[CONTRIBUTION FROM THE UNIVERSITY OF TORONTO]

Arsenobenzene-Dimetal Adducts

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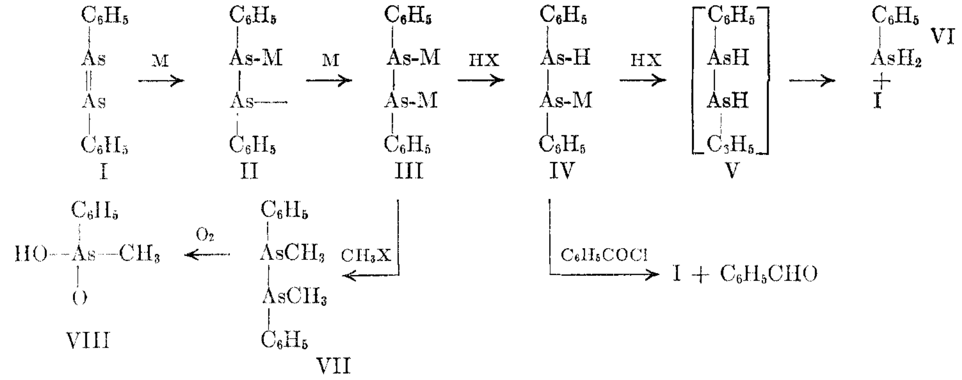
Received October 15, 1956

The preparative method for arsenobenzene has been improved. The arsenobenzene-disodium adduct has been prepared and characterized by treatment with methyl chloride, with dimethyl sulfate and with carbon dioxide. By further addition of sodium to the disodium adduct a new type, so-called arsenobenzene-tetrasodium adduct, has been prepared which gives reactions characteristic of phenyldisodiumarsine. This tetrasodium adduct and arsenobenzene exist in mobile equilibrium with the arsenobenzene-disodium adduct.

The addition of metallic lithium to arsenobenzene (I) in tetrahydrofuran was reported in 1952.[1] These workers assumed (without basis) that the radical II, "dark red," was formed initially, followed by the diadduct (III), "red." They characterized the diadduct, III, by treatment with methyl iodide to form dimethyldiphenylbiarsine VII, analyzed by iodometric titration leading to methylphenyliodoarsine and by two other reactions. The first involved reaction with one equivalent of benzoic acid to give monolithium dihydroarsenobenzene (IV) which was treated with benzoyl chloride to yield arsenobenzene and benzaldehyde according to an aldehyde synthesis proposed by Wittig *et. al.* The second reaction, with hydrogen chloride, presumably formed V, which was thought to disproportionate into arsenobenzene (I) and phenylarsine (VI).



We have treated arsenobenzene with metallic sodium in 2,5-dioxahexane and have obtained a diadduct (III, M = Na, according to sodium analysis) when 2 gram-atoms of sodium per mole of arsenobenzene are consumed in the reaction. We have little more evidence than Wittig *et al.* for the existence of a monoadduct (II, as described by them) although we have observed that addition of the relatively insoluble arsenobenzene to an arsenobenzene-dimetal adduct causes solubilization of I. Since arsenobenzene alone is sparingly soluble in 2,5-dioxahexane it would seem that some sort[2] of association between I and III is taking place. On the other hand color changes such as those discernible between mono- and dimetal combinations with azobenzene[2] and stilbene[3] have not been observed by us in studies with arsenobenzene.

Our arsenobenzene-disodium adduct, like the dilithium adduct of Wittig *et al.*, may be alkylated; we used methyl chloride and methyl sulfate. Our oxygen-sensitive product melts at 81.5–82° after purification by crystallization. This melting point is higher than that reported by Wittig *et al.* (71–74°) for dimethyldiphenylbiarsine. Also it is higher than the melting point (70°) reported[4] for VII when it is prepared by reduction of phenylarsinic acid with hypophosphorus acid. However, we have repeated the preparation of VII by the reduction of methylphenylarsine and have obtained 63% yield melting at 81.5–82°. The two products of this melting point are identical and can be air-oxidized in 42% yield to methylphenylarsinic acid. The low melting point reported by Steinkopf and Schwen may have been due to partial air oxidation of the sensitive material.

