$$\frac{-\mathrm{d}[\mathrm{D}]}{\mathrm{d}t} = (k_{\mathrm{H}}' + k_{\mathrm{D}}')[\mathrm{D}][\mathrm{NH_2}^{\ominus}] - k_{-1}\,[\text{Anion XVIII}] \quad (7)$$

Application of the steady-state approximation gives for the concentration of anion XVIII

$$[\text{Anion XVIII}] = \frac{k_{\mathrm{H}}'[\mathrm{D}][\mathrm{NH_2}^{\ominus}]}{k_{-1} + k_2} \quad (8)$$

Substitution of (8) into (7) gives

$$\frac{-\mathrm{d}[\mathrm{D}]}{\mathrm{d}t} = (k_{\mathrm{H}}' + k_{\mathrm{D}}')[\mathrm{D}][\mathrm{NH_2}^{\ominus}] - \frac{k_{-1}k_{\mathrm{H}}'}{k_{-1} + k_2}[\mathrm{D}][\mathrm{NH_2}^{\ominus}] \quad (9)$$

Similarly, expression (10) is obtained for the rate of disappearance of chlorobenzene-2-^{2}H.

$$\frac{-\mathrm{d}[\mathrm{H}]}{\mathrm{d}t} = 2k_{\mathrm{H}}'[\mathrm{H}][\mathrm{NH_2}^{\ominus}] - \frac{k_{-1}}{k_{-1} + k_2}(2k_{\mathrm{H}}'[\mathrm{H}][\mathrm{NH_2}^{\ominus}] + k_{\mathrm{D}}'[\mathrm{D}][\mathrm{NH_2}^{\ominus}]) \quad (10)$$

Let $k_{-1}/(k_{-1} + k_2) = F$ (fraction of intermediate anion returning to starting material) and $k_{\mathrm{H}}'/k_{\mathrm{D}}' = i$, then

$$\frac{\mathrm{d}[\mathrm{D}]}{\mathrm{d}[\mathrm{H}]} = \frac{[i(1 - F) + 1][\mathrm{D}]}{2i(1 - F)[\mathrm{H}] - F[\mathrm{D}]} \quad (11)$$

Division of (11) by [D] and treatment of $[i(1 - F) + 1]$, $2i(1 - F)$ and $-F$ as constants, gives on integration

$$\ln[\mathrm{D}]\Big]_{\mathrm{D}_0}^{\mathrm{D}_t} + \frac{1 + i - iF}{1 - i + iF}\ln\left[(-1 + i - iF)\frac{[\mathrm{H}]}{[\mathrm{D}]} - F\right]\Bigg]_{\frac{[\mathrm{H}]_0}{[\mathrm{D}]_0}}^{\frac{[\mathrm{H}]_t}{[\mathrm{D}]_t}} = 0 \quad (12)$$

Values of F, and hence k_{-1}/k_2, were obtained from (12). Chlorobenzene-^{2}H gave F as 0.48, 0.44 and 0.76 in runs 1, 2 and 3, respectively (Table II). The average value 0.56 ± 0.13 corresponds to a k_{-1}/k_2 on the order of 1.5.

PASADENA 4, CALIF.

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES (NO. 2027), CALIFORNIA INSTITUTE OF TECHNOLOGY, AND THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE AND ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Orientation in Aminations of Substituted Halobenzenes[1]

BY JOHN D. ROBERTS, C. WHEATON VAUGHAN, L. A. CARLSMITH AND DOROTHY A. SEMENOW[2]

RECEIVED AUGUST 22, 1955

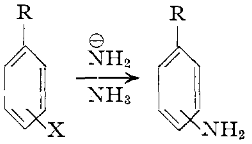
The respective orientations of amine and substituent groups resulting from aminations of a number of substituted halobenzenes have been determined qualitatively and correlated with the aid of a previously postulated elimination–addition ("benzyne") mechanism.

The degree of rearrangement in aminations of substituted halobenzenes with metallic amides is profoundly influenced by the position of the substituent relative to the halogen atom. In the aminations mentioned in the accompanying paper,[3] a number of *o*- and *m*-substituted halides gave exclusively *m*-substituted anilines while a *p*-substituted halide gave an equimolar mixture of the corresponding *m*- and *p*-substituted anilines.

