sodium amide (0.35 mole) in 250 ml. of liquid ammonia was obtained, after 5 hours, 7.1 g. (16%) of pure *m*-aminobenzotrifluoride.

Amination of *p*-Chlorobenzotrifluoride.—From 26.1 g. (0.20 mole) of *p*-chlorobenzotrifluoride and a solution of sodium amide (0.30 mole) in 250 ml. of liquid ammonia was obtained, after 10 minutes, 7.3 g. (25%) of a 1:1 mixture of *m*- and *p*-aminobenzotrifluorides, b.p. 78.0–81.5° (12 mm.).

Amination of *p*-Bromofluorobenzene.—*p*-Bromofluorobenzene (32.0 g., 0.183 mole) and a solution of potassium amide (0.36 mole) in 250 ml. of liquid ammonia yielded, after 8 minutes, 6.2 g. (31%) of a mixture of 20% *m*- and 80% *p*-fluoroanilines, b.p. 77.0–87.5° (20.5 mm.), n^{25}_{D} 1.5378–1.5386.

Amination of *o*-, *m*- and *p*-Chlorotoluenes and *m*-Bromotoluene.—A fourfold excess of potassium amide and reaction times of 6–13 min. were used in each case. *o*-Chlorotoluene gave a 66% yield of a mixture of 45% *o*- and 55% *m*-toluidine, b.p. 96.0–100.0° (21.4 mm.). *m*-Chlorotoluene gave a 66% yield of a mixture of 40% *o*-, 52% *m*- and 8% *p*-toluidine, b.p. 95.0–99.2° (23.7 mm.). *p*-Chlorotoluene gave a 35% yield of a mixture of 62% *m*- and 38% *p*-toluidine, b.p. 96.5–99.2° (21.4 mm.). *m*-Bromotoluene gave a 61% yield of a mixture of 22% *o*-, 56% *m*- and 22% *p*-toluidine, b.p. 90.0–93.1° (16.9 mm.).

_o_-Anisidine with Sodium Amide.—*o*-Anisidine (10 g., 0.081 mole) was dropped into a sodium amide solution (0.022 mole) in 150 ml. of liquid ammonia and the mixture was stirred and maintained at reflux for 1 hour. The products were isolated in the usual manner. An almost quantitative recovery of *o*-anisidine was obtained.

_p_-Aminobenzotrifluoride with Sodium Amide.—*p*-Aminobenzotrifluoride (4.2 g., 0.26 mole) was dropped slowly into a solution of sodium amide (0.009 mole) in 250 ml. of liquid ammonia. The mixture was stirred and allowed to reflux for 3 hours and the products isolated in the usual manner. *p*-Aminobenzotrifluoride (2.0 g., 46%) containing none of the *o*- or *m*-isomers was recovered; the rest of the amine was converted to a non-volatile straw-colored material.

Acknowledgment.—Thanks are due to Mr. R. Piccolini for help with some of the preparation.

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[CONTRIBUTION FROM THE COLLEGE OF PHARMACY OF THE UNIVERSITY OF CALIFORNIA]

The Dipole Moments, Spectra and Structure of Some New 2-Phenyl-, 2-Benzyl-, 2-(*p*-Halobenzylidene)- and 2,6-Bis-(*p*-halobenzylidene)-cyclohexanones[1]

BY ALAIN C. HUITRIC[2] AND W. D. KUMLER

RECEIVED MAY 24, 1955

A number of substituted 2-phenyl-, 2-benzyl-, 2-(*p*-halobenzylidene)- and 2,6-bis-(*p*-halobenzylidene)-cyclohexanones and related compounds including β-nitrostyrenes, 4-nitro-5-aryl-cyclohexenes, 6-aryl-3-cyclohexen-1-ones and 2,6-bis-(aryl)-cyclohexanones have been made. The theoretical dipole moments of the substituted phenyl and benzylcyclohexanones have been calculated and compared with the measured moments. The data are consistent with the molecules having the semi-rigid chair or *trans* form with the groups occupying equatorial positions. In the case of the *p*-(halophenyl)-cyclohexanones the possibility of the groups occupying axial positions is excluded. The α-phenylcarbonyl compounds all show an enhanced absorption around 290 mμ. Two β-phenylcarbonyl compounds also have abnormally high extinctions in this region. Two compounds with double bonds in the 3-position show additional absorption indicating that the double bond, the carbonyl and the phenyl, although chain insulated, are interacting, presumably directly through space. The dipole moments and ultraviolet spectra of the chloro-, bromo- and iodo-2-(*p*-halobenzylidene) and the chloro-, bromo- and iodo-2,6-bis-(*p*-halobenzylidene)-cyclohexanones have been measured. The dipole moments show that both groups of compounds have structures with the halobenzyl groups *trans* to the carbonyl oxygens. The ultraviolet spectra of the compounds are consistent with the structures in which the phenyl, C=C and the carbonyl are conjugated.

This work is concerned with the synthesis, stereostructure and abnormal ultraviolet carbonyl band of certain substituted cyclohexanones. The compounds were made because they gave promise of having interesting pharmacological properties.

There is considerable evidence that the rigid chair form of cyclohexane is more stable than the less rigid boat form,[3-5] and the most stable chair form of substituted cyclohexanes is that in which substituents of high steric requirements occupy equatorial positions.[6] This is generally considered also to apply to cyclohexanone and substituted cyclohexanones, but there is as yet relatively little experimental evidence in regard to this. Evidence has been obtained from dipole moment studies[7] that the structure of 2-phenylcyclohexanone is consistent with the chair form with the phenyl occupying the equatorial position. In the present work a series of substituted 2-phenylcyclohexanones is investigated in which the substituents are such that conclusive differentiation between equatorial and axial[8] isomers is possible from the dipole moments of the compounds.

Since some of these compounds belong to the α-phenylcarbonyl class their ultraviolet spectra was measured to see if they, like previous compounds studied, had abnormal carbonyl bands.[9,10] This was found to be the case. Two β-phenylcarbonyl compounds also exhibited abnormal carbonyl bands.

Dipole Moments.—The dipole moments were measured in benzene at 30°, except 2-(*p*-hydroxyphenyl)-cyclohexanone which was measured in dioxane. The moments were calculated using the equation and method of Halverstadt and Kumler.[11] The plots of ϵ_{12} *vs.* ω_2 and ν_{12} *vs.* ω_2 were straight lines within the limits of experimental error and the values of ϵ_1 and ν_1 were obtained by extrapolating

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[1] From the Ph.D. Thesis in Pharmaceutical Chemistry of Alain C. Huitric, University of California, 1954.

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[3] O. Hassel, *Quart. Revs.*, **7**, 221 (1953).

[4] O. Hassel, *Research*, **3**, 504 (1950).

[5] D. H. R. Barton, *J. Chem. Soc.*, 1027 (1953).

[6] C. W. Beckett, K. S. Pitzer and R. Spitzer, THIS JOURNAL, **69**, 2488 (1947).

[7] E. L. Alpen and W. D. Kumler, *ibid.*, **72**, 5745 (1950).

[8] D. H. R. Barton, O. Hassel, K. S. Pitzer and V. Prelog, *Science*, **119**, 49 (1954).

[9] W. D. Kumler, L. A. Strait and E. L. Alpen, THIS JOURNAL, **72**, 1463 (1950).

[10] E. L. Alpen, W. D. Kumler and L. A. Strait, *ibid.*, **72**, 4558 (1950).

[11] I. F. Halverstadt and W. D. Kumler, *ibid.*, **64**, 2988 (1942).

