

identified as idaein chloride, a pigment which Willstätter and Mallison⁵ isolated from the cranberry. The glucoside was isolated as the lead salt. By the use of differential solvents it was partially purified and was then converted to the

picrate. The pigment was eventually obtained in pure form as the chloride salt. The anthocyanin chloride on hydrolysis yields molecular proportions of cyanidin chloride and galactose.

MORGANTOWN, W. VA.

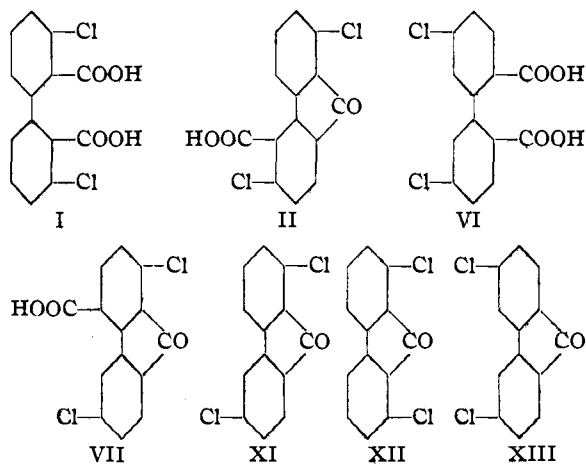
RECEIVED MARCH 16, 1936

[CONTRIBUTION NO. 139 FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Constitution of the Isomeric Dichlorofluorenone Carboxylic Acids Formed by the Action of Sulfuric Acid on 3,3'-Dichlorodiphenic Acid

BY ERNEST H. HUNTRESS AND EDWARD R. ATKINSON

Earlier work in this Laboratory¹ has shown that when 3,3'-dichlorodiphenic acid (I) is heated with concentrated sulfuric acid at 170° there is formed a ketocarboxylic acid isomeric with, but different from, the 1,6-dichlorofluorenone-5-carboxylic acid (II) quantitatively obtained at 125°. This isomeric acid (designated in the cited reference as "Acid X") has now been identified as 1,6-dichlorofluorenone-4-carboxylic acid (VII) and is identical



with the product obtained by the action of sulfuric acid upon 5,5'-dichlorodiphenic acid (VI). Experiments undertaken to elucidate such an unexpected result have now led to the further discovery that 1,6-dichlorofluorenone (XI) and 1,8-dichlorofluorenone (XII) are converted to 3,6-dichlorofluorenone (XIII) on heating in concentrated sulfuric acid. The rearrangement of fluorenones with other substituents is being examined further.

In carrying out the preparation of the isomeric ketocarboxylic acids from 3,3'-dichlorodiphenic

acid (I), it is now evident that our previous isolation of 1,6-dichlorofluorenone-5-carboxylic acid (II) after heating the 3,3'-dichlorodiphenic acid in sulfuric acid at 125° for one hour was fortuitous, since if the treatment be continued longer (*e. g.*, for five hours) the product is 1,6-dichlorofluorenone-4-carboxylic acid (VII) ("Acid X"). A brief study of the temperature at which this isomerization occurs is given in the Experimental Part.

This change does not occur when phosphoric acid is used instead of sulfuric acid. With phosphoric acid at 215°, 3,3'-dichlorodiphenic acid yields only 1,6-dichlorofluorenone-5-carboxylic acid (II); 5,5'-dichlorodiphenic acid (VI) similarly treated gives only 1,6-dichlorofluorenone-4-carboxylic acid (VII). Thus, although phosphoric acid does not effect rearrangement, it does cause ring closure.

The Evidence for the Structure of 1,6-Dichlorofluorenone-5-carboxylic Acid (II)

The original data on this acid² have been confirmed and extended. The acid gives correct analysis for halogen and the expected neutralization equivalent. On treatment with thionyl chloride it yields the corresponding acid chloride (m. p. 180–181°, uncorr.) and this with ammonium hydroxide gives an amide (m. p. 281°, uncorr.). The latter yields¹ (p. 4268) an amine (m. p. 257°, uncorr.). These three derivatives are all distinctly different from the corresponding products of the "Acid X" series, and the depression of corresponding mixed melting points has been confirmed. Furthermore, this keto acid on heating gave 1,6-dichlorofluorenone (XI). In addition to the above results, we have also been able to effect the deamination of the aminodichlorofluo-

(1) Huntress, Cliff and Atkinson, *THIS JOURNAL*, **55**, 4262–4271 (1933).

