centration at time t, in minutes. In about 90% of the cases a plot of log $a/(a - x)$ *versus* t gave a straight line for the 20 to 80% portion of the reaction while the linear portion was about 10% less than this for the remainder of the cases. Multiplication of the slope of the line by 2.303 gave k.

Standard Procedure Using Dehydration as the Indicator Reaction.—The procedure was very similar to that just described except that the reaction mixture consisted of 500 ml. of a benzene solution containing 0.125 mole of *t*-butyl alcohol, 0.125 mole of the oxygen base and 0.008 mole of *p*-toluenesulfonic acid monohydrate. The isobutene which was evolved as the reaction proceeded was, in a number of cases, absorbed in concentrated sulfuric acid and weighed. A 93 to 96% yield was obtained in each case tested.

It was found that more reproducible results could be obtained if "zero" time was taken when 0.29 ml. of water had collected. This is 0.15 ml. (6.67%) more than the water of crystallization of the catalyst. A plot of the per cent. yield of water *versus* time gave a smooth curve the slope of which increased with time until the reaction was over 97% complete; obviously no rate constant could be calculated. A plot of the per cent. yield of isobutene *versus* time gave a curve of the same shape but this curve lagged as much as 10% behind the curve based on water evolution. The times required for the reaction to proceed from 6.67 to 50.0% completion were chosen to compare the rates. This is denoted "$t_{50\%}$" in Table II for the sake of brevity.

There was a gradual increase in temperature as the reaction progressed and the temperature variations were larger than for the etherification method. For over 85% of the experiments the variation within an experiment was not more than ±0.3° for the 6.67 to 50% portion of the reaction. Among all the experiments the temperature was 80.9 ± 1.5° and among most of them it was 80.9 ± 0.8°. The yield of water was usually within 1% and always within 3% of the theoretical value except for the control which for some unexplained reason gave a 96% yield consistently. The values given in Table II for the control and for the alcohols and ethers are the average of duplicate determinations which agreed to within 5 to 8%.

Acknowledgment.—We wish to acknowledge our indebtedness to Dr. J. D. Draper who performed a number of preliminary experiments by the dehydration method. We also wish to thank the Atomic Energy Commission for a Fellowship (to K. M.) for two years and the Research Corporation for additional financial support.

COLLEGE PARK, MD.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO]

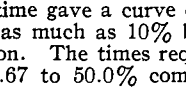
Ultraviolet Absorption Spectra of Hindered Ketones[1]

BY GREGORY D. HEDDEN AND WELDON G. BROWN

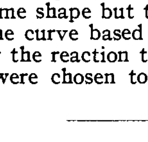
RECEIVED MARCH 21, 1953

The ultraviolet absorption spectra of ketones related to acetophenone show well-defined steric effects (decreased intensity) in the 2400 Å. bands arising from either ortho substitutions or excessive branching (tertiary ketones). The intensity variations in the weaker 2800 Å. bands are interpreted as the resultant of a normal steric effect related to carbonyl aplanarity and an opposing electronic effect of ortho (or meta) alkyl groups. In the series of cyclic ketones beginning with α-indanone the intensity changes characteristic of steric hindrance appear in benzosuberone and, to a greater degree, in benzocycloöctanone.

In a communication challenging the correctness of Remington's[2] interpretation of the influence of ring size on the spectra of the benzocyclamines (I, n = 2, 3, 4), Baddeley, Chadwick and Rawlinson[3] claimed that similar phenomena do not appear in the spectra of the benzocyclanones (II, n = 2, 3, 4). They quoted previously published[4] data and their own (unpublished) data as supporting this conclusion, but did not present a detailed analysis. Nor did they explain why their interpretation of the amine spectra, based upon the steric requirements for hyperconjugation, should not apply equally to the analogous cyclic ketones.



