

The intense long wave length band is new and is logically assigned to the exocyclic conjugation. This argument is strengthened by a study of models, which shows the interference of the extra methyl group in IX with the phenyl group, thus causing either greater strain or forcing the phenyl group to the other side of the double bond. Either would explain the slight shift of maximum from 3220 to 3258 Å. It is difficult to carry the same argument to all the compounds studied. It appears preferable to consider the chromophore  $C=C-C-C=C$  as



a whole. Just as the chromophore  $C=C-C=O$  has one intense absorption band within definite limits of the spectrum, so this more complicated chromophore has its intense long wave length absorption band within definite limits of the spectrum. For five-atom rings with saturated substituents only on the endocyclic bond this band lies at  $3075 \pm 25$  Å., for corresponding six-atom rings at  $3240 \pm 25$  Å., and for five-atom rings with aromatic substituents at  $3290 \pm 25$  Å.

**Rules for  $\alpha,\beta$ -Unsaturated Cyclopentanones.**—Our final point is incidental to the main purpose of this study, but is important. It is concerned with the "mother substances" listed in Tables I and II, derivatives of cyclopentanones with an  $\alpha,\beta$ -endocyclic ethylene bond. Although the number of such compounds whose absorption spectra have been determined is still much smaller than the number of six-atom ring ketones upon which Woodward<sup>39</sup> based his reliable rules for the relations between structure and absorption spectra of such  $\alpha,\beta$ -unsaturated cyclohexanones, we believe that the number justifies the attempt now to formulate

(39) R. B. Woodward, *THIS JOURNAL*, **64**, 76 (1942).

similar rules for the  $\alpha,\beta$ -unsaturated cyclopentanones. We include in the following list three six-atom-ring ketones with aromatic substituents on the double bond, since such compounds were not included in Woodward's<sup>25</sup> survey.

The data given in Table III are summarized roughly in Table IV, and at the same time compared with the data for cyclohexenones.<sup>25</sup>

TABLE IV

	2-Cyclohexenones	2-Cyclopentenones
<i>endo</i> -Bonds		
Saturated substituents		
Monosubstituted	2250 $\pm$ 50	2170 $\pm$ 50
Disubstituted	2350 $\pm$ 50	2270 $\pm$ 50
Trisubstituted	2470 $\pm$ 50	2360 $\pm$ 50
<i>exo</i> -Bonds		
Aromatic substituents		
Disubstituted	2850 $\pm$ 50	2860 $\pm$ 50
Saturated substituents		
Trisubstituted	2520 $\pm$ 50	2550 $\pm$ 50 <sup>1</sup>

In general, the conclusion is obvious that the five-atom ring ketones have their absorption maxima at shorter wave lengths than do the six-atom ring ketones when the ethylene bond is in the ring and all substituents are saturated. The reverse is true when the ethylene bond is outside the ring. When the substituents are phenyl groups, the size of the ring makes negligible difference.

**Acknowledgments.**—The microanalyses reported in this paper were done by the Clark Microanalytical Laboratory, Urbana, Illinois. The author makes grateful acknowledgment to Miss Anna Asadourian and to Dr. Roberta Stewart for the preparation of some of the compounds.

WELLESLEY 81, MASS.

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## Ultraviolet Absorption Spectra of Alicyclic Compounds. II. Methyl Cycloalkyl Ketones<sup>1</sup>

BY RAYMOND P. MARIELLA AND RICHARD R. RAUBE

The ultraviolet absorption spectra of methyl vinyl, methyl cyclopropyl, methyl cyclobutyl, methyl cyclopentyl, methyl cyclohexyl and several methyl alkyl ketones were measured in alcohol and isoöctane solutions. In this series, as the polarity of the solvent is increased the main maxima are shifted to shorter wave lengths. There is no simple gradation in the spectra as the ring size is increased.

The second order conjugation effect (hyperconjugation) of the cyclopropyl ring in conjugation with aromatic nuclei, ketone groups, and double bonds has been observed by several investigators.<sup>1-7</sup>

The present work was undertaken to determine whether other alicyclic systems exhibit this hyperconjugation phenomenon, and to see if there is any

correlation between ring size and ability to hyperconjugate.

