weight was 0.0050 g. and the melting point 103–108°. Mixed with pure benzoic acid, the melting point was raised to 110–114°. A second sublimation did not raise the melting point.

Summary

Catalysts have been found which initiate the decomposition of benzoic acid into benzene and carbon dioxide at temperatures as low as 245–250°. The reaction was found to be slightly reversible, benzoic acid being produced by the reaction of benzene on carbon dioxide in small amounts.

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[CONTRIBUTION FROM THE EXPERIMENTAL RESEARCH LABORATORIES, BURROUGHS WELLCOME AND COMPANY]

SOME SUBSTITUTED DI-(BETA-PHENYLETHYL)-AMINES AND BENZYL-BETA-PHENYLETHYLAMINES

BY JOHANNES S. BUCK

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A great deal of attention has been given to derivatives of β-phenylethylamine, particularly to their physiological action. This group contains compounds such as epinine, hordenine, tyramine, etc., and may also be considered as related to the hydrastinines (for example, Lodal), so that it is of great importance.

Much less work appears to have been done on secondary amines containing more than one benzene nucleus, of the type of di-(β-phenylethyl)-amine and benzyl-β-phenylethylamine, although a small number of these compounds is described in the literature and in some cases their pharmacological action has been examined. Di-(β-phenylethyl)-amine has been described by many workers; benzyl-β-phenylethylamine, *p*-methoxy-benzyl-β-phenylethylamine, *p*-hydroxybenzyl-β-phenylethylamine, *o*-hydroxybenzyl-β-phenylethylamine, and 3-methoxy-4-hydroxybenzyl-β-phenylethylamine, by Shepard and Ticknor;[1] *o*-veratrylhomopiperonylamine by Kaufmann and Müller;[2] benzyl-*p*-hydroxy-β-phenylethylamine, piperonyl-*p*-hydroxy-β-phenylethylamine, veratryl-*p*-hydroxy-β-phenylethylamine, and *o*-hydroxybenzyl-*p*-hydroxy-β-phenylethylamine, by Hoffmann and La Roche;[3] and *p,p'*-diamino-di-(β-phenylethyl)-amine and *p,p'*-dihydroxy-di-(β-phenylethyl)-amine by von Braun and Blessing.[4] The last authors also prepared cyclohexyl-*p*-hydroxy-β-phenylethylamine and cyclohexyl-*p*-amino-β-phenylethylamine. No compound containing the physiologically important catechol group (adjacent hydroxyl groups, usually in the 3,4-positions) appears to have been described. It was with the idea of prepar-

[1] Shepard and Ticknor, THIS JOURNAL, **38**, 381 (1916).

[2] Kaufmann and Müller, *Ber.*, **51**, 126 (1918).

[3] Hoffmann and La Roche, German Patent 259,874.

[4] Von Braun and Blessing, *Ber.*, **56**, 2153 (1923).

ing such compounds that the present work was undertaken. A number of the desired amines (as salts) have been obtained and their pharmacological properties will be described in another place.

The usual method for preparing benzyl-β-phenylethylamines is to condense a phenylethylamine with an aldehyde to form the Schiff base and then to reduce this, usually with sodium amalgam or (in the author's experience by far the better way) by the Adams method. This route has also been used for di-(β-phenylethyl)-amine by Rupe and Hodel.[5] In the majority of compounds prepared by the present author, this method was adopted to obtain the ethers of the hydroxyamines, and the ethers were then demethylated. Another reaction was sometimes employed. This consisted of combining a primary amine with the requisite ω-halide, to give the secondary amine salt, and this was then demethylated as before. The direct combination of a 3,4-dihydroxyamine with an aldehyde to form the Schiff base was not investigated closely as the method held little promise. Which of the two methods is used is a matter of expediency, although naturally the Schiff base method offers fewer chances of secondary reactions. In the direct combination of an amine and a halide, the formation of tertiary and quaternary compounds was not observed under the conditions employed. In the case of homoveratrylhomoveratrylamine, however, considerable amounts of homoveratrylamine hydrochloride were produced, indicating either the liberation of free secondary amine or the decomposition of the chloride into dimethoxystyrene.

