[CONTRIBUTION FROM THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Solvent Fractionation of Polycarboxylic Acids from Oxidation of Coal

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RECEIVED DECEMBER 18, 1951

Isolation of individual components from the mixture of water-soluble, polycarboxylic, aromatic acids obtained by oxidation of coal has hitherto been effected by esterification followed by vacuum fractional distillation of the esters. It has been found that separations of the acids can be made directly on the basis of molecular weight, by the solvent pair ether–pentane and on the basis of structure by acetone-benzene mixtures. The acid mixture studied was found to consist of approximately one-third benzenecarboxylic acids, one-third in the molecular weight range 200–250, with nuclei of 2 or 3 rings and the balance with molecular weights 250–450, with larger polycyclic nuclei. Of the benzenecarboxylic acids, trimellitic predominated. *o*-Phthalic, isophthalic, pyromellitic, prehnitic (1,2,3,4) and benzenepentacarboxylic acids were also isolated and characterized.

The oxidation of bituminous coals to a mixture of organic acids is readily effected in alkaline media either by chemical oxidants, such as permanganate,[2] or by the action of oxygen gas at elevated temperatures and pressures.[3,4] Acids of the benzenecarboxylic series have been isolated from the mixtures and it has also been shown that there are present significant amounts of acids with polycyclic nuclei. The benzenecarboxylic acids have been isolated and identified by conversion of the mixed acids to methyl esters, fractionation of the esters and crystallization of individual esters from the fractions.[2] The fraction of the carbon of the original coal accounted for by the actual recovery of authentic compounds by this method has, however, been low. The procedure is particularly unsatisfactory for the isolation of trimellitic acid, the 1,2,4-benzenetricarboxylic acid, since the methyl ester is not crystalline and it is necessary to fractionate the esters, saponify the ester fraction boiling in the proper range, separate the trimellitic acid by crystallization and finally purify it by conversion to the anhydride.

The purpose of the present study was to investigate the use of solvent methods of fractionating the mixture of the free acids and isolating individual components to obtain more knowledge as to the amounts of each present.

Discussion

The acids used in this study were obtained by the oxidation of an aqueous alkaline suspension of a Pocahontas No. 3 coal, by gaseous oxygen at 270° and total pressures of about 900 p.s.i.g. (61.2 atm.).[4] In the reaction approximately 50% of the carbon of the coal was converted to carbon dioxide and the balance to water-soluble, organic acids which were recovered, after acidification of the solution with sulfuric acid, by extraction with methyl ethyl ketone. The mixed acids, after vacuum drying, constitute a hygroscopic, friable, yellowish brown mass. The mixture is nearly completely soluble in oxygenated solvents such as water and the lower boiling alcohols, ketones, ethers and esters, and insoluble in low boiling aliphatic and aromatic hydrocarbons. Addition of a non-solvent, such as pentane, to an ethyl ether solution of the acids results in the formation of two phases—one, dense, viscous, and orange-colored; the other, fluid, pale yellow, consisting largely of pentane and ether and having in solution a fraction of the acids. The analytical data on the products from the two phases show that a separation on the basis of molecular weight has been effected—the higher molecular weight acids being found concentrated in the precipitated phase and those of lower molecular weight, including those of the benzenecarboxylic series in the fluid, pentane–ether-rich layer. However, attempts to isolate directly individual components from the lower molecular weight material indicated that the benzenecarboxylic acids were contaminated with yellow, resinous acids, in the same molecular weight range. Further study with other solvent systems showed that a partial separation of the pentane–ether-soluble acids, on the basis of type, could be effected by combinations of acetone and benzene.

Two procedures were developed for this purpose; in the first, the pentane–ether-soluble material was dissolved in acetone and treated with benzene until the solution became turbid. After standing at room temperature for several days in a current of air so that slow evaporation took place, a nearly white, microcrystalline precipitate appeared on the sides and bottom of the vessel. This was found to be very rich in acids of the benzenecarboxylic series while the yellow, resinous acids were chiefly in the liquid phase.

In the second procedure, a water–acetone solution of the pentane–ether-soluble material was extracted with benzene. In this modification, the benzenecarboxylic acids remained in the raffinate and the yellow, resinous acids were concentrated in the extract.

Results

The two fractionation procedures used, designated A and B are outlined in Figs. 1 and 2 and analytical data for the fractions recovered by procedure A are given in Table I. Fraction 1 was found to contain ether-insoluble acids together with about 10% of inorganic impurities resulting from the recovery procedure. Small amounts of isophthalic acid were identified as the methyl ester. Fraction 2 contained the deeply colored, high molecular weight, large nuclei, polycarboxylic acids. The analytical data indicate that Fraction 3 was largely benzenedicarboxylic acids, and isophthalic acid was isolated as the methyl ester.