There have been several reports in the literature concerning the different effects of the cyclopentyl and cyclohexyl rings.<sup>8</sup> There have been two independent correlations of four, five and six membered rings<sup>9</sup> (cyclobutanone, cyclopentanone and cyclohexanone). Comparing the maxima with the highest intensity in each case, we get the following figures:

(8) See L. N. Ferguson, *Chem. Revs.*, **43**, 392 (1948), for some leading references.

(9) (a) G. Forster, R. Skrabal and J. Wagner, *Z. Elektrochem.*, **43**, 290 (1937); (b) S. W. Benson and G. B. Kistiakowsky, *THIS JOURNAL*, **64**, 80 (1942).

(1) For the previous paper in this series see R. P. Mariella, L. F. A. Peterson and R. C. Ferris, *THIS JOURNAL*, **70**, 1494 (1948).

(2) E. P. Carr and C. P. Burt, *ibid.*, **40**, 1590 (1918).




(3) I. M. Klotz, *ibid.*, **66**, 88 (1944).

(4) J. D. Roberts and C. Green, *ibid.*, **68**, 214 (1946).

(5) M. Rogers, *ibid.*, **69**, 2544 (1947).

(6) J. F. Music and F. A. Matsen, *ibid.*, **72**, 5256 (1950).

(7) W. W. Robertson, J. F. Music and F. A. Matsen, *ibid.*, **72**, 5260 (1950).

	F. S. and W <sup>9a</sup> m $\mu$	log $\epsilon$	B. and K. <sup>9b</sup> m $\mu$	log $\epsilon$
	280	1.26	281	1.28
	299	1.30	300	1.23
	292	1.22	290	1.05

indicating in both cases that the five-membered ring does not have its maximum *between* that of similar four- and six-membered rings. Forster, Skrabal and Wagner,<sup>9a</sup> however, correlated certain maxima and claimed a gradation as the ring size increased. Unfortunately, cyclopropanone is not available in this series.

derivatives (Table II): methyl vinyl (I), methyl cyclopropyl (II), methyl cyclobutyl (III), methyl cyclopentyl (IV) and methyl cyclohexyl (V) ketones and measured their ultraviolet absorption spectra in alcohol and isoöctane solutions (Table III) (Fig. 1). The spectra of acetone (VI), methyl ethyl ketone (VII) and methyl isobutyl ketone (VIII) were also measured for comparison reasons.

Rogers<sup>5</sup> reported the spectrum of methyl cyclopropyl ketone to be anomalous since the main maximum was not between that of methyl isopropyl ketone and methyl vinyl ketone. In all other cases investigated,<sup>1-7</sup> the cyclopropyl ring showed a maximum between that of a corresponding saturated and unsaturated group.

We have verified Rogers' work and have also shown that in both solvents, methyl cyclopropyl

TABLE I

Methyl ketone	B.p., <sup>a</sup> °C.	Mm.	$n_D^{25}$	$d_4^{25}$	R <sub>t</sub>	R <sub>0</sub> <sup>b</sup>	Exalt.
I Vinyl	36.5-36.8	145	1.4083	0.8429	20.53	20.22 <sup>c</sup>	0.31
II Cyclopropyl	110.1-110.3	747	1.4224	.8938	23.93	23.10	.83
III Cyclobutyl	134.8-135.2	750	1.4300	.9002	28.16	27.72	.44
IV Cyclopentyl	94.8-95.0	99	1.4411	.9125	32.47	32.34	.13
V Cyclohexyl	76.2-77.0	25	1.4491	.9159	36.96	36.95	.01
VI Methyl	54.8	742	1.3560	.7850	16.17	16.07	.10
VII Ethyl	76.9-77.1	746	1.3762	.8014	20.65	20.68	-.03
VIII Isobutyl	112.4-112.6	737	1.3933	.7964	30.04	29.92	.12

<sup>a</sup> Boiling points of I, II, V-VIII were uncorrected, those of III and IV were determined with a calibrated iron-constantan thermocouple. <sup>b</sup> Using the atomic refractions of Glasstone, "Textbook of Physical Chemistry," 2nd Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1946, p. 530. <sup>c</sup> Includes the value of 1.73 for a double bond.

