

### Some Observations on the C-Methyl Determination

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Although the Kuhn-Roth C-methyl determination<sup>2</sup> and its various modifications<sup>3</sup> have been used extensively for structure proof, there have been some doubts expressed as to its value when applied to compounds containing several C-methyl groups and particularly to those containing *gem*-methyl groups.<sup>4</sup> Our interest in the determination arose in connection with a continuation of an earlier investigation of the structure of nepetalic acid, the principal constituent of oil of catnip. Mainly on the basis of the C-methyl values of this acid and certain of its degradation products it had been concluded in the earlier work that these compounds contained a methylcyclopentane nucleus.<sup>5</sup> However, this evidence, from what then was known, did not rigorously exclude a *gem*-dimethylcyclobutane structure.

It seemed that the C-methyl determination might be more informative if it were considered in conjunction with the amount of oxidizing agent ( $\text{Cr}_2\text{O}_7^{=}$ ) that was actually consumed by the compound during the determination. From this value it should be apparent whether sufficient oxidation had occurred to convert the compound completely to the steam-volatile acetic acid, carbon dioxide and water or if the oxidation had stopped at some intermediate stage with the formation of stable, non-volatile acidic products, *e.g.*, dibasic acids.

Table I summarizes the found C-methyl values, the corresponding amounts of oxidizing agent consumed in the reaction, and that required for conversion of the various compounds to the degradation products indicated in the footnotes to the table. It is readily apparent from the last column of the table that there is a great variation in the amounts of oxidizing agent consumed in the oxidation of the compounds listed. The monobasic saturated acids (no. 1-13) each give nearly an equivalent of titratable acid (C-methyl number), but in certain cases (no. 1, 2, 12 and 13) very little if any oxidation occurs. Obviously, the C-methyl number of these acids results from titration of the unchanged acids.

The dibasic acids no. 17-21, while having no C-methyl value, show a noteworthy difference in their resistance to the oxidizing agent. Malonic acid (no. 18) is apparently completely oxidized before it is decarboxylated to any of the stable acetic acid. The stability of succinic acid (no. 19), and to a lesser extent of glutaric and adipic acids (no. 20 and 21), to the oxidizing agent indicate that these

acids as well as acetic acid may be the end products in the oxidation of compounds of higher carbon content (*cf.* the values for no. 23-26). The ethyl groups of no. 27, however, are converted in quite high yield to acetic acid.

The *gem*-methyl groups of the isopropylidene structure of no. 15 and 52 are converted to one equivalent of acetic acid *via* oxidation to acetone (*cf.* the values for the acetone derivatives, no. 48 and 49); the same appears to be approximately true for the *gem*-methyls of the isopropyl groups of no. 10, 11 and 51. The dibasic acids with *gem*-methyl substituents (no. 28-30) are remarkably stable to oxidation and for this reason show no significant C-methyl values. Consequently, the observed C-methyl values of the *gem*-methyl compounds no. 31-35 may be readily rationalized (see appropriate footnotes to table). The structure of the acid, no. 31, which was recently proved<sup>6</sup> by other means, has now been confirmed by the isolation of  $\alpha,\alpha$ -dimethylsuccinic acid (66%) from the oxidation of its methyl ester under the conditions of the C-methyl determination. The values for hydroxypivalic acid (no. 37) indicate that it is partially oxidized to the stable dimethylmalonic acid and partially decarboxylated at the aldehyde stage to isobutyraldehyde which then shows the oxidation behavior of isobutyric acid (no. 10). Similar interpretations may be placed on the data for no. 36, 38 and 39.

The benzilidene derivative no. 44 yields benzoic acid together with some acetic acid on oxidation. This is in contrast to the corresponding anisylidene derivative no. 43, which gives a low yield of volatile acid and a high consumption of oxidizing agent because of the relatively unstable aromatic nucleus. The data for acetophenone (no. 47) also indicate that benzoic acid is the volatile acidic product. The values obtained for this acid (no. 66) show that it is quite resistant to the oxidizing agent. The other compounds containing an angular methyl group (no. 40, 41, 42, 45 and 46) give approximately one-half of the calculated amount of acetic acid.

