[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY]

The Absorption Spectra of Substituted Chalcones

BY H. HARRY SZMANT AND ARTHUR J. BASSO

RECEIVED JANUARY 14, 1952

The ultraviolet absorption spectra of a number of substituted chalcone structures are reported. An attempt is made to correlate the absorption maxima of over forty chalcones with the electronic nature of the substituents by considering the whole molecule of the chalcone as one conjugated system. The spectral properties of α,ω-diphenylpolyenes are compared with those of the related ketones.

Recent work by Lutz and co-workers[1] has demonstrated significant differences in the spectra of the *cis*- and *trans*-chalcone structures. These results have an important bearing on the interpretation of the spectra of chalcone structures which heretofore were considered in terms of two apparently non-conjugated chromophoric systems, namely, those of the benzoyl and cinnamoyl groups.[2,3]

Experimental

The chalcones were prepared in the conventional fashion by stirring equimolar quantities of the appropriate aldehyde and ketone in a 60% alcoholic solution and in the presence of catalytic amounts of sodium hydroxide. The products were crystallized from 95% ethanol and the absorption spectra were determined in 95% ethanol using a Beckman DU spectrophotometer. The physical properties, analytical data and spectral characteristics of the chalcones reported here are summarized in Table I.

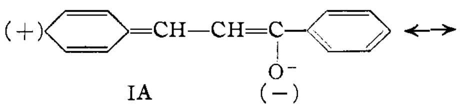
TABLE I

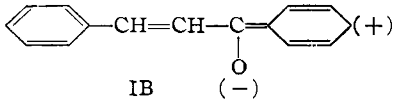
ULTRAVIOLET ABSORPTION SPECTRA OF SUBSTITUTED CHALCONES R—COCH=CH—R′

R =	R′ =	M.p., °C. (lit.)[a]	λ, mμ	ε × 10⁻⁴	Absorption maxima λ′, mμ	ε′ × 10⁻⁴
Phenyl	Phenyl	56–58 (55–58)[b]	312	2.67	230	0.89
Phenyl	*m*-Trifluoromethylphenyl	106–108[c]	299	2.82	225	1.10
p-Nitrophenyl	Phenyl	146.5 (146.5)[d]	317	1.20	264	2.80
p-Xenyl	Phenyl	155–156 (156)[e]	304	1.40	230	1.59
p-Phenoxyphenyl	Phenyl	85 (85–86)[f]	322	3.54	228	1.64
p-Phenylmercaptophenyl	Phenyl	93–95 (95)[g]	339	2.69		
p-Phenylthionylphenyl	Phenyl	135–137[h]	319	2.33	228	1.76
p-Phenylsulfonylphenyl	Phenyl	202[i]	322	2.56	265	2.00
p-Benzylphenyl	Phenyl	77–79[j]	309	1.71		
Phenyl	*o*-Chlorophenyl	51–52 (51.5)[k]	291	1.26	240	0.83
Phenyl	*p*-Chlorophenyl	114–115 (114.5)[l]	314	1.74	260	1.21
Phenyl	2,4-Dichlorophenyl	75–76[m]	289	1.29	266	1.21
Phenyl	3,4-Dichlorophenyl	114–116[n]	305	2.43	240	1.17
p-Cyclohexylphenyl	Phenyl	123–124[o]	312	2.65		
p-(4-Nitrophenyl)-phenyl	Phenyl	166 (165–166)[g]	324	4.15		

[a] All melting points are uncorrected. All analyses were performed by the Micro-Analytical Laboratory, University of Pittsburgh. [b] Michel, *Bull. soc. chim. Belg.*, **48**, 105 (1939). [c] Calcd. for $C_{16}H_{11}OF_3$: C, 69.56; H, 4.01. Found: C, 69.30; H, 3.60. [d] Alexa, *Bull. soc. chim. Romania*, 1, 77 (1939)[f]. [e] Bachmann and Wiselogle, THIS JOURNAL, **56**, 1559 (1934). [f] Dilthey, *et al.*, *J. prakt. Chem.*, 117, 337 (1927). [g] Dilthey, *et al.*, *ibid.*, **124**, 81 (1930). [h] Calcd. for $C_{21}H_{16}O_2S$: C, 75.87; H, 4.85. Found: C, 75.61; H, 4.33. [i] Calcd. for $C_{21}H_{16}O_3S$: C, 72.39; H, 4.62. Found: C, 72.32; H, 4.42. [j] Calcd. for $C_{22}H_{18}O$: C, 88.55; H, 6.08. Found: C, 88.91; H, 6.18. [k] Frederick, Dippy and Lewis, *Rec. trav. chim.*, **56**, 1000 (1937). [l] Alexa, *Bull. soc. chim. Romania*, **18A**, 93 (1936). [m] Calcd. for $C_{15}H_{10}OCl_2$: C, 65.00; H, 3.63. Found: C, 64.66; H, 3.44. [n] Calcd. for $C_{15}H_{10}OCl_2$: C, 65.00; H, 3.63. Found: C, 65.01; H, 3.62. [o] Calcd. for $C_{21}H_{22}O$: C, 86.85; H, 7.63. Found: C, 86.43; H, 7.37.