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[2] H. C. Howard, "Chemistry of Coal Utilization," Editor, H. H. Lowry, John Wiley and Sons, Inc., New York, N. Y., 1945. pp. 363–374.

[3] *Ibid.*, pp. 373–374.

[4] N. W. Franke and M. W. Kiebler, *Chemistry and Industry*, **58**, 580 (1946).

TABLE I

ANALYTICAL DATA ON FRACTIONS FROM PROCEDURE A

Fraction	%	Mol. wt.	Equiv. wt.	Funct.[b]	Nucleus[c]	Ultimate composition, % C	H	O Difference	O in carboxyls, %	O not in carboxyls, %
1	4.4	...	...	...	...	...	..	....	...	...
2	34.8	450	100	4.5	252	54.26	4.07	41.67[d]	32.0	9.67
3	2.4	172	82	2.1	79					
4a	7.2	191	91	2.1	99	56.33	4.15	39.52	35.20	4.32
4b	5.3[a]	218	139	1.5	152	58.88	4.03	37.09	22.0	15.09
5a	4.7	204	78	2.6	90					
5b	2.9	245	112	2.2	148					
6a	6.2	237	75	3.1	101	51.10	3.33	45.57	41.8	3.77
6b	1.8	242	112	2.1	150	54.94	4.02	41.04	27.7	13.34
7a	9.8	239	68	3.5	85					
7b	11.1	252	136	1.8	173					
8a	5.0	302	79	3.8	135					
8b	1.5	...	...	...	...					
Loss	2.9									

[a] The weights of subfractions b were obtained by difference in each instance. [b] Functionality = mol. wt./equiv. wt. [c] Nucleus = mol. wt.— funct. × 44. [d] Includes nitrogen and sulfur.

Each of the Fractions 4, 5, 6, 7 and 8 of Procedure A was subjected to the acetone–benzene "evaporative" separation. The products from the insoluble and soluble phases are designated as subfractions a and b, respectively, in Table I. The effectiveness of the acetone–benzene system in separating the benzenecarboxylic from the acids of larger nuclei is well shown by the marked differences in calculated nuclear sizes. The latter group of acids also shows consistently higher equivalent weights and consequently lower functionalities than the former. Further interesting differences are shown by ultimate compositions. Especially striking are the differences in per cent. oxygen not in carboxyl groups. Differences of the order of a few per cent. between oxygen "by difference" and that calculated from equivalent weights to be in carboxyl groups could be explained by the presence of nitrogen and sulfur and analytical errors, but differences of the magnitude shown are certainly significant. Since attempts to determine hydroxyl and ketone groups have been negative, one must conclude that the unaccounted for oxygen is either in some strongly hindered type of reactive group or in an ether linkage.

Trimellitic acid was isolated from both fractions 5a and 6a and appears to be the predominating

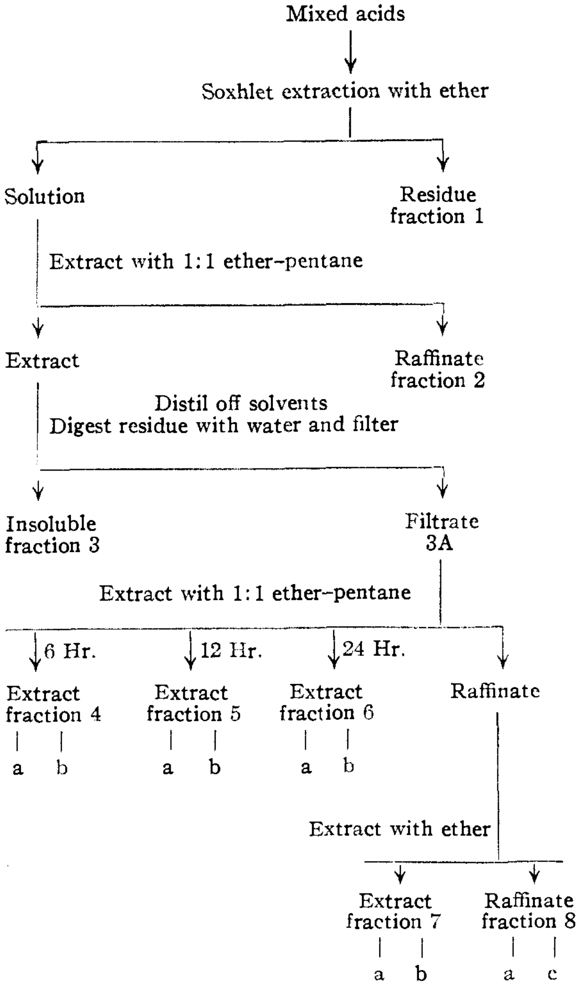

Fig. 1.—Fractionation Procedure A.

