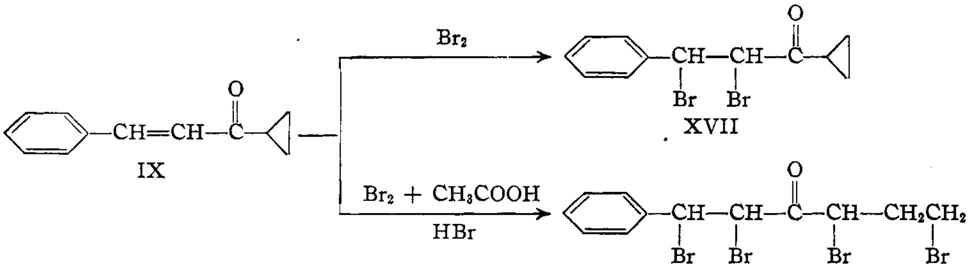
As can be seen (Table III), the spectra of all the phenyl ketones measured, with the exception of III, are essentially the same, with minor variations in the intensities of absorption of the maxima. With the exception of III, IV has the greatest intensity of absorption in both solvents.

In the styryl ketone series, the contribution of such resonance forms as C is so great that any cross-conjugation of the R groups with the carbonyl is damped out, with the exception, R = vinyl; in this case, although VIII possesses maxima at the same wave lengths as the others, it absorbs with much less intensity. This cross-conjugation effect in VIII is probably the cause of the low exaltation.

TABLE VI

Maxima

	In alcohol mμ	In alcohol log	In isoöctane mμ	In isoöctane log ε
VIII	223	3.41	219	3.46
	225	3.39	224	3.43
	289	3.54	279	3.54
IX	222	4.12	220	4.19
	291	4.38	282	4.37
X	221	4.08	219	4.16
	289	4.35	280	4.35
XI	221	4.05	219	4.13
	289	4.33	281	4.34
XII	222	4.07	220	4.12
	290	4.35	282	4.34
XIII	221	4.08	220	4.12
	...	..	225	4.05
	288	4.34	280	4.33
XIV	222	3.98	220	4.12
	...	..	226	4.05
	288	4.33	281	4.33
XV	222	4.02	220	4.11
	...	..	225	4.04
	287	4.33	280	4.33
XVI	220	4.09	218	4.18
	...	..	224	4.14
	285	4.39	278	4.41

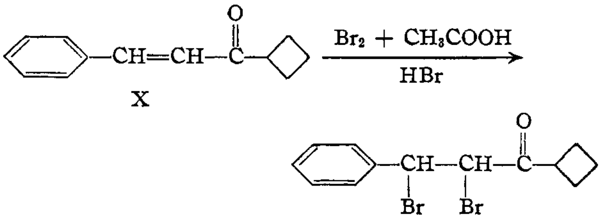


IX

XVII

XVIII

Bromination experiments showed that VIII readily absorbs two moles of bromine as would be expected. The addition of two moles of bromine to IX gave a dibromide (XVII) or a tetrabromide (XVIII) depending on the solvent and presence of a catalyst. Only in the presence of an acidic solvent and strong acid catalyst was the tetrabromide formed exclusively. As was expected, bromination of X, under conditions which converted IX into XVIII, gave only the dibromide (XIX).



X

XIX

In both series of compounds, as the polarity of the solvent was increased a bathochromic shift was noticed. This is exactly opposite to the effect noticed in the methyl cycloalkyl series.[2] This, however, does parallel the work of Scheibe[3] who showed that as the polarity of the solvent increased, the spectrum of acetophenone was shifted to longer wave lengths.

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

TABLE VII[a]

	Dibromo derivatives						2,4-Dinitrophenylhydrazones			
			Analyses, %							
			Carbon		Hydrogen				Nitrogen, %	
	Formula	M.p., °C.	Calcd.	Found	Calcd.	Found	Formula	M.p., °C.	Calcd.	Found
VIII	$C_{11}H_{10}Br_4O$[b]	..	...	...	..	..	$C_{17}H_{14}N_4O_4$[c]	...	..	..
IX	$C_{12}H_{12}Br_2O$[d]	110	43.40	43.28	3.64	3.64	$C_{18}H_{16}N_4O_4$[e]	213	15.9	15.7
X	$C_{13}H_{14}Br_2O$	134	45.11	44.82	4.08	4.13	$C_{19}H_{18}N_4O_4$	171	15.3	15.4
XI	$C_{14}H_{16}Br_2O$	134	46.69	46.64	4.48	4.39	$C_{20}H_{20}N_4O_4$	148	14.7	14.5
XII	$C_{15}H_{18}Br_2O$	139	48.15	47.99	4.85	4.67	$C_{21}H_{22}N_4O_4$	210	14.2	14.0
XIII	$C_{12}H_{14}Br_2O$	88[f]	43.14	42.96	4.22	4.35	$C_{18}H_{18}N_4O_4$	181	15.8	16.0
XIV	$C_{12}H_{14}Br_2O$	102	43.14	43.13	4.22	4.26	$C_{18}H_{18}N_4O_4$[g]	153	15.8	15.9
XV	$C_{13}H_{16}Br_2O$	100[h]	44.85	44.79	4.63	4.66	$C_{19}H_{20}N_4O_4$	172	15.2	14.9