(2) Huntress and Cliff, *ibid.*, **55**, 2559–2567 (1933).

renone obtained above from the keto acid chloride and have likewise obtained 1,6-dichlorofluorenone (XI). Finally the keto acid has been oximated and the resultant derivative hydrolyzed back to the original compound.

Characterization of "Acid X" as 1,6-Dichlorofluorenone-4-carboxylic Acid (VII)

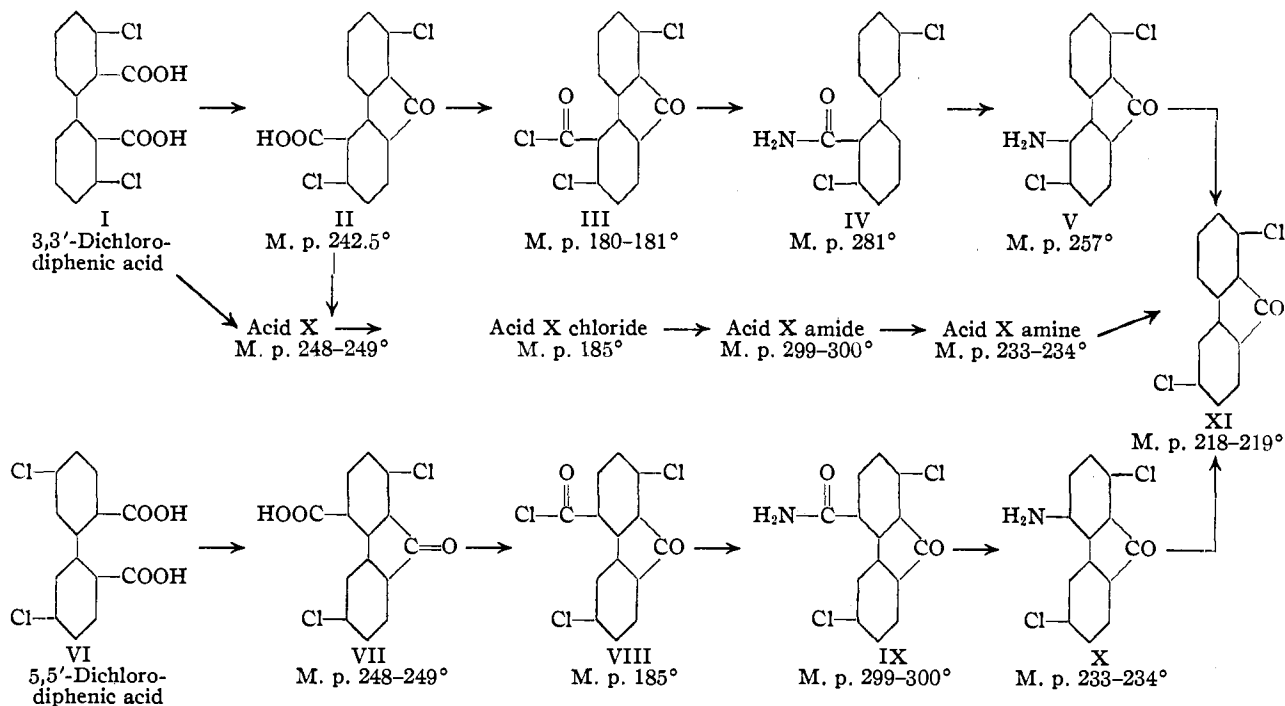
Improved Physical Constants of "Acid X" and its Derivatives.—As a result of much further experience in the preparation and purification of "Acid X" and its derivatives, products with higher melting points than those reported in the earlier paper¹ have been obtained. These are indicated in Chart I. The melting points of the acid, acid chloride, acid amide, amine, and corresponding deaminated ketone of the "Acid X" series, were found to be identical with those for the corresponding compounds of the 5,5'-dichlorodiphenic acid series. Furthermore, the melting points of mixtures of corresponding derivatives were *not depressed*. The structure of "Acid X," therefore, is that of 1,6-dichlorofluorenone-4-carboxylic acid and the relations of the various series of derivatives are portrayed in Chart I.

