that a particular orientation is no longer necessary for reaction (large $P$).

Table II contains the observed rate constants at 65° for the meta and para acids studied together with the corresponding constants calculated by means of the Hammett equation. The value of $\rho$, 0.422, was obtained by the method of least squares and the values used for $\sigma$ were those reported by Hammett.[13] The average difference between the observed rate constants and those calculated, namely, 0.082, compares favorably with the mean value of probable error in log $k$ of 0.067 found by Hammett for a series of thirty-nine reactions. The higher mean value of probable error obtained for log $k$ in this study is owing chiefly to the high differences obtained for *m*-nitro-, *p*-methoxy- and *p*-ethoxybenzoic acids. The differences of the *p*-methoxy and *p*-ethoxy acids may be related to the fact that they were the least soluble of those studied. It is interesting to note that Hartman and Gassmann[19] found high differences for *p*-methoxy-, *p*-ethoxy- and *p*-fluorobenzoic acids reacting with methanol. The results tabulated in Table II indicate that the Hammett equation might express approximately the effect of substituents on the esterification rate constant of benzoic acid with cyclohexanol.

## Summary

1. Esterification rate constants of twenty-two substituted benzoic acids with cyclohexanol are determined taking into account the reaction between catalyst and solvent.

2. The experimental values of esterification rate constants for meta and para substituents are found to be in close agreement with those predicted by the Hammett equation.

3. For the esterification reactions studied it is observed that the energy of activation increases with the non-exponential factor of the Arrhenius relation and that the data obtained verify the Fairclough–Hinshelwood equation, log $PZ = 1/\sqrt{E}$ + constant.

MIDLAND, MICHIGAN RECEIVED JULY 26, 1944

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[CONTRIBUTION FROM HERCULES EXPERIMENT STATION, HERCULES POWDER COMPANY]

# Vapor-phase Thermal Isomerization of Pinane[1]

BY A. L. RUMMELSBURG

It has been shown[1a,2,3] that $\alpha$-pinene forms the acyclic terpene *allo*-ocimene by controlled vapor-phase thermal isomerization. In addition, the acyclic terpene myrcene can be obtained by a similar isomerization of $\beta$-pinene.[3] The objective of the present work was to determine if a similar fission of the rings can occur by vapor-phase thermal isomerization of pinane (dihydropinene) to form dihydroacyclic terpenes.

## Experimental

**Pinane.**—$\alpha$-Pinene[4] was hydrogenated on a pilot plant scale using Raney nickel catalyst, a temperature of 120°, and hydrogen at a pressure of 75 lb./sq. in. to form pinane. Characteristics: $[\alpha]_D$ + 12°; $n^{20}_D$ 1.4629; $d^{20}_4$ 0.8566; b. p. 168–169° (760 mm.); bromine number 3.[5]

**Apparatus.**—Essential features of the isomerization apparatus were constructed from standard iron pipe (Fig. 1). The reaction tube had a free space of about 890 cc. The temperature within this tube was measured with a movable thermocouple. Liquid pinane was introduced through an attached glass flowmeter. During operation, the temperatures of three points ($T_1$, $T_2$ and $T_3$) within the reaction tube varied from 5 to 10° in the 500° range. This variation was in part caused by fluctuations in line voltage. The flash evaporator was kept at a temperature of about 285°. Preheating of the pinane from 285° to the reaction temperature was not employed, since this did not improve the ease of controlling the temperature within the reaction tube.[2]

**Isomerization of Pinane.**—The pinane was passed into the system at a liquid rate of 1550 cc. per hour. Thus, the contact time was about 5 sec. The maximum decrease in $n^{20}_D$ and $d^{20}_4$ of the isomerization product with increasing temperature occurred within a temperature range of 495–515°. Above these temperatures, and up to about 550–580°, $n^{20}_D$ and $d^{20}_4$ were somewhat greater, probably because of cyclization of acyclic hydrocarbons. The isomerization product obtained at 495–515° had the following characteristics: $n^{20}_D$ 1.4500; $d^{20}_4$ 0.8222; $[\alpha]_D$ +10°. A vacuum distillation indicated that terpene polymers were not present. In separate tests, similar results were obtained using a smaller all-glass pyrolysis system.

