

THE SYNTHESIS OF 12-METHYLPERHYDRORETENE
(ABIETANE) AND ITS NON-IDENTITY WITH
FICHELITE

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In a recent article in *Science*,¹ we announced the synthesis of 12-methylperhydroretene and outlined the steps by which this was accomplished. Unfortunately, mistakes in transcribing two of the structural formulas which appear in that article were overlooked. The present paper describes this synthesis in more detail and corrects the errors mentioned.

Over a century ago, it was called to the attention of chemists and others that in the fossilized remains of coniferous trees in peat and lignite beds in various parts of the world, there often occurred white or yellowish paraffin-like deposits, either crystalline or amorphous in appearance, between the annual rings, in the cracks and crevices of the wood, or disseminated throughout its mass. In general, these deposits appeared to follow the original oleoresin ducts, thus suggesting that they probably owed their genesis to the resins or resin acids of the living tree. They were, therefore, referred to as "earth resins" in some of the older handbooks.²

These deposits were given different names by their investigators—such as Fichtelite, Phylloretin, Tekoretin, Scheererite, Branchite, Hartite, Hatschetin, etc., with resulting confusion in the literature. It was soon learned, however, that practically all such naturally-occurring material was a mixture of hydrocarbons, the chief constituents of which were retene (VII) and fichtelite as we now know them, the former taking its name from the Greek *retine*, resin or gum,³ and the latter from its occurrence in fossilized pine trunks from peat beds of the Fichtelgebirge (German, *Fichte*, pine) region of Bavaria.⁴

One of the earliest investigations of these natural products was that of Trommsdorff,⁵ who examined a sample received from Dr. Fikentscher.

¹ BOGERT AND STERLING, *Science*, n.s., **87**, 196 (Feb. 25, 1938).

² *Gmelin's Handbook of Chemistry*, XVIII, 1871, p. 248.

³ FRITZSCHE, *Ann.*, **109**, 250 (1859).

⁴ BROMEIS, *ibid.*, **37**, 304 (1841).

⁵ TROMMSDORFF, *ibid.*, **21**, 126 (1837).

The latter obtained it from a peat bed near Redwitz in the Fichtelgebirge, where it occurs in fossilized trunks of conifers, particularly either *Pinus uliginosa* N,⁶ or *Pinus sylvestris*.⁷ The crystalline product he separated was apparently an impure retene. Later, from some additional material, from the same source, Bromeis⁴ succeeded in isolating pure fichtelite, which crystallizes from alcohol in tabular crystals, m.p. 46.5°, and has been studied by a number of other investigators^{6, 7, 8, 9} since.

Almost invariably it occurs associated or mixed with retene, or perhaps as a solid solution of the two. This association led early investigators to assume some genetic relationship between them, and in 1889 Bamberger and Strasser¹⁰ concluded that fichtelite was probably perhydroretene, C₁₈H₃₂. Liebermann and Spiegel,¹¹ by treatment of retene with hydriodic acid and phosphorus in sealed tubes at 250°, obtained retenedodecahydride, C₁₈H₃₀, from which Spiegel^{11b} isolated a crystalline solid, m.p. 48°, which he believed to be retene perhydride, identical with fichtelite, but which he did not secure in sufficient amount for analysis or identification. Twenty years later, Ipatiew,¹² by hydrogenation of retene under high pressure, in the presence of a nickel oxide catalyst, produced a perhydroretene as an oil, b.p. 300–315°, which refused to solidify in an ice-salt mixture, and was not identical with fichtelite. Perhydrophenanthrenes, C₁₄H₂₄, prepared by these two methods, showed similar differences.^{13, 14}

A definite connection between retene and fichtelite was established by Ruzicka, Balaš, and Schinz,¹⁵ when they obtained retene from fichtelite by heating the latter with sulfur. Later, Ruzicka and Waldman,¹⁶ dehydrogenated fichtelite quantitatively, and obtained, in addition to one mole of retene and approximately six of hydrogen, one mole of methane per mole of fichtelite, a result which indicated that fichtelite was probably a perhydromethylretene with its methyl group in tertiary union, most likely in the same relative position as in abietic acid, *i.e.* on C¹². Fichtelite would be structurally identical, then, with abietane, C₁₉H₃₄, or

⁶ HELL, *Ber.*, **22**, 498 (1889).