TABLE II<sup>a</sup>

2,4-Dinitrophenylhydrazone				$\beta$ -Nitrophenylhydrazone			
M.p., <sup>c</sup> °C.	Formula	Nitrogen, <sup>b</sup> % Calcd.	Found	M.p., <sup>c</sup> °C.	Formula	Nitrogen, <sup>b</sup> % Calcd.	Found
II 151.5-152.5 <sup>d</sup>	C <sub>11</sub> H <sub>12</sub> N <sub>4</sub> O <sub>4</sub>	21.2	21.3	144.8-145.2	C <sub>11</sub> H <sub>12</sub> N <sub>3</sub> O <sub>2</sub>	19.2	19.1
III 119.9-121.3	C <sub>12</sub> H <sub>14</sub> N <sub>4</sub> O <sub>4</sub>	20.1	20.0	128.2-129.0	C <sub>12</sub> H <sub>14</sub> N <sub>3</sub> O <sub>2</sub>	18.0	18.0
IV 126.9-127.3	C <sub>13</sub> H <sub>16</sub> N <sub>4</sub> O <sub>4</sub>	19.2	19.5	129.5-130.0	C <sub>13</sub> H <sub>16</sub> N <sub>3</sub> O <sub>2</sub>	17.0	16.9
V 136.0-136.6 <sup>e</sup>	C <sub>14</sub> H <sub>18</sub> N <sub>4</sub> O <sub>4</sub>	18.3	18.3	149.8-150.0	C <sub>14</sub> H <sub>18</sub> N <sub>3</sub> O <sub>2</sub>	16.1	16.2

<sup>a</sup> No simple derivatives of I could be prepared. <sup>b</sup> Analyses by C. Brauer and J. Anderson. <sup>c</sup> All melting points are uncorrected. <sup>d</sup> J. D. Roberts and C. Green, THIS JOURNAL, 68, 214 (1946), report a melting point of 149-150°. <sup>e</sup> C. F. H. Allen, *ibid.*, 52, 2955 (1930), reports a m.p. of 140°.

Matsen and co-workers<sup>7</sup> compared cyclopropyl, cyclopentyl and cyclohexylbenzenes, and showed a definite trend as the ring size increased, but unfortunately, cyclobutylbenzene was not included in this series. From the authors<sup>7</sup> discussion it is inferred that the maximum of cyclobutylbenzene would be between that of cyclopropyl and cyclopentylbenzene. From our work and others,<sup>9</sup> it is predicted that in the cycloalkyl-benzene series, there will not be any simple gradation as the ring size is increased.

Some recent work<sup>10</sup> on some five-, six-, seven- and eight-membered, cyclic, conjugated dienes showed the six-membered ring to have a maximum at longer wave lengths than any of the others. Unfortunately cyclobutadiene and any three-membered analog are not available for comparison purposes.

It was of interest to examine a series of compounds which included all the rings from the cyclopropyl to the cyclohexyl, and to compare these with similarly unsaturated and saturated analogs. We prepared a series of methyl ketones (Table I) and

TABLE III

	Alcohol		Isoöctane	
	m $\mu$	log $\epsilon$	m $\mu$	log $\epsilon$
I	318	1.48	331	1.40
II	271	1.37	277	1.28
III <sup>a</sup>	281	1.52	286	1.38
IV	279	1.37	283	1.29
V <sup>b</sup>	281	1.45	287	1.36
VI	270	1.20	279	1.16
VII	273	1.26	278	1.23
VIII	279	1.35	283	1.30

<sup>a</sup> III showed a minor maximum at 230 m $\mu$  (log  $\epsilon$  0.81) in isoöctane. <sup>b</sup> V showed a minor maximum in both alcohol (247 m $\mu$ , log  $\epsilon$  1.15) and in isoöctane (234 m $\mu$ , log  $\epsilon$  1.11).

ketone has the *lowest* intensity of absorption and its main maximum has the *shortest* wave length of all the cyclic relatives.