It is seen from no. 48, 49, 50, 52 and 53 that satisfactory C-methyl values may be obtained from these hydrazine derivatives of ketones. The amounts of oxidizing agent consumed for no. 68 and 69 were the basis for the calculation of the chromium values for the ketone derivatives. It is noteworthy that no titratable acid appears from the hydrochlorides no. 67 and 68, and in the case of the former no oxidizing agent was consumed. A similar observation was made with alanine hydrochloride, which gives the same C-methyl number (0.84) as does the free amino acid alanine.

A comparison of the results obtained with nepetalic acid derivatives (no. 54-60) with those from the *gem*-dimethylcyclobutane derivatives,  $\beta$ -caryophyllene<sup>7</sup> and its oxide<sup>7</sup> (no. 34 and 35) definitely shows the validity of the earlier conclusion that nepetalic acid contains a methylcyclopentane nucleus.<sup>5</sup>

(1) S. M. McElvain and C. L. Aldridge, *ibid.*, **75**, 3987 (1953).

(7) We are indebted to Professor D. H. R. Barton, Birkbeck College, University of London, England, for generous samples of these compounds.

(1) (a) Wisconsin Alumni Research Foundation Research Assistant (1952-); (b) Rohm and Haas, Philadelphia, Pa.

(2) (a) R. Kuhn, *et al.*, *Ber.*, **66**, 1274 (1933); (b) *Z. angew. Chem.*, **44**, 847 (1931); (c) F. Pregl, "Quantitative Organic Microanalysis," 3rd. ed., P. Blakiston's Son and Co., Inc., Philadelphia, Pa., 1937, p. 201.

(3) (a) L. G. Ginger, *J. Biol. Chem.*, **156**, 453 (1944); (b) W. F. Barthel and F. B. LaForge, *Ind. Eng. Chem., Anal. Ed.*, **16**, 434 (1944).

(4) (a) A. D. Campbell, *et al.*, *J. Chem. Soc.*, 1693 (1952); (b) 1942 (1953); (c) W. G. Dauben, *et al.*, *THIS JOURNAL*, **74**, 4321 (1952).

(5) S. M. McElvain, *et al.*, *ibid.*, **63**, 1558 (1941).

