simplified calculations can lead to serious misinterpretations. The comparison of half-band integrated intensities of V and *p*-nitro-*t*-butylbenzene (Table I and footnote 4) indicates that this factor does not shift the observed position of the maximum of V very far from its "true" position, but it is impossible to judge to what extent the maxima of the reference compounds have been displaced.

Summations of these effects on the alkyltrinitrobenzene spectra are: band B in II is shifted to the blue by 3–5 mμ with strongly diminished intensity relative to I due to steric inhibition of resonance; band A is displaced to the red by 10–15 mμ with slightly increased intensity as a consequence of factor 1, and somewhat further to the red due to steric enhancement of resonance. The resultant is still a fused band with $\lambda_{\max}$ displaced to a slightly greater wave length, strongly reduced $\epsilon_{\max}$ and a broadened spectral envelope. Going to III, slightly more steric inhibition in band B and steric enhancement in band A have compensating effects on half-band integrated intensity. There is further separation between band B and band A so that band A begins to emerge as an inflection. Steric inhibition decreases band B absorption intensity in IV to the point where the transition is discernible only as an inflection on the tail of a high-intensity shorter-wave length band; steric enhancement causes a bathochromic–hyperchromic displacement of band A with further broadening of the spectral envelope. In V, steric inhibition has caused complete disappearance of band B; steric enhancement has caused band A to emerge as a full maximum whose half-band integrated intensity exceeds that of *p*-nitro-*t*-butylbenzene. The spectrum has become a composite of band A and the tail of the high-intensity shorter-wave length band with no contribution from band B.

Steric enhancement of resonance appears to be a fairly prevalent phenomenon. Further examples will be discussed in subsequent papers of this series.

Experimental

1-Ethyl-2,4,6-trinitrobenzene (III)[14] and 1-*t*-butyl-2,4,6-trinitrobenzene (V)[15] were prepared by literature methods. In the preparation of 2,4,6-trinitrocumene (IV) it was found that better yields (up to 60%) resulted if the crude oil obtained by the method of Fittig, Schaeffer and Koenig[16] was renitrated as follows: 30 g. of the oil dissolved in a mixture of 120 ml. of 90% nitric acid and 600 ml. of 96% sulfuric acid was heated to 115° whereupon a vigorous reaction ensued. After holding the temperature between 120 and 130° for 30 minutes the reaction mixture was drowned on ice and the precipitate recrystallized three times from ethanol. The product had m.p. 107–110°. Other materials were commercially available and were purified by standard methods to meet conventional criteria of purity.

Absorption spectra over the range 214 to 400 mμ were determined in methanolic solutions using a Cary model 14 spectrophotometer with matched 1-cm. silica cells. Concentrations were 3 to 10 $\times$ 10^{-5} *M*. Previously described precautions[17] were taken to guard against photochemical transformations. Data of Table II are from single determinations; data of Table I in each case represent averages of two complete replicate determinations which agreed to within 1% near the maxima and to within 2% on band-edges. We are satisfied that the relative positions of the band edges of II, III and IV between 260 and 280 mμ are as shown in Fig. 1.

Half-band integrated intensities were determined as follows: Molar absorbancy index was plotted as a function of wave-number on 10 $\times$ 10 to the half-inch graph paper, Keuffel and Esser No. 359–11, 100 $\times$ 100 unit squares of which (representing 10^8 l. cm.$^{-1}$/mole cm.) weighed 754 ± 1 mg. The spectra were cut vertically at $\nu_{\max}$ and the spectral envelopes from $\nu_{\max}$ toward the red were carefully cut out and weighed. Weights were: nitrobenzene, 97 mg.; dinitrobenzene, 276 mg.; I, 468 mg.; II, 390 mg.; III, 381 mg.; V, 124 mg.; *p*-nitrotoluene, 113 mg.

Acknowledgments.—Helpful comments and suggestions by Drs. D. V. Sickman, J. C. Dacons and L. A. Kaplan are gratefully acknowledged. The work was done under NOL Task FR-44.

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[14] A. Gay-Lussac and H. Ficheroulle, *Mém. poudres*, **36**, 71 (1954).

[15] E. Liss and K. Lohmann, *Ber.*, **89**, 2546 (1956).

[16] R. Fittig, Schaeffer and Koenig, *Ann.*, **149**, 328 (1869).