Although methyl vinyl and methyl cyclopropyl ketones resemble each other by giving indications of possessing strong absorption in the near ultraviolet, it is methyl cyclopentyl ketone which seems to be most similar to methyl cyclopropyl ketone with respect to the main maximum in the ultraviolet

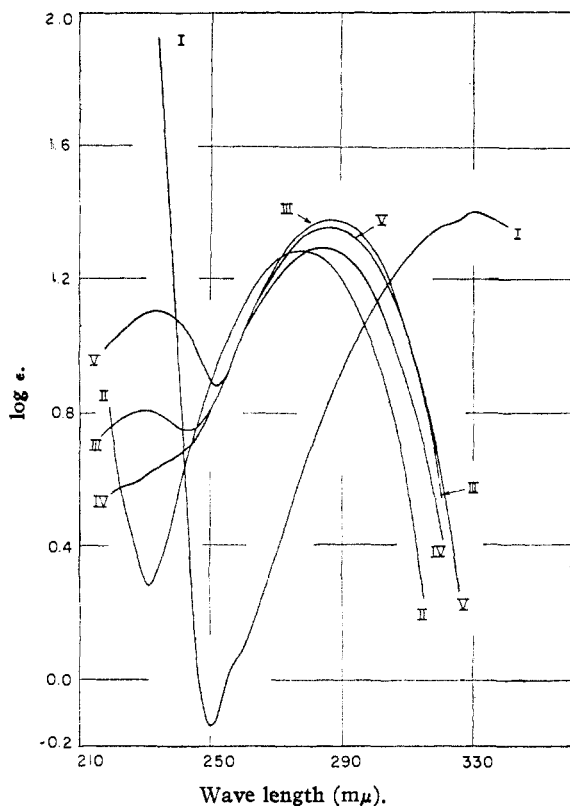


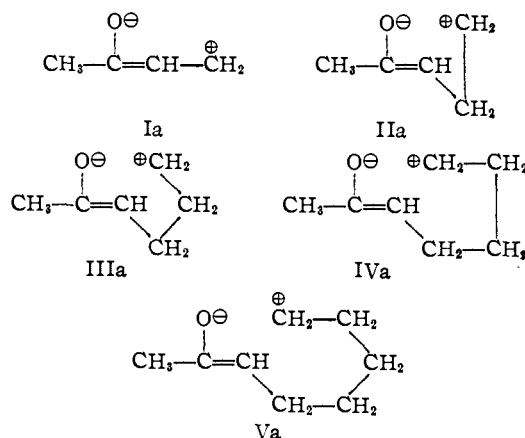
Fig. 1.—Spectra in isoöctane.

region. In addition, methyl cyclobutyl and methyl cyclohexyl ketones resemble each other very closely, with methyl cyclobutyl ketone exhibiting the *greatest* intensity of absorption in both solvents. Methyl cyclobutyl and methyl cyclohexyl ketones also have an additional maximum around 230  $m\mu$ , which the other ketones do not show. Since III absorbs at a longer wave length than do either II or IV, spectroscopically, there does not appear to be any simple gradation as the ring size is increased.

From the molecular refractions it is seen that there is a definite decrease in exaltation as the ring size is increased. This is in agreement with the strain theory, from which one would predict that as the ring size increased the polarizability of the ring would decrease.

If the ground states of all the methyl cycloalkyl ketones were approximately on the same energy level in any one solvent, then the contributions of excited states such as Ia-Va would be predominant factors in determining the position and intensity of absorption.

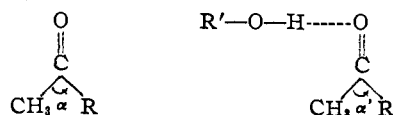
One would expect that as the ring size increased, the contribution of the excited structure would decrease. Since the results seem to be anomalous, we must conclude either that the ground states are definitely not the same in all cases, or that the contributions of the excited states are different, or the formulas above do not represent the excited states. Methyl ethyl ketone and acetone resemble methyl cyclopropyl ketone in position of maximum, but absorb with less intensity. Methyl isobutyl ketone resembles methyl cyclopentyl ketone very closely. A more complete interpretation of the spectra



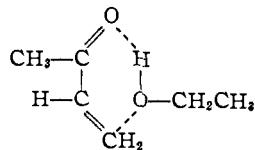
must await a critical evaluation of the ground and excited states.

In every case, the change from isoöctane to alcohol caused a shift in location of absorption maxima in the region of 290  $m\mu$ .<sup>11</sup> The differences in the positions of the maxima of II, III, IV and V were more pronounced in alcohol than in isoöctane, indicating solvent-compound interaction.

