produced a white precipitate. This was filtered off, washed with water, air-dried and recrystallized from 95% ethanol. Needle-like crystals were obtained which darkened on standing and burned explosively. Analysis of the compound for silver ion[26] gave a figure of 1.98 ± 0.06 moles of silver ion per mole of diene.

Ultraviolet Absorption Spectra.—The Cary recording spectrophotometer, model 11 PMS, serial 74, built by the Applied Physics Corp., Pasadena, Calif., was used to determine all of the spectra recorded down to 2000 Å. One spectrum of gas phase sample was determined down to 1900 Å. on the Cary model 14 by a representative of the company. This one spectrum agreed quantitatively with the other spectra.

The cells used in the determinations were standard Cary cells. They were flushed with dried nitrogen before being filled with a sample. Samples of diene deliberately exposed to air for half an hour showed no change in spectrum.

Spectroscopic quality *n*-heptane was prepared by shaking *n*-heptane (Phillips Petroleum Co., 99.5% pure) twice with concentrated sulfuric acid for a total of 28 hours. The *n*-heptane was then washed with 5% aqueous sodium bicarbonate and distilled water, dried over sodium sulfate, and distilled through a 35-cm. Vigreux column.

Infrared Absorption Spectrum.—The infrared absorption spectrum of the diene was determined neat with a model 21 Perkin-Elmer recording spectrophotometer using sodium chloride optics. The cell thickness was 0.03 mm. and the control settings were: resolution, 940; response, 1:1; gain, 5; speed, 10; suppression, 5. The recorded frequencies and corresponding percentage transmission were:

Frequency, cm.$^{-1}$	Transmission, %	Frequency, cm.$^{-1}$	Transmission, %	Frequency, cm.$^{-1}$	Transmission, %
3730	92	1390	87	1016	83
3430	95	1330	59	935	52
3050	32	1310	4	910	66
2950	8	1268	79	890	54
2845	44	1229	38	874	16
1635	77	1206	42	796	28
1596	89	1150	69	721	3
1543	30	1105	85	653	16
1451	69	1061	85		

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[26] S. Winstein and H. J. Lucas, THIS JOURNAL, 60, 836 (1938).

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

Steric Interactions in the Absorption Spectra of 2,2'-Diaroylbiphenyls and Related Compounds. III.[1] Absorption Spectra and Structure of Benzophenones

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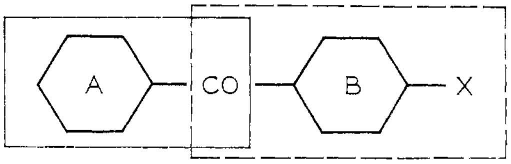
On the basis of hypotheses, postulated in previous parts of this series, substituted benzophenones may be expected to afford up to four absorption maxima (B-bands) in the region 200–360 mμ. This is, in fact, indicated by the data. The ultraviolet and infrared spectral changes on substitution are related to structural changes for a number of benzophenones on the assumption that benzophenone is initially non-planar, and that increased non-planarity may be caused by *o*-substituents.

Introduction

In previous papers of this series we have suggested the following two generalizations concerning the B-band absorptions in the ultraviolet region for 2,2'-diaroylbiphenyls, benzophenones and related compounds (for band nomenclature used, see refs.[1,3]). First, compounds of this type are assumed to absorb as partial benzenoid systems with the other benzene ring(s) exerting only a "secondary" influence on the spectra.[1] It follows from this that an unsymmetrically substituted benzophenone I may show two distinct absorption bands, one corresponding to the system –COPh involving benzene ring A, and another band corresponding to the system –COPh-*p*-X involving benzene ring B. Secondly, it was assumed[4–6] that *m*-substituted benzene derivatives may give rise to two distinct B-bands corresponding to the two monosubstituted benzene derivatives. Combining these two generalizations it follows that a *m*-disubstituted benzophenone of type II may give rise to as many as four B-bands, two involving ring A which may be associated with the partial chromophores –COPh and –PhX, and two B-bands involving ring B which may be associated with the partial chromophores –COPh and –PhY. The two –COPh absorption bands involving benzene ring A and benzene ring B are not necessarily identical because of the second-



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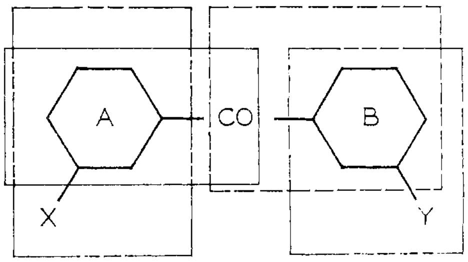

II

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[1] Part II: E. J. Moriconi, W. F. O'Connor, F. T. Wallenberger and W. F. Forbes, THIS JOURNAL, **81**, 5950 (1959).