I



II

In this paper it will be shown that the spectroscopic variations in the ketone series closely parallel those in the amines if analogous transitions are compared, and the gross effects are related to the degree of aplanarity of the carbonyl group. The pattern of steric effects will first be established with respect to ketones of the acetophenone series in which hindrance is produced by methyl groups on the ortho positions. The experimental data are new for although Biquard[4] recorded the spectra of the bicyclic ketones (II, n = 2, 3, 4) in alcohol and in cyclohexane solution, we have extended the series and have taken n-heptane as the solvent throughout.

For convenience the absorption bands in the accessible ultraviolet will be designated, in order of decreasing wave length (and increasing intensity), as K (for ketone, excitation of non-bonding oxygen electrons), B (for benzene ring absorption) and C (for conjugation, N → V transition). Attention is focussed upon the strong C bands, occurring at about 2400 Å., which like the strong 2500 Å. bands of the aromatic amines, most clearly reflect the geometrical relationship between the benzene ring and the carbonyl (or dialkylamino) group. The dependence of the B bands upon steric factors will be discussed later. The faint K bands, which have no counterpart in the amine spectra, have not been studied in detail.

The oscillator strength, f, for the C transition of a nuclear-methylated derivative of acetophenone may be represented by $f = f^{\circ} + f_{\text{para}} - f_{\text{ortho}}$, where f° is the observed oscillator strength for acetophenone (0.22, *cf.* Table I, also Fig. 1 and 2), f_{para} is the normal intensifying effect of para methyl group and f_{ortho} is the opposing effect of a methyl group in the ortho position. With the assump-

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[1] Abstracted from the Ph.D. Dissertation of Gregory D. Hedden, The University of Chicago, June, 1951.

[2] W. R. Remington, THIS JOURNAL, **67**, 1838 (1945).

[3] G. Baddeley, J. Chadwick and S. B. Rawlinson, *Nature*, **164**, 833 (1949).

[4] D. Biquard, *Bull. soc. chim. France*, [5] **8**, 55 (1941).

TABLE I

EXTINCTION COEFFICIENTS AND OSCILLATOR STRENGTHS

		Band C			Band B	
Substance	Max. (cm.$^{-1}$)	$\epsilon_{max.}$	f	Max. (cm.$^{-1}$)	$\epsilon_{max.}$	
Acetophenone	42,100	13,040	0.224	36,000	900	0.012
				35,000	700	
o-Methylacetophenone	42,000	8,600	.154	35,300	1250	.020
p-Methylacetophenone	40,500	14,300	.263	36,000^a	850^a	.011
				35,000^a	500^a	
2,4-Dimethylacetophenone	40,700	11,450	.193	35,500	1250	.020
3,4-Dimethylacetophenone	40,100	15,200	.251	35,500	1300	.018
				34,000	800	
Propiophenone	42,200	11,450	.208	36,100	880	.012
				35,000	650	
n-Butyrophenone	42,100	11,500	.208	36,100	850	.011
				34,900	600	
Isobutyrophenone	42,100	11,500	.208	36,100	850	.011
				34,900	600	
Pivalophenone	42,400	8,100	.158	^{b}	^{b}	.011
Acetomesitylene	41,800	2,900	.056	^{b}	^{b}	.004
α-Indanone	41,900	12,720	.208	35,200	2650	.031
	41,000	10,550		34,300	2550	
α-Tetralone	41,200	11,450	.196	35,000	1550	.024
				33,800	1430	
2,3-Benzosuberone	41,600	9,000	.153	35,600	1200	.019
2,3-Benzocycloöctanone	41,100	6,500	.1145	35,000	1100	.016
3-Methyl-1-indanone	42,000	12,800	.208	35,200	2600	.031
	41,200	10,500		34,300	2550	
4,7-Dimethyl-1-indanone	40,850	12,300	.179	33,100	2500	.035
	39,600	11,950		34,200	2500	
5,7-Dimethyl-1-indanone	40,000	15,650		33,850	2250	
	39,000	13,500	.244	35,200	2000	.029
				36,200^a	1350^a	
5,8-Dimethyl-1-tetralone	40,600	10,390	.169	33,300	2310	.036
	40,000	10,090				
6,9-Dimethylbenzosuberone	40,850	4,950	.088	34,750	1290	.024

^{a} Shoulder, not a maximum. ^{b} No maximum.

tion that a meta methyl group is without appreciable effect, a good fit is secured in all but one case by assigning f_{para} the numerical value 0.04, and f_{ortho} the value 0.07. The exception is acetomesitylene ($f = 0.06$) in which, presumably because of the buttressing effect, the combined effect of two ortho methyl groups (0.20) is more than twice that of one.