In the present work, amination product distributions for several substituted halobenzenes were determined qualitatively in order to ascertain whether the orientations could be rationalized on the basis of the benzyne mechanism.[3] The experimental results are summarized in Table I. It is to be emphasized that the isomer distributions in Table I may not represent more than qualitatively the actual percentages of isomers formed in the amination reactions. The yields were usually low because of partial conversion of the first-formed products to diphenyl- and triphenylamines.[4] Some preferential isomer destruction is to be expected in such secondary reactions. Indeed, in some preliminary experiments with chlorotoluenes (see Table I) using long reaction times and relatively low amide concentrations (such as would favor secondary reactions) somewhat different proportions of isomeric products were apparently obtained. In addition some of the anilines may react directly with amide ions (see later).

TABLE I

ORIENTATIONS IN AMINATIONS OF SUBSTITUTED HALOBENZENES



R	X	Yield, %	*Ortho*, %	*Meta*, %	*Para*, %
o-$\mathrm{OCH_3}$	Br[a]	33	.....	100	.....
m-$\mathrm{OCH_3}$	Br	59	.....	100	.....
p-$\mathrm{OCH_3}$	Br	31	.....	49 ± 1	51 ± 1
o-$\mathrm{CF_3}$	Cl	28	.....	100	.....
m-$\mathrm{CF_3}$	Cl	16	.....	100	.....
p-$\mathrm{CF_3}$	Cl	25	.....	50 ± 5	50 ± 5
p-F	Br	30	.....	20 ± 1	80 ± 1
o-$\mathrm{CH_3}$	Cl	66[b]	45 ± 4[b]	55 ± 4[b]	.....
o-$\mathrm{CH_3}$	Br	64	48.5 ± 2	51.5 ± 2	.....
m-$\mathrm{CH_3}$	Br	61	22 ± 4	56 ± 4	22 ± 4
m-$\mathrm{CH_3}$	Cl	66[c]	40 ± 4[c]	52 ± 4[c]	8 ± 4[c]
p-$\mathrm{CH_3}$	Cl	35[d]	.....	62 ± 4[d]	38 ± 4[d]

[a] H. Gilman and S. Avakian, THIS JOURNAL, **67**, 349 (1945). [b] One equivalent of sodium amide and a reaction time of 5 hr. gave *o*- and *m*-toluidines in the ratio of about 2:1 (19% yield). [c] One equivalent of sodium amide and a reaction time of 5 hr. gave *o*-, *m*- and *p*-toluidines in the proportions of roughly 6:3:1 (15% yield). [d] One equivalent of sodium amide and a reaction time of 5 hr. gave *m*- and *p*-toluidines in the ratio of about 1:1 (7% yield).

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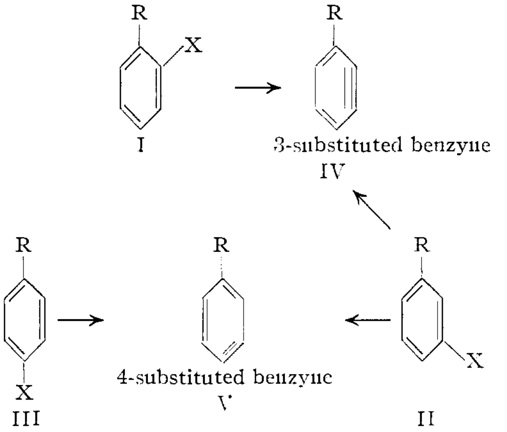
[1] (a) Supported in part by the program of research of the U. S. Atomic Energy Commission. (b) Presented in part at the Kansas City Meeting of the American Chemical Society, March 24, 1954.

[2] National Science Foundation Fellow, 1954–1955.

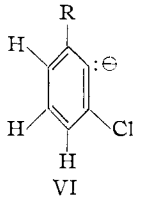
[3] J. D. Roberts, D. A. Semenow, H. E. Simmons, Jr., L. A. Carlsmith, THIS JOURNAL, **78**, 601 (1956).