**Fractional Distillation of Isomerized Pinane.**—3900 g. of the product formed in the iron pyrolysis tube at 495–515° was distilled at 760 mm. pressure through a Fenske fractionating column having approximately 100 theoretical plates. The column was packed with small metal helices. The product was separated into 20–50 g. fractions. Pertinent physical characteristics of chosen fractions are plotted in Fig. 2. Fractions A, B, C and D are composites of smaller fractions; and their characteristics are described in Table I.

**Catalytic Hydrogenation of Distillation Fractions.**—In order to measure the unsaturation of specific fractions, 0.3000-g. samples were hydrogenated in duplicate at 25–30° in a small laboratory quantitative hydrogenation unit. The catalyst was 0.1000 g. of Adams platinum oxide. Glacial acetic acid was the solvent; and the hydrogen pressure was 760 mm. The quantity of hydrogen absorbed was corrected for blanks which were run simultaneously. The accuracy of this determination is about 1–2%. In order to obtain physical constants of suitable hydrogena-

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[1] Presented before the Division of Organic Chemistry at the 106th Meeting of the American Chemical Society, September, 1943, Pittsburgh, Pennsylvania. Original manuscript received October 8, 1943.

[1a] Arbuzov, *J. Gen. Chem.* (U. S. S. R.), **3**, 21 (1933); *Ber.*, **67B**, 563 (1934).

[2] Author, unpublished work in 1937.

[3] Goldblatt and Palkin, THIS JOURNAL, **63**, 3517 (1941).

[4] Hercules $\alpha$-pinene 111, purity 95%. Characteristics: $[\alpha]_D$ +30°; $n^{20}_D$ 1.4661; $d^{20}_4$ 0.8602; b. p. 156–158° (760 mm.).

[5] The theoretical bromine number of $\alpha$-pinene is 115. However, values greater than theoretical are actually obtained, apparently because of isomerization to monocyclic terpenes containing two double bonds during the determination.

