mole of haloalkyl ether. The required volume of phenyllithium solution was added from a calibrated dropping funnel, over a period of 1.5 hours, to the haloalkyl ether in solution in 50 ml. of diethyl ether. Mechanical stirring was employed, and addition was at room temperature without cooling. The reactions proceeded smoothly, with mild refluxing. The Michler ketone color test[9] was negative a the end of the addition (except in the case of 1-ethoxy-3-chloropropane), indicating absence of phenyllithium. Occasional color tests made during the course of the addition indicated that reaction was immediate, since such tests were always negative. The reaction mixture was cooled in an ice-bath and hydrolyzed by the addition of aqueous ammonium chloride. After separation, washing with water, and drying on Drierite, the organic layer was distilled. A 42-cm. Fenske column ($^1/_8$-in. glass helices) was used to separate the diethyl ether, benzene, and other low-boiling products. The higher-boiling portion was then distilled under reduced pressure through a 25-cm. Vigreux column.

For certain reactions, data not apparent from Table I are given below.

1-Methoxy-1-chloroethane.—The 1-methoxy-1-phenylethane had b.p. 54–57° (11 mm.), n^{20}D 1.4918; the reported[10] b.p. is 55–57° (11 mm.). For derivatization, a sample of 8 g. of this product was converted to the iodide by 12 hours of refluxing with 80 ml. of 47% hydriodic acid, and the iodide was identified[11] as the S-alkylisothiouronium picrate, m.p. 168–169°.

1-Methoxy-2-bromoethane.—The reaction apparatus was attached to a series of three gas-washing bottles, each containing a solution of bromine in carbon tetrachloride. After the reaction was completed the apparatus was flushed out with nitrogen, while still connected to the absorption train. The contents of the gas-washing bottles were then washed with sodium bisulfite solution and with water, separated, dried on Drierite, and distilled to recover any ethylene dibromide. None was found in this case. However, the distillation of the main reaction mixture yielded 5.0 g. of an impure fraction, b.p. 40–66° (10 mm.), which contained some bromobenzene, as shown by its conversion, through the Grignard reagent, to benzoic acid, m.p. 122°.

The .1-methoxy-2-phenylethane, b.p. 66–70° (10 mm.), n^{21}D 1.5001, reported[12] b.p. 70–74° (12 mm.), had the characteristic sweet odor. A 7-g. sample was converted to 1-iodo-2-phenylethane by boiling for 11 hours with 80 ml. of 47% hydriodic acid, and the iodo compound was derivatized as the S-alkylisothiouronium picrate,[11] m.p. 138–139°.

In other experiments, as shown in Table I, the conditions of this reaction were varied in order to improve the yield. The best result was obtained when 0.22 mole of phenyllithium in about 200 ml. of ethyl ether was added slowly to 0.33 mole (50% excess) of 1-methoxy-2-bromoethane in 90 ml. of ethyl ether, cooled and stirred in an ice-bath.

1-Ethoxy-2-bromoethane.—Bromobenzene and 1-ethoxy-2-phenylethane, b.p. 78–79° (10 mm.), n^{20}D 1.4976, reported[13] b.p. 198–199° and n^{32}D 1.4870, were identified as indicated above. The presence of ethylene was not investigated.

1-Methoxy-2-iodoethane.—The procedure described above was used for the detection of ethylene. The ethylene dibromide, b.p. 130–134°, obtained by distillation of the product from the gas-washing bottles, was characterized as the S-alkylisothiouronium picrate,[11] identified by m.p. (259–260°) and mixed m.p. with an authentic specimen.

1-Ethoxy-1,2-dichloroethane.—In this reaction two moles of phenyllithium was used per mole of haloalkyl ether. The 1-ethoxy-1-phenylethene, b.p. 93–98° (18 mm.), n^{20}D 1.5299, reported[5] b.p. 109–112° (30 mm.) and $n^{25.5}$D 1.5287, was hydrolyzed by heating with alcoholic hydrochloric acid.[5] The resulting acetophenone was converted to the semicarbazone, which was identified by m.p. (198–199°) and mixed m.p. with an authentic specimen.