Our previous difficulty in obtaining satisfactory neutralization equivalents for "Acid X" was at first again experienced in the present work and, as might be expected, since the two are identical, a similar difficulty in obtaining satisfactory values for 1,6-dichlorofluorenone-4-carboxylic acid (VII) (in contrast to the satisfactory value for the latter obtained in our last paper where impure material was used).

Many determinations of the neutralization equivalent of this acid (either as "Acid X" or as 1,6-dichlorofluorenone-4-carboxylic acid) and also halogen analyses on various samples showed that it formed compounds with the solvents used for crystallization. The melting points of all samples, regardless of solvent present, was 248–249°. The samples were desolvated by methods described in the Experimental Part and then gave the theoretical values for the neutralization equivalent.

The Direct Decarboxylation of "Acid X."—Earlier attempts to decarboxylate "Acid X" by dry heating under reduced pressure had been unsuccessful, due to its sublimation in unchanged condition; 1,6-dichlorofluorenone-5-carboxylic acid, on the other hand, had readily lost carbon dioxide and given 1,6-dichlorofluorenone. Dur-

CHART I.—RELATIONSHIPS OF 3,3'- AND 5,5'-DICHLORODIPHENIC ACIDS AND THEIR DERIVATIVES



The substances of the "Acid X" series are identical with the substances derived from VI and represented by VII to X, respectively.

ing this present work it was noticed that certain non-acidic substances were present in the crude product from the treatment of 3,3'-dichlorodiphenic acid (I) and 5,5'-dichlorodiphenic acid (VI) with sulfuric acid at the higher temperatures. This suggested that concentrated sulfuric acid might serve as an aid in the decarboxylation of "Acid X." Such proved to be the case and experiment showed that on heating in sulfuric acid at about 200° there was obtained 3,6-dichlorofluorenone (XIII) accompanied by small quantities of unidentified material. Identification of the 3,6-dichlorofluorenone was facilitated by the fact that it is the highest melting of the three dichlorofluorenones involved in this work. That the sulfuric acid was not merely serving as a medium for heat transfer is indicated by our observation that upon its replacement by phosphoric acid neither decarboxylation nor rearrangement occurred.

The Rearrangement of the Dichlorofluorenones

In the course of the work on the decarboxylation of "Acid X" (1,6-dichlorofluorenone-4-carboxylic acid) by heating in sulfuric acid, it was discovered that under the conditions employed 3,6-dichlorofluorenone (XIII) was obtained. Since the other evidence for the 1,6-position of the chlorine atoms in the acid seemed entirely reliable, the observation suggested that 1,6-dichlorofluorenone itself (and perhaps also other dichlorofluorenones) might suffer rearrangement on heating with sulfuric acid. It was then found that although 3,6-dichlorofluorenone is stable in concentrated sulfuric acid at 185–200° for forty-five minutes, both 1,6- and 1,8-dichlorofluorenone undergo rearrangement to 3,6-dichlorofluorenone. This was identified by the failure of it and of the corresponding oxime to depress the melting point of authentic samples.

Additional Proof for the Structure of the Dichlorofluorenones.—The previous evidence for the structure of the dichlorofluorenones was as follows.

1,6-Dichlorofluorenone.—Obtained by direct heat decarboxylation of 1,6-dichlorofluorenone-5-carboxylic acid. The oxime of this fluorenone described in an earlier paper² (p. 2565) (m. p. 230°) appears to be that individual of two possible stereoisomers which is formed in preponderant amount. On hydrolysis with dilute sulfuric acid it yielded 1,6-dichlorofluorenone.

1,8-Dichlorofluorenone.—The previous work showed that this product was obtained by the ac-

tion of heat on 3,3'-dichlorodiphenic acid anhydride and that it formed an oxime with great difficulty. Its structure has now been further supported by its preparation from distillation of calcium 3,3'-dichlorodiphenate.

3,6-Dichlorofluorenone.—The structure of this product was assigned because of its previous formation by heating the anhydride of 5,5'-dichlorodiphenic acid. It has now been prepared by distillation of the calcium salt of that acid.

Experimental Part

All melting points reported in this paper were taken by the method described in Mulliken's "Identification of Pure Organic Compounds," Vol. I, page 218, on a 360° rod form melting point thermometer immersed in the sulfuric acid to the 0° point. All melting points are uncorrected.