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[3] W. F. Forbes and R. Shilton, ASTM Bulletin, in press (1960).

[4] W. F. Forbes, *Can. J. Chem.*, **36**, 1350 (1958).

[5] J. C. Dearden and W. F. Forbes, *ibid.*, **36**, 1362 (1958).

[6] W. F. Forbes and I. R. Leckie, *ibid.*, **36**, 1371 (1958).

TABLE I

ULTRAVIOLET ABSORPTION MAXIMA (B-BANDS) AND INFRARED MAXIMA (IN THE REGION 1550–1700 CM.$^{-1}$) OF MONOSUBSTITUTED BENZOPHENONES[a]

Substituent	Solvent	Ultraviolet				Infrared (in carbon tetrachloride soln.)	
		Ring A absorption		Ring B absorption		Carbonyl band	Aromatic bands
		λ_{max}, mμ	ϵ_{max}	λ_{max}, mμ	ϵ_{max}	ν_{max}, cm.$^{-1}$	ν_{max}, cm.$^{-1}$
H	Cyclohexane[1]	248	20,000			1659(s)	1592(w)
	Ethanol[1]	249	18,500				1573(vw)
p-OCH$_3$	Cyclohexane	247	10,500	274	17,000	1655(s)	1596(s)
				280.5	16,500		1577(w)
	Ethanol	249	9,000	283	16,000		
				288	15,800		
p-F	Cyclohexane	250	19,500			1663(s)	1594(s)
m-NO$_2$	Cyclohexane[1]	*ca.* 246	19,500	229	24,000[b]	1668(s)	1607(w)
	Ethanol[1]	*ca.* 248	19,000	232	21,000[b]		1592(vw)
o-NO$_2$	Hexane	244	19,000	*ca. 250*	*18,000*		
o-OH	Cyclohexane	*ca. 247*	*10,000*	256	13,000	1626(s)	1604(m)
		ca. 251	*11,500*	260	13,000		1573(w)

[a] Values in italics represent inflections in this and the subsequent table. Unresolved fine structure.

ary interactions caused by the substituents X and Y, which may affect the two –COPh absorption bands differently.

It is the purpose of the present paper to test these hypotheses and, where possible, to relate the spectral changes in any of the B-bands with structural changes in the relevant benzophenone.

Absorption Maxima of Monosubstituted Benzophenones.—The main ultraviolet and infrared absorption maxima are listed in Table I.

Benzophenone.—Benzophenone shows only one intense absorption maximum in the ultraviolet region which is ascribed to –COPh absorption. This may be deduced from the bathochromic wave length displacement between the $>$C=O chromophore ($\lambda_{max} < 200$ mμ) and the –COPh chromophore (λ_{max} *ca.* 240 mμ) which is much greater ($>$40 mμ) than the bathochromic wave length displacement between benzophenone and, for example, acetophenone which is only *ca.* 10 mμ. Therefore the effect of the second phenyl group on this absorption band is regarded only as a "secondary" effect. Following Jones,[7] who showed that the more planar anthrone molecule affords more pronounced absorption at longer wave length, we assume that the angle between the two benzene rings in benzophenone is about 30°,[7,8] and it is probable that this non-planarity contributes to inhibit effective cross-conjugation. The angle between the carbonyl group and the benzene rings in this way is assumed to be sufficiently small to permit effective conjugation between *two* adjoining chromophores and to allow "secondary" interactions to occur between all three chromophores, but the angle is assumed to be too large to prevent effective conjugation involving both benzene rings and the carbonyl group.

The infrared carbonyl band occurs at 1659 cm.$^{-1}$ (see Table I), it is symmetrical, and there is no indication of a doublet.[9] The infrared carbonyl band occurs at considerably lower frequency than the carbonyl band of acetophenone (1691 cm.$^{-1}$),[9] and hence for both ultraviolet (B-band) spectra as well as for the infrared carbonyl bands the second benzene ring in benzophenone apparently favors the respective transitions, presumably by facilitating the formation of a negative charge on the carbonyl oxygen atom. This interaction, because of the smaller effect which the second benzene ring has on the ultraviolet (B-band) spectrum, is termed a secondary effect. It may also be noted that the location of the carbonyl band in benzophenone is almost identical to that observed in a number of 2,2′-diaroylbiphenyls which have been shown to absorb essentially as benzophenones.[10]