Experimental

Starting Materials

β-Phenylethylamine.—Some was obtained from Kahlbaum, but most of it was prepared by a Hofmann reaction on phenylpropionamide.

Homoveratrylamine.—This was prepared as described by Buck[6] by a Hofmann reaction on dimethoxyphenylpropionamide.

Homoanisylamine.—Anisaldehyde, heated with malonic acid and pyridine (Rupe method) gave *p*-methoxycinnamic acid in 79% yield. On reduction (sodium amalgam) *p*-methoxyphenylpropionic acid was obtained (86% yield). Heated in a stream of dry ammonia at 210° for two hours, this gave the amide (62% yield with one heating) which was then converted, by the theoretical amount of sodium hypochlorite, into the amine; yield, 56%; b. p. 132° (10 mm.).

β-Phenylethyl chloride was prepared by the method of Barger,[7] which proved to be satisfactory.

β-Phenylethyl bromide was obtained from the Eastman Kodak Co.

3,4-Dimethoxyphenylethyl Alcohol.—Homoveratrylamine, in dilute acetic acid solution, was converted into the alcohol by the addition of the theoretical amount of sodium nitrite. The product (90% yield) boiled at 180–193° (13 mm.). Redistilled,

[5] Rupe and Hodel, *Helv. Chim. Acta*, **6**, 878 (1923).

[6] Buck, THIS JOURNAL, **52**, 4119 (1930).

[7] Barger, *J. Chem. Soc.*, **95**, 2193 (1909).

it forms a faint yellowish viscous oil, with only a slight odor; b. p. 166–168° (8 mm.); d_{20}^{20} 1.1426; n_{15} 1.5409.

Anal. Calcd. for $C_{10}H_{14}O_3$: C, 65.89; H, 7.74. Found: C, 65.94; H, 7.61.

The *p*-nitrobenzoate, prepared by the Schotten-Baumann method, and recrystallized from alcohol, forms bright yellow, glittering, jagged plates, melting at 81° and readily soluble in the usual solvents to colorless solutions.

Anal. Calcd. for $C_{17}H_{17}O_6N$: C, 61.61; H, 5.18; N, 4.23. Found: C, 61.44; H, 5.66; N, 4.03.

The urethan was prepared by warming molecular amounts of the alcohol and phenyl isocyanate and washing the product with carbon bisulfide. Recrystallized from alcohol it forms white, pearly aggregates of thin plates, somewhat soluble in hot water and readily soluble in the usual solvents. It melts at 98–99°.

Anal. Calcd. for $C_{17}H_{19}O_4N$: C, 67.74; H, 6.31; N, 4.65. Found: C, 67.62; H. 6.44; N, 4.47.

3,4-Dimethoxy-β-phenylethyl chloride could not be obtained in the pure state. The material used was obtained by treating the alcohol in carbon tetrachloride solution with the theoretical amount of phosphorus pentachloride and then removing all volatile matter under reduced pressure at 100°. A thick, reddish oil was obtained.

Schiff Bases.—In general these compounds were prepared by mixing the reactants in molecular proportions and then heating at 100° under reduced pressure until all water was evolved (usually thirty minutes). The yield is practically the theoretical. The compounds are well defined and are readily soluble in the usual solvents. They are best recrystallized by allowing their solutions in ether to evaporate spontaneously. They are tabulated below. Most of those previously known may be found in connection with the amines derived from them (see above). It is interesting to note that phenylacetaldehydes appear to give oily or ill-defined Schiff bases.[5,8]

TABLE I

SCHIFF BASES

Aldehyde	Amine	Appearance	M. p., °C.
Piperon-	H-piperonyl-	Tiny white prisms	114
Anis-	H-anisyl-	White jagged prisms	74
Veratric	β-phenylethyl-	Faint yellow pearly plates	60
Piperon-	H-veratryl-	White glittering needles	101
Anis-	H-veratryl-	Cream prisms	63
Veratric	H-anisyl-	Cream stout prisms	69
Veratric	H-veratryl-	White nodules	83