That f_{ortho} is principally a steric factor, due to out-of-plane twisting of the carbonyl group, is strongly supported by the observation that the corresponding transition in *o*-tolualdehyde has very nearly the same intensity as in benzaldehyde or *m*-tolualdehyde.[5] It is known from independent evidence[6] that the formyl group of the aldehydes is not significantly hindered by methyl groups.

The magnitude of the effect due to an ortho methyl group, expressed as $f_{ortho}/f°$ corresponding transitions, is less in the ketone series (0.32) than in the amine series (0.57). This difference is consistent with the smaller dimensions of the acetyl group. Apart from this quantitative difference there can be no doubt that the phenomena are essentially similar.

Steric hindrance also arises in pivalophenone (*cf.* Fig. 2) which shows a marked diminution in C-band intensity as compared with primary or secondary ketones of this series. An effect of similar magnitude also has been observed in 1-benzoyl-1-benzylcyclopropane[7] and it is evidently characteristic for tertiary ketones.

In the B transitions of the ketones the steric effect of an alkyl group in the ortho position is opposed by an electronic effect (increased polarizability in a direction transverse to the ring-carbonyl axis). The steric effect arises here, because of the decreased effect of the carbonyl group on the transverse polarizability as it is twisted out of the plane. At moderate degrees of twist, *e.g.*, *o*-methylacetophenone, the steric effect is overshadowed by the increased transverse polarizability due to the methyl group and the net effect is an intensification. In the extreme case, *e.g.*, acetomesitylene, the orientation of the carbonyl group is the predominant factor and the B transition has less intensity than the parent (acetophenone). In pivalophenone, where there are no substituents on the ring to produce an opposing electronic effect, the result of a moderate degree of hindrance is a diminution of the B-band intensity.

A methyl group in the para position, having no effect on the transverse polarizability, does not

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[5] J. E. Purvis, *J. Chem. Soc.*, **105**, 2488 (1914).

[6] R. G. Kadesch and S. W. Weller, THIS JOURNAL, **63**, 1310 (1941).

[7] F. Piehl, unpublished work.