TABLE I  
C-METHYL NUMBERS AND DICHROMATE CONSUMPTION

No.	Name of compound	C-Methyl number	Moles Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> consumed	Moles Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> reqd. <sup>a</sup>	% of reqd. consumed
1	Acetic acid (as sodium acetate)	0.99	0.02	1.33 <sup>b</sup>	1.5
2	Propionic acid	.97	0.11	1.00	11.0
3	Butyric acid	.93	1.07	2.00	53.5
4	Valeric acid	.94	2.33	3.00	77.7
5	Caproic acid	.90	1.86	4.00	46.4
6	Heptanoic acid	.86	2.16	5.00	43.3
7	Caprylic acid	.91	2.35	6.00	39.2
8	Pelargonic acid	.76	2.92	7.00	41.7
9	Capric acid	.87	3.30	8.00	41.2
10	Isobutyric acid	.91	1.54	2.00	77.0
11	Isovaleric acid	.87	2.45	3.00	81.7
12	Pivalic acid	.89	0.03	3.00	1.0
13	<i>t</i> -Butylacetic acid	.99	0.03	4.00	0.8
14	Crotonic acid, m.p. 72°	.94	1.67	1.67	100.0
15	$\beta,\beta$ -Dimethylacrylic acid <sup>c</sup>	.97	2.56	2.67	95.7
16	<i>cis</i> -4,5-Dimethyl- $\Delta^4$ -tetrahydrophthalic acid	1.69	5.04	5.00	100.5
17	Oxalic acid	0.00	0.32	0.33 <sup>b</sup>	97.1
18	Malonic acid	.00	1.40	1.33 <sup>b</sup>	105.2
19	Succinic acid	.00	0.09	2.33 <sup>b</sup>	3.9
20	Glutaric acid	.01	0.34	3.33 <sup>b</sup>	10.2
21	Adipic acid	.00	1.24	4.33 <sup>b</sup>	28.6
22	Methylmalonic acid	.89	0.67	1.00	67.0
23	Methylsuccinic acid	.33	0.89	2.00	44.5
24	$\alpha$ -Methylglutaric acid	.39	1.54	3.00	51.4
25	$\beta$ -Methylglutaric acid	.38	1.82	3.00	60.7
26	$\beta$ -Methyladipic acid	.28	1.95	4.00	48.7
27	$\alpha,\alpha'$ -Diethyladipic acid	1.47	3.12	3.33 <sup>j</sup>	93.6
28	Dimethylmalonic acid	0.10	0.20	2.00	10.0
29	$\alpha,\alpha$ -Dimethylsuccinic acid	.08	.04	3.00	1.3
30	$\beta,\beta$ -Dimethylglutaric acid	.01	.06	4.00	1.5
31	$\alpha,\alpha$ -Dimethyl- $\alpha'$ -methylene-glutaric acid	.10	1.73	1.67 <sup>c</sup>	103.5
32	1,1-Dimethylcyclohexanedione-3,5	.06	1.89	1.33 <sup>d</sup>	142.1
33	Isophorone semicarbazone	.46	3.57	3.00 <sup>e</sup>	119.0
34	$\beta$ -Caryophyllene	.77	5.94	6.00 <sup>f</sup>	99.0
35	$\beta$ -Caryophyllene oxide	.63	5.52	5.67 <sup>f</sup>	97.2
36	1,1-Dimethyl-2-cyclohexene-6-one semicarbazone	0.72	4.32	4.00 <sup>g</sup>	108.0
37	Hydroxypivalic acid	0.55	1.52	2.67	60.7
38	$\alpha,\alpha$ -Dimethylacetoacetamide	1.24	1.74	2.00 <sup>h</sup>	87.0
39	Ethyl $\alpha,\alpha$ -dimethylacetoacetate	2.21	2.08	2.67	77.9
40	<i>trans</i> -1-Methylcyclopentane-1,2-dicarboxylic acid	0.58	3.57	4.67	76.5
41	<i>cis</i> -9-Methyldecalone-1 semicarbazone	.56	4.64	4.67 <sup>i</sup>	99.2
42	<i>trans</i> -9-Methyldecalone-1-semicarbazone	.43	4.68	4.67 <sup>i</sup>	100.1
43	<i>cis</i> -9-Methyl-2-anisylidene-decalone-1	.34	10.70	12.33 <sup>j</sup>	86.6
44	<i>cis</i> -9-Methyl-2-benzylidene-decalone-1	1.04	6.32	6.67 <sup>k</sup>	94.8
45	<i>dl</i> -Equiselinin methyl ether	0.52	12.27	14.00	87.6
46	<i>dl</i> -Isoequilenin methyl ether	.46	11.65	14.00	83.3
47	Acetophenone <sup>l</sup>	.88	1.79	1.33 <sup>l</sup>	134.5
48	Acetone semicarbazone	.96	1.80	2.00 <sup>m</sup>	90.0
49	Acetone 2,4-dinitrophenylhydrazone	.98	5.99	6.67 <sup>n</sup>	89.9
50	Methyl ethyl ketone semicarbazone	1.84	1.69	1.67 <sup>m</sup>	101.2
51	Methyl isopropyl ketone	1.75	1.66	2.00	83.0
52	Mesityl oxide semicarbazone	1.98	3.17	3.33 <sup>m</sup>	95.2
53	1-Acetylcyclohexene semicarbazone	0.91	2.87	4.00 <sup>o</sup>	71.7
54	Nepetalic acid semicarbazone	1.20	4.44	6.33 <sup>m</sup>	70.1
55	Nepetalic anhydride	2.55	8.66	11.33	76.5
56	Nepetalinic acid, m.p. 85°	1.21	3.61	5.33	67.7
57	<i>trans</i> -Nepetic acid, m.p. 118°	0.79	4.14	4.67	88.7
58	<i>cis</i> -Nepetic acid, m.p. 132°	0.71	4.25	4.67	91.0
59	Nepetonic acid, 2,4-dinitrophenylhydrazone	1.54	9.12	10.00 <sup>n</sup>	91.2
60	Ethyl nepetonate 2,4-dinitrophenylhydrazone	2.42	9.92	10.67 <sup>n</sup>	93.0
61	<i>s</i> -Butyl alcohol	1.81	1.38	1.33	103.8