TABLE I

Cyclohexanone	ϵ_1	ν_1	α	β	P_{20}	P_{E_2}	Obsd. μ	Theoretical μ(e)	μ(a)
2-(*p*-Chlorophenyl)-	2.2676	1.14756	9.340	−0.3200	419.73	56.92	4.25	4.33	2.40
2-(*p*-Bromophenyl)-	2.2680	1.14749	7.275	− .4660	399.28	59.82	4.11	4.30	2.40
2-(*p*-Isopropylphenyl)-	2.2686	1.14768	4.267	− .1567	238.11	65.91	2.93	2.90	2.90
2-(*p*-Hydroxyphenyl)-	2.2036	0.97380	7.100	− .1240	269.59	53.58	3.28	3.37	2.56
2-(*p*-Methylphenyl)-	2.2689	1.14765	4.860	− .1820	226.89	56.67	2.91	2.90	2.90
2-(*m*-Methylphenyl)-	2.2689	1.14764	5.140	− .1990	235.90	56.67	2.99	3.02	2.90
2-(*o*-Methylphenyl)-	2.2675	1.14760	6.320	− .2060	277.57	56.67	3.31		
2-(*p*-Chlorobenzyl)-	2.2688	1.14766	5.340	− .2840	281.87	61.54	3.31	3.34	2.58
2,6-Bis-(*p*-chlorobenzyl)-	2.2690	1.14753	2.9667	− .3283	279.18	94.93	3.03		
2-(*p*-Chlorobenzylidene)-	2.2680	1.14768	3.900	− .3260	216.56	64.40	2.75		
2-(*p*-Bromobenzylidene)-	2.2680	1.14743	3.360	− .4340	236.58	68.38	2.89		
2-(*p*-Iodobenzylidene)-	2.2684	1.14770	2.880	− .5440	225.89	72.65	2.76		
2,6-Bis-(*p*-chlorobenzylidene)-	2.2683	1.14754	2.020	− .3800	209.30	109.46	2.23		
2,6-Bis-(*p*-bromobenzylidene)-	2.2680	1.14747	1.740	− .5460	219.33	113.88	2.29		
2,6-Bis-(*p*-iodobenzylidene)-	2.2684	1.14751	1.520	− .6160	234.22	126.76	2.31		

the ϵ_{12} and ν_{12} values to zero weight fraction. The solute molar electronic polarizations P_{E_2} are the molar refractions as calculated from the electron group refractions for the phenyl and benzyl compounds. For the benzylidene compounds the P_{E_2} values are the molar refractions for the D sodium line obtained from measured refractive indices of the solutions by the use of the equation

$$P_{E_2} = \frac{3\gamma\nu_1 M}{(n_1^2 + 2)^2} + M(\nu_1 + \beta)\frac{n_1^2 - 1}{n_1^2 + 2}$$

where n is the refractive index and γ the slope of the n^2_{12} *vs.* ω_2 curve. The plots of n^2_{12} *vs.* ω_2 were straight lines within the experimental error and the values of n^2_1 were obtained by extrapolating the n^2_{12} values to zero weight fraction. The results are given in Table I.

Theoretical Dipole Moments.—According to a recent review,[3] the available experimental evidence indicates cyclohexane derivatives exist in the chair form, both in the vapor and liquid state. In calculating the theoretical moments of the cyclohexanone derivatives, we have assumed the chair configuration and that no distortion takes place when one methylene group is replaced with a carbonyl group. A set of reference axes was selected with the z-axis as the principal vertical axis parallel to the *axial* bonds and the xz-plane passing through the carbonyl carbon and the number 4 carbon; the carbonyl group is pointed upward and forms angles of 35 and 55° with the xy-plane and the z-axis, respectively. The equatorial C–H bonds form an angle of 109° 28′ and also an angle of 180 − 109° 28′ = 70° 32′ with the principal vertical axis. The moment of the carbonyl group is taken as 2.90.[12] The component moments m_x, m_y, m_z along the different axes of each group moment were calculated and the resultant moment obtained by use of the equation

$$\mu = [(\epsilon m_x)^2 + (\epsilon m_y)^2 + (\epsilon m_z)^2]^{1/2}$$

The values chosen in calculating the theoretical moments including those given in Table I are as follows: p-Cl-C$_6$H$_5$-, 1.56 from the average of the best values for chlorobenzene in benzene[13] etc.;

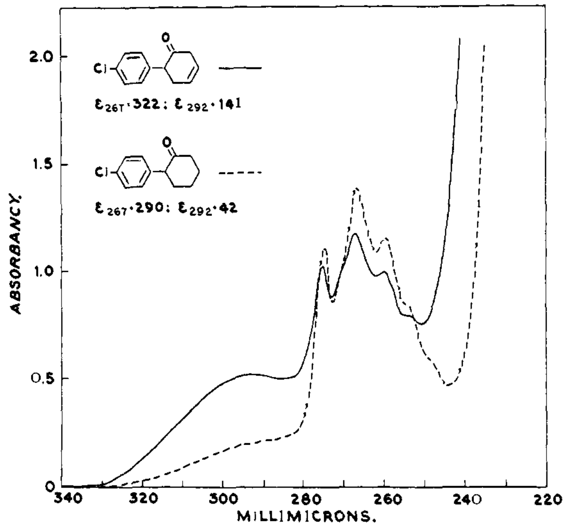

Fig. 1.—6-(*p*-Chlorophenyl)-3-cyclohexen-1-one, 0.750 g. per l., and 2-(*p*-chlorophenyl)-cyclohexanone, 1.000 g. per l., both in 95% ethanol.

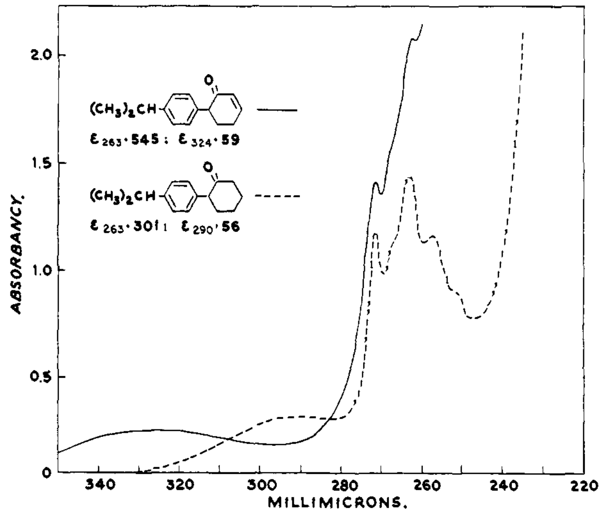

Fig. 2.—6-(*p*-Isopropylphenyl)-2-cyclohexene-1-one, 0.800 g. per l., and 2-(*p*-isopropylphenyl)-cyclohexanone, 1.000 g. per l., both in 95% ethanol.

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(12) I. F. Halverstadt and W. D. Kumler, THIS JOURNAL, **64**, 1982 (1942).

(13) L. G. Wesson, "Tables of Electric Dipole Moments," The Technology Press, Mass. Inst. of Technology, Cambridge, Mass., 1948.

p-Br-C_6H_5-, 1.52; *p*-HO-C_6H_5-CH_2-, 1.57 making an angle of 62° with the axis of rotation of the hydroxyl group; *p*-CH_3-C_6H_5-, 0.4; *p*-Cl-C_6H_5-CH_2-, 1.96; *p*-Br-C_6H_5-CH_2-, 1.92; *p*-I-C_6H_5-CH_2-, 1.71; *p*-CH_3-C_6H_5-CH_2-, 0; $(CH_3)_2$-CH-C_6H_5-CH_2-, 0; *m*-CH_3-C_6H_5-CH_2-, 0.2 in the direction of the bond by which it is attached.

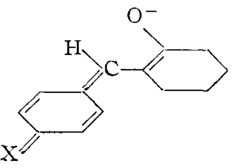
A comparison of the observed moments in Table I with the theoretical moments for the groups in the (e) and (a) positions shows that the structures of phenyl and benzyl compounds containing halogen or hydroxyl groups are consistent with these groups being in the equatorial position and are not consistent with them in the axial positions. The moments of the *p*-methyl and *p*-isopropyl compounds give no evidence as to their configuration, but the fact that these observed moments are so near that of cyclohexanone (2.90) shows that our assumption that the *p*-R-$C_6H_5CH_2$-group has a zero dipole was correct.