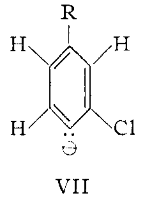
[4] F. W. Bergstrom, R. E. Wright, C. Chandler and W. A. Gilkey, *J. Org. Chem.*, **1**, 170 (1936).

Rationalization of the observed orientations in terms of the benzyne mechanism may be conveniently divided into two parts—factors governing formation of particular benzyne isomers and effects of substituent groups on directing addition of the elements of ammonia to the "triple" bond. Clearly, *o*- (I) and *p*-substituted (III) aryl halides can eliminate hydrogen halide to form *only* 3- (IV) and 4-substituted (V), benzynes, respectively. A *m*-substituted halide (II) might yield either or both isomers.



Amination experiments carried out with bromobenzene-2-^{2}H indicate that the rate for the elimination step for this halide is approximately equal to the rate of removal of the hydrogen *ortho* to the halide as a proton.[3] Consequently, the direction of elimination for a *m*-substituted aryl bromide should be predictable on the basis of which of the hydrogens adjacent to the halogen is more acidic. Experiments with chlorobenzene-2-^{2}H show that it forms benzyne in liquid ammonia by a stepwise mechanism.[3] Hence, the direction of elimination for a *m*-substituted chloride may depend not only on the relative acidities of the hydrogens adjacent to the chlorine but also on the relative rates of ejection of chloride ion by the possible isomeric anions, VI and VII.


VI


VII

As will be seen later, the latter factor may be expected to be important only when the acidities of the hydrogens adjacent to the chlorine are not very different.

The acidities of benzenoid hydrogens appear to be largely determined by the *inductive* effects of substituents[5]; thus, the acidity order is $o > m > p$ for hydrogens on benzene rings carrying electron-attracting groups and is $p > m > o$ with electron-donating groups. The order for electron-attracting groups is supported by the results of metalation studies and verified by direct measurements of the rates of deuterium–hydrogen exchange for substituted deuterobenzenes with potassium amide in liquid ammonia[5]; the deuterium exchange data are summarized in Table II.

TABLE II

PSEUDO FIRST-ORDER RATE CONSTANTS FOR DEUTERIUM-PROTIUM EXCHANGE OF SUBSTITUTED DEUTEROBENZENES (C_6H_4DR) WITH 0.6 *M* POTASSIUM AMIDE IN LIQUID AMMONIA (AT BOILING POINT)[a]

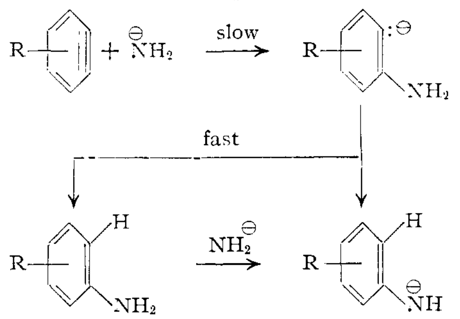
R	k, sec.$^{-1}$	R	k, sec.$^{-1}$
2-F	$>4 \times 10^{-1}$	4-CF_3	1×10^{-3}
3-F	4×10^{-4}	2-OCH_3	1×10^{-3}
4-F	2×10^{-5}	3-OCH_3	$\sim 10^{-7}$
2-CF_3	6×10^{-2}	4-OCH_3	$\sim 10^{-8}$
3-CF_3	1×10^{-3}	H	$\sim 10^{-7}$

[a] Ref. 5.

On the basis of the hydrogen acidities, the following predictions can be made. An aryl bromide with a *m*-substituent which is electron-attracting by the inductive effect should eliminate hydrogen bromide to yield preferentially the 3-substituted benzyne, since the most acidic benzenoid hydrogen is at the 2-position. Formation of a 3-substituted benzyne might also be expected for *m*-substituted aryl chlorides when R ($-OCH_3$, $-CF_3$) has a *strong* electron-attracting inductive effect, because the 2-hydrogen is then so much more acidic than the 6-hydrogen that the anion VII may not be formed at all. The corresponding *o*-substituted halides can yield only the 3-substituted benzynes so that the same final amination products should be obtained from these isomeric *o*- and *m*-substituted halides.