⁷ CLARK, *Ann.*, **103**, 236 (1857).

⁸ MALLET, *Ber.*, **5**, 817 (1872); *Chem. News* (London), **26**, 159 (1872).

⁹ BAMBERGER, *Ber.*, **22**, 635 (1889).

¹⁰ BAMBERGER AND STRASSER, *ibid.*, **22** 3361 (1889).

¹¹ (a) LIEBERMANN AND SPIEGEL, *ibid.*, **22**, 780 (1889); (b) SPIEGEL, *ibid.*, **22**, 3369 (1889).

¹² IPATIEW, *ibid.*, **42**, 2096 (1909).

¹³ LIEBERMANN, SPIEGEL, AND LUCAS, *ibid.*, **22**, 779 (1889).

¹⁴ IPATIEW, JAKOWLEW, AND RAKITIN, *ibid.*, **41**, 1000 (1908). See also Denisenko and Kotel'nikova, *J. Gen. Chem.* (U. S. S. R.), **7**, 2822 (1937).

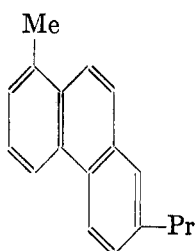
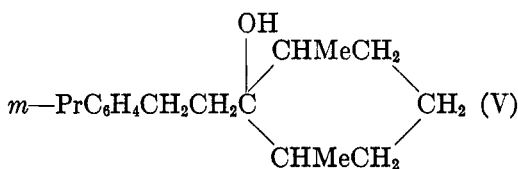
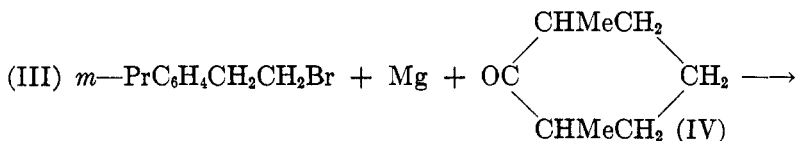
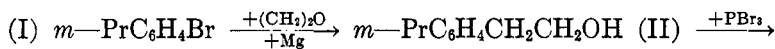
¹⁵ RUZICKA, BALAŠ, AND SCHINZ, *Helv. Chim. Acta*, **6**, 692 (1923).

¹⁶ RUZICKA AND WALDMAN, *ibid.*, **18**, 611 (1935).

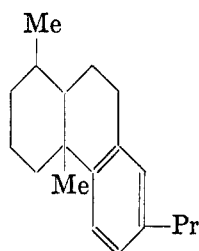
perhydroabietene, and it was to check this by synthesis that a 12-methylperhydroretene, $C_{19}H_{34}$, was built up by the steps shown in the following flow sheet.

FLOW SHEET

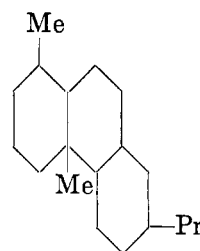
(Pr-isopropyl)



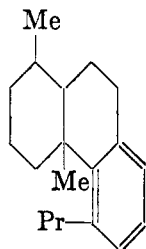
(VII) Retene



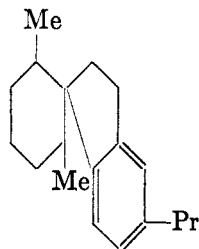
(VI) 12-Methylocta-hydroretene



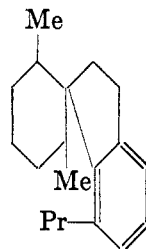
(VIII) 12-Methylperhydroretene (Abietane)



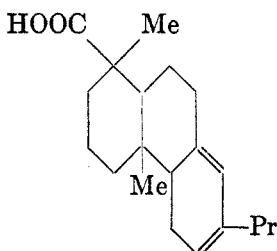
(X)



(XI)



(XII)



Theoretically, the cyclodehydration of the tertiary alcohol (V) might lead to the formation of either (VI), (X), (XI), or (XII), aside from possible stereoisomers.

When the reaction was carried out, practically all the product distilled at 180–181° at 12 mm. pressure, and yielded only retene when fused with selenium. The evidence, therefore, is that (VI) was apparently the only product of the cyclization under the conditions of our experiments.