1-Ethoxy-3-chloropropane.—When this reaction was carried out under the above conditions, reaction was much slower than in the case of the α- or β-haloalkyl ethers. The color test[9] was strongly positive at the end of the addition, and the final products included benzene in 34% yield. This is not shown in Table I, since it could have come mostly from unreacted phenyllithium. The 1-ethoxy-3-phenylpropane was converted to the iodide as above, and the latter was identified by converting it to the Grignard reagent and then carbonating with solid carbon dioxide, to give 3-phenylbutyric acid, m.p. 47–48°.

The reaction was repeated as above, except that after addition was complete the mixture was refluxed until a negative color test was obtained (3.5 hours). This treatment increased the yield of the coupling product, 1-ethoxy-3-phenylpropane, b.p. 90–95° (10 mm.), n^{23}D 1.4938, reported[14] b.p. 85–90° (20 mm.).

GRAND FORKS, NORTH DAKOTA

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[9] H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2002 (1925).

[10] W. Reppe, O. Schichting, K. Klager and T. Toepel, *Ann.*, **560**, 1 (1948).

[11] W. J. Levy and N. Campbell, *J. Chem. Soc.*, 1442 (1939).

[12] S. S. Deshapande, *J. Indian Chem. Soc.*, **15**, 509 (1938) [*C. A.*, **33**, 2281 (1939)].

[13] J. Wertheim, THIS JOURNAL, **59**, 2472 (1937).

[14] J. M. Nelson and A. M. Collins, *ibid.*, **46**, 2256 (1924).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT DAVIS]

Polymethylbenzene Complexes of Iodine and Iodine Monochloride

BY L. J. ANDREWS AND R. M. KEEFER

RECEIVED MARCH 3, 1952

Previous studies of halogen-aromatic interactions have been extended using modified procedures to include several of the polymethylbenzenes. The relative magnitudes of the equilibrium constants for the formation of 1:1 complexes with iodine or iodine monochloride of the various methylated benzenes have been found to parallel in general the tendency of the aromatic substances to undergo interaction with hydrogen fluoride–boron trifluoride solutions. Equilibrium constants for the interaction of iodine monochloride with ethyl-, isopropyl- and *t*-butylbenzene were also measured and were found to be, within close limits, the same as that for toluene. Theoretical aspects of these findings have been considered.

The generalization that increasing methyl substitution enhances the basic character of the aromatic nucleus is best illustrated by the work of McCaulay and Lien.[1] These investigators have observed that, with certain exceptions, the tendency for methylbenzenes to form complexes of the type $ArH^+BF_4^-$ in hydrogen fluoride–boron trifluoride solutions increases as the number of ring methyl substituents increases from one to six. A similar order of stability has been shown to apply to the benzene, toluene and xylene complexes of silver ion,[2] bromine,[3] iodine monochloride[4] and sulfur dioxide.[5] The mesitylene–iodine complex is more stable than that of benzene and iodine.[6] However, with silver ion mesitylene[7] yields a complex which is less stable than that formed by benz-

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[1] D. A. McCaulay and A. P. Lien, THIS JOURNAL, **73**, 2013 (1951).

[2] (a) L. J. Andrews and R. M. Keefer, *ibid.*, **71**, 3644 (1949); (b) R. M. Keefer and L. J. Andrews, *ibid.*, **74**, 640 (1952).

[3] R. M. Keefer and L. J. Andrews, *ibid.*, **72**, 4677 (1950).

[4] R. M. Keefer and L. J. Andrews, *ibid.*, **72**, 5170 (1950).

[5] L. J. Andrews and R. M. Keefer, *ibid.*, **73**, 4169 (1951).

[6] H. A. Benesi and J. H. Hildebrand, *ibid.*, **71**, 2703 (1949).

[7] L. J. Andrews and R. M. Keefer, *ibid.*, **72**, 5034 (1950).

ene. The failure of the mesitylene–silver ion complex to exhibit normal stability has been explained in terms of a steric effect (opposing complex formation) of the several methyl groups of the mesitylene molecule.