62	<i>t</i> -Butyl alcohol	0.93	2.32	2.67	86.8
63	Methyl acetoacetate semicarbazone	.97	3.02	3.00 <sup>m</sup>	100.1
64	Cyclopentanecarboxamide	.00	2.62	2.67 <sup>o</sup>	98.2
65	Hexahydrobenzamide	.00	2.35	2.67 <sup>p</sup>	88.0
66	Benzoic acid	.73	1.27	5.00 <sup>b</sup>	25.4
67	Ammonium chloride	.00	0.00	....	....
68	Semicarbazide hydrochloride	.00	0.57	0.67 <sup>q</sup>	85.0
69	2,4-Dinitrophenylhydrazone	.00	4.16	5.33 <sup>r</sup>	78.1

<sup>a</sup> Based on the assumption that the compound is oxidized to acetic acid, carbon dioxide and water except for the following cases: <sup>b</sup> complete oxidation to carbon dioxide and water, <sup>c</sup>  $\alpha,\alpha$ -dimethylsuccinic acid, carbon dioxide and water, <sup>d</sup>  $\beta,\beta$ -dimethylglutaric acid, carbon dioxide and water, <sup>e</sup> acetic acid,  $\alpha,\alpha$ -dimethylsuccinic acid, carbon dioxide, water, ammonia and nitrogen, <sup>f</sup> acetic acid,  $\alpha,\alpha$ -dimethylsuccinic acid, succinic acid, carbon dioxide and water, <sup>g</sup> acetic acid, succinic acid, carbon dioxide, water, ammonia and nitrogen, <sup>h</sup> acetic acid, carbon dioxide, water and ammonia, <sup>i</sup> acetic acid, two moles of succinic acid, carbon dioxide, water, ammonia and nitrogen, <sup>j</sup> acetic acid, succinic acid, carbon dioxide and water, <sup>k</sup> acetic acid, benzoic acid, succinic acid, carbon dioxide and water, <sup>l</sup> benzoic acid, carbon dioxide and water, <sup>m</sup> acetic acid, carbon dioxide, water, ammonia and nitrogen, <sup>n</sup> acetic acid, carbon dioxide, water, nitric acid and nitrogen, <sup>o</sup> succinic acid, carbon dioxide, ammonia and water, <sup>p</sup> glutaric acid, carbon dioxide, ammonia and water, <sup>q</sup> carbon dioxide, water, ammonia and nitrogen, <sup>r</sup> carbon dioxide, water, nitric acid and nitrogen, <sup>s</sup>  $\beta,\beta$ -dimethylacrylic acid was previously reported (ref. 2a) to give 0.26 and 0.22 mole of acetic acid, <sup>t</sup> acetophenone was previously reported (ref. 2b and c) to give 0.1 mole of acetic acid.

#### Experimental

**Apparatus.**—The 3-piece apparatus of Barthel and LaForge<sup>3b</sup> was modified to a 5-piece apparatus with ground glass joints. The reaction flask was a 50-ml. long neck (over-all length 20 cm.) flask fitted with a cold finger which extended to the bulb of the flask and served as a reflux condenser during the oxidation. When this reaction was completed the cold finger was replaced by a still head carrying a removable steam inlet tube which was made by extending a 19/38 inner joint with 7 mm. tubing to a length that reached to within 4 mm. of the bottom of the reaction flask. The side arm of the still head was attached just below the outer joint that carried the steam inlet tube and extended upward at an angle of 45° for a length of 20 cm. The central portion of this extension was enlarged to a 35 mm. diameter for a length of 7 cm. and had a square glass baffle, whose diagonal equaled the inner diameter of the enlargement, sealed across the path of the steam vapors. The still head side arm was curved downward to attach by a ball joint to an upright coil condenser with a 12-cm. cooling coil. For the steam distillation a 1-l. three-necked flask was fitted with a 30-ohm heating coil of No. 20 B and S gage oxide coated nichrome wire fastened at each end to 1/4" brass bolts passed through rubber stoppers in the side arms and then connected to a Variac outlet. The center neck of the steam flask was attached to a modified 125-ml. claisen flask which served as a condensation trap.