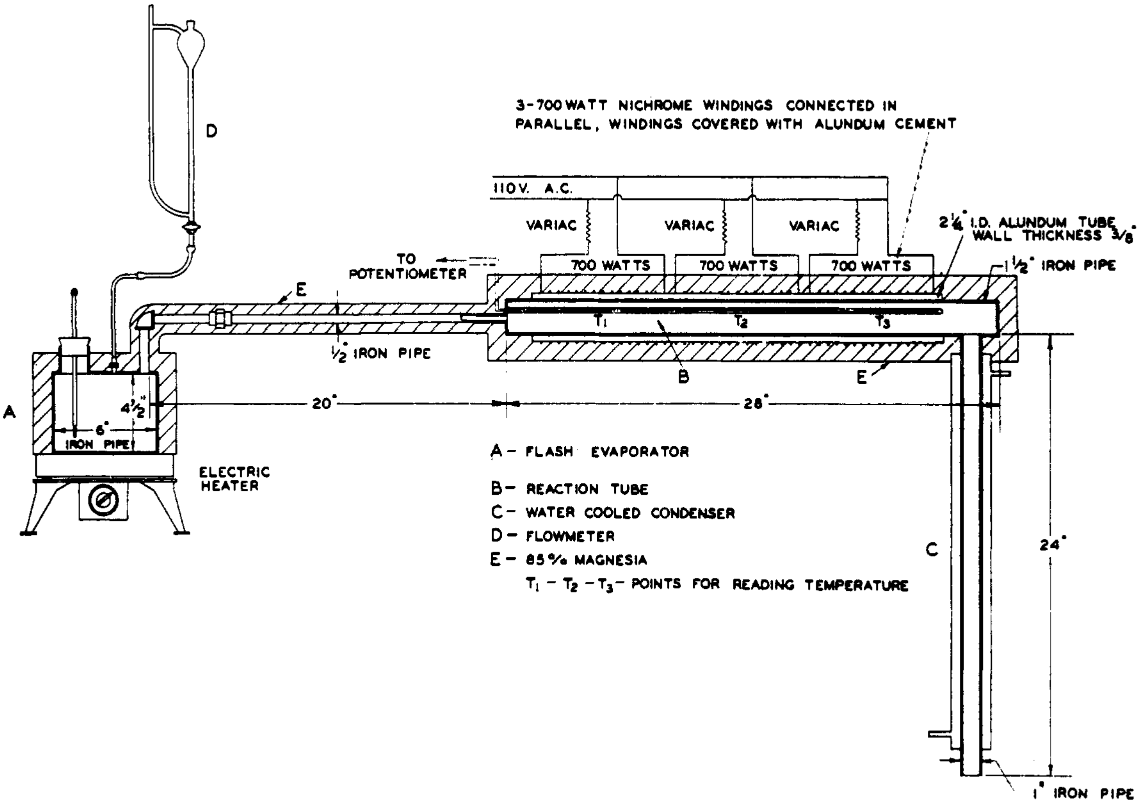

Fig. 1.—Apparatus for thermal isomerization.

tion products, 25–40 g. samples were hydrogenated in a stainless steel bomb (capacity 123 cc.) at 125° until hydrogen absorption ceased. The catalyst was Raney nickel; and the hydrogen pressure was 720–3500 lb./sq. in. The quantity of hydrogen absorbed was measured; however, the accuracy of this measurement was only about 5%. The products were filtered from catalyst, water washed, and dried over Drierite prior to measuring their physical constants. The tetranitromethane test indicated that no appreciable unsaturated material was present. Characteristics of the hydrogenation products are described in Table II.

**Attempts to Prepare Derivatives from Distillation Fractions.**—The dihydroacyclic terpenes (Fraction A) did not yield a crystalline tetrabromide when brominated in ether solution using the procedure previously employed by Goldblatt and Palkin with dihydromyrcene.[6] Furthermore, a crystalline nitrosochloride could not be prepared from this fraction. Nor could crystalline nitrosochlorides be prepared from Fractions B and D which were dihydromonocyclic terpenes.

Fraction A (20 g.) was warmed to 100° with 14.3 g. of maleic anhydride. The lower liquid maleic anhydride layer did not appreciably dissolve, and was only slightly discolored, even after heating the mixture for two hours at 150°. Hence, a Diels–Alder reaction did not occur.

**Preparation of Dihydro- and Tetrahydro-pyronenes.**—The vapor-phase thermal isomerization of α-pinene forms α- and β-pyronenes in addition to *allo*-ocimene.[2,3,7] *allo*-Ocimene is a precursor of the pyronenes[2,8]; hence, the dihydromonocyclic terpene fractions B and D could consist of dihydropyronenes.

A crude mixture of α- and β-pyronenes was prepared by isomerizing α-pinene in accordance with previous work.[2,7] The pyronenes were separated by fractional distillation through a Fenske column packed with metal helices, having approximately 60 theoretical plates. Characteristics: α-

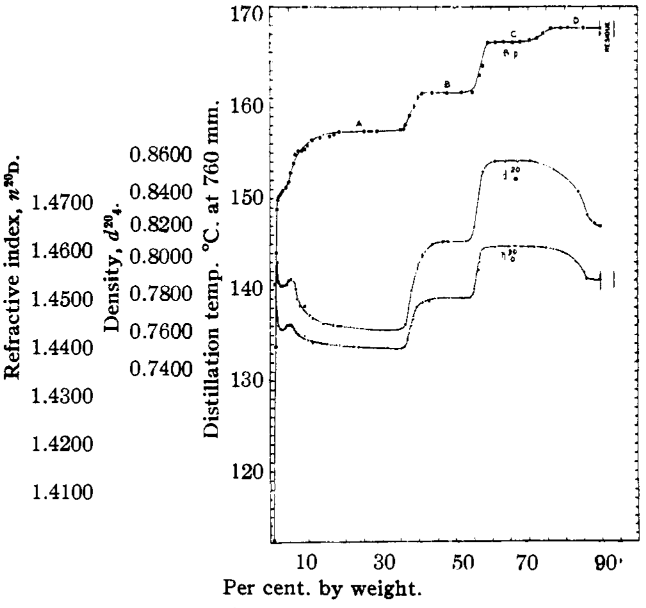

Fig. 2.—Fractional distillation of isomerization product from pinane.

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(6) Goldblatt and Palkin, THIS JOURNAL, **63**, 3522 (1941).