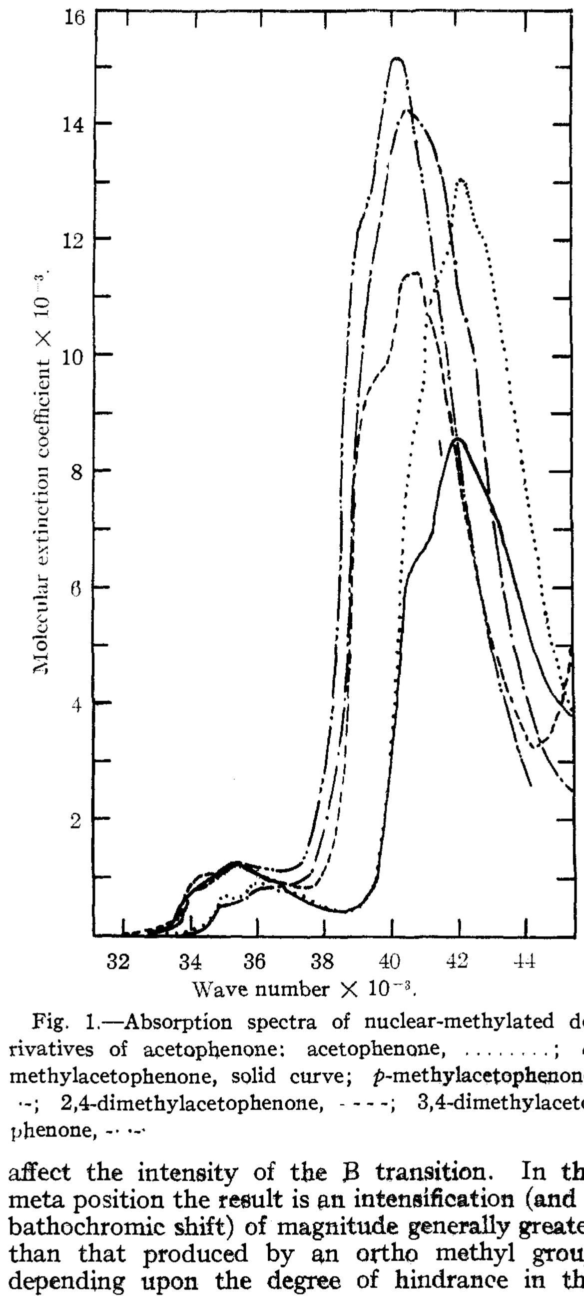


Fig. 1.—Absorption spectra of nuclear-methylated derivatives of acetophenone: acetophenone, ...; *o*-methylacetophenone, solid curve; *p*-methylacetophenone, ·–; 2,4-dimethylacetophenone, - - - -; 3,4-dimethylacetophenone, -·· –·

affect the intensity of the B transition. In the meta position the result is an intensification (and a bathochromic shift) of magnitude generally greater than that produced by an ortho methyl group depending upon the degree of hindrance in the latter case. Where no hindrance is present, as in the benzaldehyde series, methyl groups in the ortho and meta positions are equally effective in strengthening the B transition.

We are now able to interpret the principal fixtures in the spectra of the cyclic ketones. The parent series (II, n = 2, 3, 4, 5; *cf.* Fig. 3) shows substantially normal C-band intensities for n = 2 and 3 and markedly reduced intensities for n = 4 and 5. A similar phenomenon, but with a more abrupt decrease at n = 4 appears in the series of methyl-substituted cyclic ketones (III, n = 2, 3, 4; *cf.* Table I). These results are completely consistent with the view that the carbonyl group is fixed in the plane of the benzene ring for n = 2 or 3 and is twisted out-of-plane for n = 4 or 5. On the basis of the f values for the C-transitions and assuming a cosine-square relationship[8] the effective

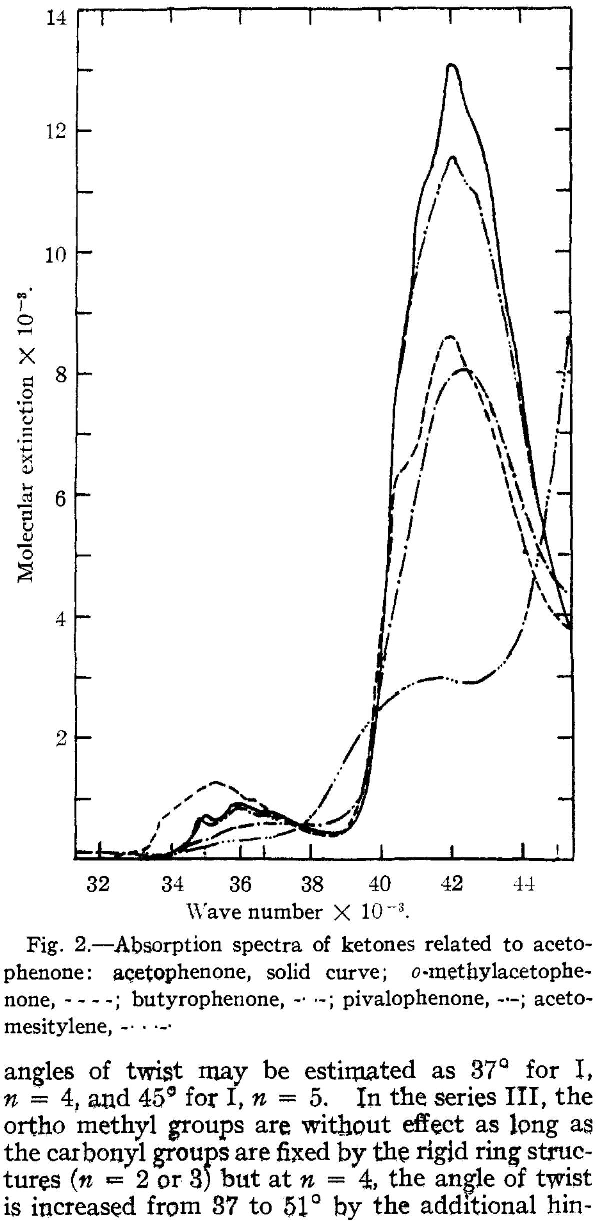
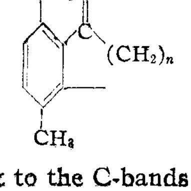