The infrared aromatic vibration bands at 1592 and 1573 cm.$^{-1}$ are weak (see Table I) and this probably indicates only a limited amount of conjugation between the carbonyl group and the two benzene rings. If conjugation of a double bond with an aromatic ring is effective, these bands are usually more intense.[11,12]

***p*-Methoxybenzophenone.**—In *p*-methoxybenzophenone the ultraviolet absorption band near 248 mμ, by analogy with the band occurring at similar wave length in benzophenone, is ascribed to ring A absorption (see Table I and structure I). The second, more intense band is ascribed to –COPh–*p*-OMe absorption because of its similarity to the absorption band in *p*-methoxyacetophenone (λ_{max} in cyclohexane 264 mμ, ϵ 18,000 with some fine structure at longer wave length, λ_{max} in ethanol 272 mμ, ϵ 16,400),[13] bearing in mind that the second benzene ring will again cause a bathochromic displacement of *ca.* 10 mμ because of the previously mentioned secondary effect. Further, the present assignments are supported by the observed B-bands in 4,4′-dimethoxybenzophenone where the peak near 248 mμ, observed in *p*-methoxybenzophenone, disappears and the 4,4′-compound affords only *one* maximum close to the second B-band in *p*-methoxybenzophenone (see Tables I and II and Fig. 1).

Closer inspection of the ultraviolet spectral data

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[7] R. N. Jones, THIS JOURNAL, **67**, 2127 (1945).

[8] I. L. Karle, H. Hauptman, J. Karle and A. B. Wing, *Acta Cryst.*, **11**, 257 (1958).

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

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

[11] G. M. Barrow, *J. Chem. Phys.*, **21**, 2008 (1953).

[12] W. F. Forbes and J. J. J. Myron, unpublished information.

[13] J. C. Dearden and W. F. Forbes, *Can. J. Chem.*, **38**, 896 (1960).

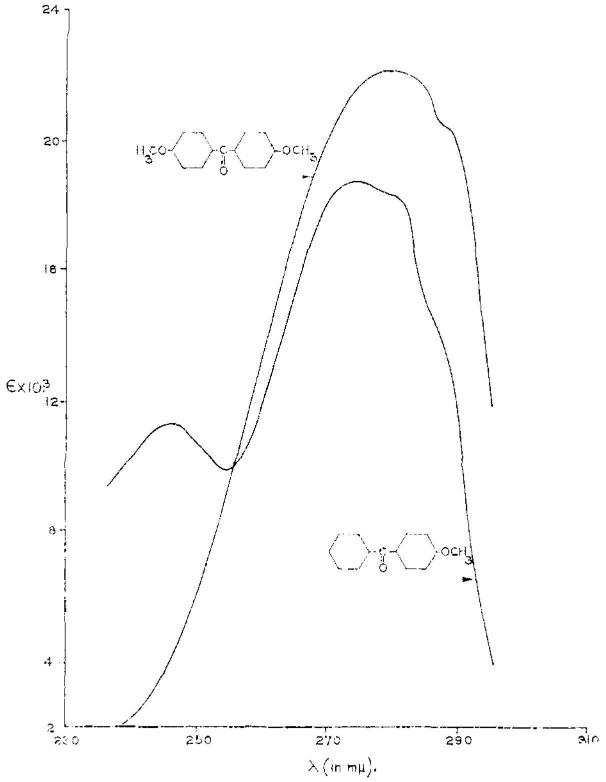

Fig. 1.—The ultraviolet absorption spectra of *p*-methoxy- and 4,4′-dimethoxy-benzophenone in cyclohexane solution.

listed in Table II indicates that under identical conditions 4,4′-dimethoxybenzophenone absorbs at slightly longer wave length (λ_{max} 278 mμ with some fine structure at longer wave length) than the otherwise similar band of *p*-methoxybenzophenone (λ_{max} 274 mμ with some fine structure at longer wave length). This spectral change can be explained readily by assuming that in 4,4′-dimethoxybenzophenone, the second *p*-methoxy substituent will facilitate the formation of a partial negative charge on the carbonyl oxygen atom and thus the observed bathochromic wave length displacement will be further enhanced in 4,4′-dimethoxybenzophenone.