The dipole moment of 2-(*o*-methylphenyl)-cyclohexanone with the *o*-methylphenyl group in the 2-axial position will be something less than that of cyclohexanone and have a value around 2.5. The rotation of the group is highly restricted and the position with the least steric interference is one where the methyl group is lined up so its dipole opposes that of the carbonyl. With the *o*-methylphenyl group in the equatorial position free rotation is impossible and the methyl can be either up or down with respect to the plane of the cyclohexanone ring. The down position has the least steric interference and the calculated moment for this position with the plane of the benzene ring at right angles to the plane of the cyclohexanone ring is 3.42. This is in good agreement with the observed moment of 3.31 particularly when it is realized that the tendency for dipole attraction between the methyl and the carbonyl may pull the phenyl group somewhat out of the perpendicular position and reduce the actual dipole somewhat.

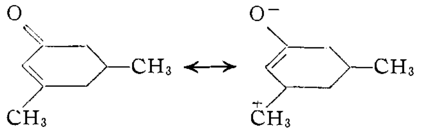
Models indicate that the *p*-chlorobenzyl group in 2-(*p*-chlorobenzyl)-cyclohexanone should have freedom of rotation in the equatorial compound, but may be restricted in the axial isomer. The calculated moments are 3.34 for the equatorial and 2.58 for the axial isomer, assuming freedom of rotation in both cases. The observed moment of 3.31 is in good agreement with the calculated moment for the equatorial compound.

For 2,6-bis-(*p*-chlorobenzyl)-cyclohexanone three possibilities exist: both groups equatorial, one equatorial and one axial, and both axial. The calculated moments are 3.68, 2.86 and 2.40, respectively, assuming freedom of rotation in each case. The models indicate that freedom of rotation with the groups in an axial position is highly unlikely. In the isomer with both groups equatorial, there is considerable freedom of movement, but one would expect dipole attractive forces to favor those positions, other things being equal, in which the chlorine and carbonyl dipoles augment each other to a lesser extent. The observed moment of 3.03 is not consistent with either the 2-axial, 6-axial configuration or the 2-equatorial, 6-axial configuration, but is in accord with the 2-equatorial, 6-equatorial structure with the groups spending more time in those positions which give rise to a smaller resultant moment.

The 2-(*p*-halobenzylidene)-cyclohexanones may exist in either a *cis* or *trans* form. For the 2,6-bis-(*p*-halobenzylidene)-cyclohexanones there are three possibilities, both benzylidene groups *cis*, both *trans*, and one *cis* and the other *trans*. With a group such as a halogen in the *para* position, the dipole moments should give an unambiguous answer to the structure. Resonance is, however, a complicating factor. In the conjugated 2-(*p*-halobenzylidene)-cyclohexanones the effect of resonance will be to increase the negative charge on the carbonyl oxygen and decrease that on the halogen atom as a result of the contribution of the form

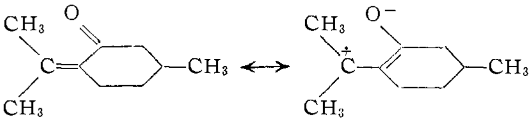


The result of this effect on the dipole moment will be to increase the moment of the *trans* configuration, but in the *cis* configuration the differences brought about in the moments of the two groups by the resonance will tend to cancel each other. This view is supported by the observed moments of 3,5-dimethylcyclohexenone and of pulegone of 3.79 and 2.95, respectively.[14] In 3,5-dimethylcyclohexenone there is an arrangement similar to that in the *trans* compound



3,5-dimethylcyclohexenone

and in pulegone there is an arrangement similar to that in the *cis* compound.



pulegone

The dipole moment of pulegone is very close to that of cyclohexanone 2.90, indicating a virtual cancellation of any effect from the conjugated C=C and its resonance with C=O, while in the case of the other compound the conjugated double bond and resultant resonance effects have raised the moment by about 0.9.

The conjugated systems in the 2-(*p*-halobenzylidene)-cyclohexanones will tend to assume a coplanar configuration. To calculate the theoretical dipole moments of these compounds, a set of axes was selected with the carbon–carbon double bond parallel to the *x*-axis and the *y*-axis passing through the carbonyl carbon.

Calculations were made assuming coplanarity of the conjugated parts and also a non-coplanar struc-

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(14) O. Hassel and E. Naeshagen, *Z. physik. Chem.*, **B15**, 373 (1952).

ture in which there was no distortion of the chair form of the cyclohexane ring.

The values in Table II clearly rule out the *cis* configuration for the 2-(*p*-halobenzylidene)-cyclohexanones. The molecules are *trans* and the actual structure may be somewhere between the coplanar and the non-distorted chair form for which we have made calculations. Since the resonance increased the moment of the *trans* form the observed moment would be expected to be larger than the calculated moment, as is the case.

TABLE II

OBSERVED AND THEORETICAL MOMENTS

Benzilidene)-cyclohexanone	Obsd.	*trans* Co-planar	*trans* Non-co-planar	*cis* Co-planar	*cis* Non-co-planar
2-(*p*-Chloro-	2.75	2.56	2.30	4.85	4.40
2-(*p*-Bromo-	2.89	2.55	2.30	4.82	4.36
2-(*p*-Iodo-	2.76	2.53	2.29	4.61	4.18
		Both aryl groups *trans* to carbonyl	Both aryl groups *cis* to carbonyl		One aryl *cis* other *trans* to carbonyl
2,6-Bis-(*p*-chloro-	2.23	0.94	6.82		4.24
2,6-Bis-(*p*-bromo-	2.29	0.98	6.74		4.20
2,6-Bis-(*p*-iodo-	2.31	1.19	6.32		4.05

From Table II it is also evident that the 2,6-bis-(*p*-halobenzylidene)-cyclohexanones do not have both aryl groups *cis* to the carbonyl nor is one *cis* and the other *trans*. The compounds have both aryl groups *trans* to the carbonyl. Since the resonance forms with a separation of charge are expected to make a larger contribution here than in the monosubstituted compounds, the enhancement of the observed moments over the calculated moments would be expected to be greater, which is the case. The rigid chair form will not exist in these molecules because of the presence of three sp^2-carbon atoms in the ring. To calculate the theoretical moments of these compounds coplanarity was assumed and a set of reference axes selected with the plane of the molecule parallel to the xy-plane and the carbonyl bond parallel to the y-axis. Perfect coplanarity probably is not attained because of steric interference.

Ultraviolet Spectra.—The ultraviolet spectra were obtained in 95% ethanol using a Cary recording spectrophotometer, model 11PMS with fused silica cells. The 2-(*p*-halobenzylidene)-cyclohexanones and the 2,6-bis-(*p*-halobenzylidene)-cyclohexanones have two peaks in their ultraviolet spectrum as shown in Table III. The maxima are in the same regions as the maxima for *p*-chlorobenzalacetone and di-*p*-chlorobenzalacetone,[15] respectively, and the spectra are in all respects very similar. This is confirmatory evidence that the structures with the phenyl, C=C and carbonyl groups conjugated, which have been assigned to these compounds are correct.

It was observed by Kumler, Alpen and Strait[9,10] that the carbonyl absorption peak is more intense and is shifted to longer wave lengths in α-phenylcarbonyl compounds as compared with simple aliphatic carbonyl compounds. This was originally explained in terms of no-bond resonance,[9] but it was also pointed out[10] that an interaction directly through space between the π-electrons of the phenyl and carbonyl groups could also account for the observed anomaly. A number of other workers have reported evidence of interaction between chain-insulated unsaturated systems.[16]

TABLE III

Compound	λ_{max}	ϵ
2-(*p*-Chlorophenyl)-cyclohexanone	260	240
	267	290
	275	230
	292	42
6-(*p*-Chlorophenyl)-3-cyclohexen-1-one	260	273
	267	322
	275	284
	292	141
2-(*p*-Bromophenyl)-cyclohexanone	254	235
	259	276
	266	294
	275	200
	290	48
2-(*p*-Bromophenyl)-3-cyclohexen-1-one	259	289
	267	312
	275	251
	293	140
2-(*p*-Isopropylphenyl)-cyclohexanone	257	238
	263	301
	271	240
	290	46
6-(*p*-Isopropylphenyl)-2-cyclohexen-1-one	263	545
	271	358
	324	59
2-(*p*-Hydroxyphenyl)-cyclohexanone	277	1630
With NaOH added	295	2800
2-(*p*-Methylphenyl)-cyclohexanone	258	249
	264	318
	272	286
	290	54
2-(*m*-Methylphenyl)-cyclohexanone	264	302
	271	266
	290	45
2-(*o*-Methylphenyl)-cyclohexanone	263	282
	271	244
	290	34
2-(*p*-Chlorobenzyl)-cyclohexanone	262	306
	269	400
	277	360
	290	41
2,6-Bis-(*p*-chlorobenzyl)-cyclohexanone	262	581
	267	780
	277	695
	290	57
2-(*p*-Chlorobenzylidene)-cyclohexanone	224	7,400
	294	18,300
2-(*p*-Bromobenzylidene)-cyclohexanone	222	8,300
	295	20,200
2-(*p*-Iodobenzylidene)-cyclohexanone	227	6,900
	302	21,500
2,6-Bis-(*p*-chlorobenzylidene)-cyclohexanone	236	18,800
	332	31,500
2,6-Bis-(*p*-bromobenzylidene)-cyclohexanone	236	18,700
	335	37,400
2,6-Bis-(*p*-iodobenzylidene)-cyclohexanone	240	22,400
	336	29,800

Table III contains the spectra of a number of

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[15] V. Alexa, *Bull. soc. chim. Romania*, **17**, 67 (1935).