Temperatures at which 1,6-Dichlorofluorenone-5-carboxylic Acid (II) Isomerizes to 1,6-Dichlorofluorenone-4-carboxylic Acid ("Acid X") (VII).—As indicated in the following table, the isomerization has been found to occur at a temperature considerably lower than that previously described. Since "Acid X" was much less soluble in solvents than its isomer, its detection in mixtures of the two compounds (even when present in small proportion) was readily effected. Such was not the case, however, with the isomeric acid.

The crude products were purified by the method previously described for the individual acids. Only those experiments are here cited in which the product consisted mainly of one isomer. In general 3 cc. of C. P. concd. sulfuric acid was used for every gram of original material. The identity of the purified substances was established by mixed melting points with authentic samples.

TABLE I

Original substance	Temp. of H ₂ SO ₄ , °C.	Time of heating, hr.	Product
3,3'-Dichlorodiphenic acid	150–160	1	"Acid X"
	135–145	4	"Acid X"
	125	1	1,6-dichlorofluorenone-5-carboxylic acid
	125	5	"Acid X"
	95–104	1	1,6-dichlorofluorenone-5-carboxylic acid
	80–90	24	1,6-dichlorofluorenone-5-carboxylic acid
"Acid X"	95–99	10	"Acid X"

Phosphoric Acid as a Condensing Agent.—Sirupy phosphoric acid (85%) was heated at 160° for one hour until evolution of water ceased. One-tenth gram of 3,3'-dichlorodiphenic acid was heated in 2 cc. of this phosphoric acid at 200° but no solution occurred. At 215°, however, a brown solution formed after two hours and from this, by the purification used in the sulfuric acid condensations, there was obtained pure 1,6-dichlorofluorenone-5-carboxylic acid, with no detectable amounts of "Acid X." A similar experiment with 5,5'-dichlorodiphenic acid gave 1,6-dichlorofluorenone-4-carboxylic acid ("Acid X").

Oximation of 1,6-Dichlorofluorenone-5-carboxylic Acid (II).—Three-tenths of a gram of the acid in 15 cc. of alcohol was refluxed for forty-five minutes with 0.43 g. of hy-

droxylamine hydrochloride in 5 cc. of water. The oxime separated after further dilution. In some runs sodium bicarbonate solution was used and the oxime precipitated by acidification. The melting point of the resulting oxime varied irregularly on recrystallization from various solvents, but the product from dilute acetone generally melted at 263°, dec. No attempt was made to separate the possible stereoisomeric forms. The oxime was not hydrolyzed by boiling 6 *N* sodium hydroxide, nor by concentrated sulfuric acid, but when refluxed for two hours with 50% sulfuric acid, the original keto acid was regenerated.

1,6-Dichlorofluorenone (XI) from 1,6-Dichloro-5-amino-fluorenone (V).—In a typical run, 0.1 g. of amine was suspended in a mixture of 10 cc. of alcohol with 0.8 cc. of concentrated sulfuric acid. To the suspension at 0° a concentrated aqueous solution of sodium nitrite was added slowly until excess was present, motor stirring being used. After a heavy precipitate of diazonium salt formed 20 cc. of alcohol was added and the mixture stirred ten minutes at 0°. One-half gram of copper bronze was added and the mixture warmed until evolution of acetaldehyde ceased. After standing for twelve hours the pale yellow product was filtered off and sublimed at 150–190° under 18 mm. pressure. The product weighed 0.05 g. and melted at 217–218°. It did not depress the melting point of an authentic sample of 1,6-dichlorofluorenone. It was converted to the oxime by the procedure previously described² (p. 2565); the product so obtained melted at 230° dec. and did not depress the melting point of an authentic sample of the oxime.

The Neutralization Equivalent of 1,6-Dichlorofluorenone-4-carboxylic Acid ("Acid X") (VII).—The titrations were carried out in neutral alcohol using 0.1 *N* sodium hydroxide with phenolphthalein as indicator. If a pure sample (m. p. 248–249°) was crystallized from glacial acetic acid and then titrated, values from 177.8 to 261.2 were obtained (calcd. 293). Either the material recovered from these determinations or fresh material again recrystallized from dilute alcohol, gave neutralization equivalents varying from 296.8 to 301.4. Similar results were obtained on products from aqueous dioxane.