In view of the low stability of the mesitylene–silver ion complex it has seemed desirable to determine whether the stabilities of the halogen complexes of highly methylated benzenes are also abnormally low. The equilibrium constants for formation of 1:1 complexes with iodine and iodine monochloride of mesitylene, durene, pentamethyl-, hexamethyl- and hexaethylbenzenes have now been determined by a modification of the spectrophotometric procedure used previously. The equilibrium constants for complex formation of benzene, toluene and the xylenes with the halogens have been redetermined by these improved procedures, and the interaction of iodine monchloride with ethyl-, isopropyl- and *t*-butylbenzenes has also been investigated. Equilibrium constants for halogen interaction of several other aromatic compounds have also been determined.

Experimental

Materials.—Samples of Eastman Kodak Co. white label grade durene and of pentamethyl-, hexamethyl- and hexaethylbenzenes were used without purification. The mesitylene, a sample which had been purified by the procedure of Smith and Cass,[8] was furnished by Mr. John H. Blake. All other materials were purified as described in connection with the silver ion complex studies.

The Absorption Spectrum Measurements.—As in earlier work[3,4,6] a series of carbon tetrachloride solutions of varying concentrations of the halogen and the aromatic substance were prepared at 25°. The optical densities of these solutions at the complex absorption maximum (usually in the neighborhood of 300 mμ) were determined using as a blank a halogen free solution of the aromatic compound, of the same concentration as that of the solution under measurement. In the present procedure,[9] which was designed to permit the investigation of aromatic compounds which are solids at room temperature, the concentration of the aromatic material in the complex solutions generally did not exceed values much greater than 1 *M*. The concentration of halogen in solution was so adjusted that the optical density at the complex absorption maximum ranged between 0.300 and 1.00 when 1-cm. absorption cells were used. The cell housing of the Beckman spectrophotometer used in these measurements was maintained at 25°. Insofar as possible measurements were made at slit width settings of 0.6. All optical densities were corrected for the slight absorption of the uncomplexed halogen.

In making optical measurements on solutions of iodine monochloride and certain of the aromatic substances (noticeably with the polymethylbenzenes), it was observed that the optical densities at the complex absorption maximum diminished with time. Whenever this phenomenon was encountered, a series of optical density measurements as a function of time over a short time interval were made immediately after preparation of the solutions. These data were used to estimate by extrapolation the optical density of the freshly prepared solution.

The cause of the observed changes in optical density with time is now under investigation. Preliminary work indicates that iodine is formed as a product of the reaction which occurs.

Results

In this investigation, as in previous investigations, the spectrophotometric data obtained using carbon tetrachloride solutions containing both halogen and aromatic substance have been utilized to calculate equilibrium constants for the formation of 1–1 complexes by means of equation 1.

$$\frac{(\mathrm{X_2})_t l}{d_c} = \frac{1}{K_c \epsilon_c} \times \frac{1}{(\mathrm{A})_t} + \frac{1}{\epsilon_c} \text{ where } (\mathrm{A})_t \gg (\mathrm{X_2})_t \quad (1)$$

The terms $(\mathrm{X_2})_t$ and $(\mathrm{A})_t$ represent the total molar concentrations, respectively, of halogen and aromatic compound. Values of K_c have been calculated in terms of molar concentrations $\{i.e., K_c = (\mathrm{A{\cdot}X_2})/(\mathrm{A})(\mathrm{X_2})\}$ for all reacting species rather than by the method of earlier investigations in which the concentration of the aromatic substance was expressed in terms of its mole fraction. This procedure was adopted to facilitate calculations based on measurements on the dilute solutions employed in dealing with aromatic compounds which are solids at room temperature.[9] The use of dilute solutions of the aromatic substances eliminates the shift in the wave length of maximum absorption of the halogen complexes noted in studies on more concentrated solutions. Values of d_c were obtained by correcting the measured optical densities for the absorption of free halogen in the solutions. These corrections were calculated by procedures described previously.[10] For each series of measurements plots of $(\mathrm{X_2})_t/d_c$ against $1/(\mathrm{A})_t$ (based on at least 5 points) gave straight lines, and the values of $1/\epsilon_c$ and $1/K_c\epsilon_c$ obtained from the intercepts and slopes of the plots were utilized to calculate the values of ϵ_c and K_c appearing in Table I. (ϵ_c represents the molar extinction coefficient of the complex at its absorption maximum.) The equilibrium constants reported here are, insofar as there is duplication, in fair agreement with those obtained in previous work using more concentrated solutions of the aromatic substances. In general the wave lengths of maximum absorption of the complexes in dilute solutions of the aromatic compounds (*i.e.*, about 1 *M*) are shifted 4 to 5 mμ toward the ultraviolet from those found for the concentrated solutions ($N_A = 1$). However the values of ϵ_c reported here agree (within the limits of error) with the values obtained in working with concentrated solutions.