Catalytically hydrogenated, it absorbed three moles of hydrogen per mole of hydrocarbon, with formation of a saturated $C_{19}H_{34}$ hydrocarbon, as an odorless, colorless, transparent, viscous oil (VIII), which could not be obtained in crystals.

Since fichtelite is a white crystalline solid, m.p. 46.5°, it is obviously different from our synthetic product. Whether the difference between the two is stereochemical,¹⁵ or is due to a difference in the location of the angular methyl group, remains to be determined. A critical comparison of the synthetic with the natural product awaits the receipt from Europe of an additional supply of fichtelite.

The recent X-ray crystallographic and related studies of fichtelite by Crowfoot,¹⁷ give a molecular weight of 264 ± 4 ($C_{19}H_{34} = 262$) for this hydrocarbon. Her investigation also indicates that the molecules are roughly lath-shaped and that their arrangement, taken together with their low crystal density, is additional evidence for the presence of a methyl group in tertiary linkage.

The synthetic product, however, appears to be identical with the major component of a mixture of saturated hydrocarbons obtained by the catalytic hydrogenation of "abietene" according to the Hasselstrom and Hull patent,¹⁸ and supplied to us through the courtesy of the G. and A. Laboratories of Savannah, Ga. This major component was separated as a colorless mobile oil by repeated fractional distillation over sodium until its boiling point remained practically constant (183–184° at 12 mm.);

¹⁷ CROWFOOT, *J. Chem. Soc.*, **1938**, 1241.

¹⁸ HASSELSTROM AND HULL, *U. S. Pat.* **2,095,548** (Oct. 12, 1937); *Chem. Abstr.*, **31**, 8547 (1937).

its physical constants were those shown in the appended Table, and its percentage composition agreed with that calculated for $C_{19}H_{34}$.

Inasmuch as this abietane may be regarded as the fundamental hydrocarbon of the entire abietic group of resin acids and related compounds, we hope to be able to study it somewhat more fully.

We are now attempting to synthesize abietic acid by a process similar to that described above for the 12-methylperhydroretene.

Acknowledgement.—We are under especial obligations to Professor Homer Adkins, of the University of Wisconsin, for carrying out, in his hydro-

TABLE
PHYSICAL CONSTANTS OF COMPOUNDS DISCUSSED

COMPOUND	M.P.	B.P., °C.	PRES- SURE, (MM.)	SP. GR.	REFR. INDEX	OPT. ROT.
Fichtelite	46.5°	235.6 355.2	43 719	0.938 (d_4^{25})	1.5052 (n_D^{20}) ^a	+19.° (α_D^{20}) +18.08° (α_D^{20})
Abietane	Liq.	183-4 345-8	12 760	0.9368 (25°)	1.5022 (n_D^{25})	+10.45° (α_D^{25}) +12.53° (α_D^{25}) (CHCl ₃)
12-Methylper- hydroretene	Liq.	179-80	12	0.9374 (d_4^{25})	1.5025 (n_D^{25})	0°
Vocke $C_{19}H_{34}$	Liq.	128	1			

^a On supercooled liquid material.¹⁵

genation apparatus, the catalytic reduction of our octahydromethylretene (I).

EXPERIMENTAL

The thermometers used in these experiments were calibrated with the aid of U. S. Bureau of Standards certified thermometers. All melting points were determined in an open beaker with vigorous agitation, while raising the temperature at the rate of three degrees per minute, and the readings were corrected for stem exposure. Refractive indices were measured at 25° with an Abbé refractometer. The analytical work was carried out by Dr. Donald Price and Mr. Saul Gottlieb, and was of the micro type.

Fichtelite.—The fichtelite used in our experiments came from "near Wunsiedel, Fichtelgebirge, Bavaria," and was imbedded in and disseminated through some pieces of partially fossilized coniferous wood. This wood was shredded and extracted with petroleum ether in a continuous extractor. The extract was shaken with successive portions of sulfuric acid to remove retene and other contaminants, and was then crystallized from petroleum ether. The product formed white crystals, m.p. 46.5°, in agreement with the literature.¹⁶

Nitrocumenes.—A mixture of 86 g. of nitric (sp. gr. 1.42) and sulfuric (sp. gr. 1.84) acids was slowly stirred into 100 g. of cumene, prepared from benzene, isopropylbromide, and amalgamated aluminum. Maintaining the temperature at 10–20°, the stirring was continued for 2 hrs., after which the product was poured into cold water, washed, and distilled repeatedly at 12 mm. pressure. Three fractions were collected as follows: (1) 18 g., b.p. 117–119°; (2) 67 g., b.p. 128°; and (3) 7 g., b.p. 168–170°.