The infrared carbonyl band of *p*-methoxybenzophenone is again symmetrical and occurs at slightly lower frequency (γ_{max} 1655 cm.$^{-1}$) than for benzophenone (ν_{max} 1659 cm.$^{-1}$) (see Table I). This displacement to lower frequency is approximately half that between acetophenone (ν_{max} 1691 cm.$^{-1}$) and *p*-methoxyacetophenone (ν_{max} 1681 cm.$^{-1}$) under identical conditions, and this suggests that the carbonyl group in the ground state of benzophenone is about equally affected by the two benzene rings. In terms of conformation this is consistent with the explanation that *p*-methoxybenzophenone is again non-planar but near-planar with the carbonyl group situated in a plane which is at a similar angle to the planes of *both* benzene rings. The aromatic vibration bands (see Table I) of *p*-methoxybenzophenone, compared with those of benzophenone, are again intensified in a similar manner in which these bands are ntensified for *p*-methoxyacetophenone compared with acetophenone or for *p*-methoxybenzoyl chloride compared with benzoyl chloride.[12]

***p*-Fluorobenzophenone.**—*p*-Fluorobenzophenone in cyclohexane solution affords one intense band at 250 mμ and since a fluoro substituent generally tends to lower the **B**-band absorption intensity of a benzene derivative of this type,[14] we assume that the observed absorption band corresponds more predominantly to ring A absorption (see Table I and structure I). The band corresponding to ring **B** absorption would be expected to occur close to the band associated with ring A absorption and this therefore presumably accounts for the occurrence of only one intense absorption band in the region 220–280 mμ.

The frequency of the symmetrical, structureless, infrared carbonyl band in *p*-fluorobenzophenone is slightly raised by 4 cm.$^{-1}$ relative to the carbonyl band in benzophenone, and as for *p*-fluorobenzoyl chloride compared with benzoyl chloride, the infrared aromatic vibration bands near 1590 cm.$^{-1}$ are again considerably more intense in the *p*-fluoro-substituted compound (see Table I and *cf.* also ref. 12). There is no reason to suppose that the *p*-fluoro substituent appreciably affects the conformation of the benzophenone molecule.

***m*-Nitrobenzophenone.**—*m*-Nitrobenzophenone again shows the expected maximal absorption between 245 and 250 mμ which is ascribed to ring A absorption, that is, to the benzoyl chromophore *not* involving the nitro group. The other maximal absorption near 230 mμ (see Table I), which is accompanied by an appreciable amount of unresolved fine structure, is ascribed to ring B absorption (see structure II), that is, to nitrobenzene absorption with the *m*-substituent exerting its usual secondary effect which gives rise to the observed hypsochromic wave length displacement. A third ultraviolet band (B-band), corresponding to ring **B** benzoyl absorption (*cf.* structure II), might be expected to occur near 230 mμ (*cf.* ref. 1) and absorption of this type may indeed account for the observed fine structure in that region.

The infrared carbonyl band of *m*-nitrobenzophenone is again symmetrical and structureless and occurs at 1668 cm.$^{-1}$. The displacement of 9 cm.$^{-1}$ to higher frequency relative to the band in benzophenone (see Table I) is similar to the displacement observed between *m*-nitroacetophenone (ν_{max} *7101* cm.$^{-1}$) and acetophenone (ν_{max} *1691* cm.$^{-1}$).[9] This may imply that the carbonyl stretching vibration in *m*-nitrobenzophenone is affected by the nitro group in much the same way as the carbonyl stretching vibration is affected by the *m*-nitro group in *m*-nitroacetophenone. This in turn may tentatively be assumed to imply similar conformations in *m*-nitrobenzophenone and *m*-nitroacetophenone as far as the nitro and carbonyl groups are concerned, presumably the groups being non-planar but near-planar in both molecules.

The aromatic vibration bands are weak and occur at higher frequency than for benzophenone (see Table I). Analogous spectral changes in these bands are observed between benzoyl chloride and *m*-nitrobenzoyl chloride.[12]

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[14] W. F. Forbes, *Can. J. Chem.*, **37**, 1977 (1959).

TABLE II

ULTRAVIOLET ABSORPTION MAXIMA (B-BANDS) AND INFRARED MAXIMA (IN THE REGION 1550–1700 CM.$^{-1}$) OF DISUBSTITUTED BENZOPHENONES