(7) Du Pont and Doulou, *Compt. rend.*, **202**, 1861 (1936).

(8) Goldblatt and Palkin, THIS JOURNAL, **66**, 655 (1944).

TABLE I

CHARACTERISTICS OF ISOMERIZED PINANE FRACTIONS

| Fractionation products Distillation range, %[a] | Distillation temperature, °C. | $H_2$ absorbed, %[b] | $n^{20}D$ | $d^{20}_4$ | Molecular refraction Found | Molecular refraction Calcd. |
|---|---|---|---|---|---|---|
| 2.5–4 | 150.5 | 2.31 | 1.4435 | 0.7875 | ... | ... |
| 9 | 155.3 | 2.35 | .... | .... | ... | ... |
| 22–36 (Fraction A)[c] | 158–159 | 2.75 | 1.4393 | .7636 | 47.61 | 47.44[d] |
| 37 | 159.5 | 2.23 | .... | .... | ... | ... |
| 42–54 (Fraction B) | 161 | 1.39 | 1.4501 | .8121 | 45.72 | 45.71[e] |
| 58–70 (Fraction C)[f] | 167 | 0.02[g] | 1.4612 | .8551 | ... | ... |
| 87–89 (Fraction D) | 168.5 | 1.41[g] | 1.4538 | .8202 | 45.59 | 45.71[e] |
| Comparative dihydroterpenes | | | | | | |
| Dihydro-*allo*-ocimene[h] | 168–170[i] | .. | 1.4560 | .7708 | 48.71 | 47.44[d] |
| Dihydromyrcene[j,k] | 166–168[i] | .. | 1.4489 | .7755 | 47.74 | 47.44[d] |
| Dihydro-α-pyronene[l] | 163[i] | 1.51 | 1.4659 | .855 | 44.74 | 45.71[e] |

[a] By weight of the total. [b] Based on the weight of the sample, using the quantitative laboratory method. Theory 2.92% for $C_{10}H_{18}$ with two double bonds; 1.46% with one double bond. [c] $[\alpha]_D$ +8°. *Anal.* Calcd. for $C_{10}H_{18}$: C, 86.87; H, 13.13. Found: C, 86.79; H, 13.15. [d] $C_{10}H_{18}$ containing two double bonds. [e] $C_{10}H_{18}$ containing one double bond. [f] $[\alpha]_D$ +10°. [g] Using the high pressure method with Raney nickel catalyst. [h] By Arbuzov, *J. Gen. Chem.* (U. S. S. R.), **3**, 28 (1933). [i] B. p. at 760 mm. [j] By Enklaar, *Rec. trav. chim.*, **26**, 166 (1907); **27**, 433 (1908). [k] By Goldblatt and Palkin, ref. 6. [l] Prepared by reducing α-pyronene with sodium.

TABLE II

HYDROGENATED[a] ISOMERIZED PINANE FRACTIONS

| Product | B. p., °C. (760 mm.) | $n^{20}D$ | $d^{20}_4$ | Molecular refraction Found | Molecular refraction Calcd. |
|---|---|---|---|---|---|
| Hydrogenated Fraction A[b] | 160–162 | 1.4158 | 0.7370 | 48.38 | 48.37[c] |
| Hydrogenated Fraction B[d] | 161–162.5 | 1.4370 | .7955 | 46.16 | 46.18[e] |
| Hydrogenated Fraction D[f] | 168–171 | 1.4425 | .8048 | 46.12 | 46.18[e] |
| Comparison hydrocarbons | | | | | |
| 2,6-Dimethyloctane[g,h] | 159 | 1.4101-1.4117 | 0.7274–0.7301 | 48.43 | 48.37[c] |
| 2,4-Dimethyloctane[g] | 158 | 1.4095 | 0.7262 | 48.43 | 48.37[c] |
| 2,3,4-Trimethylheptane[g] | 162 | 1.4219 | .7502 | 48.15 | 48.37[c] |
| 2,3,6-Trimethylheptane[g] | 155 | 1.4130 | .7345 | 48.25 | 48.37[c] |
| *o*, *m*, and *p*-Menthanes[i,j,k] | 168–172 | 1.438–1.447 | 0.795–0.8137 | 46.29–46.02 | 46.18[e] |
| Tetrahydro-α-pyronene[l] | 164–166 | 1.4505 | 0.8291 | 45.47 | 46.18[e] |
| Tetrahydro-β-pyronene[m] | 166–168 | 1.4462 | .8124 | 46.03 | 46.18[e] |