An aryl bromide with a *m*-substituent which is *weakly* electron-donating by the inductive effect should give both the 3- and 4-substituted benzynes with the 4-isomer predominating. The corresponding chloride should also give a mixture of the 3- and 4-substituted benzynes, but less of the latter may be formed than from the bromide because the anion VI from the chloride with its more localized negative charge, may lose chloride ion (to form the 3-substituted benzyne) more readily than the isomeric anion VII (to form the 4-substituted benzyne). No complications of this sort are to be expected when the elimination can only occur in one direction and, in agreement with this idea, the same mixture of toluidines was obtained from the amination of *o*-bromo- and *o*-chlorotoluenes.

The amination of a benzyne intermediate seems most likely to occur in two steps, the first being a rate-determining addition of amide ion and the second being a fast abstraction of a proton from solvent or an intramolecular proton shift.



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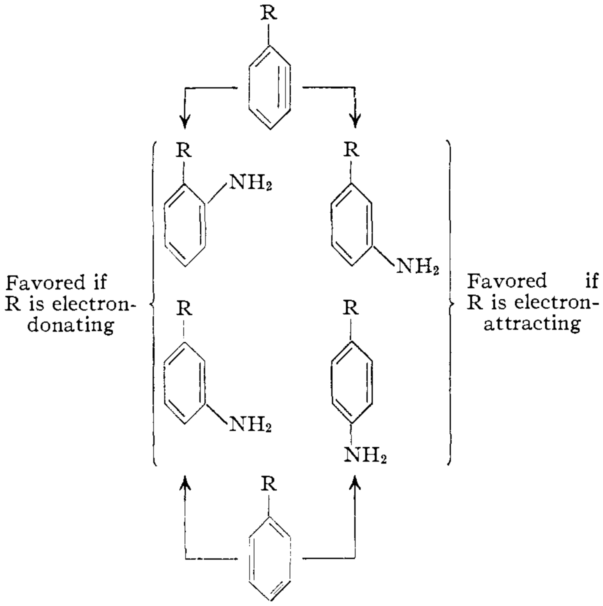
(5) G. E. Hall, R. Piccolini and J. D. Roberts, THIS JOURNAL, **77**, 4540 (1955).

The direction of addition might be predicted by considering the amide ion to add so as to provide the most favorable location of the negative charge with respect to the inductive effect of R.[6] On this basis, the benzenoid hydrogen acidity data may be employed to predict the pattern of addition. Where R is electron-attracting by its inductive effect, a 3-substituted benzyne should give predominantly the *m*-substituted aniline and a 4-substituted benzyne may show some preference for forming the *p*-substituted aniline. Where R is weakly electron-donating by its inductive effect 3- and 4-substituted benzynes may give preferentially the *o*- and *m*-substituted anilines, respectively; however, the preference in the case of the 3-substituted benzyne may be diminished by steric hindrance to formation of the *o*-substituted anilines.



In general, the orientations observed with the various substituents (Table I) are in accord with the above predictions based on the benzyne mechanism. Thus, all of the halides with electron-attracting *o*- and *m*-substituents give exclusively *m*-substituted anilines. The results obtained from aminations of the halotoluenes are consistent with the formation of 60% of 4- and 40% of 3-methylbenzyne from *m*-bromotoluene and 21% of the 4- and 79% of the 3-isomer from *m*-chlorotoluene. The predominance of the 4-benzyne formed from *m*-bromotoluene is in accord with the electron donating effect of the methyl group whereas the greater amount of the 3-isomer from *m*-chlorotoluene is explicable on the basis that the 2-anion (VI, R = CH_3) loses chloride ion faster than the 4-anion (VII, R = CH_3). 4-Methylbenzyne gives the *m*- and *p*-toluidines in the ratio of approximately 2:1, a result which is also qualitatively in accord with the electrical effect of the methyl group. Although the inductive effect alone should lead to a preponderance of *o*-toluidine from the amination of 3-methylbenzyne, the *o*- and *m*-isomers were actually obtained in the ratio of about 1:1; the low value for this ratio may well be due to steric hindrance to attack of amide ion at the 2-position.