[a] Microanalyses by Misses Hines, Guy, Hobbs, Sorensen and Brauer. [b] The vinyl compound absorbed 2.2 moles by titration in ethanol, and the resulting product boiled at 120–130° at 7 mm. This tetrabromo derivative was very unstable and lost hydrogen bromide immediately. [c] Attempts to prepare this derivative resulted only in an amorphous red material, melting over a wide range (75–145°). [d] Tetrabromo derivative, m.p. 118°. Calcd. for $C_{12}H_{12}Br_4O$: C, 29.30; H, 2.46. Found: C, 29.13; H, 2.46. [e] *p*-Nitrophenylhydrazone, m.p. 119°. Calcd. for $C_{18}H_{17}N_3O_2$: N, 13.7. Found: N, 13.4. Phenylhydrazone, m.p. 104°. Calcd. for $C_{18}H_{18}N_2$: N, 10.7. Found: N, 10.5. [f] C. Harries and P. Bromberger, *Ber.*, **35**, 3090 (1902), report a m.p. of 90°. [g] *p*-Nitrophenylhydrazone, m.p. 131°. Calcd. for $C_{18}H_{19}N_3O_2$: N, 13.6. Found: N, 13.6. [h] C. V. Gheorghiu and B. Arwentiew, *J. prakt. Chem.*, **118**, 295 (1928), report a m.p. of 101°.

It may be, here, that the excited states are more stabilized by solvent interaction than the ground states, thus causing a smaller gap to exist between the two states (in the more polar solvent) and consequently a shift to longer wave lengths. The nature of the solvent effect is being further pursued.

Acknowledgment.—This research was supported by a Frederick G. Cottrell Grant-in-Aid by the Research Corporation, and by a grant from the Graduate School of Northwestern University.

Experimental

Spectra.[2]—Concentrations in the phenyl ketone series were approximately 7 × 10^{-5} molar, except in the case of phenyl propenyl ketone, where a concentration of 1 × 10^{-5} was sufficient. In the styryl ketone series, concentrations were approximately 1 × 10^{-5} molar, except in the case of styryl vinyl ketone, where a 1 × 10^{-4} molar solution was necessary.

Phenyl Ketones.—The acid chlorides were added, dropwise, to a mixture of a slight excess of aluminum chloride in dry benzene. Benzaldehyde and acetophenone were obtained from the Eastman Kodak Company and were fractionated through 10-plate columns. The former was washed with potassium carbonate solution and dried before distillation.

Styryl Ketones.—With the exception of VIII, all the styryl ketones were prepared by the following method: One-half mole each of freshly distilled benzaldehyde and the appropriate methyl ketone was dissolved in one-half liter of water and 25 ml. of 10% aqueous sodium hydroxide was added. The mixture was set aside, with occasional shaking, for a period of seven to nine days. At the end of this time, the originally colorless organic layer had assumed yellow-green color. The layer was separated, and the water layer was extracted several times with ether. The combined organic layer and ether extracts were dried over sodium sulfate, and the ether was evaporated. The residue was either distilled or crystallized. Both IX and X were originally obtained as supercooled liquids (purified by distillation), and did not crystallize for two weeks. Subsequent preparations of IX and X crystallized immediately.

Styryl Vinyl Ketone.—A 2-liter flask equipped with a mechanical stirrer was immersed in an ice-bath and connected by means of a rubber tubing to a 300-ml. flask immersed in another ice-bath. This latter flask also carried a connection to an air line which contained a needle valve. In the larger flask were placed: 500 ml. of water, 240 ml. of freshly distilled benzaldehyde and 30 ml. of 10% aqueous sodium hydroxide, and in the smaller flask was placed 250 ml. of 85% aqueous solution of methyl vinyl ketone. By regulation of the needle valve, the methyl vinyl ketone was forced into the larger flask at such a rate that the temperature remained at 8–10° while the mixture was stirred. After the addition was complete, the mixture was stirred at 10° for one hour; the rather pasty reaction mixture was dissolved in ether, causing the formation of two layers. The aqueous layer was separated and extracted with ether several times. The combined ether extracts and organic layer were dried over sodium sulfate, the ether was evaporated and the residue fractionated at reduced pressure. Approximately 150 ml. of benzaldehyde was recovered, after which the distillate assumed the characteristic yellow-green color of the ketone. The yield of this colored fraction was 36 g. (10%). Although this fraction boiled in a narrow range, 79–81° at 1.4 mm., it still contained benzaldehyde. Subsequent refractionations produced pure product. The residue after each distillation was a clear thermoplastic solid. In each preparation of VIII, the product was fractionated until the spectrum showed no characteristic peak at 241 mμ for benzaldehyde and the ketone gave a negative Schiff test for aldehyde. The data listed in the various tables are those obtained for this highly purified ketone.

Bromination Experiments.—The ketone was dissolved in the appropriate solvent and a slight excess of liquid bromine added from a calibrated pipet. The solution was heated for a few minutes on the steam-bath. Cooling brought down a mass of faint yellow crystals which were crystallized several times from 70% alcohol to white needles. Compound VIII in carbon disulfide readily formed the tetrabromide upon addition of two moles of bromine. Compound IX in either carbon disulfide or ethanol and using either one or two moles of bromine gave exclusively the dibromide (XVII). When IX was dissolved in glacial acetic acid and two moles of bromine added, a mixture of the di- and tetrabromides was formed. However, when this experiment was repeated in the presence of two drops of 48% hydrobromic acid, the tetrabromide was formed exclusively. Repetition of the latter experiment using X gave only the dibromide (XIX).

EVANSTON, ILLINOIS

RECEIVED MAY 21, 1951