	Analyses					
	Carbon, %		Hydrogen, %		Nitrogen, %	
Formula	Calcd.	Found	Calcd.	Found	Calcd.	Found
$C_{17}H_{15}O_4N$	68.67	68.39	5.08	5.06	..	..
$C_{17}H_{19}O_2N$	...	...	..	..	5.20	4.99
$C_{17}H_{19}O_2N$	75.78	75.52	7.13	7.14	..	..
$C_{18}H_{19}O_4N$	68.97	68.77	6.12	6.34	4.47	4.46
$C_{18}H_{21}O_3N$	...	...	..	..	4.68	4.77
$C_{18}H_{21}O_3N$	...	...	..	..	4.68	4.85
$C_{19}H_{13}O_4N$	69.27	69.55	6.99	7.15	..	..

[8] Späth and Berger, *Ber.*, **63**, 2098 (1930).

Amines.—The Schiff bases are very readily reduced in acetic acid solution by platinum oxide and hydrogen, after the method of Adams. Excess acetic acid was removed under reduced pressure, the acetate dissolved in water and aqueous ammonia or sodium hydroxide solution added. The amine was then extracted with ether, the extract dried over potassium hydroxide and the ether removed. The amine was then recrystallized from alcohol–aqueous ammonia mixture or distilled under reduced pressure. The yield is practically the theoretical. Those amines not prepared *via* the Schiff base were obtained from the salts in an analogous manner.

In the second method of preparation, the halide and amine were mixed in molecular amounts and heated on the water-bath until the reaction was complete. Bromides react much more rapidly than the chlorides and the reaction mixture may not require heating. With the chlorides up to twenty hours' heating may be required. Usually the amine hydrobromide separates in the solid state, but the hydrochlorides remain oily. In all cases, ether is added to the reaction mixture and the salt filtered off and recrystallized.

The amines tend to form carbonates in air. Two salts were made from each amine, the hydrochloride, wherever possible, for pharmacological test, and another salt for analytical check. The amines and salts are tabulated.

Phenolic Amines.—β-Phenylethylamine derivatives are somewhat unstable to strong acids, but by carefully regulating the reaction it was found possible to obtain, in most cases, the demethylated (phenolic) derivatives in good yield. The demethylation, which goes extraordinarily easily, was carried out by means of hydriodic acid (52%, *d* 1.7), which must be colorless. The amine, mixed with ten times its weight of acid, was cautiously heated in a current of carbon dioxide until the evolution of methyl iodide had ceased. One-fifth of the acid was then distilled over and the rest removed under reduced pressure. The hydriodide usually remained as a crystalline mass.

The phenolic amine salts are generally well-defined, crystalline compounds, stable when quite pure. They possess, as might be expected, powerful reducing properties, reducing gold and silver salts in the cold. Those containing two adjacent hydroxyl groups give intense green colors with ferric chloride. Aqueous alkalies, when not present in excess, give white precipitates of the bases, at once soluble in excess to unstable yellowish solutions which rapidly oxidize.

In one case, 4-hydroxybenzyl-4′-hydroxy-β-phenylethylamine, no adjacent hydroxyl groups are present and only a faint violet color is obtained with ferric chloride. The powerful reducing properties are also absent and the base is stable.