Of these, (1) gave *o*-nitrobenzoic acid, and (2) *p*-nitrobenzoic acid, when oxidized with chromium trioxide in glacial acetic acid solution. By reduction with tin and hydrochloric acid, both (1) and (2) yielded bases whose oxalates, crystallized from water, melted respectively at 170° (corr.) and 157° (corr.). Constam and Goldschmidt¹⁹ have reported for *o*-cumidine oxalate a m.p. of 173°, and for the *para* isomer 159°. As noted beyond, fraction (3) consisted of dinitrocumene. The approximate composition of our nitrated cumene was 19% *ortho*, 73% *para*, and 8% dinitro.

By varying slightly the proportion of acid (83 g. nitric and 125 g. of sulfuric) to 100 g. of cumene, and operating at a temperature of 40–50°, a yield of 77% of the *p*-nitrocumene was secured, with but very small amounts of the *o*-nitro and dinitro derivatives, and most of the unnitrated cumene was recovered.

2,4-Dinitrocumene.—As already mentioned, the nitration product obtained in fraction (3) above had a b.p. of 168–170° at 12 mm. Purified by freezing, it was obtained in yellow crystals, m.p. 18.5° (corr.), b.p. 136° at 2 mm.

Anal. Calc'd for C₉H₉N₂O₄: C, 51.40; H, 4.81.

Found: C, 51.79; H, 4.79.

By careful oxidation in glacial acetic acid solution with chromium trioxide and a few drops of hydrochloric acid, a small quantity of *m*-dinitrobenzene was isolated. Considerable difficulty was experienced in achieving an oxidation without complete destruction of the molecule, with separation of oxides of nitrogen.

The nitration of cumene has been carried out before by other investigators^{19, 20, 21, 22} but in none of these cases was any description given of the properties of the pure nitro derivatives. The crude product was either reduced direct, or after a partial purification (washing, or steam distillation), to a mixture of amino cumenes.

p-Cumidine was prepared by reduction of *p*-nitrocumene with tin and hydrochloric acid, and was purified by distillation with steam, followed by fractionation at atmospheric pressure; b.p. 222.5° (literature; 217–220°¹⁹, 225°²¹); yield, 77%.

Attempts to produce *p*-cumidine by heating a mixture of aniline, isopropyl alcohol, and zinc chloride under pressure,²³ or by the action of high temperature and pressure upon *N*-isopropylaniline hydrochloride,²⁴ proved much less satisfactory.

Acetyl derivative.—By the action of acetic anhydride upon a solution of *p*-cumidine in dilute acetic acid. White leaflets, from dilute alcohol, m.p. 102.5° (corr.), in agreement with the figure found by other investigators;¹⁹ yield, 92%.

3-Bromo-4-acetamidocumene.—The foregoing acetyl derivative was brominated in glacial acetic acid solution, at 45°, and the crude product was purified by crystallization from water; white leaflets, m.p. 129° (corr.).

¹⁹ CONSTAM AND GOLDSCHMIDT, *Ber.*, **21**, 1158 (1888).

²⁰ CAHOURS, *Compt. rend.*, **26**, 315 (1847).

²¹ NICHOLSON, *Ann.*, **65**, 59 (1849).

²² POSPJECOW, *J. Russ. Phys.-Chem. Soc.*, **18**, 52 (1886).

²³ LOUIS, *Ber.*, **16**, 111 (1883).

²⁴ HOFMANN, *ibid.*, **7**, 527 (1874).

Anal. Calc'd for $C_{11}H_{14}BrNO$: C, 51.56; H, 5.51; Br, 37.34.

Found: C, 51.93; H, 5.78; Br, 37.21.

3-Bromo-4-aminocumene, obtained by refluxing the preceding crude compound for three hours with a mixture of alcohol and concentrated hydrochloric acid, followed by liberation of the free base with caustic alkali, formed a pale-yellow liquid, b.p. 141–143° at 16 mm. pressure; yield, 46%, calculated upon the basis of initial unbrominated acetocumide.