[17] M. J. Kamlet and L. A. Kaplan, *J. Org. Chem.*, **22**, 576 (1957)

[JOINT CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FORDHAM UNIVERSITY, NEW YORK, N. Y., AND THE DIVISION OF PROTEIN CHEMISTRY, C.S.I.R.O., MELBOURNE, AUSTRALIA]

Steric Interactions in the Absorption Spectra of 2,2′-Diaroylbiphenyls and Related Compounds. IV.[1] Absorption Spectra and Electronic Interactions in Halogen-substituted Benzophenones

BY EMIL J. MORICONI,[2a] WILLIAM F. O'CONNOR[2a] AND WILLIAM F. FORBES[2b]

RECEIVED AUGUST 7, 1961

The infrared and ultraviolet absorption spectra of a number of halogen-substituted benzophenones have been determined. The main ultraviolet absorption bands can be rationalized in terms of locally excited states; that is, it is assumed that the molecule does not preferentially absorb as one conjugated system. The reason for this may be the non-planarity of the molecule. In 2-halogen-substituted benzophenones this non-planarity is clearly indicated by the spectral data. For 4-halogen substituted benzophenones the ultraviolet data indicate an order of apparent mesomeric (resonance) interaction of I > Br > Cl > F in the electronic excited state. Information concerning the actual conformation of some of the benzophenones is also deduced using infrared data. This indicates that a number of substituted benzophenones exist in more than one conformation. In most of the monosubstituted benzophenones investigated, the unsubstituted benzene ring is probably more coplanar with the carbonyl group. As a preliminary observation it is reported that some of the halogen-substituted benzophenones in the solid state afford a strong e.s.r. signal on irradiation with 2537 Å. light.

Introduction

Halogen-substituted benzophenones, like other compounds discussed in this series of papers, are of interest because they represent examples of conjugated molecules which do not absorb ultra-

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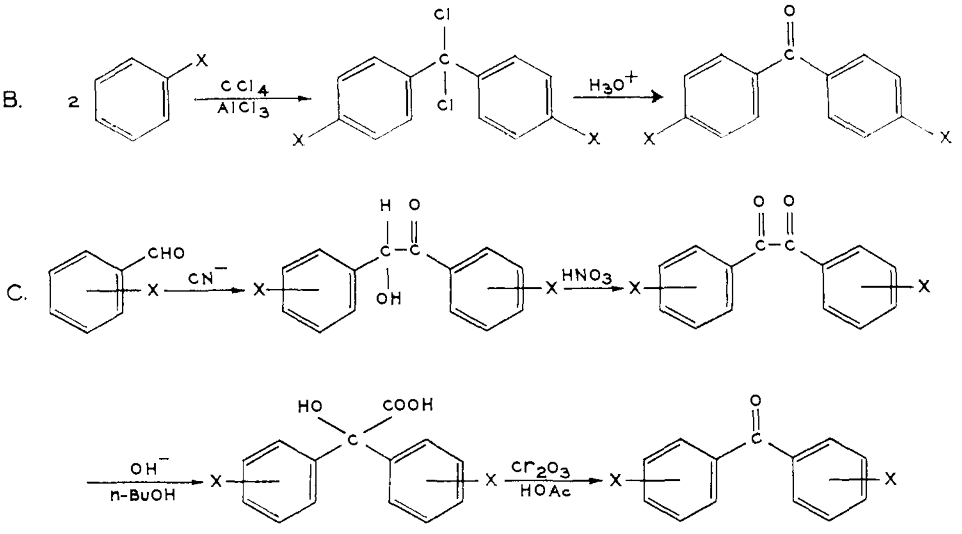
[1] Part III, E. J. Moriconi, W. F. O'Connor and W. F. Forbes, *J. Am. Chem. Soc.*, **82**, 5454 (1960).

[2] (a) Fordham University. (b) Department of Chemistry, University of Waterloo, Ont., Canada (to whom all correspondence should be addressed).

A. Friedel–Crafts aroylation reaction



violet light as one conjugated system. Instead portions of the molecule are raised to electronically excited states by the absorbed light and these parts of the molecule give rise to characteristic ultraviolet absorption spectra associated with the relevant locally excited state. Halogen substitution gives rise to characteristic spectral changes in more simple compounds like acetophenones and benzaldehydes, and these changes can be used to identify some of the locally excited states. Also, in the infrared carbonyl bands of halogen-substituted acetophenones characteristic doublet formation is sometimes observed, which can be related to conformational isomerism, and doublet formation in substituted benzophenones is therefore of interest. Moreover, some benzophenones show promise as protective agents for textiles against light[3] and against weathering and it has also been suggested[4] that certain benzophenones can act as radical suppressors.

Experimental

Infrared Absorption Spectra.—The infrared spectra were determined on a Beckman model IR 7 spectrophotometer, calibrated against a polystyrene film, using an NaCl prism and a diffraction grating. The frequency reproducibility in the 1700 cm.$^{-1}$ region was *ca.* 0.5 cm.$^{-1}$ and frequencies are believed to be accurate to ±2 cm.$^{-1}$.

The integrated absorption intensities (A) were calculated from the equation

$$A = K(1/cl)\log(T_0/T)_{\max}\,\Delta\nu_{1/2} \times 2.303 \times 10^{-4}$$

where c is the concentration in moles per liter, l the cell length in cm., $\log(T_0/T)_{\max}$ the optical density at the absorption maximum and $\Delta\nu_{1/2}$ the band width in cm.$^{-1}$ at half maximum intensity; K was taken as $\pi/2$ (*cf.* ref. 5 and refs. cited therein). Solute concentrations were usually of the order of 5×10^{-2} mole/l., cell thickness (NaCl windows) 0.5 mm. The accuracy of A-values is estimated to be ±5%.