Fig. 2.—Absorption spectra of ketones related to acetophenone: acetophenone, solid curve; *o*-methylacetophenone, - - - -; butyrophenone, -· ·–; pivalophenone, -·–; acetomesitylene, -· · ·-·

angles of twist may be estimated as 37° for I, n = 4, and 45° for I, n = 5. In the series III, the ortho methyl groups are without effect as long as the carbonyl groups are fixed by the rigid ring structures (n = 2 or 3) but at n = 4, the angle of twist is increased from 37 to 51° by the additional hindrance due to the methyl group.



III

With respect to the C-bands the phenomena are similar to those noted by Remington[2] for the 2500 Å. bands of the analogous cyclic amines. The B-band intensities of the cyclic ketones, II, parallel those of the C-bands, but it will be noted that the B-band intensities for n = 2 and 3 are substantially higher than, and at n = 4 approximately equal to, the intensity of the corresponding transition in acetophenone. This situation is perhaps the basis for the statement of Baddeley, Chadwick and Rawlinson[3] to the effect that it is the compounds with five- and six-membered rings, not the seven-, that are abnormal. Actually, the higher B-

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(8) H. B. Klevens and J. R. Platt, THIS JOURNAL, 71, 1714 (1949).

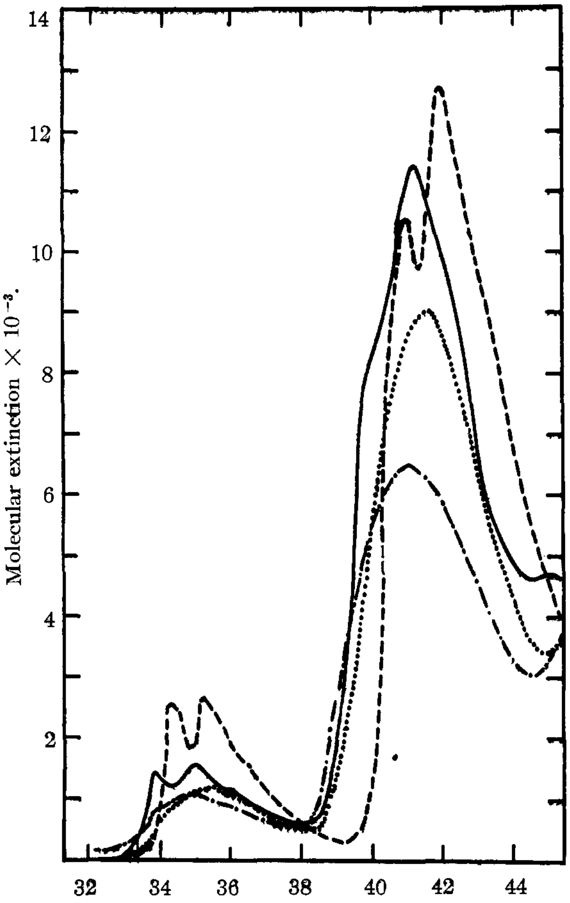

Fig. 3.—Absorption spectra of benzocyclanones: α-indanone, ----; α-tetralone, solid curve; benzosuberone, ...; benzocycloöctanone, -·-.