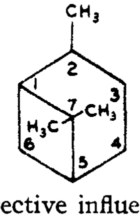
[a] Raney nickel catalyst; high pressure $H_2$. [b] $H_2$ absorbed, 2.76%. [c] $C_{10}H_{22}$. [d] $H_2$ absorbed, 1.51%. [e] $C_{10}H_{20}$. [f] $H_2$ absorbed, 1.41%. [g] Constants calcd. by Francis, *Ind. Eng. Chem.*, **33**, 554 (1941). [h] Arbuzov, *J. Gen. Chem.* (U. S. S. R.), **3**, 28 (1933), by hydrogenating *allo*-ocimene. [i] By Kishner, *Chem. Zentr.*, **83**, **I**, 1713 (1912). [j] By Smirnov, *Chem. Zentr.*, 81, i, 780 (1910). [k] By Sabatier and Murst, *Compt. rend.*, **156**, 186 (1913). [l] $H_2$ absorbed by α-pyronene during this preparation, 3.1%; theory, 2.96% for $C_{10}H_{16}$ containing two double bonds. [m] $H_2$ absorbed by β-pyronene during this preparation, 2.85%.

pyronene, distilled at 158–159° (760 mm.), $n^{20}D$ 1.4707, $d^{20}_4$ 0.8469; β-pyronene, distilled at 166–166.5° (760 mm.), $n^{20}D$ 1.4787, $d^{20}_4$ 0.8437.

α- and β-pyronenes (27 g.) in alcohol solutions were reduced with sodium using a procedure previously applied to myrcene to prepare dihydromyrcene.[6] Only α-pyronene yielded a dihydropyronene. The α- and β-pyronenes were also hydrogenated using the previously described procedure with Raney nickel catalyst and high pressure hydrogen. The resulting tetrahydropyronenes did not contain appreciable unsaturated material according to the tetranitromethane test. Constants of the dihydro- and tetrahydropyronenes are listed in Tables I and II.

## Discussion

Fraction A (Table I) of the pinane isomerization product consists of dihydroacyclic terpenes, as is indicated by its physical constants and degree of hydrogen absorption. The formation of *allo*-ocimene and myrcene from α- and β-pinenes, respectively, involves the rupture of the $C_1$-$C_7$ and $C_5$-$C_6$ bonds in the cyclobutane ring. Rupture of the same bonds in pinane (I) would yield the dihydroacyclic terpene, 2,6-dimethyloctadiene. However, in the case of pinane, the ab-



(I)

sence of the directive influence of a double bond can be expected to increase the number of fission possibilities in the cyclobutane ring. For example, rupture of the $C_1$–$C_6$ and $C_5$–$C_7$ bonds in pinane would yield other dihydroacyclic terpenes, 2,4-dimethyloctadienes. Furthermore, rupture of the $C_5$–$C_6$ and $C_5$–$C_7$ or the $C_1$–$C_6$ and $C_1$–$C_7$ bonds in pinane would yield still other dihydroacyclic terpenes, 2,3,4- and 2,3,6-trimethylheptadienes.

The physical constants of the dihydroacyclic terpenes from pinane (Fraction A) differ from those of dihydro-*allo*-ocimene and dihydromyrcene (Table I). In addition, the refractive index and density of the completely hydrogenated Fraction A are somewhat greater than those of 2,6-dimethyloctane, the hydrogenation product of both *allo*-ocimene and myrcene (Table II). This increase could be caused by the presence of hydrocarbons having a relatively more compact structure, probably trimethylheptanes. Accordingly, the dihydroacyclic terpenes resulting from the isomerization of pinane are apparently mixtures of dimethyloctadienes and trimethylheptadienes. Since the mixture does not react with maleic anhydride, appreciable conjugation is not present.