The energy levels of the various excited states in this series are so high that they are probably unaffected by the nature of the solvent. For this reason, any solvent effects would result in a change primarily in the ground states. Such a change would probably cause a stabilization of the ground state and consequently a shift to shorter wave lengths. In the more polar solvent, hydrogen bonding of the ketone group with the solvent results in the formation of a less strained configuration about the ketonic carbon ( $\alpha'$  would be more close to the normal tetrahedral carbon valence angle than  $\alpha$ ).



When R is a cycloalkyl or alkyl, the change from isoöctane to alcohol caused an average hypsochromic shift of about 5.5  $m\mu$ . When R is vinyl, the shift is slightly more than twice this value. This rather large shift may be due to the formation of a somewhat stable "quasi" six-membered ring, thus markedly stabilizing the ground state.



**Acknowledgment.**—This research was supported by a Frederick G. Cottrell Grant-in-Aid by the Research Corporation.

#### Experimental

**Spectra.**—All spectra were measured on a model DU Beckman quartz spectrophotometer. The concentration used was approximately  $2 \times 10^{-2}$  molar with the exception

(11) This is in agreement with the work of G. Scheibe, *Ber.*, **58**, 586 (1925), who showed that as the polarity of the solvent increased, the position of the wave length of acetone was shifted toward shorter wave lengths.

of I, where a concentration of  $2 \times 10^{-3}$  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<sup>13</sup> 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<sup>13,14</sup> 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.

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

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

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

EVANSTON, ILLINOIS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

## Ultraviolet Absorption Spectra of Alicyclic Compounds. III. Phenyl Cycloalkyl and Styryl Cycloalkyl Ketones<sup>1</sup>

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<sup>2</sup> 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

TABLE I

Phenyl ketone	°C.	B.p. <sup>a</sup>	Mm.	$n_D^{20}$	$d_4^{20}$	R <sub>t</sub>	R <sub>b</sub> <sup>b</sup>	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 <sup>d</sup>		...	....	....	...	...	...

<sup>a</sup> Uncorrected. <sup>b</sup> Atomic refractions taken from Glasstone, "Textbook of Physical Chemistry," 2nd Ed., D. Van Nostrand Co., New York, N. Y., 1946, p. 530. <sup>c</sup> 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. <sup>d</sup> Melting point. Analysis for C<sub>12</sub>H<sub>16</sub>O: C, 82.93; H, 8.57. Found: C, 83.08; H, 8.61.

TABLE II<sup>a,b</sup>

2,4-Dinitrophenylhydrazone				<i>p</i> -Nitrophenylhydrazone			
Formula	M.p., °C.	Nitrogen, %		Formula	M.p., °C.	Nitrogen, %	
		Calcd.	Found			Calcd.	Found
IV C <sub>18</sub> H <sub>14</sub> N <sub>4</sub> O <sub>4</sub>	211–213 <sup>d</sup>	17.2	17.2	C <sub>16</sub> H <sub>11</sub> N <sub>3</sub> O <sub>3</sub>	130–131	14.9	14.7
V C <sub>17</sub> H <sub>14</sub> N <sub>4</sub> O <sub>4</sub>	172–173	16.4	16.3	C <sub>17</sub> H <sub>13</sub> N <sub>3</sub> O <sub>3</sub>	148–149	14.2	14.5
VI C <sub>18</sub> H <sub>14</sub> N <sub>4</sub> O <sub>4</sub>	143–144	15.8	15.5	C <sub>18</sub> H <sub>13</sub> N <sub>3</sub> O <sub>3</sub>	121–123	13.6	13.9
VII C <sub>18</sub> H <sub>20</sub> N <sub>4</sub> O <sub>4</sub>	201–202	15.2	15.2	C <sub>19</sub> H <sub>21</sub> N <sub>3</sub> O <sub>3</sub>	149	13.0	13.2

<sup>a</sup> Analyses by C. Brauer and J. Sorensen. <sup>b</sup> 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. <sup>c</sup> Uncorrected. <sup>d</sup> C. F. H. Allen and R. Boyer, *Can. J. Research*, **9**, 159 (1933), report a m.p. of 151°.

(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).

(I) and acetophenone (II) were compared with phenyl propenyl (III), cyclopropyl (IV), cyclobutyl (V), cyclopentyl (VI) and cyclohexyl (VII) ketones.