intensities at $n = 2$ and 3, are adequately explained as the normal $+f$ effect of an ortho alkyl group which does not hinder coplanarity of the carbonyl-group. Except insofar as it may be a part of the normal $+f$ mechanism it appears unnecessary to invoke hyperconjugation, and its dependence upon the orientation of the methylene groups, as these authors have done. There is as yet no clear spectroscopic evidence that the hyperconjugation between an aromatic ring and an alkyl group depends in any great degree upon either the orientation or the number of α-hydrogen atoms. Nor is the present series a suitable one for the demonstration of such minor effects since, by varying the ring size, the orientation of the ortho methylene groups cannot be altered without also affecting the orientation of the carbonyl group.

Experimental

The measurements of spectra were made with a Beckman quartz spectrophotometer, Model DU, on solutions of the ketones at concentrations from 10^{-3} to 10^{-4} M in purified n-heptane. Except as noted below, the compounds were either available from earlier work or were prepared by conventional procedures. The physical constants are listed in Table II.

The conventional Friedel–Crafts ketone synthesis fails for pivalophenone.[9] It was prepared by an inverse Grignard reaction, an ether solution of phenylmagnesium bromide being added slowly to an ether solution of pivaloyl chloride.

TABLE II

PHYSICAL CONSTANTS OF KETONES

Ketone	B.p. or m.p., °C.	n^{20}D (obsd.)	n^{20}D (lit.)
Acetophenone	82 (12 mm.)	1.5342	1.5342[a]
o-Methylacetophenone	107–108 (25 mm.)	1.5303	1.5320[b]
p-Methylacetophenone	112 (23.5 mm.)	1.5332	1.5331[c]
2,4-Dimethylacetophenone	115 (18 mm.)	1.5339	1.5340[d]
3,4-Dimethylacetophenone	....	1.5310	1.5381[d]
Propiophenone	85 (7.5 mm.)	1.5274	1.5269[e]
Butyrophenone	124 (29 mm.)	1.5198	1.5196[e]
Isobutyrophenone	115 (29 mm.)	1.5180	1.5190[e]
Pivalophenone	98 (11.5 mm.)	1.5102	1.5086[f]
Acetomesitylene	....	1.5168	1.5175[g]
α-Indanone[h]	M.p. 41–42	....	.....
α-Tetralone	129 (12 mm.)	1.5691	1.5691[b]
2,3-Benzosuberone	154 (15 mm.)	1.5638	1.5650[i]
2,3-Benzocycloöctanone[j]	142 (10 mm.)	1.5618	
3-Methyl-1-indanone	135 (15 mm.)	1.5573	1.5568[k]

[a] J. W. Brühl, *J. prakt. Chem.*, **50**, 119 (1894). [b] K. V. Auwers, *Ann.*, **408**, 242 (1951). [c] P. H. Groggins and R. H. Nagel, *Ind. Eng. Chem.*, **26**, 1313 (1934). [d] C. S. Marvel, J. H. Saunders and C. G. Overberger, THIS JOURNAL, **68**, 1085 (1946). [e] D. P. Evans, *J. Chem. Soc.*, 788 (1936). [f] At 19.2°. K. V. Auwers, *Ber.*, **45**, 2772 (1912). [g] C. R. Noller and R. Adams, THIS JOURNAL, **46**, 1893 (1924). [h] Material prepared by R. G. Kadesch, *ibid.*, **66**, 1207 (1944). [i] Lit. value is n^{18}D, Plattner, *Helv. Chim. Acta*, **27**, 801 (1944). [j] C. F. Koelsch, H. Hochmann and C. D. LeClaire, THIS JOURNAL, **65**, 59 (1943).