[16] Reference 11 of the paper by D. J. Cram and H. U. Daeniker, THIS JOURNAL, **76**, 2743 (1954).

additional α-phenylcarbonyl compounds that are derivatives of 2-phenylcyclohexanone and have abnormal carbonyl bands with extinctions from 34 to 56 around 290 mμ. These compounds usually have several maxima in the range 250 to 280 mμ due to the substituted benzene ring and the extinction coefficients and wave lengths of these λ_{max} are also given. In some of the cases, the value given at 290 mμ does not represent a distinct peak. Since cyclohexanone itself has a λ_{max} at 283 with an extinction of only 16.6 measured in 95% ethanol in which the other measurements were also made, it is apparent that all of these compounds give evidence of an enhanced carbonyl absorption.

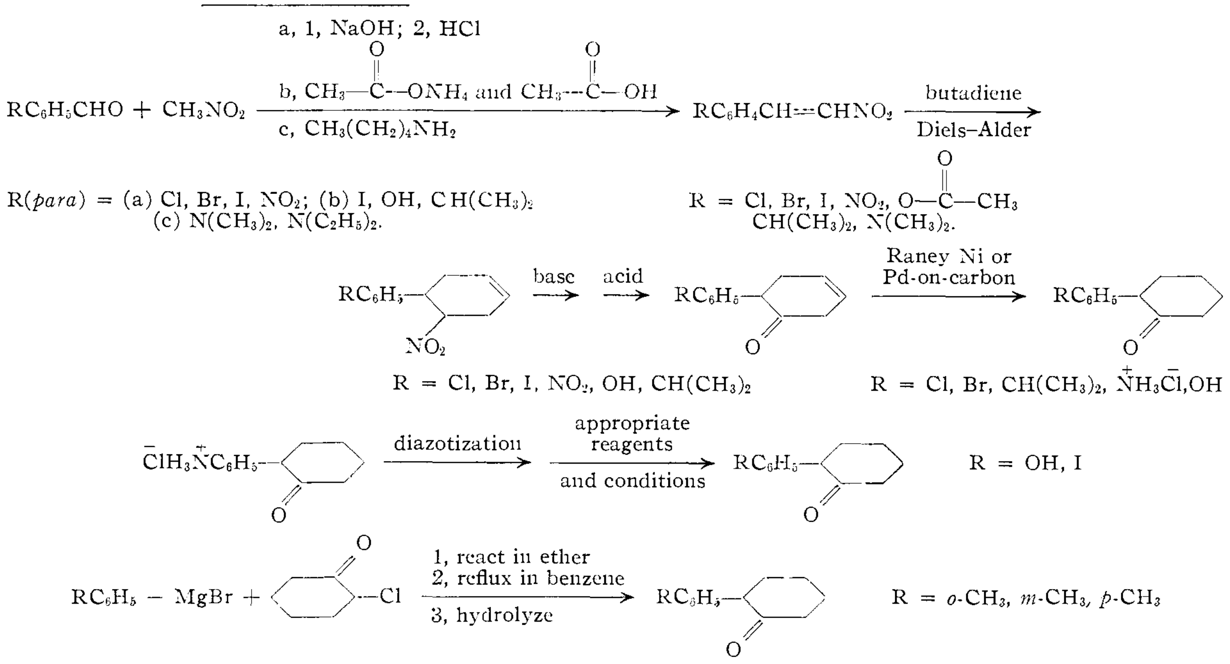
The extinction at 292 and 293 mμ of 141 and 140 for the compounds with double bonds in the 3-position suggest that these double bonds also interact with the other unsaturated groups although they are chain insulated.

The extinction coefficient of 41 and 57 at 290 mμ for the 2-(*p*-chlorobenzyl)-cyclohexanone and 2,6-bis-(*p*-chlorobenzyl)-cyclohexanone indicate that these effects are present in β-phenylcarbonyl compounds as well as in α-phenylcarbonyl compounds. In these compounds with two intervening CH_2 groups hyperconjugation is not a plausible explanation and the idea of direct interaction through space between the orbitals of the phenyl and carbonyl groups is clearly favored. The Fisher–Hirschfelder–Taylor models indicate that the phenyl groups can come in very close proximity to the carbonyl group in these compounds. However, the phenyl groups are not held in permanent juxtaposition to the carbonyl group because if this were the case the dipole moments of these compounds would be much higher than the observed values. With the benzyl group rotating, the theoretical dipole moment would be in keeping with the observed moment and since the phenyl group for part of the time would be in close proximity to the carbonyl, the enhanced extinction around 290 mμ is accounted for.

The spectra of *p*-chloro- and *p*-bromophenylcyclohexenone are typical of the spectra of related β,γ-unsaturated phenylcyclohexenones[17] while the spectrum of *p*-isopropylphenylcyclohexenone exhibits a maximum in the region 320 to 330 mμ shown[17] to be characteristic of α,β-unsaturated phenylcyclohexenones. This latter compound, therefore, has been assigned the structure 6-(*p*-isopropylphenyl)-2-cyclohexen-1-one.

Experimental

The compounds were made as follows:



Substituted β-Nitrostyrenes.—Three methods were used for the synthesis of these compounds. Method a is essentially that described in reference 18 for the synthesis of β-nitrostyrene. The preparation of *p*-bromo-β-nitrostyrene is described as an example of method a.

***p*-Bromo-β-nitrostyrene.**—A solution of 37.5 g. (0.202 mole) of *p*-bromobenzaldehyde and 12.7 g. (0.208 mole) of nitromethane in 90 ml. of methanol was cooled to 5° in an ice-bath. Twenty-five milliliters of ice-cold aqueous solution of sodium hydroxide, containing 8.73 (0.218 mole) of NaOH, was added dropwise with stirring at such a rate that the temperature was maintained between 10 to 15°. A white precipitate occurred which upon addition of about two-thirds of the NaOH solution became too thick for efficient stirring. An additional 20 ml. of methanol was added and stirring continued for 15 min. after all the NaOH solution had been added. A water–ice mixture (150 ml.) was added and the resulting solution was slowly added with stirring to a mixture of 50 ml. of concentrated hydrochloric acid and 75 ml. of water. The resulting yellow precipitate was washed free of chloride, giving 23 g. (50%) of dry crude product. Recrystallization from 95% ethanol gave a light yellow crystalline product, m.p. 150.5–151°.

Anal. Calcd. for $C_8H_6BrNO_2$: Br, 35.04. Found: Br, 35.17.

This compound has been made by Dominguez, *et al.*,[19]

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[17] W. C. Wildman and R. B. Wildman, *J. Org. Chem.*, **17**, 581 (1952).

[18] "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 413.

[19] X. A. Dominguez, J. S. S. Elizondo and A. Elizondo, THIS JOURNAL, **75**, 4581 (1953).