TABLE II

DATA ON AMINES

Amine	Prepd. from	Cryst. solvent	Properties	B. p. or m. p., °C.	Formula	Analyses: Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Homoveratryl-β-phenylethyl-	Salt	.....	Faint yellow oil	178[a] (0.48 mm.)	$C_{18}H_{23}O_2N$					4.91	4.57
Hydrochloride	2	Dil. HAc + HCl	White pearly crusts	183	$C_{18}H_{24}O_2NCl$	67.15	67.19	7.52	7.67		
Hydrobromide	2	Dil. HAc	Bulky cryst. powder	172	$C_{18}H_{24}O_2NBr$	58.99	59.37	6.61	6.79		
Homoveratrylhomoveratryl-	Salt	.....	White crystals	*ca.* 240 (1.0 mm.) (m. p. 51°)	$C_{20}H_{27}O_4N$					4.06	4.33
Hydrochloride	2	Abs. alc.	Pearly cryst. masses	196	$C_{20}H_{28}O_4NCl$	62.83	62.54	7.37	7.48		
Hydriodide	Chloride	Water	Pearly plates	182 soft 175	$C_{20}H_{28}O_4NI$	50.72	50.58	5.97	6.13		
Veratrylhomoanisyl-	1	.....	Pale yellow oil	197 (0.48 mm.)	$C_{18}H_{23}O_3N$					4.65	4.59
Hydrochloride	Amine	Dil. HCl	Pearly plates	223	$C_{18}H_{24}O_3NCl$	63.94	64.17	7.13	7.36		
Hydrobromide	Amine	Dil. HAc-HBr	Pearly plates	233	$C_{18}H_{24}O_3NBr$	56.52	56.83	6.33	6.62		
Anisylhomoanisyl-	1	Alc. + NH_4OH	Fluffy, whitish leaves	44	$C_{17}H_{21}O_2N$					5.16	5.31
Hydrochloride	Amine	Dil. HCl	Small rhombs	271	$C_{17}H_{22}O_2NCl$	66.31	66.46	7.21	7.54		
Hydrobromide	Amine	Dil. HBr	Glittering hexagons	254	$C_{17}H_{22}O_2NBr$	57.94	58.09	6.29	6.02		
Piperonylhomoveratryl-	1	.....	White crystals	203[b] (0.44 mm.) (m. p. 34)	$C_{18}H_{21}O_4N$					4.44	4.32
Hydrochloride	Amine	Dil. HCl	Fluffy tiny needles	219	$C_{18}H_{22}O_4NCl$	61.43	61.50	6.31	6.65		
Hydrobromide	Amine	Water	Tiny nodules	204	$C_{18}H_{22}O_4NBr$	54.54	54.56	5.59	5.56		
Hydriodide	Amine	Dil. HAc	Faint yellow prisms	198	$C_{18}H_{22}O_4NI$	48.75	48.65	5.00	5.09		

TABLE II (*Concluded*)

Amine	Prepd. from[d]	Cryst. solvent	Properties	B. p. or m. p., °C.	Formula	Analyses: Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Anisylhomoveratryl-	1	Cold ether	Large yellowish crysts.	47	$C_{18}H_{23}O_3N$					4.65	4.79
Hydrochloride	Amine	Dil. HAc	Long prisms	234	$C_{18}H_{24}O_3NCl$	63.97	64.15	7.14	7.18		
Perchlorate	Amine	Dil. HAc	Small prisms	198	$C_{18}H_{24}O_7NCl$	53.78	53.79	6.02	5.79		
Veratryl-β-phenylethyl-	1	.....	Pale yellow oil	182 (0.35 mm.)	$C_{17}H_{21}O_2N$					5.16	5.01
Perchlorate	Amine	Alc.–ether	Faint yellow tables	177	$C_{17}H_{22}O_6NCl$	54.89	54.77	5.97	6.15		
Hydriodide	Amine	Alc.–ether	Faint yellow nodules	170	$C_{17}H_{22}O_2NI$	51.11	51.06	5.56	5.78		
Benzylhomoveratryl-	1	.....	Faint yellow oil	178 (0.75 mm.)	$C_{17}H_{21}O_2N$					5.16	5.08
Hydrochloride	Amine	Water	Pearly leaves	200	$C_{17}H_{22}O_2NCl$	66.32	65.99	7.22	7.35		
Picrate	Amine	HAc	Canary yellow needles	160	$C_{23}H_{24}O_9N_4$	55.17	54.85	4.84	4.54		
Piperonylhomopiperonyl-[9]	1	Cold ether	Faint yellow crystals	51	$C_{17}H_{17}O_4N$					4.68	4.97
Hydrochloride	Amine	Dil. HCl	Pearly leaves	243	$C_{17}H_{18}O_4NCl$	60.79	60.89	5.43	5.50		
Acid sulfate	Amine	Water	Granular cryst. powder	Indef.	$C_{17}H_{17}O_4N \cdot H_2SO_4$	51.37	51.54	4.83	4.95		
Veratrylhomoveratryl-	1	Aq. alc.	White glittering plates	79	$C_{19}H_{25}O_4N$	68.84	68.68	7.61	7.58		
Hydrobromide	Amine	Water	Chalky aggregates	187	$C_{19}H_{26}O_4NBr$	55.33	55.57	6.36	6.51		
Oxalate	Amine	Aq. alc.	Pearly plates	230	$C_{21}H_{27}O_8N$	59.83	59.43	6.46	6.42		
Di-(β-phenylethyl)-[e]	.....	.....	.....	...	$C_{18}H_{19}N$	...	...	..	..	..	..
Hydrochloride	2	Dil. HCl	White needle-prisms	233[c]	$C_{16}H_{20}NCl$	73.38	73.08	7.71	7.39	5.36	5.71
Hydrobromide	2	Dil. HAc	Stout white prisms	193	$C_{16}H_{20}NBr$	62.78	62.55	6.58	6.86	4.58	4.69