The cyclization of ε-phenylcaproyl chloride, with aluminum chloride, which under ordinary conditions does not occur,[10] produced 2,3-benzocycloöctanone in 19% yield when carried out by the high-dilution technique applied by Plattner.[11] The yield was increased to 41% by the application of an extreme-dilution technique which employs the device shown in Fig. 4. In this device the dilute solution of the acid chloride, added from the dropping funnel, is further diluted by condensate from the reflux condenser before being admitted to the reaction vessel. In a typical experiment, the acid chloride obtained as a residue after treatment of 36.7 g. of ε-phenylcaproic acid, in benzene solution, with phosphorus pentachloride was dissolved in 500 ml. of carbon disulfide. This was placed in the dropping funnel; the dilution flask was filled with 500 ml. of carbon disulfide and

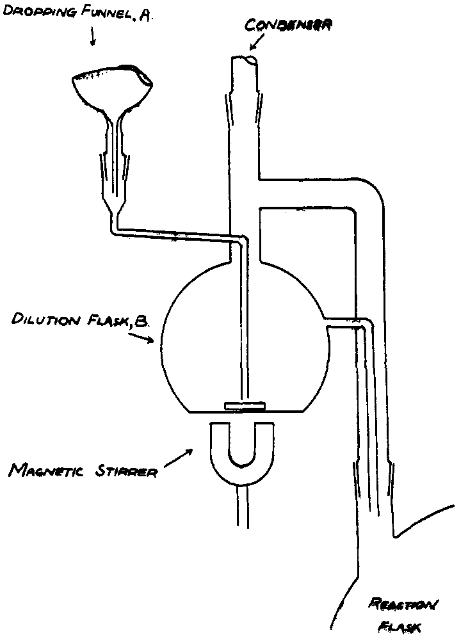

Fig. 4.—High dilution apparatus used in the preparation of benzocycloöctanone.

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(9) E. Rothstein and R. W. Saville, *J. Chem. Soc.*, 1950 (1949).

(10) J. V. Braun and Deutsch, *Ber.*, **45**, 2183 (1912).

(11) P. A. Plattner, *Helv. Chim. Acta*, **27**, 801 (1944).

the reaction flask contained 1200 ml. of carbon disulfide and 55 g. of sublimed aluminum chloride. The drip rate from the funnel was adjusted to one-fifteenth that of the reflux rate and the total time of addition was 78 hours. The reaction mixture was stirred vigorously throughout this period. After removal of carbon disulfide and treatment of the residue with ice, the product, 13.5 g., having the physical constants shown in Table II was isolated by steam distillation, extraction, and vacuum distillation. *Anal.* Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.71; H, 7.84.

The ketone formed an oxime, m.p. 92.5°, and a semicarbazone, m.p. 220°. Upon oxidation with permanganate a mixture of phthalic and phthalonic acids was formed.

There was no advantage in the extreme dilution technique as applied to the preparation of benzosuberone which is formed in excellent yield by Plattner's high dilution technique. An attempt to prepare benzocyclononanone by the cyclization of 7-phenylheptanoyl chloride using the extreme dilution technique resulted in the formation of a polymeric product and no volatile ketone was found.

The values for the oscillator strength were derived from ϵ–ν plots by planimetric integration of curves which, in the regions of overlapping, were drawn to zero extinction in a somewhat arbitrary way. The resulting uncertainty is negligible for the strong C bands, but the estimates for the B bands in some cases depend appreciably upon the manner of extrapolating to zero extinction.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE DEPARTAMENTO DE QUÍMICA, FACULDADE DE FILOSOFIA, CIÊNCIAS E LETRAS, UNIVERSIDADE DE SÃO PAULO]

Ultraviolet Absorption Spectra of Fully Aromatic Esters and Thiolesters[1]