In this paper we wish to report a number of new chalcones and their spectral characteristics, and also we intend to show that the spectra of chalcones can be better interpreted and correlated if the principal absorption band is assumed to originate from electronic oscillations represented by I.


IA


IB

Discussion

The results of Lutz[1] with *cis*- and *trans*-chalcone as well as those with the dibenzoylethylene structures clearly demonstrate that the long wave lengths band of *trans*-chalcone (298 mμ in hydrocarbon solution, 312 mμ in alcoholic solution)[4] depends on the coplanarity of the whole molecule. These results imply that the whole molecule is responsible for the electronic excitations which give rise to the long wave lengths peak and not the cinnamoyl group as has been previously stated in the literature.[2,3] The characteristic maximum of the cinnamoyl chromophore lies at 286 mμ and the application of this relationship was found to be very useful in the determination of the structures of unsaturated ketones.[5] There is little reason to believe

---

(1) R. E. Lutz, *et al.*, THIS JOURNAL, **72**, 4090, 5058 (1950).

(2) E. R. Katzenellenbogen and G. E. K. Branch, *ibid.*, **69**, 1615 (1947).

(3) L. F. Ferguson and R. P. Barnes, *ibid.*, **70**, 3907 (1948).

(4) Unless otherwise specified all maxima mentioned in this paper refer to alcoholic solutions.

(5) A. L. Wilds, *et al.*, THIS JOURNAL, **69**, 1985 (1947).

that the replacement of a methyl group when attached to the cinnamoyl structure (in benzalacetone) by a phenyl group (to give chalcone) should cause a bathochromic shift of 26 mμ in the respective maxima unless the chromophoric system is enlarged in the process. Thus, we conclude that while the two phenyl groups in benzophenone are not conjugated because of steric interference of the ortho hydrogen atoms,[6] the insertion of an ethylene unit removes the steric interference and permits conjugation throughout the whole molecule.[7]

In connection with the problem of the chalcone spectra it is advisable to point out the relationship between the spectra of α,ω-diphenylpolyenes and the related structures in which a carbonyl group is inserted into the polyene chain. The α,ω-diphenylpolyenes represent a typical convergent series[8]

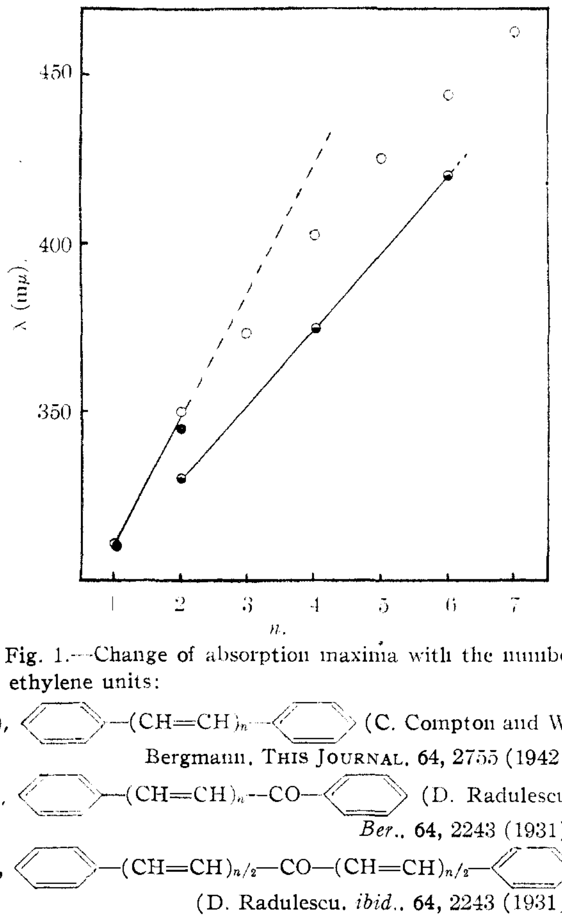
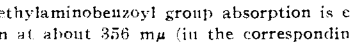
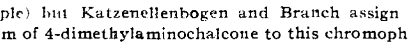
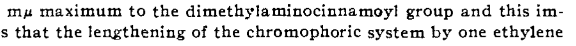