Halogen analyses on the products from acetic acid or from dilute alcohol were always low: *e. g.*, from acetic acid, Cl found, 21.67, 22.41; from dilute alcohol: Cl found, 23.32, 22.75; calculated for C₁₄H₁₀Cl₂O₂: Cl, 24.23%. This suggested possibility of solvation.

The product from acetic acid was desolvated by drying in a vacuum oven for five hours at 110°, during which time the needle-like crystals effloresced completely. In some cases samples were desolvated by solution in anhydrous benzene, boiling with decolorizing carbon, and adding ligroin, the precipitated solid being dried at 110°. In one instance no ligroin was added and on cooling, brilliant yellow needles formed which apparently consisted of an addition compound with benzene since they effloresced rapidly at 110°.

All desolvated samples showed the same melting point as the solvates from which they were derived (248–249° in every case). Titration of the desolvated samples gave neutralization equivalents of 294.3, 291.6, 293.3, 291.6, calculated 293.

Direct Decarboxylation of 1,6-Dichlorofluorenone-4-carboxylic Acid ("Acid X") (VII).—In a typical experiment, 0.1 g. of the acid was heated in 1 cc. of c. p. concd. sulfuric acid at 200–215° for one hour. Gas evolution was noticed. The solution was poured on ice and the dark brown solid shaken with dilute sodium bicarbonate solution to remove acidic substances. The undissolved residue was then filtered off, dried and sublimed. At one atmosphere and 140–165° a light sublimate melting at 205–230° first formed which represented about 10% of the total product. The pressure was then reduced to 10 mm. and at 160–180° a bright yellow sublimate, melting at 299–300°, formed. There was also a non-sublimable sulfur-containing residue of high melting point. In other experiments the crude product was recrystallized from dilute acetone before sublimation. The low melting sublimate, obtained in all runs, was not identified.

The sublimate melting at 299–300° was shown to be 3,6-dichlorofluorenone. It did not depress the melting point of an authentic sample and it gave an oxime of m. p. 246–247° which also did not depress the melting point of authentic 3,6-dichlorofluorenone oxime. This portion usually represented about 90% of total sublimate.

The same results were obtained when 3,3'-dichlorodiphenic acid, 5,5'-dichlorodiphenic acid and 1,6-dichlorofluorenone-5-carboxylic acid, all of which are known to yield "Acid X" at the temperatures used, were heated in sulfuric acid at about 200°. The non-acidic material obtained during preparative runs on "Acid X" at 170° also consisted chiefly of 3,6-dichlorofluorenone.

The Rearrangement of the Dichlorofluorenes.—Fifty milligrams of pure 3,6-dichlorofluorenone (m. p. 300°) was heated in 1 cc. of c. p. concentrated sulfuric acid at 185–200° for forty-five minutes. The color of this solution was deep violet. After pouring on ice, the resulting solid was dried and sublimed. At 140–165° and 1 atm. a small amount of light yellow sublimate formed, but at 180° and 10 mm. pure 3,6-dichlorofluorenone was recovered. There was also a small sulfur-containing residue which did not sublime under these conditions.

Approximately 500 mg. of pure 1,8-dichlorofluorenone (m. p. 254°) was heated in 5 cc. of c. p. concd. sulfuric acid for forty-five minutes at 180–190°. The deep brown solution slowly changed to the violet color characteristic of 3,6-dichlorofluorenone. The product was separated in the usual way. At 140–160° and 1 atm., 20 mg. of a sublimate, m. p. 200–225°, was removed and at 180° and 10 mm. 70 mg. of pure 3,6-dichlorofluorenone sublimed. There was also a residue which did not sublime. The product of 3,6-dichlorofluorenone was converted into the oxime (m. p. 246–247°, dec.) and this oxime did not depress the melting point of an authentic sample.