	Ultraviolet (in cyclohexane soln.)				Infrared (in carbon tetrachloride soln.)	
	Ring A absorption		Ring B absorption		Carbonyl band	Aromatic bands
Substituents	λ_{max}, mμ	ϵ_{max}	λ_{max}, mμ	ϵ_{max}	ν_{max}, cm.$^{-1}$	ν_{max}, cm.$^{-1}$
H, H	248	20,000			1659(s)	1592(w) 1573(vw)
4-OCH_3, 4′-OCH_3	278 *ca. 282* *ca. 287*	27,000 *26,000* *24,500*			1648(s)	1596(s) 1574(w)
3-OCH_3, 3′-OCH_3	220.5 254 306	28,000 10,000 4,200				
4-Cl, 4′-Cl	261	27,500			1662(s)	1585(s) 1568(vw)
4-Cl, 4′-OCH_3	257	15,000	280 284 *ca. 290*	17,500 17,500 *15,000*	1653(s)	1595(s) 1570(shoulder)
3-NO_2, 4′-OCH_3	225 *ca. 255*	30,000 *11,500*	286 *ca. 292*	16,000 *15,000*	1658(s)	1595(s) 1571(w)

***o*-Nitrobenzophenone.**—The ultraviolet absorption maxima of *o*-nitrobenzophenone, as listed in Table I, again show what is assumed to be ring A absorption, occurring near 245 with slightly decreased absorption intensity. The second B-band now occurs at longer wave length than for *m*-nitrobenzophenone, the absorption being more characteristic of ordinary nitrobenzene absorption.[4] This implies that the secondary interaction of the carbonyl group is no longer important, and this in turn may be explained by assuming that steric interactions cause the molecule to exist in non-planar forms.[15] This would be expected to lead to two absorption bands, corresponding to the –COPh and –$PhNO_2$ chromophores, while the absorption associated with –$COPhNO_2$ is no longer observed. This is in contrast to previously discussed ultraviolet B-bands where both absorption bands, each involving the carbonyl group as shown in structure I, could usually be detected. It is therefore assumed that there is no longer any appreciable overlap between the π-electrons of the carbonyl group and the π-electrons of the benzene ring containing the nitro group because of increased steric interactions and in this way the secondary interaction between the benzene ring and the carbonyl group is assumed to be inhibited, although the nitrobenzene conjugation is maintained.

***o*-Hydroxybenzophenone.**—It may first be noted that absorption characteristic of an intramolecularly hydrogen-bonded carbonyl compound occurs in the ultraviolet absorption spectrum of *o*-hydroxybenzophenone. That is, a doublet occurs near 260 mμ (see Table I) and a corresponding doublet occurs in the C-band (see Experimental). Analogous doublets are observed in the B- and C-bands of *o*-hydroxybenzaldehyde and in the B- and C-bands of *o*-hydroxyacetophenone,[13] except that in the case of the benzophenone the B-band maxima, as anticipated, again occur at slightly longer wave length. Next, the ultraviolet spectrum of *o*-hydroxybenzophenone shows inflections near 250 mμ (see Table I) which are ascribed to ring A absorption. A third B-band might be expected, corresponding to the phenol chromophore, but in cyclohexane solution this band, if it occurs, is hidden by A-band absorption. In alkaline media, however, a band does occur at 236 mμ, ϵ 19,000, and this band may be associated with the phenolic B-band absorption.[16]

The infrared carbonyl band of *o*-hydroxybenzophenone shows an intense peak which occurs at considerably lower frequency than in benzophenone (see Table I). This is as expected for an intramolecularly hydrogen-bonded carbonyl group, and the presence of an intramolecular hydrogen bond is further confirmed by the absence of any intense absorption near 3600 cm.$^{-1}$ which might have been associated with free hydroxyl absorption (see Experimental). The displacement in the carbonyl band relative to the carbonyl band in benzophenone is 33 cm.$^{-1}$ (see Table I) and it may be noted that this is slightly less than the frequency displacement between the bands in *o*-hydroxyacetophenone and acetophenone (48 cm.$^{-1}$; see Experimental) or between salicylaldehyde and benzaldehyde (44 cm.$^{-1}$; see Experimental and ref. 9). All these observations are consistent with the hypothesis that *o*-hydroxybenzophenone exists in one non-planar conformation, with the hydroxy group linked by means of an intramolecular hydrogen bond to the carbonyl group, since in a non-planar molecule the effect of an intramolecular hydrogen bond might be expected to be less pronounced. The nonplanarity of the molecule in this way may account for the above-mentioned smaller frequency displacement in the infrared carbonyl band.

Absorption Maxima of Disubstituted Benzophenones.—The main ultraviolet and infrared absorption maxima are listed in Table II.

4,4′-Dimethoxybenzophenone.—The ultraviolet absorption of this compound exhibits one absorption band in the region 230–300 mμ and, as noted in the discussion of *p*-methoxybenzophenone, this band is ascribed to –COPh–*p*-OMe absorption. This assignment is supported by the data in Fig. 1 which illustrate the essential similarity of the main

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[15] H. H. Szmant and C. M. Harmuth, THIS JOURNAL, **81**, 962 (1959).