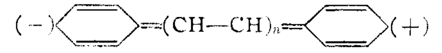
Fig. 1.—Change of absorption maxima with the number of ethylene units:

○,  (C. Compton and W. Bergmann, THIS JOURNAL, 64, 2755 (1942))

●,  (D. Radulescu, *Ber.*, 64, 2243 (1931))

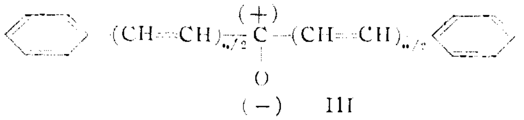
◒,  (D. Radulescu, *ibid.*, 64, 2243 (1931))

and this behavior is attributed to the decrease in stability of the extreme resonance structures (II) as the charge separation increases with an increase

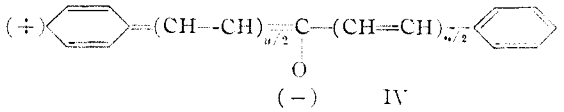


II

in *n*. In Fig. 1 there are compared the maxima of the symmetrical ketones with the α,ω-diphenylpolyenes of corresponding chain lengths and two noteworthy observations are made. Firstly, the maxima of the two series coincide in the lower range and, secondly, the available data in the ketone series indicate *non*-convergence. Both these observations are explained by regarding the ground state structure of the ketones as being predominately III, and the excited states as IV. Thus, with the ketones we are not dealing so much with a



III



IV

structure in which charge separation counteracts the effect of lengthening the chromophoric system. Rather the situation approaches that of the cyanines where the lengthening of the chromophoric system permits a greater distribution of the ionic charge and, therefore, causes a proportional stabilization of the excited states. The chromophoric system in the diphenylpolyethylene ketones extends therefore throughout the whole length of the molecule and chalcone is an example of an unsymmetrical diphenylpolyethylene ketone.[8a]

An attempt to systematize the absorption spectra of the chalcones reported in the literature and in this paper is shown in Table II. The substituents present on the two aromatic rings are tabulated together with the observed displacement of the principal band which in the parent compounds is located at 312 mμ. If the displacements of the principal band are viewed in the light of the usual electromeric and/or inductive effects ascribed to the substituents, one can arrive at the following generalizations: (In the discussion that follows the numbers in parentheses refer to the compounds listed in Table II, and almost all substituents are located at the *para* positions.)

A. Substituents on One Ring.—1. The bathochromic effects of strongly positive electromeric

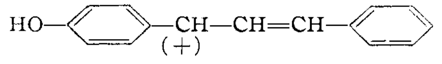
---

(6) R. N. Jones, *ibid.*, **67**, 2127 (1945).

(7) The following objections can be raised with regard to the *x* and *y* axes interpretation of the dimethylaminochalcones in ref. 2. The 4-dimethylaminobenzoyl group absorption is characterized by a maximum at about 356 mμ (in the corresponding benzophenone, for example) but Katzenellenbogen and Branch assign the 387 mμ maximum of 4-dimethylaminochalcone to this chromophore. Furthermore, in the case of the 4-dimethylaminochalcone these authors assign the 419 mμ maximum to the dimethylaminocinnamoyl group and this implies that the lengthening of the chromophoric system by one ethylene group causes a bathochromic shift of 65 mμ. Finally, the interpretation of the singly protonated chalcone spectra in terms of *x* and *y* axes does not agree with previous observations (W. D. Kumler, *ibid.*, **68**, 1184 (1946), and ref. 11) that the maxima of protonated *p*-aminobenzaldehyde and *p*-aminoacetophenone are shifted to shorter wave lengths than those of the unsubstituted carbonyl compounds.

(8) L. G. S. Brooker, "Advances in Nuclear and Theoretical Organic Chemistry," Interscience Publ., Inc., New York, 1945, Chap. 4.