This ease with which the As—As bond can be broken makes credible the explanation by Wittig *et al.* that treatment of their diadduct (III, M = Li) with hydrogen chloride leads to phenylarsine (VI) and arsenobenzene (I) *via* dihydroarsenobenzene (V) which disproportionates. Indeed we have found another, though typically different, example of As—As bond fission. We have observed that the

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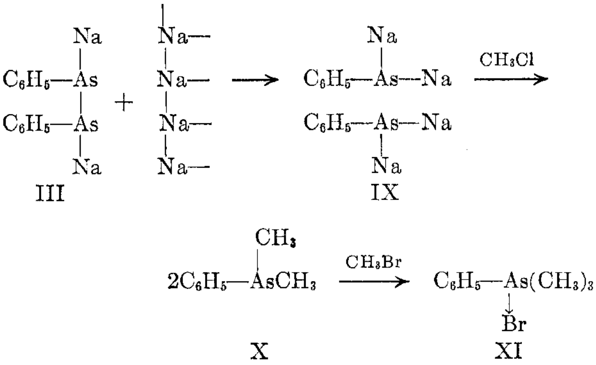
[1] G. Wittig, M. A. Jesatis, and M. Gloz, *Ann.*, **577**, 1 (1952).

[2] J. W. B. Reesor and G. F Wright, *J. Org. Chem.*, **22**, 375 (1957).

[3] J. W. B. Reesor, J. Smith, and G. F Wright, *J. Org. Chem.*, 19, 940 (1954).

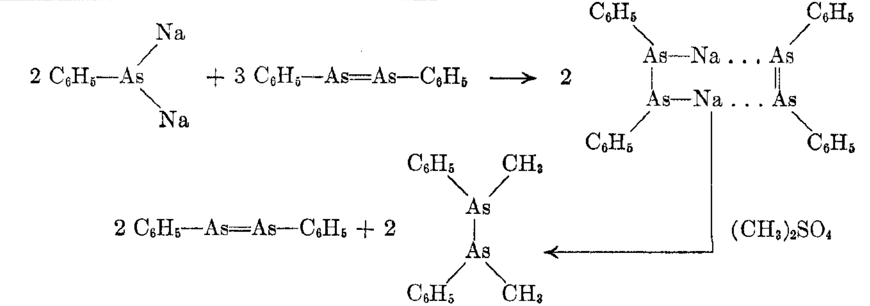
[4] W. Steinkopf and G. Schwen, *Ber.*, **54B**, 1437 (1921).

deep red solution of the disodium adduct, which is formed within 24 hr. from arsenobenzene and sodium, is split during four subsequent days by the action of excess sodium into a yellow-green solution. Whereas the analysis of the deep red solution shows that about two atoms of sodium are present per molecule of arsenobenzene, the yellow-green solution contains 4 atoms of sodium. We call the latter system the arsenobenzene-tetrasodium adduct although it seems to contain phenyldisodium arsine (IX). Treatment of this system with methyl chloride immediately produces the characteristic arsine-like odor in the effluent nitrogen, and a 75% yield of dimethylphenylarsine (X), identified as phenyltrimethylarsonium bromide (XI), is obtained from IX.


III IX X XI

$$2C_6H_5\text{—}As(CH_3)_2 \xrightarrow{CH_3Br} C_6H_5\text{—}As(CH_3)_3Br$$

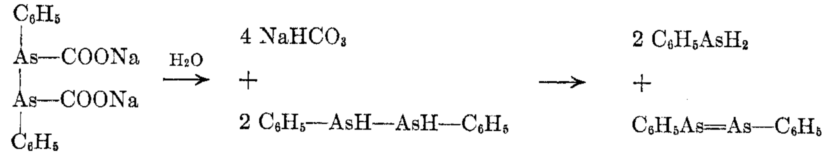
Moreover the arsenobenzene-tetrasodium adduct (largely IX) is in reversible equilibrium with the di-adduct (III) and arsenobenzene (I). Addition of an equivalent of I to the yellow-green system (IX) first produces a color change to a dark brown color during the first 20 min. and then slowly causes the deep red color of the arsenobenzene-disodium adduct (III) to appear during 24 hr. Of course part of the delay is due to the insolubility of arsenobenzene in 2,5-dioxahexane, and the system is not quite homogeneous at the end of the reaction period. Proof that the final system comprises the di-adduct is provided by subsequent treatment with methyl chloride. No odor of dimethylphenylarsine is apparent and a 74% yield of dimethyldiphenylbiarsine is obtained together with 2% of arsenobenzene. A similar study has been made in which 3 equivalents of arsenobenzene dissolve completely into the arsenobenzene-tetrasodium adduct system during 15 min. to give a homogeneous red solution. When this system is treated with methyl sulfate a 60% yield of dimethyldiphenylbiarsine is obtained, together with a recovery of 81% of the arsenobenzene, expected on the basis of the following reaction scheme.