Ultraviolet Absorption Spectra.—The ultraviolet absorption spectra were determined in 1-cm. cells using a Unicam SP 500 and a model DK 2 spectrophotometer, calibrated against a didymium filter and standard solutions of potassium nitrate and potassium chromate. Wave length readings obtained on the two instruments were found to be within 1 mμ of each other. The accuracy of $\lambda_{\max}$ values is estimated to be ±1 mμ, and the precision of $\epsilon_{\max}$ values ±5% or better. Values were reproducible for most compounds to ±2%. For each compound at least two independent sets of observations were made (ultraviolet and infrared spectrum).

Preparation of Compounds.—The halogenated benzophenones were prepared by one of the procedures A–C.

2- and 4-Fluorobenzophenones, 4-chlorobenzophenone, 4,4'-dichlorobenzophenones and 4-bromobenzophenone were best grade commercially available materials. The liquids were carefully distilled until their physical properties agreed with values reported in the literature; they showed single peaks on vapor phase chromatography indicative of greater than 99% purity. Solids were recrystallized or sublimed to constant m.p. All of the compounds afforded the calculated C,H values on elemental analysis. New compounds include (method of preparation in parentheses):

3-Fluorobenzophenone (A), m.p. 53°, light tan needles from 95% ethanol followed by sublimation. *Anal.* Calcd. for $C_{13}H_9OF$: C, 77.97; H, 4.53. Found: C, 77.91; H, 4.72.

2,2'-Difluorobenzophenone (C), b.p. 158–159° (8.1 mm.), colorless liquid, $n^{23.5}D$ 1.5685. *Anal.* Calcd. for $C_{13}H_8OF_2$: C, 71.55; H, 3.70. Found: C, 71.45; H, 3.93.

3,3'-Difluorobenzophenone (C), m.p. 61.5°, white platelets from petr. ether (60–75°). *Anal.* Calcd. for $C_{13}H_8OF_2$: C, 71.55; H, 3.70. Found: C, 71.39; H, 3.92.

3,3'-Diiodobenzophenone (C), m.p. 152.5–153.5°, white needles from ethanol. *Anal.* Calcd. for $C_{13}H_8OI_2$: C, 35.98; H, 1.88. Found: C, 36.09; H, 1.82.

Electron Spin Resonance Spectra.—A spectrometer possessing a transmission type TE 210 cavity with the magnetic field at the samples modulated at 110 kc./sec. by a single wire loop inside the cavity was used. The klystron was of type 723 A/B automatically locked to the cavity frequency by a control circuit. A small electromagnet with gap 5/8" and pole-diameter 2 1/4" was used. The magnet current was controlled by a stabilizer and the magnetic field was swept over the desired region. At $g = 2$, the current needed for 3000 gauss was about 110 ma. and the required voltage was about 300. The microwave frequency was about 8800 Mc./s. (X-band). About 10^{13} molecules of diphenylpicrylhydrazyl were needed for detection at room temperature. Spectra were determined, before and after irradiation, in sealed silica tubes in the absence of air.

Results

Infrared Carbonyl Bands.—The infrared carbonyl bands in carbon tetrachloride solution are listed in Table I. The following may be noted: (i) A 4-halogen substituent slightly raises the carbonyl stretching frequency by *ca.* 1 wave num-

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[3] J. E. Moore and H. P. Lundgren, U. S. Patent 2,888,315; *cf. C. A.*, **53**, 15590g (1959).

[4] J. H. Chaudet and J. W. Tamblyn, Reps. A.C.S. Meeting, Sept., 1960, p. 19-T.

TABLE I

THE INFRARED CARBONYL BANDS (MAIN MAXIMA) OF HALOGEN-SUBSTITUTED BENZOPHENONES IN CARBON TETRACHLORIDE SOLUTION

Substituent	ν_{max}, cm.$^{-1}$	App. mol. extinction coefficient, ϵ^a_{max}	Band widths, $\Delta\nu_{1/2}$ cm.$^{-1}$	Integrated absorption intensity A, mole^{-1} l. cm.$^{-2}$ $\times 10^{-4}$
H	1665.5	650	10.0	2.34
2-F	1670.5	367	18.2	2.41
3-F	1667^c	415	13.1	1.98
4-F	1666	600	9.4	2.01
2-F, 2′-F	1665.5 1677.5^a	391 202^a		
3-F, 3′-F	1671.5	..	10.5	..
4-F, 4′-F	1665.5	..	10.7	..
2-Cl	1679^b	460	13.8	2.28
3-Cl	1668.5	507	11.3	2.07
4-Cl	1666.5	580	10.5	2.21
2-Cl, 2′-Cl	1667^a 1684	200^a 240		
3-Cl, 3′-Cl	1671.5	415	11.4	1.78
4-Cl, 4′-Cl	1668.5	527	12.3	2.38
2-Br	1678	440	13.5	2.14
3-Br	1668.5	505	10.8	1.94
4-Br	1666.5	554	10.8	2.15
2-Br, 2′-Br	1666^a 1684	170^a 267		
3-Br, 3′-Br	1671.5	485	11.4	1.99
4-Br, 4′-Br	1667.5	622	10.0	2.25
2-I	1676.5	420	12.3	1.90
3-I	1668	468	10.5	1.76
4-I	1666	564	10.7	2.18
3-I, 3′-I	1670^b			
4-I, 4′-I	1666^c			