The methylbenzene complexes with both iodine and iodine monochloride fall in the same order of stability as has been reported by McCaulay and Lien[1] for the interaction of these hydrocarbons with $\mathrm{HF{-}BF_3}$. This order of stability is as follows: toluene < xylene < durene < mesitylene < pentamethylbenzene < hexamethylbenzene. Contary to the findings of McCaulay and Lien the results of this investigation indicate that of the xylene–iodine monochloride complexes that formed by the para isomer is the most rather than the least stable. However the observed stability differences for the halogen complexes of the three xylenes are small.

Although an ethyl substituent appears to enhance the basicity of the benzene ring to the same degree as does a methyl substituent (*cf.* K_c values for the benzene, toluene and ethylbenzene complexes with iodine monochloride), hexaethylbenzene is an extremely poor base as compared to hexamethylbenzene. The hexaethylbenzene–iodine complex has a lower K_c value than that of benzene,

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(8) L. I. Smith and O. W. Cass, THIS JOURNAL, **54**, 1606 (1932).

(9) This method is similar to that employed by N. W. Blake, H. Winston and J. A. Patterson, *ibid.*, **73**, 4337 (1951).

(10) R. M. Keefer and L. J. Andrews, *ibid.*, **74**, 458 (1952).

TABLE I

EQUILIBRIUM CONSTANTS FOR I_2 AND ICl COMPLEXES OF AROMATIC SUBSTANCES IN CARBON TETRACHLORIDE AT 25°

Aromatic	λ_{max}, mμ	$\epsilon_{max} \times 10^{-3}$	K_c
Iodine Complexes			
Benzene	292	16.4	0.15
Toluene	302	16.7	.16
o-Xylene	316	12.5	.27
m-Xylene	318	12.5	.31
p-Xylene	304	10.1	.31
Mesitylene	332	8.85	.82
Durene	332	9.00	.63
Pentamethylbenzene	357	9.26	.88
Hexamethylbenzene	375	8.20	1.35
Hexaethylbenzene	378	16.7	0.13
Bromobenzene	290	10.4	.13
Phenanthrene	396	13.0	.15
Naphthalene	360	7.64	.25[a]
Styrene	330	7.35	.31
Stilbene	373	7.14	.31
Bibenzyl	304	11.2	.46
Iodine monochloride complexes			
Benzene	282	8.13	0.54
Toluene	288	8.00	.87
Ethylbenzene	290	8.26	.88
Isopropylbenzene	290	8.06	.88
t-Butylbenzene	290	7.94	.88
o-Xylene	298	7.87	1.24
m-Xylene	298	9.18	1.39
p-Xylene	292	6.54	1.51
Mesitylene	307	7.87	4.59
Durene	306	7.25	4.25
Pentamethylbenzene	322	7.81	6.43
Hexamethylbenzene	334	4.0	22.7
Hexaethylbenzene	340	6.60	1.24
Bromobenzene	286	5.91	0.32
Naphthalene	341	3.88	1.39
Bibenzyl	292	8.20	1.48

[a] N. W. Blake, H. Winston and J. A. Patterson, THIS JOURNAL, **73**, 4437 (1951), report for the naphthalene–iodine complex in carbon tetrachloride the values λ_{max} 360 mμ, ϵ_{max} 7250, K_c 0.257.

and with iodine monochloride the equilibrium constant for the interaction with the hexaethyl derivative is about the same as those for the xylenes. The low stability of the hexaethylbenzene complexes can be explained in terms of unfavorable steric effects resulting from the high concentration of ethyl substituents on the aromatic nucleus. A consideration of molecular models shows that, regardless of the structural configuration of the addition complexes,[11] six ethyl substituents on the benzene ring offer much more inhibition to the approach of reacting halogen to within the sphere of interaction of the aromatic π-electrons than do six methyl substituents.