TABLE IV

4-NITRO-5-ARYLCYCLOHEXENES

Phenyl)-cyclohexene	Yield crude product, one crystln., %	M.p. purified product, °C.	Recrystn. solvents	Reacting solvent	Analyses, % Calcd.	Found
4-Nitro-5-(*p*-chloro-	89	88.5–89.5	Ethanol, *i*-PrOH	Tol.	Cl, 14.92	14.81
4-Nitro-5-(*p*-bromo-	96	110.6–111.5	Ethanol, *i*-PrOH	Tol.	Br, 28.32	28.39
4-Nitro-5-(*p*-iodo-	71	145–146	Ethanol, *i*-PrOH	Tol.	I, 38.56	38.76
4-Nitro-5-(*p*-nitro-	91	138–139	Ethanol	Tol.	N, 11.29	11.15
4-Nitro-5-(*p*-acetoxy-	87	113.5–114.5	Ethanol, *i*-PrOH	Diox.	N, 5.36	5.38
4-Nitro-5-(*p*-isopropyl-	90	75.0–75.5	Iso., pet. ether	Tol.	N, 5.71	5.60

by a different method. They gave a melting point of 156–158°. Repeated purification of the compound prepared by us failed to raise the melting point above 150.5–151°.

***p*-Chloro-β-nitrostyrene.**—This compound was obtained in 52% yield from *p*-chlorobenzaldehyde by method a, m.p. 113–114° (lit.[20] m.p. 113–114°).

***p*,β-Dinitrostyrene.**—This compound was obtained in 58% yield from *p*-nitrobenzaldehyde by method a. Recrystallization from a mixture of 95% ethanol and dioxane gave a light yellow crystalline product, m.p. 206–207°. (lit.[21] m.p. 196–199°).

Anal. Calcd. for $C_8H_6N_2O_4$: N, 14.43. Found: N, 14.14.

Method b is the general method of Gairaud and Lappin.[22] The preparation of *p*-iodo-β-nitrostyrene describes the method.

***p*-Iodo-β-nitrostyrene.**—A mixture of 20 g. (0.086 mole) of *p*-iodobenzaldehyde, 10.4 g. (0.17 mole) of nitromethane and 8 g. of ammonium acetate in 80 ml. of glacial acetic acid was heated under reflux for 2 hours. The hot mixture was poured into 500 ml. of ice–water mixture. The resulting precipitate was washed with water and recrystallized from a mixture of 95% ethanol and dioxane, giving 14.3 g. (60%) of yellow crystalline product, m.p. 186.5–187.5°. A small portion was treated with decolorizing carbon in ethanol–dioxane mixture for analysis, m.p. 188.5–189.5°.

Anal. Calcd. for $C_8H_6INO_2$: I, 46.14. Found: I, 46.33.

p-Iodo-β-nitrostyrene was also prepared in 40% yield by method a, m.p. 188.5–189.5°. Dominguez, *et al.*,[19] report a melting point of 183–184° for this compound.

***p*-Isopropyl-β-nitrostyrene.**—This compound was obtained in 41% yield from *p*-isopropylbenzaldehyde by method b. The product was recrystallized from isopropyl alcohol and from petroleum ether, m.p. 37–38°.

Anal. Calcd. for $C_{11}H_{13}NO_2$: N, 7.33. Found: N, 7.42.

***p*-Diethylamino-β-nitrostyrene.**—This compound was prepared by method c which is the same as that described by Worrall and Cohen[23] for the synthesis of the dimethylamino analog. A mixture of 17.7 g. (0.1 mole) of *p*-diethylaminobenzaldehyde and 18.3 g. (0.3 mole) of nitromethane was heated on a water-bath for 5 minutes and 0.5 g. of *n*-amylamine was added, whereupon a bright red color developed. The heating was continued for one minute and the reaction mixture allowed to stand overnight. Cooling in ice gave a red crystalline material which was recrystallized from 2-nitropropane, giving 6 g. (27%) of product. The product was recrystallized from 95% ethanol giving bright red crystals, m.p. 96–97°.

Anal. Calcd. for $C_{12}H_{16}N_2O_2$: N, 12.72. Found: N, 12.67.

***p*-Acetoxy-β-nitrostyrene.**—This compound was prepared by the acetylation of *p*-hydroxy-β-nitrostyrene. A mixture of 30 g. (0.18 mole) of *p*-hydroxy-nitrostyrene[22] and 90 g. (1.15 mole) of acetyl chloride was maintained at 45° for 7 hours. The excess acetyl chloride was removed *in vacuo* and the crude product washed with ice-cold absolute ethanol and recrystallized from an ethanol–benzene mixture, giving 24 g. (64%) of product, m.p. 159.5–161°. A small portion was treated with decolorizing carbon in 95% ethanol, giving a light yellow crystalline product, m.p. 160–161°.

Anal. Calcd. for $C_{10}H_9NO_4$: N, 6.76. Found: N, 6.49.

4-Nitro-5-arylcyclohexenes.—These compounds were prepared by the method of Wildman and Wildman.[17] The Diels–Alder condensation of each β-nitrostyrene with 1,3-butadiene was carried out under pressure in a Pyrex bomb or in a steel bomb with a Pyrex liner by heating at 100° for 75 to 90 hours. The solvent, toluene unless otherwise stated, was removed under a stream of nitrogen or air at room temperature and the product recrystallized from an appropriate solvent. There was no noticeable difference in yield when the solvent was removed under a stream of nitrogen or of air.

4-Nitro-5-(dimethylaminophenyl)-cyclohexene.—Unchanged *p*-dimethylamino-β-nitrostyrene was recovered quantitatively when heated in a Pyrex bomb at 100° for 70 hours with butadiene and trace of hydroquinone in toluene. The desired product was obtained in poor yield when the reaction was carried out in dioxane in the presence of a slight excess of trichloroacetic acid. A steel bomb was loaded with 27 g. (0.14 mole) of *p*-dimethylamino-β-nitrostyrene,[23] 25 g. (0.153 mole) of trichloroacetic acid, traces of hydroquinone, 35 ml. of dioxane and butadiene in excess. The bomb was heated at 100° for 82 hours. The dioxane was removed *in vacuo* under a stream of nitrogen and the residue washed with 10% sodium carbonate. The residue was then washed with 5% hydrochloric acid, leaving 13.5 g. of unreacted *p*-dimethylamino-β-nitrostyrene. The acid washings were neutralized with sodium carbonate. The resulting precipitate was washed with water, dried *in vacuo* and washed repeatedly with hot petroleum ether, leaving a dark residue which was insoluble in petroleum ether. Evaporation of the petroleum ether gave 2.5 g. of orange crystalline material which was recrystallized from isopropyl alcohol, m.p. 133–134°.

Anal. Calcd. for $C_{14}H_{18}N_2O_2$: N, 11.37. Found: N, 11.42.

The reaction was also investigated in dioxane with a slight excess of hydrochloric acid. A grayish-black material with melting point above 250° was recovered after heating at 100° for 15 hours. There was no evidence of any desired product or of any unreacted styrene. The reaction was also investigated at room temperature in glacial acetic acid with a slight excess of hydrochloric acid. Only unreacted starting material was recovered after shaking the bomb at room temperature for one week.

6-Aryl-3-cyclohexen-1-ones.—These compounds were prepared from the corresponding 4-nitro-5-arylcyclohexenes by the Nef reaction, using essentially the method described by Wildman and Wildman.[17] There was no appreciable difference in yield when the reaction was carried out in an atmosphere of nitrogen or in the presence of air. The synthesis of 6-(*p*-chlorophenyl)-3-cyclohexen-1-one is described in detail as a typical example of the method used to prepare compounds of this series.

Anal. Calcd. for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.12; H, 8.59.

2-Arylcyclohexanones.—2-Arylcyclohexanones, with the exception of 2-(*p*-iodophenyl)-cyclohexanone, were obtained in almost quantitative yield by low pressure catalytic hydrogenation of the corresponding 6-aryl-3-cyclohexen-1-ones at room temperature, using Raney nickel W-2[24] or 10% palladium-on-carbon (J. T. Baker) as catalysts.

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[20] N. Campbell, W. Anderson and J. Gilmore, *J. Chem. Soc.*, 446 (1940).

[21] J. Thiele, *Ber.*, **32**, 1293 (1899).

[22] C. B. Gairaud and G. R. Lappin, *J. Org. Chem.*, **18**, 1 (1953).