[a] Values are those as obtained directly from the instrument. If the two bands are graphically resolved (*cf.* Figs. 2 and 3), slightly different ϵ_{max} and ν_{max} values are obtained. [b] Some unresolved fine structure occurs on the low frequency side of the band. [c] Some unresolved fine structure occurs on the high frequency side of the band.

ber relative to this frequency in benzophenone. A comparable change has been observed for 4-halogen-substituted acetophenones.[5] The carbonyl stretching band frequency of these benzophenones remains constant to within ±0.5 cm.$^{-1}$ (1666 ± 0.5 cm.$^{-1}$). (ii) Introduction of substituents in the 2- or 3-positions causes larger displacements to higher frequency. Comparing the carbonyl band frequencies of 2-, 3- and 4-substituted benzophenones, the 2-isomer generally affords maxima at the highest and the 4-isomer at the lowest frequency. (iii) Carbonyl band asymmetry occurs in some of the 2- and 3-halogen substituted benzophenones (see Figs. 2 and 3), and is most pronounced for 2,2′-dihalogen substituted benzophenones when two bands can readily be identified. (iv) The intensity of the carbonyl band (as measured by A) is lowest in the 3-isomer. This observation conforms to the behavior observed for the corresponding acetophenones.[6]

Ultraviolet Absorption Bands.—The main ultraviolet maxima in cyclohexane solution are listed in Table II. The band nomenclature is that employed in previous parts of this series (*cf.* also ref. 7). Three different band types are observed, *B*-bands (corresponding to $^1A \rightarrow {}^1L_A$ transitions), *C*-bands (corresponding to $^1A \rightarrow {}^1L_B$ transitions) and *D*-bands (corresponding to ($n \rightarrow \pi$) absorption).

***B*-Bands.**—Following the hypotheses previously postulated,[1] a monosubstituted benzophenone may afford two *B*-bands: one associated with ring A, the benzene ring to which the substituent is attached, and the other associated with ring B, the unsubstituted benzene ring. The following may now be noted: (i) In monohalogen substituted benzophenones two *B*-bands can sometimes be identified. One of these *B*-bands, if it occurs near 248 mμ, that is, near the absorption in benzophenone, is associated with the non-substituted benzene ring B. This absorption in monosubstituted halogen benzophenones is near the absorption associated with ring A, and therefore band assignments cannot always be carried out with certainty. For example, the two bands can tentatively be identified in 4-bromo- and 4-iodobenzophenone but not for 4-fluoro- or 4-chlorobenzophenone. Moreover, because of the closeness of the two bands, one of the bands usually occurs only as an inflection; sometimes even this cannot be discerned.

(ii) In the disubstituted benzophenones the two *B*-bands are identical and only one *B*-band would be anticipated. This has been illustrated[1] previously for the spectra of 4-methoxy- and 4,4′-dimethoxybenzophenone, which showed the absence of the second *B*-band in the latter compound.

(iii) The *B*-bands of 4,4′-disubstituted and of 4-substituted benzophenones occur at progressively longer wave length and generally with increased absorption intensity (except for the iodo compound which shows some fine structure at the long wave length side characteristic of a number of 4-substituted iodobenzenes) as the mass of the halogen substituent increases. This order is the same as that previously noted for benzenes, acetophenones and for other compounds.[6,8] The maximal absorption of 4-substituted benzophenones generally occurs at shorter wave length and with reduced absorption intensity than for the corresponding 4,4′-dihalogen substituted benzophenones.

(iv) The *B*-bands (like the infrared carbonyl bands) tend to occur at progressively longer wave length (lower frequency) in the order 2-isomer < 3-isomer < 4-isomer < 4,4′-isomer. An exception is provided by 2-iodobenzophenone where the *B*-bands associated with ring A occur at longer wave length than for the 3-isomer. However, 2-iodobenzophenone is believed to be exceptional for reasons to be discussed. The *B*-bands in 2-substituted benzophenones, particularly if the 2-substituent is large, normally occur with reduced absorption intensity compared with those in the 3-isomer (*cf.* Rekker and Nauta[9,10] who have

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[5] R. N. Jones, W. F. Forbes and W. A. Mueller, *Can. J. Chem.*, **35**, 504 (1957).

[6] W. F. Forbes and W. A. Mueller, *ibid.*, **35**, 488 (1957).

[7] W. F. Forbes and R. Shilton, ASTM Special Technical Publication No. 269, p. 176 (1959).

[8] W. F. Forbes, *Can. J. Chem.*, **39**, 2295 (1961); *cf.* also W. M. Schubert, J. M. Craven and H. Steadly, *J. Am. Chem. Soc.*, **81**, 2695 (1959); A. Burawoy and A. R. Thompson, *J. Chem. Soc.*, 4314 (1956).