Fractions B and D consist of dihydromonocyclic terpenes. Fraction B could not be a dihydropyronene, since the physical constants of its hydrogenation product are dissimilar to those of tetrahydro-α- and β-pyronenes (Table II). By comparing the physical constants of the hydrogenation product of Fraction D with those of the tetrahydropyronenes and menthanes, it is apparent that Fraction D could consist of mixtures of dihydromonocyclic terpenes, probably mostly menthenes.

Fraction C is saturated, and its physical constants (Table I) indicate that it is unchanged pinane.

## Summary

Vapor-phase thermal isomerization of pinane at temperatures of 495–515°, and a contact time of about five seconds has been carried out, in order to determine whether dihydroacyclic terpenes are formed.

About 30–40% of dihydroacyclic terpenes are formed by the isomerization. In addition, about 20–40% of dihydromonocyclic terpenes, probably including some menthenes are formed. The remainder of the identified material (20–30%) in the reaction mixture is unchanged pinane.

WILMINGTON, DEL. RECEIVED JULY 28, 1944

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[CONTRIBUTION FROM STARCH AND DEXTROSE DIVISION, NORTHERN REGIONAL RESEARCH LABORATORY,[1] PEORIA, ILLINOIS]

# Extraction of Fatty Substance from Starch

BY ROY L. WHISTLER AND G. E. HILBERT

Considerable importance has been attached to the "fatty" constituents in starch. Fatty material interferes with the fractionation of starch[1a] into amylose and amylopectin and is responsible, at least in part, for the initial flocculent precipitate (starch, hemicellulose, amylocellulose, γ-amylose, etc.) which forms when cereal starch solutions are treated with amylases.[2] Many other properties of cereal starch pastes, such as their opacity, viscosity, gelling power, retrogradation rate, and iodine absorption capacity are affected by fats.

Before the modifying influence of native fatty material can be fully determined for corn starch, it is necessary to understand the type of combination which exists between the fatty substance and the starch. Considerably different effects would be expected if the fat were bound by primary valence bonds than if it were bound by secondary valence forces.

That the fatty material of cereal starches is not removed by a typical fat solvent, such as ether or carbon tetrachloride, has been known for some time. This, in part, caused Taylor and coworkers[3] to believe that the fatty acids are present as esters of starch, the esters being associated with the *a*-amylose fraction. Schoch[4] has shown that the fatty substance of cereal starches can be largely removed by extraction with neutral hydrophilic solvents such as methanol and aqueous dioxane. Such extraction reduces the fat content of corn starch to about 0.1 to 0.2%. These results were interpreted by Schoch as indicating that most of the fat is combined mechanically with the starch. The fact that palmitic acid is strongly adsorbed by starch has been shown by Lehrman.[5] The adsorption follows a typical Freundlich isotherm and the fatty acid is not removed by extraction with carbon tetrachloride. It is interesting to note that, according to Lehrman's results, the adsorption of palmitic acid by potato, corn, and rice starches is roughly proportional to their surface areas rather than to their original content of fatty acid. Although the evidence is strong that most of the fatty acid in starch is held by forces other than primary valence bonds, the nature of the combination of the residual non-extracted fat with starch is less well known.

Information on this point was obtained from experiments dealing with the extraction of intact and of disintegrated corn starch granules with methanol. The rate of removal of fatty material from raw, intact corn starch granules by Soxhlet extraction with methanol was determined and

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[1] This is one of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

[1a] Schoch, THIS JOURNAL, **64**, 2957 (1942).

[2] Wilson, Schoch and Hudson, *ibid.*, **65**, 1380 (1943).

[3] Taylor and Nelson, THIS JOURNAL, **42**, 1726 (1920); Taylor and Iddles, *Ind. Eng. Chem.*, **18**, 713 (1926); Taylor and Werntz, THIS JOURNAL, **49**, 1584 (1927); Taylor and Walton, *ibid.*, **51**, 3431 (1929); Taylor and Sherman, *ibid.*, **55**, 2584 (1933).

[4] Schoch, *ibid.*, **64**, 2954 (1942); see also Kerr, *Cereal Chem.*, **20**, 299 (1943). Evans and Briggs, *ibid.*, **18**, 443 (1941).

[5] Lehrman, THIS JOURNAL, **64**, 2144 (1942); **61**, 212 (1939).