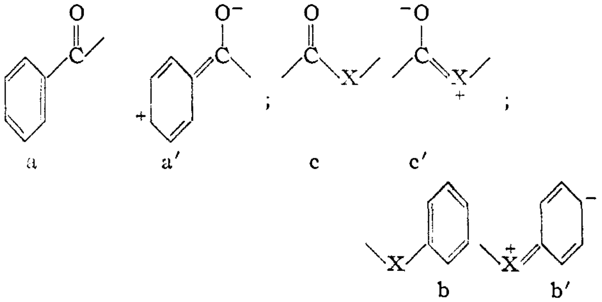
BY G. CILENTO

RECEIVED OCTOBER 23, 1952

In aromatic esters or thiolesters, three main electronic transitions may be expected, which in several cases might give rise to two systems of cross-conjugation. Although there are some cross-conjugation effects, the electronic transitions are largely independent of one another. A certain band appearing in the spectra of certain thiolesters is attributed to an activated state in which the sulfur atom expands its valence shell to a decet.

The present paper reports the ultraviolet absorption spectra (above 220 mμ) of 20 phenyl benzoates or phenyl thiolbenzoates substituted in the two para-positions by methoxyl, nitro or chlorine, as listed in Table I.

Three main electronic transitions may be anticipated in such molecules: (1) that associated with the aroyl absorption of ring A corresponding to structures a and a′; (2) interaction of ring B with the oxygen or the sulfur atom of the ester grouping (structures b and b′); (3) excitation of the ester group proper, symbolized by c and c′. When R_1 and R_2 are suitable substituents two systems of cross-conjugation may arise, but it appears that the three transitions take place independently although some cross-conjugation effects are present in the spectra.



For an interpretation of the position of the bands observed the following considerations seemed important. The ground state of the transition a,a′ might be slightly higher than that found in ordinary aroyl groups because the aroyl resonance a ↔ a′ is opposed by the ester resonance c ↔ c′, although this effect is to some extent compensated by the resonance b ↔ b′ which opposes the ester group resonance. Regarding the excited state a′ the same considerations are applicable but are more important, because a′ is established at the expense of the strong ester resonance c ↔ c′; thus one would expect a′ to be farther from its ground state than, *e.g.*, the excited state of benzaldehyde is from its ground state, and, as above, any weakening of c ↔ c′ by effects of ring would reapproximate a′ to the ground state a. Perhaps such stabilization of the excited state explains the fact that the benzoyl band of phenyl thiolbenzoate lies at a longer wave length than that of cyclohexyl thiolbenzoate, λ_{max} 239 and 235 mμ, respectively.[2]

Furthermore, Table I shows that nitration of ring B (compounds V and VI) causes bathochromic displacement of the benzoyl absorption. When the A-ring contains methoxyl (Compounds III and IV) the benzoyl maxima are again shifted bathochromically, but on subsequent introduction of NO_2-groups into the B-ring the two aromatic bands overlap although the maximum of the resultant band lies at longer wave length than do any of the bands in the parent compounds III and V; IV and VI.[3]

Thiolesters exhibit aroyl absorption at longer wave length than their oxygen analogs. This is probably due to the stronger tendency of sulfur, as compared to oxygen, to interact with the B-ring; thus the thiolester resonance c ↔ c′ would suffer a greater reduction with accompanying stabilization of the excited state a′. Accordingly nitration in the ring B causes a more pronounced red shift of the benzoyl absorption in the case of the thiolester (from 239 to 248 mμ) than in the case of the oxygen ester (from 232 to 235 mμ). It is apparent, however, that there must also be other factors, for phenyl benzoate absorbs at 230 mμ (in C_6H_{12})

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[1] From a paper presented at the 4th meeting of the Sociedade Brasileira para o progresso da Ciência, Porto Alegre, November, 1952.

[2] H. P. Koch, *J. Chem. Soc.*, 387 (1949).

[3] The comparison is not strictly valid in the set of thiolesters IV, VI and VIII, because these were not studied in the same solvent.