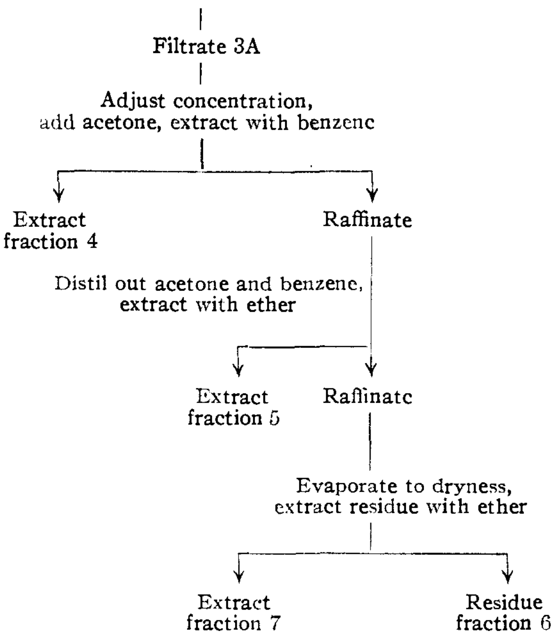

Fig. 2.—Fractionation Procedure B.

benzenecarboxylic acid. Pyromellitic acid (1,2,4,5-benzenetetracarboxylic acid) was isolated from fraction 7a.

The fractionation procedure outlined in Fig. 2 is somewhat simpler than the one just discussed. By its use *o*-phthalic, trimellitic, prehnitic[5] (1,2,3,4-benzenetetracarboxylic acid) and benzenepentacarboxylic acids were isolated from fractions 4,5,6 and 7, respectively.

These solvent separations permit an estimation of the distribution of the acids in the original mixture. About one-third of the mixture consists of acids in the molecular weight range 250–450 large polynuclear structures, another one-third is in the range 200–250, with nuclei of two or three rings and the remaining third appears to be made up of benzenecarboxylic acids. Of these, the trimellitic acid is estimated to constitute about half, or approximately 16% of the original mixture.

Experimental

Fractionation Procedure A. (See Fig. 1).—Approximately 200 g. of the mixed acids, vacuum dried at 100°, was refluxed about 5 hours with 1 liter of reagent grade ethyl ether. The separation of the insoluble material by filtration in an open funnel was troublesome in humid weather and was best carried out in a large paper thimble in a Soxhlet extractor. Final washing of the ether-insoluble material in the thimble was effected in the extractor by reflux. The insoluble material is designated as fraction 1. The filtrate was adjusted to a concentration of about 200 g. per liter and, while being agitated, was treated with an equal volume of pentane. After agitation the phases were allowed to separate and the upper fluid phase decanted. The viscous, lower phase, which partly adhered to the vessel, was dissolved in ether and the acids recovered by evaporation of the ether; they were vacuum dried at 100°, weighed and analyzed. They are designated as fraction 2. The acids were recovered from the fluid phase by evaporation of the solvents and digestion with water. The insoluble acids were separated by filtration, dried and analyzed and are designated as fraction 3. The filtrate, concentration about 30 g./100 ml., was placed in a continuous liquid phase extractor and three separate, successive extracts, with 1-1 ether–pentane, recovered by extraction periods of 6, 12 and 24 hours, were collected. These make up fractions 4, 5 and 6. The ether–pentane mixture was replaced with ether and extraction continued with this solvent alone for 24 hours. The acids recovered from the ether extract are designated as fraction 7. The residual acids were recovered by evaporation of the raffinate and constitute fraction 8. Fractions 4, 5, 6, 7 and 8 were then each resolved into sub-fractions by the following procedure: the fraction was made up to a concentration of about 20 g./100 ml. in reagent ether and treated with an equal volume of pentane. Small amounts of a viscous, colored phase separated and was discarded. The fluid phase was decanted and the acids recovered by evaporation. A solution of the acids in reagent acetone, 20 g./100 ml., was prepared and treated with sufficient benzene to produce turbidity. A crystalline phase appeared after a few days of slow evaporation and was recovered after decantation of the liquid phase. In each instance the solid phase is designated as sub-fraction a and the product recovered by evaporation of the liquid phase as sub-fraction b.

Fractionation Procedure B. (See Fig. 2).—This procedure was the same as in A except that following the separation of fraction 3, the aqueous filtrate 3A was adjusted to a concentration of about 20 g./100 ml. and an equal volume of acetone added. The acetone–water solution was then extracted three times with 100-ml. portions of benzene. Fraction 4 was recovered by evaporation of the extract. The acetone and residual benzene were distilled out of the raffinate and the resulting aqueous solution was exhaustively extracted with ether. Fraction 5 was recovered from the extract. The raffinate was evaporated to dryness, the dried acids transferred to a Soxhlet thimble and exhaustively extracted with ether. Fraction 6 was recovered from the residue and the extract constitutes fraction 7.