[23] D. E. Worrall and L. Cohen, THIS JOURNAL, **66**, 842 (1944).

[24] *Org. Syntheses*, **21**, 15 (1941).

TABLE V

6-ARYL-3-CYCLOHEXEN-1-ONES

Phenyl)-3-cyclohexen-1-one	Yield crude product, %	M.p. purified product	Analyses, % Calcd.	Found	M.p., °C. 2,4-Dinitrophenylhydrazones[a]
6-(*p*-Chloro-	38.5	64–64.5	Cl, 17.16	17.26	144.5–145.5
6-(*p*-Bromo-	33	63.5–64.5	Br, 31.82	31.74	149–150
6-(*p*-Iodo-	73	62–63	I, 42.57	42.59	
6-(*p*-Nitro-	53	112.5–113.5	N, 6.45	6.95	174.5–175
6-(*p*-Hydroxy-	55	126–127	C, 76.57	76.52	
			H, 6.43	6.53	214.5–215.5
6-(*p*-Isopropyl-[b]		66.5–67.5	C, 84.07	84.12	
			H, 8.47	8.59	

[a] Prepared according to method of A. J. Birch, *J. Chem. Soc.*, 593 (1946). [b] Purified by use of Girard T reagent according to "Substances Naturelles de Synthese," Vol. II, Masson et Cie, Paris, 1951, p. 117.

TABLE VI

2-ARYLCYCLOHEXANONES

Phenyl)-cyclohexanone	M.p., purified product, °C.	Catalyst	Recrystn. solvents	Analyses, % Calcd.	Found
2-(*p*-Chloro-[a]	77.5–78.5	Ni	EtOH, pet. eth.	C, 69.06	68.93
				H, 6.28	6.52
				Cl, 16.99	17.06
2-(*p*-Bromo-	84–85	Ni	EtOH, pet. eth.	C, 56.93	56.79
				H, 5.18	5.37
				Br, 31.57	31.56
2-(*p*-Isopropyl-	70.0–70.5[b]	Ni, Pd	*i*-PrOH-water	C, 83.28	83.10
				H, 9.32	9.12
2-(*p*-Hydroxy-	168.5–170	Ni	50% EtOH–water	C, 75.76	75.56
				H, 7.42	7.53

[a] R. L. Huang (*J. Org. Chem.*, **19**, 1363 (1954)) reported a m.p. of 154–156° for the 2,4-dinitrophenylhydrazone of this compound for which we get a m.p. of 163–164°. He, however, did not isolate the *p*-chlorophenylcyclohexanone. [b] W. E. Backman, D. I. Fujimoto and L. B. Wick, THIS JOURNAL, **72**, 1995 (1950), report a m.p. of 68–69°.

2-(*p*-Aminophenyl)-cyclohexanone Hydrochloride.—Two and a half grams of 6-(*p*-nitrophenyl)-3-cyclohexen-1-one, dissolved in 200 ml. of 95% ethanol containing 2.5 ml. of concentrated hydrochloric acid, was hydrogenated at 10 lb. pressure with 200 mg. of 10% palladium-on-carbon as catalyst. The calculated amount of hydrogen was taken up within 6 minutes. The catalyst was removed by filtration, 5 ml. of concentrated hydrochloric acid was added and the alcohol removed *in vacuo* at 40–45° until about 30 ml. of alcohol remained. Some salt had precipitated out at this point. One hundred and fifty milliliters of anhydrous ether was added and the mixture was allowed to stand in the refrigerator overnight. The precipitate was filtered with suction, washed with anhydrous ether and dried *in vacuo* giving 2.4 g. (93%) of product.

2-(*p*-Hydroxyphenyl)-cyclohexanone was also prepared by diazotization of 2-(*p*-aminophenyl)-cyclohexanone hydrochloride. A solution of 1.7 g. (0.00754 mole) of 2-(*p*-aminophenyl)-cyclohexanone hydrochloride in 4 ml. of water and 1.5 ml. of concentrated sulfuric acid was cooled to 0° and 4 g. of crushed ice was added. The diazotization was carried out by adding, all at once, a solution of 0.65 g. of sodium nitrite in 1.6 ml. of water, cooled at 10°. The mixture was allowed to stand in an ice-bath for 10 minutes and a small amount of urea was added to remove the excess nitrous acid. The cold diazonium salt solution was then added dropwise to 100 ml. of boiling *N* sulfuric acid. A precipitate occurred during the addition. The mixture was cooled in ice, the precipitate filtered with suction and dried *in vacuo*, giving 1.2 g. of crude product. The crude product was treated with decolorizing carbon in 95% ethanol and recrystallized from 50% ethanol, giving 0.8 g. (56%) of colorless crystalline material, m.p. 168.5–170°. The melting point of a mixture of the compounds obtained by the two different methods was not depressed. The ultraviolet spectra of the two compounds were found to be identical.

When the diazonium salt solution was added to *N* sulfuric acid at 50°, and warmed at 55° until evolution of nitrogen had stopped, a dark red color developed, which is indicative of coupling reactions. There was no evidence of coupling when the cold diazonium salt solution was added dropwise to boiling *N* sulfuric acid.

2-(*p*-Iodophenyl)-cyclohexanone.—Catalytic hydrogenation of 6-(*p*-iodophenyl)-3-cyclohexen-1-one, with Raney nickel W-2 as catalyst, was not successful. Only a fraction of the calculated amount of hydrogen was taken up at the end of 4 hours of hydrogenation at 12 lb. pressure. Unreacted starting material and a small amount of dark oily substance were recovered from the reaction.

2-(*p*-Iodophenyl)-cyclohexanone was obtained through diazotization of 2-(*p*-aminophenyl)-cyclohexanone hydrochloride. 2-(*p*-Aminophenyl)-cyclohexanone hydrochloride, 1.7 g. (0.00754 mole), in a mixture of 4 ml. of water and 5 ml. of concentrated hydrochloric acid, was diazotized at 0° by dropwise addition of a solution of 0.54 g. of sodium nitrite in 2 ml. of water. A solution of 1.41 g. of potassium iodide in 8 ml. of water, cooled to 5°, was added dropwise with stirring to the ice-cold diazonium salt solution. The mixture was kept in ice for 90 minutes, allowed to come to room temperature, extracted with chloroform and the chloroform extracts were washed with 5% sodium thiosulfate solution, followed by water. Evaporation of the chloroform left a dark oily substance which was washed repeatedly with hot ligroin, leaving a small amount of dark resinous material. Removal of the ligroin gave 1.2 g. (53%) of light yellow material, m.p. 86-89°. The crude material was treated with decolorizing carbon in 95% ethanol and recrystallized from ethanol-water mixture, giving colorless crystalline material, m.p. 96–97°.

Anal. Calcd. for $C_{12}H_{13}IO$: C, 48.02; H, 4.37; I, 42.49. Found: C, 47.80; H, 4.32; I, 42.42.

2-(*o*-Methylphenyl)-cyclohexanone.—The method used for the preparation of this compound is essentially the same as that described by Newman and Farbman[25] for the synthesis of 2-phenylcyclohexanone. A solution of *o*-methylphenylmagnesium bromide was prepared from 81 g. (0.474 mole) of freshly distilled *p*-bromotoluene, 11.9 g. (0.49 mole) of magnesium turnings and 170 ml. of anhydrous ether, under the usual conditions of the Grignard reaction. The Grignard was started by the addition of four drops of *n*-butyl bromide. A solution of 47.5 g. (0.36 mole) of 2-chlorocyclo-

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(25) M. S. Newman and Morris D. Farbman, THIS JOURNAL, **66**, 1550 (1944).

hexanone (prepared by the method of reference 26) by chlorination of cyclohexanone) in 130 ml. of anhydrous ether was added with stirring to the *o*-methylphenylmagnesium bromide solution at a rate which caused moderate refluxing. At the end of the addition of this amount of 2-chlorocyclohexanone the reaction mixture became turbid and the refluxing subsided. Anhydrous benzene (175 ml.) was then added and the ether was distilled off. The mixture was refluxed for 7 hours, then cooled to room temperature and hydrolyzed by pouring into 300 ml. of ice-cold water. The magnesium salts were dissolved by acidifying with 10% sulfuric acid, the benzene layer separated, and the aqueous layer extracted with benzene. The benzene extracts were washed with 5% sodium bicarbonate solution, followed by water, and dried over anhydrous sodium sulfate. The benzene was removed *in vacuo* (water-pump) and the product distilled at reduced pressure. The fraction boiling at 115–130° at 1 mm. (20 g. or 29.6% on basis of 2-chlorocyclohexanone) solidified upon cooling. Several recrystallizations from petroleum ether gave a colorless crystalline product, m.p. 55.5–56.5°.