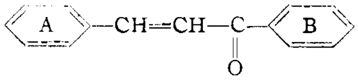
(8a) The situation in the chalcone approaches that of the related carbonium ions recently reported by Pew (THIS JOURNAL, **73**, 1678 (1951)). The simplest of these ions reported in that paper



exhibits a maximum at 480 mμ which corresponds to a bathochromic displacement of approximately 130 mμ when compared to compound 7 in Table II. The 2,4,3′,4′,-tetrahydroxycarbonium ion described by Pew absorbs 195 mμ toward longer wave lengths than the analogous chalcone 40 in Table II. The difference between the chalcone and carbonium ion spectra are understandable if one considers the relative stabilities of the ground states of these two structures.

TABLE II

THE EFFECT OF SUBSTITUENTS ON THE 312 mμ BAND OF CHALCONE



No.	Ring A	Ring B	Δλ$_{312}$mμ[a,b]
1	4-Me$_2$N	.....	105,^{1} 116^{2}
2	.....	4-Me$_2$N	74,^{1} 84^{2}
3	4-H$_2$N	.....	91^{2}
4	.....	4-H$_2$N	61^{2}
5	4-MeO	.....	32-36^{2}
6	.....	4-MeO	11^{2}
7	4-HO	.....	42-46^{2}
8	.....	4-HO	12,^{2} 13^{4}
9	4-Me	.....	21^{2}
10	.....	4-Me	−1^{2}
11	4-Cl	.....	3,^{2} 2^{3}
12	.....	4-Cl	1^{2}
13	4-C$_6$H$_5$S	.....	46^{5}
14	.....	4-C$_6$H$_5$S	27^{3}
15	4-Me$_2$NH	.....	−18^{1}
16	.....	4-Me$_2$NH	3^{1}
17	4-O$_2$N	.....	8^{2}
18	.....	4-O$_2$N	16,^{2} 5^{3}
19	3-F$_3$C	.....	−13^{3}
20	3,4-DiCl	.....	−7^{3}
21	3,4-CH$_2$O$_2$	.....	53^{2}
22	2-Cl	.....	−14^{2}
23	.....	4-C$_6$H$_5$	−8^{3}
24	.....	4-C$_6$H$_5$O	10^{3}
25	.....	4-C$_6$H$_5$SO	7^{3}
26	.....	4-C$_6$H$_5$SO$_2$	10^{3}
27	.....	4-Cyclohexyl	0^{3}
28	.....	4-(*p*-O$_2$NC$_6$H$_5$)	12^{3}
29	.....	3-HO	3^{4}
30	.....	4-Br	−4^{2}
31	4-MeO	4-EtO	34^{6}
32	4-MeO	4-Br	35.5^{6}
33	4-MeO	2,4,6-TriMe	17^{6}
34	2,4,6-TriMe	4-MeO	6^{6}
35	3-O$_2$N	2,4,6-TriMe	−35^{6}
36	4-Br	4-MeO	9^{6}
37	4-H$_2$N	2,3,4-TriMeO	77^{7}
38	3-H$_2$N	2,3,4-TriMeO	1^{7}
39	3,4-Di-HO	3,4-di-HO	72^{8}
40	3,4-Di-HO	2,4-Di-HO	72.5^{9}
41	3,4-Di-AcO	2,4-Di-AcO	−3^{9}
42	4-C$_6$H$_5$S	4-C$_6$H$_5$S	43^{5}
43	4-C$_6$H$_5$S	4-C$_6$H$_5$	40^{5}
44	4-C$_6$H$_5$S	4-Cl	48^{5}
45	2-O$_2$N	2,4,6-TriMe	−61^{6}
46	2,4,6-TriMe	2-O$_2$N	−3^{6}

[a] The displacement of the principal band is calculated on the basis of a 312 mμ value for the parent compound unless a given author reported a different maximum for chalcone. In the latter case the reported value is listed together with the literature reference and it is used to calculate the displacements of the substituted chalcones. All of the spectral data refer to alcoholic solutions. [b] The superscripts refer to the following literature sources: (1) Ref. 2. (313 mμ). (2) Alexa, *Bull. soc. chim. Romania*, **18A**, 93 (1936); **1**, 77 (1939) (309 mμ). (3) This study. (4) Shibata and Nagai, *J. Chem. Soc. Japan*, **43**, 101 (1922). (5) Szmant, Segedi and Dudek (manuscript in preparation) report the syntheses of these chalcones. The spectra were determined by Mr. H. J. Planinsek. (6) Ref. 3. (7) Price, Dingwall and Bogert, THIS JOURNAL, **56**, 2483 (1934). (8) Russel, Todd and Wilson, *J. Chem. Soc.*, 1940 (1934). (9) Seikel and Geissman, THIS JOURNAL, **72**, 5720 (1950) (309.5 mμ).

substituents are 1.4–3.2 times greater when the groups are located on ring A rather than on ring B (compare 1–2, 3–4, 5–6, 7–8, 13–14).