[9] R. F. Rekker and W. Th. Nauta, *Rec. trav. chim.*, **73**, 969 (1954); **77**, 714 (1958).

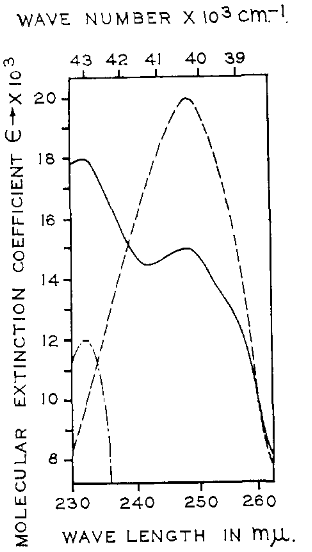


Fig. 1.—Ultraviolet absorption spectra of 2-iodobenzophenone (———), 2-iodotoluene (— · —) and benzophenone (— —) (all in cyclohexane solution).

shown that alkyl groups in 2-positions cause the absorption intensity of benzophenones to be appreciably decreased). In 2,2′-dihalogen substituted benzophenones these absorptivity decreases tend to be much more pronounced (see Table II).

***C*-Bands.**—These bands frequently occur only as inflections. Their absorptivity generally increases in the 2- and 3-isomers. The *C*-bands resemble the *C*-band of the parent compound, benzophenone.

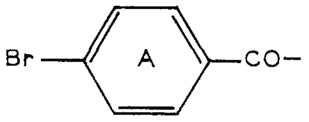
***D*-Bands.**—Bands of considerably lower intensity also occur near 330 mμ which are assumed to be *D*-bands (*cf.* ref. 11 for the *D*-band of benzophenone). Their location of maximal absorption is not appreciably affected by substitution, but they appear to become more intense for some of the 4-substituted benzophenones as the mass of the molecule increases.

Electron Spin Resonance Spectra.—Of the benzophenones tested the 4-fluoro-, the 4-chloro-, the 3- and 4-bromo- and the 3-nitro- derivatives gave intense, relatively stable, signals (*g*-value approx. 2) after irradiation with ultraviolet light (maximum emission of 2537 Å.). Much less intense signals were obtained for benzophenone and the 2-bromo-, 2-hydroxy-, 3-fluoro-, 4,4′-dichloro- and 4,4′-dibromo- derivatives. The benzophenones were also tested as protective agents for wool against damage by light irradiation. None of the compounds tested proved particularly successful as a protective agent against this irradiation. 3-Nitrobenzophenone considerably promoted yellowing. This work will be more fully described elsewhere.

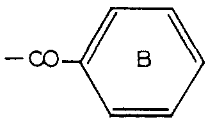
Discussion

The ultraviolet *B*-band absorption of 4-halogen-substituted benzophenones at progressively longer wave length in the order I > Br > Cl > F indicates this same order of mesomeric interaction in the electronic excited state. This is the opposite from the order suggested by the majority of *ground state* data. A possible explanation is that the excited states, involving π-orbital overlap with the halogen atoms, are energetically more stable for the heavier halogens, thus accounting for the observed order of mesomeric interaction in the excited levels under consideration. This order of mesomeric interaction must be supposed to differ from the order prevailing in the activated complexes involved in chemical reactions (*cf.* ref. 8 and refs. cited therein).

Ultraviolet *B*-band spectra show some evidence that locally excited states are involved in the corresponding transitions; that is, di-substituted benzophenones show only one *B*-band, whereas monosubstituted benzophenones may give rise to two absorption bands, one of which may be associated with a chromophoric system such as I and the other with the chromophoric system II[1] (a similar observation has been made for thiobenzophenones[12]). This occurrence of locally excited states may be facilitated by steric interactions. For example, sterically hindered biphenyls, in which the interplanar angle is large, are well known to absorb essentially as two separate benzene systems (*cf.* ref. 13 and references cited there), and this is ascribed to the operation of steric interactions. In the halogen-substituted benzophenones, 2-iodobenzophenone is assumed to represent a compound where steric interactions are large and where consequently the molecule absorbs as two distinct entities: *i.e.*, that of a sterically hindered iodobenzene (*cf.* ref. 8) and that associated with the chromophoric system II. This is illustrated in Fig. 1 which shows the similarity of the spectrum of 2-iodobenzophenone on the one hand and the spectra of a sterically hindered iodobenzene (2-iodotoluene) and of benzophenone on the other hand. While in other monohalogen substituted benzophenones the interplanar angle would not be anticipated to be as large as in 2-iodobenzophenone (where it would be expected to be of the order of 45° or greater; *cf.* ref. 14), none of the benzophenones is believed to be planar for reasons previously discussed (see ref. 1 and refs. cited therein).



I



II

Additional evidence for steric interactions, particularly in 2-halogen substituted benzophenones, can be deduced from the ultraviolet data since it is well known that a decreased absorption intensity in the *B*-bands of the ultraviolet absorption spectra is indicative of steric interactions; in fact, such decreased absorption is consistently obtained in the *B*-bands of most 2-halogen and 2,2′-dihalogen substituted benzophenones (see Table II). Displace-

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(10) R. F. Rekker and W. Th. Nauta, *Spectrochim. Acta*, **8**, 348 (1957).