[a] B. p. rises to 220°. [b] Possibly some change. [c] Literature gives 260, 265°. [d] Under the heading "Preparation" 1 signifies that the amine was prepared via the Schiff base, and 2 signifies that the compound was obtained from a phenylethyl chloride and an amine. [e] Previously obtained by various other methods. Beilstein, 4 Auf., Bd. XII, p. 1098; Rupe and Glenz, *Helv. Chim. Acta*, **5**, 940 (1922); Rupe and Hodel, *ibid.*, **6**, 865 (1923); v. Braun, Blessing and Zobel, *Ber.*, **56**, 1988 (1923).

[9] *Cf.* Malan and Robinson, *J. Chem. Soc.*, 2653 (1927).

TABLE III

PHENOLIC AMINES

Phenolic amine salt	Parent amine and preparation	Cryst. solvent	Appearance	M. p., °C.	Formula	Analyses: Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Benzyl-3,4-dihydroxy-β-phenylethylamine hydrochloride	Benzylhomoveratryl-, by AgCl on hydriodide	Dil. HCl, alc.–ether	Chalky, cryst. powder	87, solid, 120, remelts 180	$C_{15}H_{18}O_2NCl$	64.37	64.49	6.49	6.58
Picrate	Alc. picric acid and hydrochloride	Dil. HAc	Red-brown irreg. prisms	131	$C_{15}H_{17}O_2N\cdot 2C_6H_3O_7N_3$	46.28	46.26	3.36	3.87
Methylenedioxybenzyl-3,4-dihydroxy-β-phenylethylamine hydriodide[a]	Piperonylhomoveratryl-, demethylation	Dil. acetic	Buff, tiny nodules	237	$C_{16}H_{18}O_4NI$	46.26	46.34	4.37	4.52
Hydrochloride	By AgCl on hydriodide	Dil. HCl	Buff, cryst. powder	219	$C_{16}H_{18}O_4NCl$	59.33	59.41	5.61	5.77
4-Hydroxybenzyl-4′-hydroxy-β-phenylethylamine hydriodide	Anisylhomoanisyl-, demethylation	Dil. HI	Tiny prisms	192	$C_{15}H_{18}O_2NI$	48.51	48.43	4.89	5.16
Hydrochloride	By AgCl on hydriodide	Dil. HCl	Stout rect. prisms	234	$C_{15}H_{18}O_2NCl$	64.38	64.50	6.49	6.96
Base	Aq. ammonia on salts	Dil. alc.	White prisms	118 frothing	$C_{15}H_{17}O_2N$	N, 5.76	5.77		
4-Hydroxybenzyl-3′,4′-dihydroxy-β-phenylethylamine hy'chloride	Anisylhomoveratryl-, by AgCl on hydriodide	Dil. HCl	Tiny nodules	200–205	$C_{15}H_{18}O_3NCl$	60.89	61.06	6.17	6.33
Picrate	Aq. picric acid and hydrochloride	Dil. HAc	Red-brown nodules	97, solidifies, remelts *ca.* 140	$C_{15}H_{17}O_3N\cdot 2C_6H_3O_7N_3$	45.18	45.08	3.23	3.28

TABLE III (*Concluded*)