**Procedure.**—Exactly 5 ml. of the oxidizing solution, prepared by the addition of 250 ml. of sulfuric acid (sp. gr. 1.84) to a solution of 168 g. chromic anhydride (CrO<sub>3</sub>) in 1000 ml. of distilled water,<sup>2a</sup> was pipetted into the reaction flask containing the weighed sample (10–20 mg.). The cold finger was inserted in the flask and the reaction mixture heated in an oil-bath held at 130° for 1.5 hr. After this time the reaction mixture was cooled slightly, the cold finger rinsed with a minimum of distilled water, 7 g. of anhydrous magnesium sulfate<sup>3b</sup> added, and the cold finger replaced by the still head. The flask was returned to the oil-bath and the reaction mixture steam distilled until 50 ml. of distillate had been collected.<sup>8</sup> The distillate was titrated from a microburet with 0.05 *N* sodium hydroxide to the phenolphthalein end-point. The C-methyl number was calculated as the moles of titratable acid per mole of the compound used.

(8) In three runs using 20.2, 12.2 and 31.1 mg. of sodium acetate and collecting the distillate in 5-ml. increments, it was found that 98% of the acetic acid appeared in the first 30–35 ml. of distillate.

The solution remaining in the reaction flask after the steam distillation was washed into a volumetric flask and diluted to 1 l. The amount of dichromate anion remaining in this solution was determined on a 50-ml. aliquot by the procedure of Kolthoff and Sandell.<sup>9</sup> The difference between the dichromate value so obtained and that obtained from 5.00 ml. of the original chromic acid oxidizing mixture, which had been carried through the entire procedure but without the addition of any organic material, gave the values of  $\text{Cr}_2\text{O}_7^{2-}$  consumed that are recorded in the table.

(9) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd ed., The Macmillan Co., New York, N. Y., 1952, p. 594.

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### $\beta$ -Propiolactone. XV. Use in the Diene Synthesis

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$\beta$ -Propiolactone may be used in place of acrylic acid as the dienophile component in the Diels-Alder diene synthesis. Cyclohexene-4-carboxylic acid (from butadiene) and the corresponding substituted adducts from isoprene and cyclopentadiene have thus been prepared in excellent yield.

A catalyst (potassium carbonate) known to aid polymerization of the lactone to a polyester and assist in the pyrolysis of the latter to acrylic acid,<sup>1</sup> was used to accelerate the reaction. In the absence of such a catalyst a major portion of the lactone was recovered as its polymer (polyester), as evidenced by the formation of acrylic acid during distillation of the crude reaction product.

#### Experimental

**Butadiene and  $\beta$ -Propiolactone.**—Following is one set of conditions which gave the optimum yield. In a chilled 2900-ml. stainless steel autoclave were placed 576 g. of  $\beta$ -propiolactone (97% purity, 7.75 moles), 500 g. of butadiene (9.25 moles), 6 g. of potassium carbonate and 2 g. of hydroquinone. The mixture was heated to 200°; exothermic reactions took place at about 100° and 200°, raising the temperature to 270° for a short time. The temperature was maintained at 200° for 1.5 hours. The crude reaction product was distilled; 937 g. of cyclohexene-4-carboxylic acid (96% of theory, based on the  $\beta$ -propiolactone content of the starting material) was obtained, b.p. 126° (16 mm.). The product was identical in every respect with that produced by reaction of acrylic acid and butadiene.<sup>2</sup>

**Isoprene and  $\beta$ -Propiolactone.**—Potassium carbonate, 5 g., and 1 g. of hydroquinone were heated to 170° in a 2900-ml. stainless steel autoclave. A mixture of 432 g. of  $\beta$ -propiolactone (97% purity, 5.82 moles) and 476 g. (7.0 moles) of isoprene was pumped in. The temperature rose to 205° and was maintained there during the addition, which took one hour. The resulting reaction mixture, on distillation, gave 750 g. of a mixture of methylcyclohexene-carboxylic acids,<sup>3</sup> b.p. 93° (0.9 mm.), 129° (10 mm.), m.p. 75–90° (lit.<sup>4</sup> 97–98° for a single acid, after recrystallization).