(11) F. Dörr, *Z. Elektrochem.*, **61**, 950 (1957).

(12) P. Brocklehurst and A. Burawoy, *Tetrahedron*, **10**, 118 (1960).

(13) W. F. Forbes, F. T. Wallenberger, W. F. O'Connor and E J. Moriconi, *J. Org. Chem.*, **23**, 224 (1958).

(14) A. Olivi and A. Ripamonti, *Ricerca Sci.*, **28**, 2102 (1958).

TABLE II

MAIN ULTRAVIOLET ABSORPTION MAXIMA OF HALOGEN-SUBSTITUTED BENZOPHENONES IN CYCLOHEXANE SOLUTION

Substituent	*B*-Band				*C*-Band		*D*-Band	
	Ring A absorp.		Ring B absorp.					
	λ_{max}, mμ	ϵ_{max}	λ_{max}, mμ	ϵ_{max}	λ_{max}, mμ	ϵ_{max}	λ_{max}, mμ	ϵ_{max}
H	248	20,000	..	....	*ca. 280*	*2250*	*ca. 325* 338 347	*80* 105 115
2-F			248	18,000	*ca. 281* *ca. 292*	*2900* *1350*	*ca. 321* 333 345 359	*85* 100 105 80
3-F			248	19,000	*ca. 280*	*3200*	*ca. 322* *336* 348	*75* *105* 110
4-F	250	20,250			*ca. 280*	*1750*	*ca. 322* 334.5 344.5	*90* 120 125
2-F, 2′-F	248 *ca. 259*	18,000 *12,000*	..	....	283.5	4000	*ca. 324* 336 346	*95* 105 105
3-F, 3′-F	248	17,500	.	....	285 *ca. 297*	4000 *2500*	*ca. 326* 338 349.5	*75* 95 105
4-F, 4′-F	252	20,500	..	....	..	..	*ca. 320* 330 342 *ca. 357*	[b]
2-Cl	*ca. 254*	*15,250*[a]	248	17,500	*ca. 280* *ca. 291*	*2000* *1200*	*ca. 321* 332 344	*75* 90 95
3-Cl	*ca. 255*	*17,000*[a]	249	19,000	*ca. 285*	*2250*	321.5 333.5 347	130 125 120
4-Cl	255.5	20,500					*ca. 322* 337 347.5	*95* 125 135
2-Cl, 2′-Cl	250 *ca. 253*	10,500 *10,250*	..	....	287	2200	338 *ca. 354*	140 *115*
3-Cl, 3′-Cl	251	16,500	..	....	290	2500	*ca. 326* 338.5 349.5	*80* 100 105
4-Cl, 4′-Cl	262	27,000	..	....	..	..	*ca. 324* 337 348	*135* 175 185
2-Br	*ca. 255*	*13,500*[a]	248.5	15,500	*ca. 282* *ca. 292*	*1900* *1200*	*ca. 320* 332 344	*70* 90 90
3-Br	*ca. 255*	*16,500*[a]	250	18,000	*ca. 282* *ca. 290*	*2250* *1800*	339 348	105 110
4-Br	259	23,500	*ca. 253*	*22,000*	*ca. 280* *ca. 287*	*7000* *2300*	*ca. 322* 337 347	*110* 150 160
2-Br, 2′-Br	252 *ca. 257*	9,500 *9,000*	..	....	290	2400	338	160
3-Br, 3′-Br	252	17,500	..	....	291	2500	*338* 350	*95* 100
4-Br, 4′-Br	266	30,000	..	....	*ca. 281*	*17,000*	*ca. 325* 337 348	*150* 190 200
2-I	232 *ca. 255*	17,500 *13,500*	248.5	15,000	*ca. 283* *ca. 293*	*2250* *1600*	*332* 344.5	*105* 100
3-I	229 *251*	27,000 *17,250*[a]			*ca. 285*	*1950*	*ca. 334* 346	*120* 110
4-I	270 *282*	18,000 *14,500*	*ca. 256*	*15,000*	..	..	*ca. 318* *ca. 332* *ca. 349*	*510* *290* *235*

3-I, 3′-I	233	30,500	..	....	298.5	1700	338.5	80
	255	*12,500*					350.5	80
4-I, 4′-I	278	21,000	..	....	..	....	*ca. 335*	[b]
	288	*19,000*					*ca. 350*	

[a] Band assignment doubtful. [b] Intensities not determined.

ments to higher frequency are also observed in the infrared carbonyl bands (and sometimes in the ultraviolet *B*-bands) of 2-halogen substituted benzophenones and particularly in 2,2′-disubstituted benzophenones; these spectral changes may therefore also be associated, at least partly, with steric interactions.