Due to evidence of a coupling side reaction producing some bitolyl (see 2-(*p*-methylphenyl)-cyclohexanone) a small amount of product was purified by treating with Girard T reagent by the method previously described (footnote *b*, Table V); 2,4-dinitrophenylhydrazone, m.p. 143.4–144.5°. Huang reported *o*-tolylcyclohexanone having a b.p. of 110–112° at 0.7 mm. and the 2,4-dinitrophenylhydrazone a m.p. of 145–147°.

Anal. Calcd. for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.87; H, 8.47.

2-(*m*-Methylphenyl)-cyclohexanone.—This compound was obtained in 26% yield from *m*-bromotoluene and 2-chlorocyclohexanone by the method described for 2-(*o*-methylphenyl)-cyclohexanone, b.p. 125–134° at 1 mm. The product was purified by treating with Girard T reagent, giving colorless crystalline material, m.p. 37–38°; 2,4-dinitrophenylhydrazone, m.p. 132–133°.

Anal. Calcd. for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 83.01; H, 8.42.

2-(*p*-Methylphenyl)-cyclohexanone.—This compound was obtained in 40% yield from *p*-bromotoluene and 2-chlorocyclohexanone by the method described for 2-(*o*-methylphenyl)-cyclohexanone. Purification by treatment with Girard T reagent gave colorless crystalline product, m.p. 50.5–51.5°; 2,4-dinitrophenylhydrazone, m.p. 153.5–154.5°.

Huang (Footnote *a*, Table VI) reported *p*-tolylcyclohexanone having a m.p. of 50° and the 2,4-dinitrophenylhydrazone a m.p. of 153°.

Anal. Calcd. for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 83.22; H, 8.31.

There is evidence of a coupling side reaction producing a certain amount of 4,4′-bitolyl in the above reaction. Purification of the crude 2-(*p*-methylphenyl)-cyclohexanone through recrystallization, and later through Girard T reagent, yielded a small amount of colorless material which was found to be insoluble in concentrated sulfuric acid and to have a melting point of 121–122°. This material is more soluble in petroleum ether and less soluble in ethanol than is 2-(*p*-methylphenyl)-cyclohexanone. The reported melting point of 4,4′-bitolyl is 121–122°.[27] The reported melting point of 3,3′-bitolyl is 5–7° and that of 2,2′-bitolyl 18°.[27] No attempt was made to identify the oily residues obtained as impurities from the treatment of 2-(*o*-methylphenyl)-cyclohexanone and 2-(*m*-methylphenyl)-cyclohexanone with Girard reagent.

2,6-Bis-(*p*-chlorobenzylidene)-cyclohexanone.—A mixture of 21 g. (0.15 mole) of *p*-chlorobenzaldehyde (Heyden Chemical Corp.) and 7.35 g. (0.075 mole) of cyclohexanone in 150 ml. of 50% ethanol, containing 0.9 g. of sodium hydroxide, was heated under reflux for 90 minutes. A yellow precipitate occurred after a short period of heating. The reaction mixture was allowed to cool to room temperature. The precipitate was then filtered with suction, washed with water and dried *in vacuo*, giving 23.6 g. (91.6%) of bright yellow crystalline material, m.p. 136–144°. Recrystallization from an ethanol–benzene mixture gave m.p. 147–148°.

Anal. Calcd. for $C_{20}H_{16}Cl_2O$: Cl, 20.66; C, 69.98; H, 4.70. Found: Cl, 20.65; C, 70.36; H, 4.73.

The 2,4-dinitrophenylhydrazone could not be obtained by the usual method.

2,6-Bis-(*p*-chlorobenzylidene)-cyclohexanone was obtained in 30% yield when the method used by Colonge and Sibeuf[28] for the synthesis of 2-benzylidenecyclohexanone was used in an attempt to obtain 2-(*p*-chlorobenzylidene)-cyclohexanone. The method consists of refluxing a mixture of about equivalent amounts of benzaldehyde and cyclohexanone in a 4% aqueous solution of potassium hydroxide.

2,6-Bis-(*p*-bromobenzylidene)-cyclohexanone.—A mixture of 6.0 g. (0.0325 mole) of *p*-bromobenzaldehyde and 1.59 g. (0.0162 mole) of cyclohexanone in 100 ml. of 50% ethanol, containing 0.3 g. of sodium hydroxide, was heated under reflux for 90 minutes. A yellow precipitate occurred after a short period of heating. After cooling to room temperature the precipitate was filtered with suction, washed with water and dried *in vacuo*, giving 6.5 g. of bright yellow crystalline material, m.p. 161–164°. Recrystallization from ethanol–benzene mixture gave m.p. 166–167°.

Anal. Calcd. for $C_{20}H_{16}Br_2O$: Br, 36.98. Found: Br, 36.78.

2,6-Bis-(*p*-iodobenzylidene)-cyclohexanone.—A mixture of 10 g. (0.043 mole) of *p*-iodobenzaldehyde and 2.11 g. (0.0215 mole) of cyclohexanone in 200 ml. of 50% ethanol, containing 0.6 g. of sodium hydroxide, was refluxed for 90 minutes. A yellow precipitate occurred after a short period of heating. After cooling to room temperature, the precipitate was filtered with suction, washed with water and dried *in vacuo*, giving 9.5 g. (84%) of bright yellow crystalline material. Recrystallization from a mixture of ethanol and benzene gave m.p. 190.5–191.5°.

Anal. Calcd. for $C_{20}H_{16}I_2O$: I, 48.24. Found: I, 48.47.

2,6-Bis-(*p*-chlorobenzyl)-cyclohexanone.—To a solution of 5 g. of 2,6-bis-(*p*-chlorobenzylidene)-cyclohexanone in a mixture of 125 ml. of thiophene-free benzene and 25 ml. of absolute ethanol was added about 1.5 g. of Raney nickel W-2[24] and hydrogenation carried out at 30 lb. pressure at room temperature. The calculated amount of hydrogen was taken up in one hour. The catalyst was filtered off and the benzene and ethanol removed *in vacuo* under a stream of nitrogen, leaving some colorless crystalline material and a small amount of yellow oily residue. The crystalline material was filtered with suction and washed with isopropyl alcohol, giving 4 g. of crude product. The crude product was treated with decolorizing carbon in 95% ethanol and recrystallized from isopropyl alcohol, giving colorless needles, m.p. 146–147°.

Anal. Calcd. for $C_{20}H_{21}Cl_2O$: Cl, 20.42; C, 69.18; H, 5.81. Found: Cl, 20.60; C, 68.90; H, 5.78.

2,6-Bis-(*p*-bromobenzyl)-cyclohexanone.—To a solution of 3.5 g. of 2,6-bis-(*p*-bromobenzylidene)-cyclohexanone in 125 ml. of thiophene-free benzene was added about 1 g. of Raney nickel W-2,[24] and hydrogenation carried out at 30 lb. pressure at room temperature. The uptake of hydrogen stopped slightly short of the calculated amount after one hour. The benzene solution was found to be slightly acidic to moist litmus, suggesting the possibility of some dehalogenation. The catalyst was filtered off and the benzene removed at room temperature under a stream of air, leaving some crystalline material and a small amount of viscous yellow residue. The crystalline material was filtered with suction, treated with decolorizing carbon in 95% ethanol, and recrystallized from 95% ethanol and from methanol, giving a colorless crystalline product, m.p. 154–155°.

Anal. Calcd. for $C_{20}H_{20}Br_2O$: Br, 36.64; C, 55.07; H, 4.62. Found: Br, 36.52; C, 55.27; H, 4.72.