Phenolic amine salt	Parent amine and preparation	Cryst. solvent	Appearance	M. p., °C.	Formula	Analyses: Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
3,4-Dihydroxybenzyl-4′-hydroxy-β-phenylethylamine hydriodide	Veratrylhomoanisyl-, demethylation	Dil. HI	Faint yellow prisms after softening	*ca.* 163	$C_{15}H_{18}O_3NI$	46.50	46.22	4.69	5.04
Hydrochloride	By AgCl on hydriodide	Dil. HCl	Tiny nodules	180	$C_{15}H_{18}O_3NCl$	60.89	61.06	6.14	6.33
3,4-Dihydroxybenzyl-3′,4′-dihydroxy-β-phenylethylamine hydrochloride	Veratrylhomoveratryl-, by AgCl on hydriodide	Dil. HCl	Flesh-colored tiny prisms	182	$C_{15}H_{18}O_4NCl \cdot H_2O$	H_2O, 5.46	5.44	Cl, 10.76	10.87
Anhydrous	Dried at 110°		White cryst. powder		$C_{15}H_{18}O_4NCl$	57.78	57.57	5.78	5.80
						N, 4.50		4.80	
Picrate	Aq. picric acid and hydrochloride	Water	Red-gold plates	173	$C_{15}H_{17}O_4N \cdot 2C_6H_3O_7N_3$	44.19	44.19	3.16	3.19
3,4,3′,4′-Tetrahydroxy-di-(β-phenylethyl)-amine hydriodide	Homoveratrylhomoveratryl-, demethylation	Alc.–ether	Powdery prisms	187	$C_{16}H_{20}O_4NI$	46.02	45.95	4.83	5.07
Hydrochloride	By AgCl on hydriodide	Alc.–ether	Chalky crusts	230	$C_{16}H_{20}O_4NCl \cdot 2.5H_2O$	51.80	51.66	6.79	6.68

[a] This demethylation was carried out by adding 3.3 moles of hydriodic acid (as 52% solution) to the amine, and keeping the mass just fused for five minutes. On adding alcohol the product crystallized.

In general, the solubility of all the salts is of the same order. They are readily soluble in warm water, warm alcohol and warm acetic acid, but are much less soluble in a dilute solution of the acid from which they were formed. A number of the salts have distinct colors when freshly recrystallized (usually a pink tint) due to water of crystallization. The color disappears on drying the salt at 110°.

Veratrylphenylethylamine and homoveratrylphenylethylamine failed to demethylate normally with hydriodic acid. The products formed are being examined.

The melting points above cited are corrected. Boiling points were taken on Anschütz thermometers. The author is indebted to Mr. Walter S. Ide for the majority of the micro analyses in this paper.

Summary

A series of 3,4-dihydroxybenzyl-β-phenylethylamines and 3,4-dihydroxydi-(β-phenylethyl)-amines is described, together with the intermediate Schiff bases and secondary amines.

TUCKAHOE, NEW YORK

[CONTRIBUTION NO. 70 FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

CATALYSIS IN ORGANIC CHEMISTRY. IV. DECOMPOSITIONS OF ESTERS AND ACIDS BY ANHYDROUS ZINC CHLORIDE

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The types of decomposition of esters by anhydrous zinc chloride described in a previous paper[1] may be represented by the equations

$$RCOOC_nH_{2n+1} = RCOOH + C_nH_{2n} \quad (I)$$
$$RCOOC_nH_{2n+1} = RH + CO_2 + C_nH_{2n} \quad (II)$$
$$RCOOC_nH_{2n+1} = RC_nH_{2n+1} + CO_2 \quad (III)$$

The transformation of ethyl benzoate into benzoic acid, benzene and ethylene and the conversion of methyl salicylate into *o*-cresol and carbon dioxide are typical decompositions. It has been noted that diethyl oxalate and succinate react with anhydrous zinc chloride, yielding ethyl chloride and zinc salts. The present paper gives an account of the behavior of twelve esters and seven acids.

Discussion of Experiments

Pure freshly distilled or crystallized esters or acids and 0.5 mole of anhydrous zinc chloride per mole of ester or acid were used. Unless otherwise stated, the decomposition products were isolated by the proced-

[1] Underwood and Baril, THIS JOURNAL, 52, 395 (1930).