2. Weakly positive groups (whether by electromeric or inductive effect) have small bathochromic effects when present on ring A and are practically of no consequence when present on ring B (compare 9–10, 11–12, 27).

3. Electron attracting groups on ring A cause large hypsochromic shifts but when present on ring B they tend to give *bathochromic* effects (compare 15–16, 17–18, 19, 20, 25, 26, 28, 29).

B. Substituents on Both Rings.—4. With both substituents of strongly positive electromeric character the resulting bathochromic effects are of the same magnitude as those caused by only one group present on ring A (compare 31-5, 37-3, 42-13).

5. The bathochromic effects caused by a strong positive electromeric group is retained in the presence of weakly positive groups (compare 34-6, 36-6, 44-13).

6. The effect of electron attracting groups (stated in generalization 3) overshadows the effects of the other types of groups (see 35, 45, 46), but it can be compensated to a large extent by the presence of electron attracting groups in ring B (see 41).

In addition to the above generalizations it is noted that groups present in the ortho positions on either ring tend to cause unusually large hypsochromic effects (see 22, 45, 46) and this is probably due to steric effects discussed by Lutz.[1]

The effects of the substituents on the principal absorption band of chalcone can be readily explained if one considers that the two extreme electron distributions in the excited state are not at the same energy levels[9] and that structure IA should be less favored because of the greater charge separation. Since a positive electromeric group in ring A can aid in the stabilization of IA and thus can decrease the inequality of IA and IB, it follows that bathochromic effects should vary in accord with generalizations 1 and 2. Electron attracting groups on ring A lower the stability of electron distribution I-A and further increase the difference between the energy levels of I-A and I-B. The same groups on ring B also lower the stability of structure I-B but thereby the energy levels of the two extreme distributions are brought closer together and the unexpected bathochromic (generalization 3) effect is explained.[10]

In addition to the principal absorption band at the long wave lengths there appear in the spectra of chalcones also minor absorption peaks in the 225–260 mμ range. Some of these bands apparently correspond to the "second primary band" of Doub and Vandenbelt,[11] while others are due to the absorption of a specific portion of the molecule. In the case of the sulfone group-containing chalcone, for example, the 265 mμ peak is probably due to the absorption of the phenylsulfonyl group.

---

(9) In the language of the electron-gas model (H. Kuhn, *J. Chem. Phys.*, **17**, 1198 (1949)) this implies a non-symmetrical sine wave of the potential field throughout the molecule.

(10) In terms of the electron-gas model (ref. 9) this implies an increase in the uniformity of the potential field.

(11) L. Doub and J. M. Vandenbelt, THIS JOURNAL, **69**, 2714 (1947).

Acknowledgment.—We wish to thank the Monsanto Chemical Company and the Heyden Chemical Company for the gifts of several substituted acetophenones and chlorinated benzaldehydes, respectively, which were employed in the syntheses.

Pittsburgh 19, Pa.

[Contribution from the Chemistry Department, Brookhaven National Laboratory]

The Gross Mechanism of the Victor Meyer and Hartmann Reaction[1]

By Aksel A. Bothner-By and C. Wheaton Vaughan, Jr.

Received March 20, 1952

Iodosobenzene-I^{131} and iodoxybenzene have been allowed to react in the presence of alkali to yield diphenyliodonium iodate. It has been shown that the radioactivity of the product occurs almost exclusively in the diphenyliodonium ion. A mechanism which is consistent with this and other previous observations is suggested for the reaction.

The reaction between an aryliodoso compound (I) and an aryliodoxy compound (II) in the presence of alkali to yield a diaryliodonium iodate (III) has been termed the Victor Meyer and Hartmann reaction.[2] A mechanism involving a cyclic complex has been proposed for it,[2a] which, however, does not account for the alkali catalysis observed.