Ratios of *m*- to *p*-substituted anilines obtained from *p*-substituted phenyl halides can be roughly correlated with k_m/k_p for exchange (see Table II). When k_m/k_p is nearly unity as for $-CF_3$, the *m*- and *p*-substituted anilines are formed in substantially equal amounts.[7] With fluorine, k_m/k_p is about 20 which correlates well with the substantially greater amount of *p*- with respect to *m*-fluoroaniline obtained from *p*-bromofluorobenzene. The behavior of *p*-bromoanisole is exceptional in that roughly equal amounts of *m*- and *p*-anisidines are formed despite the fact that k_m/k_p for exchange seems to be substantially greater than unity.

Generally speaking, the orientation resulting from ammonia addition to 3-substituted benzynes appear to be predictable in a straightforward manner. With 4-substituted benzynes the situation is complicated because the inductive effects of the substituents are less strong and the conjugative electrical effects possessed by groups like $-OCH_3$ and $-CF_3$ may become relatively important. An added difficulty is the fact that amide ion almost certainly attacks the "triple" bond in the plane of the six-membered ring and hence the aromatic π-electron system can only be involved in a secondary way. The fundamentally different reaction locus makes uncertain applications of electronic theory such as used for aromatic nitrations which primarily involve attack on the benzenoid π-electron system.

Experimental Part

Amination Reactions.—The procedures were similar to those previously described for iodobenzene-1-^{14}C.[3] The compositions of the product mixtures were determined by infrared analyses. No attempt was made to isolate the di- or triarylamines formed in the reactions.

Amination of *m*-Bromoanisole.—*m*-Bromoanisole (9.27 g., 0.049 mole) and a solution of sodium amide from sodium metal (2.2 g., 0.096 g.-atom) and 300 ml. of liquid ammonia gave, after 15 minutes, 3.6 g. (59%) of pure *m*-anisidine, b.p. 118.5–119.5° (11 mm.).

Amination of *p*-Bromoanisole.—*p*-Bromoanisole (30.0 g., 0.16 mole) and a solution of potassium amide (0.64 mole) in 300 ml. of liquid ammonia gave, after 6 minutes, 6.1 g. (31%) of a 1:1 mixture of *m*- and *p*-anisidines, b.p. 125.0–127.5° (15.4 mm.).

Amination of *o*-Chlorobenzotrifluoride.—From 45.6 g. (0.25 mole) of *o*-chlorobenzotrifluoride and a solution of sodium amide (0.28 mole) in 250 ml. of liquid ammonia was obtained, after 5 hours, 13.0 g. (28% based on the unrecovered aryl halide) of pure *m*-aminobenzotrifluoride, b.p. 85–87° (20 mm.), n^{25}_{D} 1.4773. From the non-acid soluble portion of the reaction mixture was recovered 20.7 g. of *o*-chlorobenzotrifluoride containing no *m*-chlorobenzotrifluoride.

Amination of *m*-Chlorobenzotrifluoride.—From 48.8 g. (0.27 mole) of *m*-chlorobenzotrifluoride and a solution of

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(6) An additional but probably secondary influence would be the gain in resonance energy in the transition state due to conjugation between the orienting substituent and the entering amino group.

(7) The agreement in this case may be fortuitous and actually substantially more *p*-isomer might have been formed than indicated by the infrared product analysis for the following reasons. The yield in the amination was only 25% and a separate experiment showed that *p*-aminobenzotrifluoride is converted to polymeric material by sodium amide in liquid ammonia (see Experimental Part). The work of R. G. Jones, THIS JOURNAL, **69**, 2346 (1947), on the relative stabilities of *m*- and *p*-trifluoromethylphenolate ions provides a rationale for preferential destruction of *p*-aminobenzotrifluoride by amide ions in mixtures with the *m*-isomer. If a substantially greater proportion of the *p*-isomer is formed from the 3-benzyne than indicated by the product analysis, this may well be due to resonance interaction between the $-CF_3$ group and attacking amide ion,[6] *cf.* J. D. Roberts, R. L. Webb and E. A. McElhill, *ibid.*, **72**, 408 (1950).

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

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

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

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

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

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

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

PASADENA 4, CALIFORNIA

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

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

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

RECEIVED MAY 24, 1955

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

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

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

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

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

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

[2] Fellow of the Foundation for Pharmaceutical Education 1952–1954. Now at the University of Washington College of Pharmacy.

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

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

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

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

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

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