*Anal.* Calcd. for  $\text{C}_8\text{H}_{12}\text{O}_2$ : neut. equiv., 140.2. Found: neut. equiv., 141.9.

(1) T. L. Gresham, J. E. Jansen and F. W. Shaver, *THIS JOURNAL*, **70**, 998 (1948).

(2) F. X. Werber, J. E. Jansen and T. L. Gresham, *ibid.*, **74**, 532 (1952).

(3) J. S. Meek and co-workers (Abstracts, 115th American Chemical Society Meeting, San Francisco, Calif., 1949, p. 59L) state that the reaction of acrylic acid with isoprene gives "predominantly" the para isomer (1-methylcyclohexene-4-carboxylic acid).

(4) French Patent 672,025, to Société M. Naef & Cie. (C. A., **24**, 2213 (1930)).

**Dicyclopentadiene and  $\beta$ -Propiolactone.**—A mixture of 241 g. of  $\beta$ -propiolactone (97% purity, 3.25 moles) and 300 g. of dicyclopentadiene (technical) were pumped into a 1-l. stainless steel bomb at 180° and containing 5 g. of potassium carbonate and 7 g. of hydroquinone. The temperature was maintained at 170–180° for a total of 1.25 hours, including the addition period. The crude reaction product was distilled. About 23% of the dicyclopentadiene was recovered; 415.3 g. of 3,6-endomethylenecyclohexene-4-carboxylic acid (92.5% of theory, based on  $\beta$ -propiolactone) was recovered. It boiled at 120.5–121.5° (10 mm.) (lit.<sup>5</sup> 132–134° (22 mm.)),  $n_D^{25}$  1.4955.

*Anal.* Calcd. for  $\text{C}_8\text{H}_{10}\text{O}_2$ : neut. equiv., 138.2. Found: neut. equiv., 144.1.

**Acknowledgment.**—The authors wish to thank Mr. Harry Davis and associates for carrying out the pressure reactions.

(5) O. Diels and K. Alder, *Ann.*, **460**, 98 (1928).

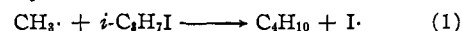
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### Free Radical Displacement Reactions

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A study of the system, methyl-isopropyl iodide-helium at 8–9 mm. and 300–330° has demonstrated the relatively small contribution of the reaction



either in the gas phase or as a heterogeneous reaction. Although the above was the reaction sought, the extraction of hydrogen or iodine atoms by the methyl radical was believed to be the favored reaction in view of the probable activation energy of (1) associated with inversion of the iodide. Methyl radicals were produced by the reaction of sodium vapor and methyl bromide in a modification of the Polanyi "sodium flame" technique.<sup>1</sup> The radicals thus formed were transported at high velocity on a helium stream into a reactor section where they came in contact with isopropyl iodide. The reactor section contained silver gauze, which served as a means of detection for any iodine displaced according to reaction 1.

#### Experimental

A helium stream was saturated with sodium in a heated Pyrex U-tube and then introduced through a 1-mm. jet into the preheater consisting of a 6" section of 25-mm. Pyrex tubing. In the preheater the sodium reacted with methyl bromide, carried on a second helium stream, to form methyl radicals and sodium bromide with the emission of the characteristic yellow sodium radiation when the mixing zone was illuminated with a sodium resonance lamp. The radicals thus generated were carried very rapidly through a jet of 2 mm. diameter into the reactor zone. The high gas velocities prevailing in the jets prevented backmixing. Depending on the experiment, an additional helium stream brought either isopropyl iodide or iodine into the reactor. In the preliminary experiments iodine was employed as a means of identifying methyl radicals by the formation of methyl iodide. In the investigation of the displacement reaction itself the iodine was replaced with isopropyl iodide. The reactor itself consisted of a 5.5" length of 25-mm. Pyrex tubing electrically wound. After being treated with acid and sulfide, silver gauze was placed in the reactor to detect any displaced iodine. Deposits on the gauze were subsequently analyzed for iodine polarographically, after the io-

(1) E. Horn, M. Polanyi and D. W. G. Style, *Trans. Faraday Soc.*, **30**, 189 (1934).