2,6-Bis-(*p*-dimethylaminobenzylidene)-cyclohexanone.—A mixture of 10 g. (0.067 mole) of *p*-dimethylaminobenzaldehyde and 3.2 g. (0.0326 mole) of cyclohexanone in 150 ml. of 50% ethanol, containing 3 g. of sodium hydroxide, was heated under reflux for 3 hours. A dark orange precipitate began to separate out after 10 minutes of refluxing. After cooling to room temperature, the precipitate was filtered with suction, washed with water and dried *in vacuo*, giving 7.5 g. (64%) of dark orange crystalline material. The product was recrystallized from toluene, the crystals washed with ice-cold ethanol and dried *in vacuo*, m.p. 246–248°.

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(26) *Org. Syntheses*, **25**, 22 (1945).

(27) Lange's "Handbook of Chemistry," Seventh Ed., Handbook Publishers, Inc., Sandusky, Ohio, 1949.

(28) J. Colonge et J. Sibeuf, *Bull. soc. chim.*, 786 (1952).

Anal. Calcd. for $C_{24}H_{28}N_2O$: N, 7.77. Found: N, 8.05.

When two equivalents of *p*-dimethylaminobenzaldehyde and one equivalent of cyclohexanone were refluxed in a solution of 0.3% sodium hydroxide in 50% ethanol, the yield of 2,6-bis-(*p*-dimethylaminobenzylidene)-cyclohexanone was only 12.5%. A considerable amount of lower melting point material, 66–68°, was recovered from the reaction mixture by diluting the filtrate with water.

2,6-Bis-(*p*-dimethylaminobenzyl)-cyclohexanone.—One gram of 2,6-bis-(*p*-dimethylaminobenzylidene)-cyclohexanone was dissolved in a mixture of 150 ml. of ethanol, 6 ml. of concentrated hydrochloric acid and 15 ml. of water. Two hundred milligrams of 10% palladium-on-carbon (J. T. Baker) was added and the hydrogenation carried out at 20 lb. pressure at room temperature. The calculated amount of hydrogen was taken up within 15 minutes. The catalyst was filtered off and the colorless solution was neutralized with 10% sodium carbonate and diluted with an equal volume of water. The resulting colorless precipitate was filtered with suction, washed with water and recrystallized from 95% ethanol, m.p. 136–137°.

Anal. Calcd. for $C_{24}H_{32}N_2O$: N, 7.69; C, 79.08; H, 8.85. Found: N, 7.92; C, 79.30; H, 9.03.

2-(*p*-Acetoxyphenyl)-nitrocyclohexane.—To a solution of 1 g. (0.00383 mole) of 4-nitro-5-(*p*-acetoxyphenyl)-cyclohexene in 200 ml. of absolute ethanol was added 0.1 g. of 10% palladium-on-carbon (J. T. Baker) and hydrogenation was carried out at 30 lb. pressure at room temperature. About a one-to-one molar ratio of hydrogen was taken up within 15 minutes and the uptake of hydrogen then came to a stop. The catalyst was filtered off and the ethanol removed *in vacuo*. The crude product was recrystallized from 95% ethanol, giving a colorless material, m.p. 92–93°. The product is not soluble in 10% hydrochloric acid, indicating that the nitro group was not reduced.

Anal. Calcd. for $C_{14}H_{17}NO_4$: N, 5.32; C, 63.86; H, 6.51. Found: N, 5.36; C, 64.11; H, 6.46.

Analyses.—Analyses are by the Microanalytical Division of the Department of Chemistry, University of California.

Melting points.—All melting points are corrected.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

Spectra as a Guide to Structure in the Hydroxypyrone and Hydroxypyridone Series

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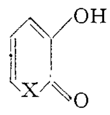
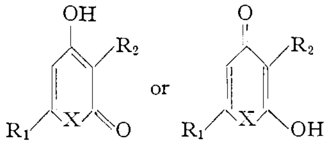
The ultraviolet spectra of 4-hydroxy-2-pyrones and pyridones (or their enol tautomers) are shifted hypsochromically in alkaline solution, while those of 3-hydroxy-4-pyrones or pyridones and of 2-hydroxy-3-pyridones are shifted bathochromically.

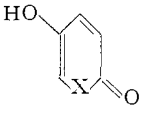
In the course of a recent structural investigation,[1] certain degradation products were shown to be N-alkylated hydroxypyridones, although no basis existed for a choice of a detailed expression from among the alternative types I–V(X = N).[2] Since the confirmation of structure by independent synthesis of even simple members of these classes of substances is often tedious and difficult,[3] a simple diagnostic procedure was desirable. Although the work we report here does not deal with all of the structures I–V, it provides a simple method for distinguishing pyridones (X = N) or pyrones (X = O) of the type II from those of types I and IV.



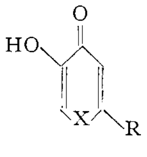
I, X = NCH$_3$



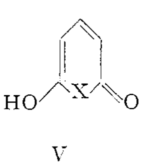
IIa, $R_1 = CH_3$; $R_2 = H$; X = O
b, $R_1 = CH_3$; $R_2 = C_2H_5$; X = O
c, $R_1 = CH_3$; $R_2 = COCH_3$; X = O
d, $R_1 = CH_3$; $R_2 = C_2H_5$; X = NCH$_3$
e, $R_1 = CH_3$; $R_2 = H$; X = NCH$_3$



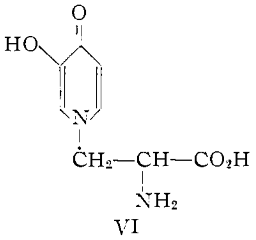
III



IVa, R = CH$_2$OH; X = O
b, R = H; X = NCH$_3$
c, R = CH$_2$OH; X = NCH$_3$



V



VI

We were led to investigate a spectroscopic approach for two reasons: (i) the expectation that any distinguishing criteria found in the ultraviolet behavior of pyrones would apply to pyridones[4]; and (ii) the unusual *hypsochromic* shift of the ultraviolet absorption maximum in alkaline solution observed[5] with pyrones of the type II (*e.g.*, triacetic lactone, IIa). Accordingly, we measured the ultraviolet absorption spectra in neutral and basic methanol or ethanol of I, IIa-d and IVa-c. All of these substances except IVc and IId were known.[6] We have prepared IVc from methylamine and kojic acid (IVa), and IId from methylamine and desoxodehydroacetic acid (IIb). Table I shows the data.

Conclusions.—(i) The general similarities between the spectra of pyrones and the corresponding pyridones apply to this series as well as to the simpler mother substances previously examined.[4] However, certain other regularities of behavior observed with the simple models[4] are not obeyed here. In particular, it was previously observed[4] that the integrated absorption intensity could be correlated with the square of the distance between the hetero

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(1) J. A. Berson and W. M. Jones, THIS JOURNAL, **78**, in press (1956).

(2) A classical example of the same kind of problem developed during the determination of the structure of the alkaloid leucenol (leucaenine), VI.[3]

(3) (a) R. Adams, S. J. Cristol, A. A. Anderson and A. A. Albert, THIS JOURNAL, **67**, 89 (1945); (b) A. F. Bickel and J. P. Wibaut, *Rec. trav. chim.*, **65**, 65 (1946); (c) J. P. Wibaut, *Helv. Chim. Acta*, **29**, 1669 (1946); (d) J. P. Wibaut and R. J. C. Kleipool, *Rec. trav. chim.*, **66**, 24, 459 (1947); (e) A. F. Bickel, THIS JOURNAL, **69**, 1801, 1805 (1947); (f) R. Adams and T. R. Govindachari, *ibid.*, **69**, 1806 (1947); (g) R. Adams, V. V. Jones and J. L. Johnson, *ibid.*, **69**, 1810 (1947); (h) R. Adams and V. V. Jones, *ibid.*, **69**, 1803 (1947).

(4) J. A. Berson, *ibid.*, **75**, 3521 (1953).

(5) J. A. Berson, *ibid.*, **74**, 5172 (1952).

(6) We are greatly indebted to Professor J. P. Wibaut (Amsterdam) for samples of I and IVb, and to Dr. W. M. McLamore (Charles Pfizer and Company) for a sample of kojic acid (IVa).