Anal. Calc'd for $C_9H_{12}BrN$: C, 50.47; H, 5.61.

Found: C, 51.04; H, 5.79.

Hydrochloride.—Fine white needles, from water or alcohol, melting at 190–195° (corr.) with decomposition and sublimation.

m-Bromocumene (I).—The amino group was eliminated from the antecedent compound in the customary manner, by digesting the diazonium salt with copper-bronze powder and distilling the resulting mixture with steam. The crude product thus driven over was purified by washing with alkali, to remove phenols, then with concentrated sulfuric acid, followed by water, and finally was distilled at atmospheric pressure. The purified compound formed a colorless clear oil, b.p. 208–210°; yield, 50%.

Anal. Calc'd for $C_9H_{11}Br$: C, 54.23; H, 5.57.

Found: C, 54.50; H, 5.60.

Oxidized by alkaline permanganate, it gave *m*-bromobenzoic acid, m.p. 155° (corr.), in agreement with the literature.²⁵

The *o*-nitrocumene, obtained as a by-product in the nitration of cumene, was reduced to *o*-cumidine (b.p. 220–221°) (Constam and Goldschmidt,¹⁹ 213.5–214.5° at 732 mm.), which was acetylated, and the acetyl derivative was then brominated. The product was probably chiefly the 2-acetamido-5-bromocumene mixed with some of the 3-bromo isomer. For our purpose, it was not necessary to separate these isomers, since both gave only *m*-bromocumene when the acetamido group was eliminated. The *m*-bromocumene prepared in this way was identical with that prepared from the *p*-cumidine, and the overall yield was equally good.

beta-m-Cumylethanol (II), prepared from *m*-bromocumene, ethylene oxide, and magnesium, by the usual Grignard procedure, was fractionated twice with a Widmer column, and a 55% yield of the alcohol was obtained; b.p. 124° at 10 mm. pressure.

Anal. Calc'd for $C_{11}H_{16}O$: C, 80.42; H, 9.83.

Found: C, 80.01, H, 9.92.

3,5-Dinitrobenzoate.—Pale-yellow needles, from dilute alcohol, m.p. 82° (corr.).

Anal. Calc'd for $C_{15}H_{13}N_2O_6$: C, 60.34; H, 5.06.

Found: C, 60.33; H, 5.23.

beta-m-Cumylethylbromide (III), from the alcohol (II) and phosphorus tribromide; yield, 88%; b.p. 120° at 10 mm. pressure.

Anal. Calc'd for $C_{11}H_{15}Br$: C, 57.89; H, 6.60.

Found: C, 57.72; H, 6.59.

2,6-Dimethyl-1-beta-(m-cumylethyl)cyclohexanol (V).—By condensation of the foregoing bromide (III) with 2,6-dimethylcyclohexanone (IV) (synthesized through *alpha, alpha'*-dimethylpimelic acid,^{26, 27}) by the Grignard reaction, and fractionation

²⁵ FRIEDBURG, *Ann.*, **158**, 19 (1871).

²⁶ (a) KIPPING, *J. Chem. Soc.*, **67**, 350 (1895); (b) KIPPING AND EDWARDS, *Proc. Chem. Soc.*, **1896**, 188.

²⁷ ZELINSKY, *Ber.*, **28**, 781 (1895); **30**, 1541 (1897).

of the crude product under diminished pressure, there resulted a 43% yield of the tertiary alcohol (V) sought. It formed a pale-yellowish oil, b.p. 144–146° at 2 mm. pressure, which could not be crystallized, but congealed to a glassy solid at low temperature.

Anal. Calc'd for $C_{15}H_{30}O$: C, 83.14; H, 11.03.

Found: C, 83.50; H, 10.98.

Attempts to prepare from this alcohol either a phenylurethane or a 3,5-dinitrobenzoate, led only to dehydration with formation of the olefin.