In an effort to obtain some evidence bearing on the question of the mechanism, diphenyliodonium iodate has been prepared by the reaction of iodoxybenzene and iodosobenzene-I^{131}.

$$\underset{\text{I}}{\text{Ar-IO}} + \underset{\text{II}}{\text{Ar-IO}_2} \xrightarrow{\text{OH}^-} \underset{\text{III}}{\text{Ar}_2\text{I}^+ + \text{IO}_3^-}$$

The iodosobenzene-I^{131} was prepared by a standard procedure.[3] The diphenyliodonium iodate was analyzed by precipitation of the diphenyliodonium ion from aqueous solution as the bromide, followed by precipitation of the iodate as the barium salt. The purified samples were mounted and counted, utilizing the γ-radiation of the I^{131} only, in order to avoid complications from self-absorption and back-scattering. The results are shown in Table I.

Table I

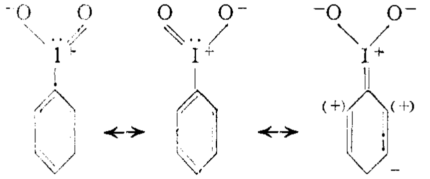
Substance	Wt. sample	Obsd. ct./min.[a]	ct./min. mg. I
C_6H_5IO	0.0192	792	71 (single detn.)
$C_6H_5I^+Br$	.0279	1765	63 ± 1
	.0455	2874	
$Ba(IO_3)_2$	.1050	105	1 ± 1
	.0939	95	

[a] Corrected for background.

It can be seen that it is the iodine of the iodosobenzene which turns up in the diphenyliodonium ion, the iodine of the iodoxybenzene being oxidized to iodate. In view of these results, one may draw two conclusions: (1) there is no symmetrical intermediate involving both iodine atoms; (2) the isotope exchange reaction between iodosobenzene and iodoxybenzene is slow, compared to the rate of formation of the iodonium salt.

The specific activity of the diphenyliodonium bromide is slightly lower than that of the starting material. This may be explained by the previously observed formation of diphenyliodonium salts from iodoxybenzene alone in the presence of alkalies.[2a] The slight activity in the iodate fraction may arise from impurity, or by disproportionation of iodosobenzene to iodobenzene and iodoxybenzene followed by reaction of the iodoxybenzene-I^{131} so produced with more iodosobenzene.

Since the structures of the polyvalent organic iodine compounds are not yet very well understood, any proposals concerning the mechanism of this reaction must be highly speculative. Nitration of iodoxybenzene (probably in the form of its salt with sulfuric acid) leads practically exclusively to *m*-nitroiodoxybenzene.[2a] In view of this strong meta-directing influence, and by natural analogy to the nitro group, one is tempted to write resonance structures for iodoxybenzene such as IV, V and VI.



IV V VI

However, the simple valence bond picture of these forms with a double bond to the iodine requires the utilization of the iodine 5d orbitals. If the energy required for this electronic structure is comparatively large, then these forms will not contribute as much to the resonance hybrid as do the corresponding forms of nitrobenzene. The question of valence-shell expansion has been discussed fully by Sutton and co-workers.[4]

Accepting the current view of the mechanism of aromatic nucleophilic substitution reactions,[5] it is of interest to note that the reaction of azide ion with *p*-nitroiodoxybenzene gives *p*-nitrophenylazide, with nucleophilic displacement of the iodoxy group.

---

[1] Research carried out under the auspices of the U. S. Atomic Energy Commission. While this paper was in process, the paper by J. B. Th. Aten and A. H. W. Aten, Jr., This Journal, **74**, 2411 (1952), appeared in which were reported the results of experiments similar to ours. However since our work differs from theirs in point of experimental detail and interpretation, we are presenting it here.

[2] (a) I. Masson, E. Race and F. E. Pounder, *J. Chem. Soc.*, 1669 (1935); (b) C. Hartmann and Victor Meyer, *Ber.*, **27**, 504 (1894).

[3] H. J. Lucas and E. R. Kennedy, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, New York, N. Y., 1943, p. 331; *Org. Syntheses*, **22**, 69 (1942); H. J. Lucas, E. R. Kennedy and M. W. Formo, *ibid.*, **22**, 70 (1942).

[4] L. E. Sutton, *Ann. Repts.*, **37**, 73 (1940); C. M. Phillips, J. S. Hunter and L. E. Sutton, *J. Chem. Soc.*, 146 (1945); Z. Z. Hugus, Jr., This Journal, **74**, 1076 (1952), in which the use of 4f orbitals in iodine bonding is discussed.

[5] J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 297 (1951).