[16] J. C. Dearden and W. F. Forbes, *Can. J. Chem.*, **37**, 1294 (1959).

B-bands for *p*-methoxybenzophenone and 4,4′-dimethoxybenzophenone.

Figure 1 shows that the second peak at 247 mμ in *p*-methoxybenzophenone has, as expected, disappeared for the 4,4′-dimethoxy compound. The differences in the main absorption bands between the two compounds are ascribed to secondary interactions (see the discussion of the spectrum of *p*-methoxybenzophenone).

The infrared carbonyl band is again symmetrical and structureless and occurs at 1648 cm.$^{-1}$; the frequency displacement to lower frequency of 11 cm.$^{-1}$ compared to the band in benzophenone (see Table II) is analogous to the observed frequency displacement of 9 cm.$^{-1}$ between the carbonyl bands in acetophenone and *p*-methoxybenzophenone (see Experimental). The aromatic vibration bands remain similar for *p*-methoxyacetophenone (see Experimental), for *p*-methoxybenzophenone (see (Table I) and for 4,4′-dimethoxybenzophenone (see Table II).

3,3′-Dimethoxybenzophenone.—3,3′-Dimethoxybenzophenone in the region 220–320 mμ affords three absorption bands. The intense band at 220.5 mμ is associated with anisole absorption (chromophore AX in structure II) and is assumed to correspond to the B-band of anisole at 220 mμ.[17] The second B-band at 254 mμ is assumed to correspond to the –COPh chromophore with the –OMe substituent exerting its usual secondary effect of *ca.* 7 mμ,[17] by displacing the –COPh absorption band toward longer wave length. The third band at 306 mμ is assumed to be a C-band,[3] because of its lower intensity (see Table II), and because it occurs at a similar wave length as the C-band of compounds like *m*-methoxybenzaldehyde (λ_{max} 304 mμ, ϵ 3000).[17]

4,4′-Dichlorobenzophenone.—4,4′-Dichlorobenzophenone in the region 220–300 mμ affords one intense, structureless band at 261 mμ which is ascribed to –COPh–*p*-Cl absorption. The corresponding bands in *p*-chlorobenzaldehyde and *p*-chloroacetophenone occur at 253 and 249 mμ, respectively,[5,18] that is, the usual bathochromic wave length displacement of about 10 mμ is again observed.

The symmetrical, structureless, infrared carbonyl band occurs at 1662 cm.$^{-1}$ close to the infrared carbonyl band of benzophenone (see Table II). This frequency displacement of 3 cm.$^{-1}$ to higher frequency may be compared with the similar frequency displacement of 1 cm.$^{-1}$ observed between acetophenone and *p*-chloroacetophenone.[9] The aromatic vibration bands occur at slightly lower frequency for 4,4′-dichlorobenzophenone than for benzophenone (see Table II).

4-Chloro-4′-methoxybenzophenone.—The ultraviolet absorption spectra of 4-chloro-4′-methoxybenzophenone, not unexpectedly, are intermediate between the spectra of 4,4′-dimethoxybenzophenone and 4,4′-dichlorobenzophenone (see Table II). A secondary effect is that the band associated with –COPh–*p*-Cl absorption in 4-chloro-4′-methoxybenzophenone (at 257 mμ) is slightly displaced to *shorter* wave length compared with the similar band (at 261 mμ) in 4,4′-dichloroacetophenone; and conversely the band associated with –COPh–*p*-OMe absorption in 4-chloro-4′-methoxybenzophenone (at 280 mμ) is slightly displaced to *longer* wave length compared with the similar band (at 278 mμ) in 4,4′-dimethoxybenzophenone. This can be explained in terms of a preferential alignment of the carbonyl group *toward* the plane of the benzene ring containing the methoxy substituent, and *away* from the plane of the benzene ring containing the chloro substituent. Support for such a proposed conformation may also be deduced from the infrared carbonyl bands since the symmetrical, structureless, carbonyl band of 4-chloro-4′-methoxybenzophenone at 1653 cm.$^{-1}$ lies closer to that of 4,4′-dimethoxybenzophenone (1648 cm.$^{-1}$) than to that of 4,4′-dichlorobenzophenone (1662 cm.$^{-1}$; *cf.* also ν_{max} of *p*-methoxybenzophenone, as given in Table I, 1655 cm.$^{-1}$). The more intense aromatic vibration at 1595 cm.$^{-1}$ for 4-chloro-4′-methoxybenzophenone is also more similar to that in 4,4′-dimethoxybenzophenone (1596 cm.$^{-1}$) than to that in 4,4′-dichlorobenzophenone (1585 cm.$^{-1}$) (see Table II; *cf.* also ν_{max} of *p*-methoxybenzophenone, as given in Table I, 1596 cm.$^{-1}$).