Since in the silver ion studies the experimental evidence indicated that even with mesitylene a methyl group steric effect opposing aromatic–silver ion coördination existed, it seemed of interest to determine equilibrium constants for the interaction of polymethylbenzenes with silver ion to ensure that the mesitylene reaction did not represent an anomalous case. It was found, however, that with the exception of durene the available polymethylbenzenes were insufficiently water soluble for argentation studies. Argentation constants for durene were determined by measuring the solubility of the aromatic compound in aqueous silver nitrate solutions adjusted to an ionic strength of unity. The method of measurement and of calculations to determine the equilibrium constants were the same as those used previously. The argentation constants for benzene, mesitylene and durene at 25° for the reactions

$$Ag^+ + Ar = AgAr^+ \qquad K_1 = (AgAr^+)/(Ag^+)(Ar) \quad (2)$$

$$Ag^+ + AgAr^+ = Ag_2Ar^{++}$$
$$K_2 = (Ag_2Ar^{++})/(Ag^+)(AgAr^+) \quad (3)$$

are as follows: benzene, $K_1 = 2.41$, $K_2 = 0.21$; mesitylene, $K_1 = 1.8$ (no K_2)[12]; and durene, $K_1 = 2.05$, $K_2 = 0.34$. Although durene gives a slightly greater argentation constant than does benzene, its reactivity is considerably lower than would be anticipated in terms of the electronic effects of the methyl groups. The fact that these methyl group steric effects were not observed in the halogen interaction studies lends credibility to the suggestion made earlier that the steric effects observed in argentation studies may result from interference between ring methyl groups and water molecules in the hydration sphere of silver ion.

Ethyl-, isopropyl- and *t*-butylbenzene within close limits give the same K_c values for interaction with iodine monochloride as does toluene. If these complexes were subject to appreciable stabilization because of enhanced ring electron density resulting from hyperconjugation involving α-hydrogen atoms of the alkyl substituents, the K_c values for these benzene derivatives should decrease with change in alkyl substituents in the order $CH_3- > CH_3CH_2- > (CH_3)_2CH- > (CH_3)_3C-$. On the basis of the inductive effects of these groups one would predict the opposite order of reactivity. It is possible that the almost identical reactivities of the alkylbenzylenes as noted in the present study may result fortuitously through combination of these opposing electronic effects. Lichtin and Bartlett have offered interesting comments on the problems inherent in theorizing on the basis of a series of measurements which reflect the resultant of both effects.[13]

The remaining compounds for which equilibrium constants were reported in Table I were investigated primarily to determine whether the stabilities of their halogen complexes parallel those observed for their silver ion complexes. The halogen complexes of bromobenzene, naphthalene, stilbene and bibenzyl have the same order of stability as do the silver complexes of these compounds. One marked deviation in behavior was noted in the case of the styrene–iodine complex. In this case a K_c value approximating that for the xylene complexes was obtained. The argentation constants for styrene, however, were sufficiently large as to suggest that

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(11) See for various viewpoints references 2-6 and also R. S. Mulliken, THIS JOURNAL, **72**, 600 (1950); **74**, 811 (1952).

(12) The K_1 value for mesitylene was checked with carefully purified material and found to agree very well with that reported previously.

(13) N. N. Lichtin and P. D. Bartlett, THIS JOURNAL, **73**, 5530 (1951).

the silver ion in this complex was coördinated mainly at the vinyl side chain rather than with the ring.

Although phenanthrene forms a more stable silver ion complex than does benzene, the K_c values for the iodine complexes of these aromatics are the same. It is possible that the phenanthrene-iodine results are somewhat in error as spectrophotometer readings, in this case, were made at high slit width settings, a procedure which is undesirable where high precision is required.