The absence of large absorptivity decreases (which are associated with steric interactions, and which *are* observed in the corresponding acetophenones) in the *B*-band of 2-substituted benzophenones may be ascribed to the hypothesis that 2-halogen substituted benzophenones will tend to absorb by means of transitions to locally excited states involving the unsubstituted portion II of the benzophenone molecule. When two 2-substituents are present the absorptivities are, as anticipated, greatly reduced (*cf.* also refs. 9 and 10).

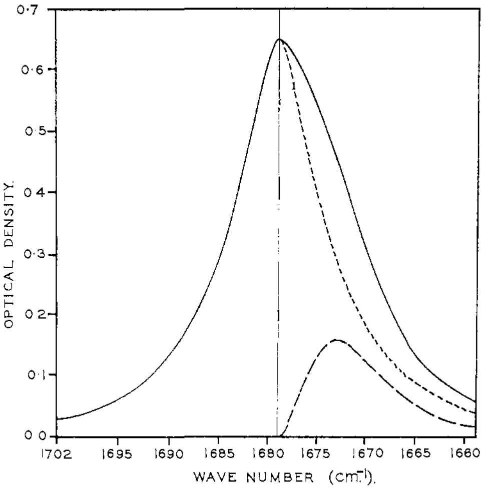
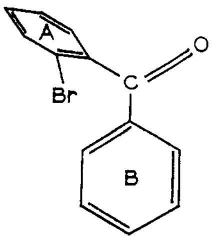
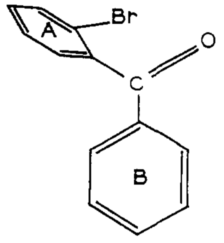


Fig. 2.—Infrared carbonyl band of 2-chlorobenzophenone in carbon tetrachloride solution: observed spectrum (———); band reflected about ordinate through $\nu_{\max}$ (- - - -) and difference curve (— —).

Since doublet formation may also be caused by steric interactions and since this has previously been observed in certain halogen-substituted acetophenones (such as 2-chloro- and 2-bromo-acetophenone),[5] doublet formation in the infrared carbonyl bands was carefully looked for, using high resolution screening. However, although minor deviations of symmetry frequently were observed in the carbonyl band, no clear-cut asymmetry could be observed in most of the monosubstituted compounds studied except for the 2-chloro- and 2- and 3-fluoro compounds. The 2,2′-dichloro- and the 2,2′-dibromo- compounds, on the other hand, afford well-defined doublets. A probable explanation is that such asymmetry or doubled formation is caused by an *s-cis*, *s-trans* equilibrium involving structures III and IV, and that this equilibrium is partly determined by the steric interactions operating in the two structures.



III (*s-trans*)



IV (*s-cis*)

Most other monohalogen substituted (except 2-substituted) benzophenones absorb maximally between 1665.5 and 1671.5 cm.^{-1}. This is in contrast to, for example, the halogen-substituted benzoyl chlorides where appreciable frequency displacements are observed between the locations of the maximal absorption in benzoyl chloride and in the corresponding 3- and 4-halogen-substituted benzoyl chlorides.[15] A possible explanation is to suppose that the carbonyl group in halogen-substituted benzophenone is more coplanar with the unsubstituted aromatic ring B than with the halogen-substituted aromatic ring A. The reason for this may be that the halogen-substituent withdraws electrons from the aromatic ring to which it is attached and consequently overlap between the π-electrons of this ring and the π-electrons of the carbonyl group is more limited. Consequently, the force constant of the carbonyl group may be determined more by the adjoining unsubstituted (coplanar) benzene ring. Hence in 3-halogen substituted benzophenones, but not in the corresponding benzoyl chlorides, a 3-substituent will only slightly affect the $C{=}O$ maximal frequency.

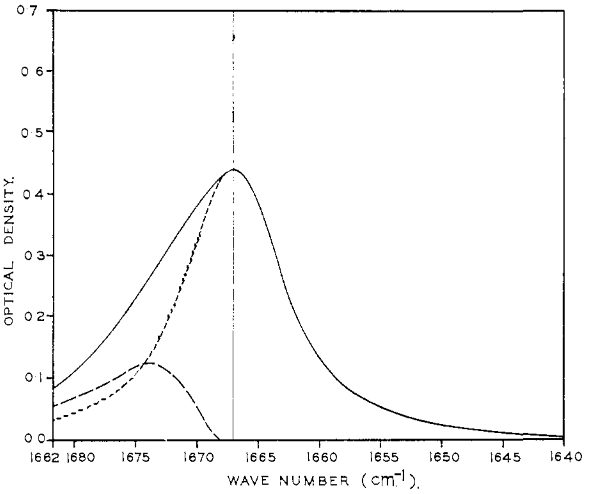


Fig. 3.—Infrared carbonyl band of 3-fluorobenzophenone in carbon tetrachloride solution: observed spectrum (———); band reflected about ordinate through $\nu_{\max}$ (- - - -) and difference curve (— —).

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(15) W. F. Forbes and J. J. J. Myron, *Can. J. Chem.*, **39**, 2452 (1961).