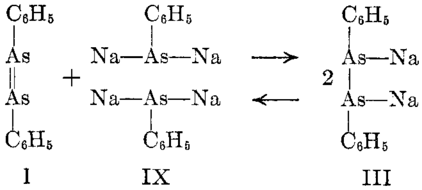
The mobile equilibrium (I) + (IX) $\rightleftarrows$ 2(III) is probably responsible for the behavior of the arsenobenzene-tetrasodium adduct when it is treated with air. The color of the system changes from yellow-green to red and then to white. Arsenobenzene is recovered from the oxidized system.

Treatment of both the arsenobenzene di- and tetrasodium adducts with carbon dioxide results in the immediate precipitation of light-colored solids.

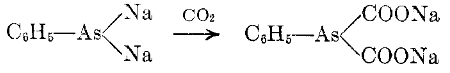
Upon treatment with water, the product of the di-adduct reaction with carbon dioxide decomposes vigorously (presumably with decarboxylation). The presence of phenylarsine can then be demonstrated together with arsenobenzene, thus indicating the disproportionation of dihydroarsenobenzene as postulated by Wittig *et al.*


XII

$$C_6H_5As(COONa)\text{—}As(COONa)C_6H_5 \xrightarrow{H_2O} 4\,NaHCO_3 + 2\,C_6H_5\text{—}AsH\text{—}AsH\text{—}C_6H_5 \longrightarrow 2\,C_6H_5AsH_2 + C_6H_5As{=}As\text{—}C_6H_5$$


I IX III

The recovery of product from carbon dioxide and the arsenobenzene-tetrasodium adduct is indicative of the reaction


XIII

$$C_6H_5\text{—}AsNa_2 \xrightarrow{CO_2} C_6H_5\text{—}As(COONa)_2$$

Subsequent treatment of the carboxylated product with water results, as in the previous case, *in an exothermic reaction and in the production of a soluble carbonate.* Only arsenobenzene, which may arise through the oxidation of phenylarsine, has been isolated from the reaction mixture.

The authors are grateful to the Defence Research Board for generous financial aid.

EXPERIMENTAL

Melting points have been corrected against authentic standards. In general, *all* operations have been carried out under nitrogen. When petroleum ether is used it is the grade boiling at 60–70° and is free from alkenes and peroxides.

Arsenobenzene. (*a*) *Preparation.* A solution of 40 g. (0.2 mole) of phenylarsonic acid (E. K. White Label) in 200 ml. of absolute ethanol was heated to 50–60° and 80 g. (0.6 mole) of 50% aqueous hypophosphorous acid (B.D.H. reagent) was added. After 5 min. a white precipitate began to separate. The system was stirred for 5 hr. at 50–60°. The warm suspension was suction-filtered and the light yellow solid was washed with 100 ml. of absolute ethanol. The yield of the vacuum-dried crude material was 25 g. (80%), m.p. 191–204°.

(*b*) *Purification.* The structure and purity of arsenobenzene have been conjectural. Melting points have been reported as 195°,[5] 196°,[6] 208°,[7] 209–212°[1] and 212–213°[8] while molecular weights employing both cryoscopic and ebullioscopic methods have ranged from 334, 402, and 642[5] to 895 and 915.[8] The material found to be adequate for the present research was purified by two methods.