Fifty milligrams of pure 1,6-dichlorofluorenone (m. p. 218°) was heated at 150° in 2 cc. of c. p. concd. sulfuric acid for thirty minutes. The color change from brown to violet was again noted. On subliming the product there was obtained at 150° and 1 atm. a small amount of sublimate, m. p. 195–215°, and at 180° and 10 mm., pure 3,6-dichlorofluorenone. This experiment was repeated using 70 mg. of 1,6-dichlorofluorenone and heating at 125° for forty minutes. The sublimate was separated into two fractions as before, which, however, were *equal* in amount.

the one having m. p. 199–230°, the other m. p. 299–300° (3,6-dichlorofluorenone). There was no residue from these sublimates. This experiment indicates that while the rearrangement occurred at 125° it was not complete in forty minutes. As before the product of 3,6-dichlorofluorenone gave an oxime identical with authentic 3,6-dichlorofluorenone oxime.

1,6-Dichloro-4-aminofluorenone (X) and its Deamination.—Both the preparation and deamination of this amine have been described previously¹ (p. 4268) when the substance was derived from "Acid X." In this work the substance has been derived from 1,6-dichlorofluorenone-4-carboxylic acid which had been prepared from 5,5'-dichlorodiphenic acid.

The preparation of the amine was carried out by a modified method which gave much better results. Potassium hydroxide was used; the ratio of excess alkali to hypobromite was 3/1; the amide-hypobromite ratio was 1/1.2; the concentration of the hypobromite was about 0.0002 mole per cc. of solution; motor stirring was used. Recrystallization from benzene and ligroin gave the amine of m. p. 233–234°, dec. The deamination of this amine was carried out by the procedure previously described for the amine derived from "Acid X."

Summary

1. "Acid X," formed by the rearrangement of 1,6-dichlorofluorenone-5-carboxylic acid in sulfuric acid, is identical with 1,6-dichlorofluorenone-

4-carboxylic acid formed when 5,5'-dichlorodiphenic acid is heated with sulfuric acid.

2. The temperatures at which the two isomeric dichlorofluorenone carboxylic acids (formed from 3,3'-dichlorodiphenic acid) are stable have been examined.

3. Phosphoric acid has been found to condense both the 3,3'- and the 5,5'-dichlorodiphenic acids but not to effect the *rearrangement* by which "Acid X" is produced.

4. Certain anomalous observations in the determination of the neutralization equivalent of "Acid X" appear to have been due to formation of solvates with the recrystallizing solvents.

5. "Acid X" has been decarboxylated directly by heating in sulfuric acid to give 3,6-dichlorofluorenone.

6. 1,6-Dichlorofluorenone and 1,8-dichlorofluorenone rearrange in hot concentrated sulfuric acid to give 3,6-dichlorofluorenone.

7. The condensations of other substituted diphenic acids and the rearrangements of the fluorenones and fluorenone carboxylic acids derived from them are being examined.

CAMBRIDGE, MASS.

RECEIVED APRIL 10, 1936

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Properties of Unsaturated Sulfur Compounds. III. Alpha Beta Unsaturated Ketosulfones

BY E. P. KOHLER AND R. G. LARSEN

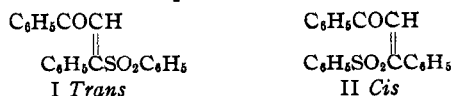
In continuation of our investigation of unsaturated ketosulfones¹ we have prepared a representative in which one of the unsaturated carbon atoms holds both a phenyl and a phenylsulfonyl group, the relation between the present and the former sulfones being shown by the formulas



The preparation of this substance enabled us to compare a number of similarly constituted compounds with respect to their stereoisomerism, the facility with which they enter into addition reactions and the mode of addition of unsymmetrical addenda.

The new ketosulfone, like the one described in the earlier paper, occurs in two forms of which one is yellow and the other colorless. From the analogy with the most closely related compounds of

which the configuration is known—dibenzoyl ethylene and phenyl- β -benzoylpropionic ester—one would expect the polar groups to be in the *trans* position in the more stable yellow form. We therefore represent this form with I and designate it the *trans* compound.



The relative melting points and solubilities of the two forms are the reverse of those of the unphenylated ketosulfones but the relative stabilities remain the same; a trace of base immediately produces a yellow color in solutions of the *cis* compound and in a short time converts it completely into the *trans* isomer. Owing to the reversal of the solubilities the effect of exposing concentrated solutions of the unphenylated and phenyl-

(1) Kohler and Larsen, *THIS JOURNAL*, **57**, 1448 (1935).