For 2-substituted benzophenones the effect may be more pronounced and the molecule may, moreover, exist in two forms such as III and IV; however, essentially the same argument applies. This general hypothesis receives further support from the observation that the more intense ultraviolet *B*-band for 2- and 3-halogen-substituted benzophenones is most frequently the *B*-band associated with ring B (see Table II) as would be anticipated from predominant conformations of types III and IV. In 4-substituted benzophenones the abovementioned short-range interactions are presumably of less importance and resonance-type interactions may predominate. These can adequately account for the ultraviolet spectral changes and also for the relatively higher intensities in the infrared carbonyl band of 4- (and 2-) substituted benzophenones.

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(16) NSF Undergraduate Research Participants.

[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY, EVANSTON, ILL.]

Alumina: Catalyst and Support. XV.[1] Dehydration of 2-endo- and 2-exo-Bornanol and of endo- and exo-Norbornanol over Alumina Catalyst[2,3]

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The dehydration of 2-*endo*- and 2-*exo*-bornanol, and *endo*- and *exo*-norbornanol over alumina catalysts were studied. The major primary products correspond to those expected from the removal of the hydroxyl group and the hydrogen on the third carbon atom with respect to the one which originally carried the hydroxyl. This process involves either rearrangement of the carbon skeleton (leading to camphene and 2-norbornene) or to the formation of a three-membered ring (leading to tricyclene and nortricyclene). The rate of dehydration of the *exo*-alcohols is faster than that of the corresponding *endo* isomers. The camphene obtained from active 2-*endo*-bornanol was found to retain optical activity. The norbornanols also underwent dehydrogenation to 2-norbornanone over the catalyst. These results are discussed from a mechanistic point of view. While confirming the earlier observation that amines modified the alumina, reducing its ability to bring about olefin isomerizations, it was also observed that the solvent itself may exert this effect to some extent. Thus benzene was capable of reducing the isomerizing ability of the catalyst to a greater extent than *n*-hexane. Equilibrium compositions of 2-bornene, camphene and tricyclene at 275° and of 2-norbornene and nortricyclene at 280° and 310° were established.

In previous papers of this series the differences in catalytic activity of aluminas prepared by various methods were discussed.[5,6,7] It was shown that the dehydration of certain aliphatic and cyclic alcohols may undergo secondary isomerizations accompanying dehydration, depending on the type of alumina used.[8a,b] These secondary isomerizations could be avoided by using aluminas containing only relatively weak acid sites or by modification of aluminas by the use of ammonia or organic bases.[9-11]

The present paper deals with the dehydration of 2-*endo*- and 2-*exo*-bornanol and of 2-*endo*- and 2-*exo*-norbornanol over an "acidic" alumina prepared from aluminum isopropoxide and over the same alumina but modified by the addition of piperidine to the alcohols.[5]

Experimental Part

Alcohols. 1. *d*-2-*endo*-**Bornanol** was purchased from Smith–New York Co., Freeport, L. I., N.Y. It was purified by treating a boiling ethanolic solution of the borneol with activated charcoal, followed by recrystallization from ethanol. *d*-2-*endo*-Bornanol melted at 208° and had $[\alpha]_D$ + 15.8° in ethanol.

2. 2-*exo*-**Bornanol** was prepared by reducing optically pure *d*-camphor with lithium aluminum hydride in tetrahydrofuran solution.[12] The infrared spectrum showed the absence of carbonyl group. The alcohol was composed, according to gas chromatography, of 89% 2-*exo*- and 11% 2-*endo*-bornanol and the observed rotation was $[\alpha]_D$ −28° in ethanol. The literature value of pure 2-*exo*-bornanol was reported[13] to be $[\alpha]_D$ − 34.34°.

3. 2-*endo*-**Norbornanol** was prepared from cyclopentadiene and vinyl acetate by the method of Winstein and Trifan[14]; the alcohol melted at 151–152° and was over 99% pure as determined by gas chromatography.

4. 2-*exo*-**Norbornanol** was prepared by the method of Walborsky and Loncrini,[15] which consisted in epoxidation of bicyclo[2.2.1]-2-heptene (2-norbornene) with peracetic acid and reduction of 2,3-epoxybicyclo[2.2.1]heptane with lithium aluminum hydride.[16]

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(1) For paper XIV of these series see H. Pines and S. M. Csicsery, *J. Am. Chem. Soc.*, **84**, 292 (1962).

(2) Paper V of the series: Dehydration of Alcohols.

(3) For IV see C. N. Pillai and H. Pines, *J. Am. Chem. Soc.*, **83**, 3274 (1961).

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(12) Prepared by C. Goetschel, University of Michigan.

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(15) H. M. Walborsky and D. F. Loncrini, *ibid.*, **76**, 5396 (1954).

(16) Although the experimental conditions used in the epoxidation reaction apparently were similar to those described,[15] the epoxynorbornene after distillation melted at 110–123° (literature,[15] m.p. 125–127°) and was composed of three isomers which on reduction with lithium aluminum hydride formed 2-*exo*-norbornanol admixed with a small amount of *endo*-norbornanol. The epoxides are probably 2,3-