(*i*) *Crystallization.* Crude arsenobenzene (3.0 g.) was completely dissolved in 12 ml. of refluxing purified chlorobenzene. The crystals obtained upon cooling to 25° were filtered by suction and washed with two 5-ml. portions of chlorobenzene, and three 10-ml. portions of diethyl ether. After drying 2 hr. at 25° (2 mm.) the recovery was 60%, m.p. 204–208°.

(*ii*) *Elution.* Crude arsenobenzene (3.0 g.) was suspended in 15 ml. of pure chlorobenzene at 25°. After 5 min. the suspension was filtered by suction and washed with two 5-ml. portions of chlorobenzene and three 10-ml. portions of ethyl ether, then dried at 25° (2 mm.). Recovery 80%, m.p. 201–207°.

Arsenobenzene-disodium adduct and methyl chloride. Arsenobenzene-disodium adduct was prepared in a modified Schlenk tube[3] containing an excess of sodium in a single block together with 3.07 g. (0.01 mole) of arsenobenzene in 40 ml. of 2,5-dioxahexane (purified by distillation from sodium benzophenone ketyl). An 82% yield (based on sodium analysis eventually made on inorganic residues from the reaction) was obtained when the adduct solution was decanted from excess metallic sodium after 19 hr. The decantate in a 100-ml. stirred flask was treated with methyl chloride at such a rate that ice water bath cooling maintained the temperature at 0–5°. The reaction was complete in 15 min.

To the reaction system was added 20 ml. of water freed from dissolved oxygen; then the dioxahexane was evaporated under reduced pressure (10 mm.) at room temperature. That part of the residue which was insoluble in water was dissolved in 40 ml. of petroleum ether leaving 0.30 g. (10%) of arsenobenzene, m.p. 191–200°, insoluble in the water–petroleum ether mixture. The petroleum ether phase was separated from the aqueous phase and evaporated, leaving 2.40 g. (87% calcd. on yield of diadduct) of *sym*-dimethyldiphenylbiarsine, m.p. 70–76°. Two crystallizations from petroleum ether (6 ml. per g.) at 0° raised the melting point to 81.5–82°. The aqueous phase was made up accurately to a 100-ml. volume with distilled water. Duplicate aliquots (1 or 2 ml. depending on the concentration of sodium ion) were analyzed for sodium content (in order to determine the adduct yield) according to the method of Barber and Kolthoff.[9] Methyl sulfate, used in place of methyl chloride in the above reaction, gave similar results.

Arsenobenzene-disodium adduct and carbon dioxide. To an arsenobenzene-disodium adduct prepared as described above (from 3.38 g., 0.011 mole, of arsenobenzene) and chilled with an ice water bath was added gaseous carbon dioxide at 0–5° during 30 min. Addition of water to the white suspension caused much evolution of heat and a color change to a light chocolate brown. The precipitate was filtered off, 2.32 g., m.p. 203–207°. This yield of arsenobenzene exceeds the theoretical (2.18 g.) slightly on the basis of a sodium analysis of the aqueous filtrate which indicates that the di-adduct is formed in 71% yield, and therefore should yield half of this molar 71% as arsenobenzene according to the scheme of Wittig *et al.*

The filtered reaction mixture had a characteristic arsine odor which eventually disappeared within 12 hr. because of air oxidation. Evaporation of the oxidized system yielded 0.12 g. of arsenobenzene and 0.74 g. of phenylarsonic acid.

Arsenobenzene-tetrasodium adduct and methyl chloride. Arsenobenzene-tetrasodium adduct was prepared identically with the adduct described above except that the reaction was allowed to continue for 5 days, then was decanted and treated with methyl chloride at 0–5°. The foul odor of an arsine was immediately noticeable. After 1 hr. the reaction was complete so 30 ml. of water freed from dissolved oxygen was added. The volatile components of the system were distilled under reduced pressure (10 mm.) at 25° and were condensed in a dry-ice-cooled receiver.