DAVIS, CALIFORNIA

[CONTRIBUTION FROM THE ISTITUTO DI CHIMICA FISICA DELL' UNIVERSITA DI FIRENZE]

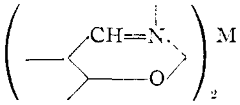
Chemical Reactions of Complexes. I. Action of Hydrazides on Nickel Disalicylaldehyde

BY LUIGI SACCONI

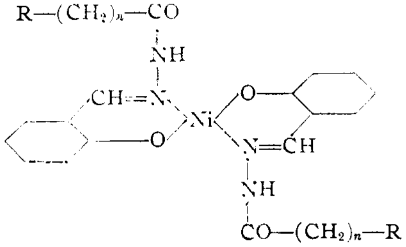
RECEIVED MARCH 31, 1952

The reaction of hydrazides of the type $H_2N-NH-CO-R$ with nickel disalicylaldehyde (or with nickel acetate and salicylaldehyde) is dependent on the nature of the R group. If R = alkyl or arylalkyl, symmetrical paramagnetic ionic compounds are formed. If R = Ph or substituted Ph, bicyclic planar complexes are formed.

Starting with the first syntheses of Pfeiffer and co-workers,[1] many complexes of metal *o*-oxyazomethines have been described.

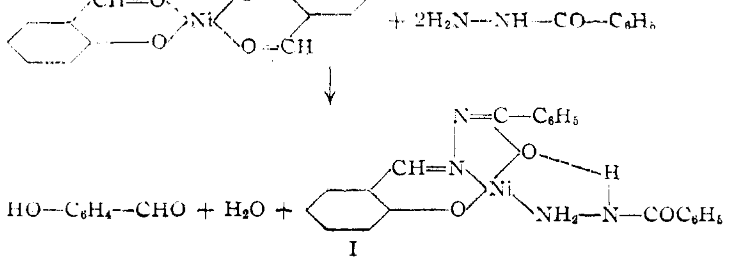


On treating nickel disalicylaldehyde with hydrazides of the type $H_2N-NH-CO-(CH_2)_n-R$, where R represents methyl or phenyl groups, nickel bis-salicylidenehydrazides of the following structure are formed



These complexes, green in color, are paramagnetic with a moment of about 3.3 Bohr magnetons. They therefore have four ionic sp^3 bonds and a tetrahedral configuration.

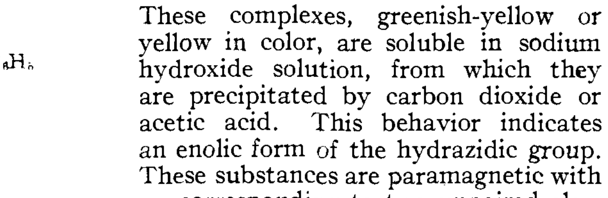
If R = phenyl and n = 0, two series of compounds are obtained. Initially formed are bicyclic complexes containing a tridentate group produced by a molecule of salicylidenebenzoylhydrazine reacting in enolic form, as represented by the reactions shown.



I

These complexes, orange to red in color, are insoluble and stable in concentrated aqueous alkalies. They are diamagnetic and therefore have a planar arrangement of dsp^2 covalent bonds. The H---O bond in formula I accounts for the stability of the four planar bonds as well as the stability toward alkalies. The formation of bicyclic complexes when R = phenyl and n = 0 is undoubtedly due to the greater enolizing influence of the C_6H_5-CO- group, compared with that of the alkyl -CO- and the phenylalkyl -CO- groups.[2]

The bicyclic complexes are slowly transformed into symmetrical complexes by reaction with salicylaldehyde, either liberated from nickel disalicylaldehyde or added as such. This type of reaction can be represented by



II

These complexes, greenish-yellow or yellow in color, are soluble in sodium hydroxide solution, from which they are precipitated by carbon dioxide or acetic acid. This behavior indicates an enolic form of the hydrazidic group. These substances are paramagnetic with μ_{eff} corresponding to two unpaired electrons, indicating a probable tetrahedral structure.

o-Aminobenzoylhydrazine is an exception, however, since the following asymmetrical paramagnetic complex is first formed

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[1] P. Pfeiffer and co-workers, *J. prakt. Chem.*, **129**, 163 (1931); **145**, 243 (1936); **150**, 261 (1938); *Ann.*, **503**, 84 (1933); *Angew. Chem.*, **62**, 201 (1950); L. Hunter and J. A. Marriott, *J. Chem. Soc.*, 2000 (1937).

[2] R. A. Morton, A. Hassan and T. C. Calloway, *ibid.*, **883** (1934).