3-Nitro-4′-methoxybenzophenone.—Following the hypothesis developed in the introduction, this compound might be expected to give rise to three ultraviolet absorption bands (B-bands); one corresponding to –COPh–*p*-OMe absorption, one corresponding to nitrobenzene absorption and one corresponding to –COPh absorption with the nitro group exerting a secondary influence. In fact, by analogy with previous assignments the three bands can tentatively be identified. Thus, as shown in Table II, the band at 286 mμ with accompanying fine structure at longer wave length is ascribed to ring B absorption, that is, to absorption associated with –COPh–*p*-OMe absorption and the band at 225 mμ is ascribed to ring A absorption by analogy with the similar band occurring in *m*-nitrobenzophenone (see discussion of this compound and the data listed in Table I). The assignment of the remaining weak inflection near 255 mμ is doubtful. A possible explanation is that the nitrobenzene group in 3-nitro-4′-methoxybenzophenone, unlike the nitrobenzene group in *m*-nitrobenzophenone, is twisted away from the carbonyl group and that in this way the nitrobenzene absorption tends to appear near 255 mμ, near the nitrobenzene absorption in *o*-nitrobenzophenone; whereas the –COPh absorption in compounds like 3-nitro-4′-methoxybenzophenone occurs near 225 mμ, as in compounds like *m*-nitroacetophenone but not as in compounds like *m*-nitrobenzophenone (see Tables I and II and *cf.* ref. 1).

This preferential alignment of the carbonyl group *away* from the nitrobenzene ring in 3-nitro-4′-methoxybenzophenone is again supported by the bathochromic wave length displacement of the ultraviolet absorption associated with the –COPh–*p*-OMe chromophore (*cf.* discussion of compound 4-chloro-4′-methoxybenzophenone) and it is also supported by the infrared bands. That is, the symmetrical, structureless, infrared carbonyl band of

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(17) J. C. Dearden and W. F. Forbes, *Can. J. Chem.*, **37**, 1305 (1959).

(18) W. F. Forbes, W. A. Mueller, A. S. Ralph and J. F. Templeton, *ibid.*, **35**, 1049 (1957).

TABLE III

PREPARATION OF BENZOPHENONE DERIVATIVES

Substituent	Reagents Acylating	 Aromatic	 Condensing	M.p., °C. (cor.)	Lit. m.p., or b.p., °C.
3-NO_2	3-$NO_2C_6H_4COCl$	C_6H_6	$AlCl_3$	94.5–95.5	94–95[a]
2-NO_2	2-$NO_2C_6H_4COOH$	C_6H_6	CF_3CO_3H	103–104	103–104[b]
4-OCH_3	C_6H_5COCl	$C_6H_5OCH_3$	$AlCl_3$	62–63	61[c]
2-OH	4-$CH_3OC_6H_4COCl$	C_6H_6	$AlCl_3$	39–40	41[c]
4,4′-$(Cl)_2$					146.5–148.5[d]
4,4′-$(OCH_3)_2$					143.5–145[e]
3,3′-$(OCH_3)_2$[f]					144–145 (0.3)[f]
4-Cl-4′-OCH_3	4-ClC_6H_4COCl	$C_6H_5OCH_3$	I_2	125–127	124.5[g]
4-OCH_3–3′-NO_2	3-$NO_2C_6H_4COCl_3$	$C_6H_5OCH_3$	$AlCl_3$	92.5–95	95[h]

[a] R. Geigy and W. Koenigs, *Ber.*, **18**, 2400 (1885). [b] H. H. Szmant and C. M. Harmuth, THIS JOURNAL, **81**, 962 (1959). [c] F. Ullman and I. Goldberg, *Ber.*, **35**, 2811 (1902). [d] Eastman Org. Chem. P-1440. [e] *Ibid.*, 4395. [f] Graciously supplied by Professor L. H. Klemm and Dr. Emilios P. Antoniades; see L. H. Klemm, R. Mann and C. D. Lind, *J. Org. Chem.*, **23**, 349 (1958). [g] I. A. Kaye, H. C. Klein and W. J. Burlant, THIS JOURNAL, **75**, 745 (1953). [h] W. Blakey, W. I. Jones and H. A. Scarborough, *J. Chem. Soc.*, 2865 (1927).