The distillate from the reaction system was treated with 5 g. (excess) of methyl bromide and the system, tightly stoppered, was maintained at 25° for 3 days. When the reaction vessel was opened, the arsinelike odor was absent. The solution was evaporated to dryness by an air stream leaving 4.96 g. (90%) of phenyltrimethylarsonium bromide, m.p. 259–270°. This product was purified by crystallization from absolute ethanol (3 ml. per g.) at 0° and two crops were obtained which were washed with cold ethanol (2 ml. per g.) and dried *in vacuo*, 4.13 g. (75%), m.p. 279–281°. Two more crystallizations from ethanol raised the melting point to 283–284° (dec.). The x-ray diffraction pattern (Cu $K\alpha$, Ni filtered) in *d* spacings (A) at relative intensities (I/I_1) are: [10] 3.056; [9] 3.705; [8] 6.104, 3.814; [7] 6.366, 4.371, 5.640; [5] 3.587, 3.437, 3.173, 2.657.

The bromide salt (25 mg.) was converted to its picrate (20 mg.) by treating the bromide in 1 ml. of absolute ethanol with 1 ml. (excess) of a saturated ethanol solution of picric acid. The melting point of the picrate, 142.5–143.2°, was raised to 144.2–144.7° by crystallization from 1 ml. of 50% aqueous ethanol. The x-ray diffraction pattern: [10] 3.49; [9] 11.33; [8] 8.665; [7] 4.35; [6] 4.766; [5] 5.64, 4.979; [4] 3.831.

Arsenobenzene-tetrasodium adduct and carbon dioxide. Arsenobenzene-tetrasodium adduct prepared as described above (from 2.00 g., 0.0066 mole, of arsenobenzene) and chilled with an ice water bath was treated with gaseous carbon dioxide at 0–5° during 6 hr. The solvent was removed under reduced pressure (10 mm.) at room temperature from the light tan colored precipitate. The product, pro-

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(5) C. S. Palmer and A. B. Scott, *J. Am. Chem. Soc.*, **50**, 536 (1928).

(6) A. Michaelis and C. Schulte, *Ber.*, **14**, 912 (1881); **15**, 1953 (1882).

(7) A. Binz, H. Bauer, and A. Hallstein, *Ber.*, **53**, 427 (1920).

(8) F. F. Blicke and F. D. Smith, *J. Am. Chem. Soc.*, **52**, 2937 (1930).

(9) H. H. Barber and I. M. Kolthoff, *J. Am. Chem. Soc.* **50**, 1625 (1928).

tected from air and moisture throughout its isolation, weighed 3.60 g., 96% calculated as $C_6H_5As(COONa)_2$.

Treatment of the product with water in the presence of air resulted in an exothermic reaction. A strong arsinelike odor was noticeable and a dark brown water-insoluble solid (1.47 g.) was produced. Crystallization of this solid from chlorobenzene (25 mg./ml.) at 0° gave 0.42 g. (21%) of arsenobenzene, m.p. 201–204°.

Potentiometric titration of the water-soluble carbonate confirmed the sodium analysis of 2.0 atoms of sodium for each atom of arsenic.

1 Arsenobenzene-tetrasodium adduct: 1 arsenobenzene: 4 methyl chloride. The arsenobenzene-tetrasodium adduct was prepared from 2.92 g. (0.009 mole) of arsenobenzene and was added to 2.92 g. (0.009 mole) of arsenobenzene. An exothermic reaction ensued and the yellow-green color gradually deepened as the suspended arsenobenzene changed from white to dark brown while it dissolved. The supernatant liquid phase changed to a red color during 45 min. The system was stirred at 25° for a total of 23 hr., after which there was only a little solid in the dark red solution.

Treatment with methyl chloride and subsequent processing was the same as that used for the experiment with the di-adduct: yield of dimethyldiphenylbiarsine, 4.74 g. (74%), m.p. 73–77°, crystallized from petroleum ether, m.p. 81.5–82.0°. Arsenobenzene was recovered in a 2% yield.

An experiment of this type where methyl sulfate was used in place of methyl chloride gave similar results.

1 Arsenobenzene-tetrasodium adduct:3 arsenobenzene:2 methyl sulfate. The arsenobenzene-tetrasodium adduct was prepared from 0.53 g. (0.0019 mole) of arsenobenzene and was added to 1.91 g. (0.0057 mole) of arsenobenzene. The sequence of color changes was identical to that observed in the previous experiment and all but a trace of the arsenobenzene went into solution.