12-Methyl-1,2,3,4,9,10,11,12-octahydroretene (VI).—With efficient cooling, 12 g. of the hexanol (V) was stirred into 30 cc. of 85% sulfuric acid; the mixture then washed into a separatory funnel with 30 cc. of petroleum ether, and shaken with separate portions of 85% sulfuric acid until the acid layer was colorless. The petroleum ether layer, which had acquired a bluish fluorescence, was removed, washed with a 10% sodium carbonate solution, then twice with a 10% sodium sulfate solution, after which it was dried over anhydrous sodium sulfate, and distilled under a pressure of 12 mm. Practically the entire product came over at 177–183°, as a clear, viscous oil, with a faint bluish fluorescence, which boiled at 180° when redistilled over sodium at the same pressure (12 mm.), and possessed a refractive index of n_D^{25} 1.5354; yield, 81%. It could not be obtained in crystalline form.

Anal. Calc'd for $C_{15}H_{28}$: C, 88.99; H, 11.01.

Found: C, 88.97; H, 11.01.

Dehydrogenated by fusion with selenium for 6 hrs. at 300°, this hydrocarbon gave a large yield of retene (VII) (m.p. 100°, corr., mixture m.p. 99.5°, corr.), which was identified also by its picrate (m.p. 126°, corr.; mixture m.p. 125.5°, corr.).

Anal. Calc'd for $C_{15}H_{18}$: C, 92.26; H, 7.74.

Found: C, 92.48; H, 7.80.

Anal. of picrate, $C_{15}H_{13}C_6H_3O_7N_3$: N, 9.07. Found: N, 9.41.

No other hydrocarbon could be isolated from this dehydrogenation reaction.

It will be noted that the m.p. (100°) recorded above for our retene, is slightly higher than that usually found for this compound, and agrees more closely with the m.p. (100.5–101°, corr.) reported by Ruzicka and Waldmann¹⁶ for the retene they obtained by the action of palladium charcoal upon abietic acid. Retene, of course, like other phenanthrene derivatives, may exist in different spatial configurations, and this may account for the different melting-points observed for products obtained by different methods.

12-Methylperhydroretene (VIII).—Through the courtesy of Professor Homer Adkins, of the University of Wisconsin, 3 g. of the above octahydro compound (VII), in methylcyclohexane solution, was hydrogenated at 225° and 150 atmospheres pressure, using Raney nickel as the catalyst. The calculated quantity (3 moles) of hydrogen was absorbed in 4 hrs. Distillation of the product, under 12 mm. pressure, yielded 2.5 g. of liquid, b.p. 180–181°. This was rectified over sodium at the same pressure (12 mm.), and the fraction b.p. 179–180° (1.2 g.) used for analysis and various tests. It was a colorless, water-clear, viscous oil, which slowly congealed to a glassy solid, of indefinite m.p., when chilled by a mixture of "dry ice" and methanol. Futile attempts were made to crystallize it from various solvents, by seeding with pure fichtelite. It was unaffected by cold concentrated sulfuric acid, cold neutral or alkaline permanganate, or by bromine in carbon tetrachloride solution. Its physical constants were: b.p. 179–180° at 12 mm.; d_4^{25} 0.9374; n_D^{25} 1.5025; M_D calc'd 83.25, obs. 82.66. It was optically inactive.

Anal. Calc'd for $C_{16}H_{34}$: C, 86.93; H, 13.07.

Found: C, 87.20; H, 13.22.

Vocke²⁸ agitated a partially purified tetrahydroabietic acid (m.p. 175–180°, instead of 190°) with concentrated sulfuric acid at 60°, and collected with petroleum ether some oily drops which he observed floating in the liquid. The petroleum ether extract, after washing and evaporation, left a colorless mobile oil (yield not stated), b.p. 128° at 1 mm., whose analysis agreed with that calculated for C₁₉H₃₄, but concerning which no further information was given except that the major portion of the reaction product was something else.

The Table (page 24) gives the physical constants of fichtelite, of the abietane from the G. and A. Laboratories' crude product, of the Vocke C₁₉H₃₄, and of the 12-methylperhydroretene whose synthesis is described in the foregoing.

SUMMARY

1. 12-Methylperhydroretene has been synthesized from *m*-bromocumene and 2,6-dimethylcyclohexanone as initial materials, and is a colorless clear viscous oil. Hence it is not identical with the fossil resin fichtelite, for which this formula was suggested by Ruzicka and Waldman.

2. It does appear, however, to be identical with a perhydroabietene (abietane) obtained by catalytic hydrogenation of abietene at high temperature and high pressure.

²⁸ VOCKE, *Ann.*, **497**, 257 (1932).