3-nitro-4′-methoxybenzophenone at 1658 cm.$^{-1}$ lies closer to that of *p*-methoxybenzophenone (ν_{max} 1655 cm.$^{-1}$) than to that of *m*-nitrobenzophenone (ν_{max} 1668 cm.$^{-1}$), and the main aromatic vibration band of 3-nitro-4′-methoxybenzophenone is similar to that of *p*-methoxybenzophenone (see Tables I and II).

Experimental

Infrared Absorption Spectra.—The infrared spectra were determined on a Unicam SP 100 instrument, using a NaCl prism and a diffraction grating; concn. 3.5–4.5·10^{-2} moles/l., cell thickness 0.5 mm., CCl_4 solvent. Most of the data are listed in Tables I and II. Other data are: acetophenone, ν_{max} 1691(s) cm.$^{-1}$ (carbonyl band); *p*-methoxyacetophenone, ν_{max} 1681(s) cm.$^{-1}$ (carbonyl band); ν_{max} 1598(s) and ν_{max} 1571(w) cm.$^{-1}$ (aromatic vibration bands); *o*-hydroxyacetophenone, ν_{max} 1642(s) cm.$^{-1}$ (carbonyl band); ν_{max} 1613(m), ν_{max} 1592(vw) and ν_{max} 1576(m) cm.$^{-1}$ (aromatic vibration bands); salicylaldehyde, ν_{max} 1665(s) cm.$^{-1}$ (carbonyl band); ν_{max} 1643(s) cm.$^{-1}$ ν_{max} 1617 (m) and ν_{max} 1575(m) cm.$^{-1}$ (aromatic vibration bands); *o*-hydroxybenzophenone (concn., 0.2 mole/l.), ν_{max} 3031 cm.$^{-1}$ (aromatic C–H band) and no maximal absorption near 3600 cm.$^{-1}$.

Ultraviolet Absorption Spectra.—The ultraviolet absorption spectra were determined in 1-cm. cells using a Unicam SP 500 spectrophotometer calibrated against a didymium filter. For each compound at least two independent sets of observations were made. The accuracy of λ_{max} values is estimated to be $\pm$ 1 mμ, and the precision of ϵ_{max} values $\pm 5\%$ or better. Values were reproducible in most cases to $\pm 2\%$. Most of the B-band data are listed in Tables I and II. Also, *o*-hydroxybenzophenone was found to exhibit C-band absorption in cyclohexane at λ_{max} 328 mμ, ϵ 3500, and at λ_{max} 334 mμ, ϵ 4,000. The same compound in alkaline media absorbed maximally at 236 mμ, ϵ 19,000.

Preparation of Compounds.—The substituted benzophenones were invariably prepared by a Friedel–Crafts reaction. Reagents and product m.p. data are summarized in Table III. Salicylaldehyde and the acetophenones were best-grade commercially available materials. These compounds were carefully redistilled until their boiling point and refractive indices agreed with the values reported in the literature and until further distillation did not cause any change in their spectral properties. Most of the compounds afforded the calculated C,H values on elemental analysis.

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Overlap Control of Organic Reactions. III. The Stereochemistry of the Darzens Reaction

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The Darzens condensation of benzaldehyde with ethyl α-chlorophenylacetate affords predominantly ethyl 2,3-*cis*-diphenyl-2,3-epoxypropionate. A carbene mechanism is excluded. The synthesis of two possible Darzens intermediates, the diastereomeric ethyl 2-chloro-3-hydroxy-2,3-diphenylpropionates, is described. Under Darzens reaction conditions each of these affords ethyl 2,3-*cis*-diphenyl-2,3-epoxypropionate. Evidence is presented that the initial aldolization step is rapidly reversible and that the reaction stereochemistry is overlap controlled in the subsequent cyclization step. For facile ring closure, the carbonyl group must be unhindered.

The present investigation stemmed from an earlier study[2a] in which configurations were assigned to the stereoisomeric 2,3-diphenyl-2,3-epoxypropionic acids which first had been described by Kohler.[3] It was shown[2a] that the 122° acid and its 58° ester are 2,3-*cis*-diphenyl-2,3-epoxypropionic acid and ethyl 2,3-*cis*-diphenyl-2,3-epoxypropionate

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(2) (a) Paper I of this series: H. E. Zimmerman, L. Singer and B. S. Thyagarajan, THIS JOURNAL, **81**, 108 (1959); (b) paper II, H. E. Zimmerman and L. Ahramjian, *ibid.*, **81**, 2086 (1959).

(3) E. P. Kohler and F. W. Brown, *ibid.*, **55**, 4299 (1933).