Treatment of the mixture with 0.57 g. (0.0045 mole) of methyl sulfate and subsequent processing by the method outlined above gave recoveries of 0.92 g. (81%) of arsenobenzene and 0.75 g. (60%) of dimethyldiphenylbiarsine, calculated on the basis of the equations which we have suggested for this reaction.

Benzoic acid titration of arsenobenzene-disodium adduct. Disodium arsenobenzene, prepared from 2.44 g. (0.008 mole) of arsenobenzene in 40 ml. of 2,5-dioxahexane was titrated with a dioxahexane solution of benzoic acid (0.306 g./ml.). During this process the mixture became so viscous, due to the precipitation of sodium benzoate, that adequate stirring was difficult. Complete decolorization occurred after 5.0 ml. of the acid solution had been added. The diadduct content, calculated on the basis of the titration was 78.4%. A value of 72.7% was obtained by sodium analysis of the residues.

On the basis of the sodium analyses and the reaction scheme proposed by Wittig *et al.*, 1.55 g. of arsenobenzene should have been found. A recovery of 1.61 g. actually was obtained.

Dimethyldiphenylbiarsine. Phenylmethylarsinic acid (0.374 g., 0.0019 mole), m.p. 179–179.5°, with 0.66 g. (0.01 mole) of aqueous 50% hypophosphorous acid and 5 ml. of absolute ethanol was refluxed for 6 hr. under nitrogen. The system rapidly became murky and a rust-colored precipitate appeared. Upon cooling the ethanol was vacuum-evaporated from the suspension of white crystals. The remainder was extracted at 25° with 5 ml. of petroleum ether. This extract was filtered and cooled to 0° to yield 0.18 g. (63%), m.p. 81.5–82°. A mixture melting point with other samples was not lowered. Microanalysis for arsenic gave low results: As, 43.4, 43.7, 43.4; calcd. for $C_{14}H_{16}As_2$: As, 44.8.[10]

Oxidation of dimethyldiphenylbiarsine. A mixture of 20 ml. of petroleum ether and 10 ml. of water was added to 1.58 g. (0.0047 mole) of dimethyldiphenylbiarsine, m.p. 74–77°, and the whole was shaken at 25° in contact with air for 11 hr. Then the two phases were separately evaporated to dryness. The aqueous layer yielded 0.892 g. (0.0045 mole) of impure methylphenylarsinic acid, m.p. 158–166°; solution in 2 ml. of water and precipitation by addition of 10 ml. of acetone raised this melting point to 179–179.5°, recovery 42%. The oil (0.55 g.) from the petroleum ether phase spontaneously crystallized slowly to give 0.35 g., m.p. 167–171°, and 0.21 g., m.p. 163–169°. Total recovery of methylphenylarsinic acid, m.p. 158–174°, was 1.14 g. (60%).

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[10] O. Wintersteiner and H. Hannel, *Mikrochemie*, **4**, 155 (1926).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TORONTO]

Phosphorobenzene-Alkali Metal Adducts

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Received October 18, 1956

Phosphorobenzene has been shown to exist in mono-, di-, and polymeric forms. Each of these forms is converted by treatment with metallic sodium in 2,5-dioxahexane to the phosphorobenzene-disodium adduct. This adduct is converted by methyl chloride into the oxygen-sensitive dimethyldiphenylbiphosphine and by benzoyl chloride into dibenzoyldiphenylbiphosphine.

The addition of alkali metals to phosphorus-phosphorus double bonds has not been reported. Indeed the literature relating to phosphorobenzene (V) itself is sparse and confused. Michaelis and Kohler[1] first reported phosphorobenzene as the final product of a reaction series commencing with phenylphosphonous acid, I. When the acid was heated it disproportionated into phenylphosphonous acid (III) and phenylphosphine (II). The latter compound when heated with phenyldichlorophosphine, IV, yielded a pale yellow crystalline mass of melting point 149–150°, the carbon hydrogen analysis of which corresponded to that expected for $C_6H_5PPC_6H_5$. This product (V) was decomposed by hydrogen chloride into II and IV and by chlorine[2] into IV alone.

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[1] A. Michaelis and H. Kohler, *Ber.*, **10**, 807 (1877).

[2] W. Schlenk and F. Bergmann, *Ann.*, **463**, 1 (1928).