Separation and Characterization of Individual Acids. *o*-Phthalic Acid.—This acid appeared as a sublimate in vacuum drying of the original mixture as well as during the drying of fraction 3, Procedure B. The chief contaminant was oxalic acid. This was separated by washing with cold water and the phthalic acid crystallized from hot water.

Anal. Calcd. for $C_8H_6O_4$: C, 57.82; H, 3.64; equiv. wt., 83.06. Found: C, 57.71; H, 3.60; equiv. wt., 83.

Isophthalic Acid.—Fraction 3 was treated with phosphorus pentachloride and converted to the methyl ester,[6] which after crystallization from methanol melted at 65–66°.

Anal. Calcd. for $C_{10}H_{10}O_4$: C, 61.84; H, 5.19. Found: C, 61.56; H, 5.08.

Trimellitic Acid.—The analytical data, Table I, for fractions 5a and 6a from Procedure A, indicated the presence of benzenetricarboxylic acids. Higher equivalent weight, colored acids were, however, found difficult to eliminate completely. The best procedure found for this purpose was as follows: a 2-g. sample was placed in a small beaker, heated slowly to 230° and maintained at this temperature for about 10 minutes to form the anhydride. The crude anhydride was vacuum sublimed, the sublimate dissolved in warm water, the solution cooled and extracted with ether. From the ether extract the acid was precipitated by addition of benzene. This acid was also isolated from fraction 4, Procedure B. Final purification in each instance was by crystallization from nitric acid.

Anal. Calcd. for $C_9H_6O_6$: C, 51.41; H, 2.85; mol. wt., 210; equiv. wt., 70. Found: C, 51.71; H, 2.84; mol. wt., 215; equiv. wt., 71.

Pyromellitic Acid.—This acid was recovered from fraction 7b (Procedure A). The fraction was treated with hot 16 *N* nitric acid, evaporated to incipient crystallization, allowed to cool and the crystal mush separated by filtration on a fritted glass crucible. After washing with a little cold, 16 *N* nitric acid and drying, the crude acid was esterified with diazomethane. Crystallization of the esterified product from methanol resulted in the separation of a crystal mush, m.p. 143–145°. *Anal.* C, 54.19; H, 4.52. The m.p. and composition are intermediate between the methyl esters of pyromellitic and benzenepentacarboxylic acids. Repeated crystallization from methanol resulted in the separation of glistening plates of tetramethyl pyromellitate, m.p. 142°.

Anal. Calcd. for $C_{14}H_{14}O_8$: C, 54.19; H, 4.55. Found: C, 54.25; H, 4.57.

Prehnitic Acid.[5]—This acid was recovered from fraction 6 (Procedure B), which was very rich in this acid. The crude acid was recrystallized from 16 *N* nitric acid and characterized by conversion to the methyl ester by diazomethane. The pure ester was recovered in fine needles by crystallization from methanol, m.p. 133°.

Anal. Calcd. for $C_{14}H_{14}O_8$: C, 54.19; H, 4.55. Found: C, 54.19; H, 4.23.

Benzenepentacarboxylic Acid.—Fraction 7 (Procedure B), was crystallized from nitric acid and esterified with diazomethane as in the purification of pyromellitic acid. Recrystallization of the ester from methanol gave large blunt needles melting at 148°.

Anal. Calcd. for $C_{16}H_{16}O_{10}$: C, 52.17; H, 4.38. Found: C, 52.26; H, 4.17.

Special Procedure for Isolation of Trimellitic Acid.—To get further information as to the amount of trimellitic acid in the original mixture, the following procedure was employed. An ether solution of the mixed acids (33 g. in 150 ml.) was treated with an equal volume of pentane. The fluid, upper layer was separated by decantation and the ether and pentane evaporated. The recovered acids (wt.

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[5] Much confusion has existed due to the frequent interchange of the names prehnitic and mellophanic. Smith and Byrkit (THIS JOURNAL, 55, 4305 (1933)) made the logical proposal that the name prehnitic be used for the acid derived from prehnitene, 1,2,3,4-tetramethylbenzene. "Chemical Abstracts" has continued to designate these acids in the reverse fashion.

[6] E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1946, p. 177.

19 g.) were redissolved in ether and the process repeated. The acids (12.5 g.) were digested with about 100 ml. of warm water and after standing for 24 hours, the small amount of isophthalic acid, which had separated, was filtered off. The filtrate was diluted to about 150 ml. with water, 10 ml. of glacial acetic acid added and the solution heated to boiling. While boiling, 100 ml. of an aqueous, 1 *N* solution of calcium acetate was added slowly, with stirring. After digestion for 1 hour on a steam-bath, the solution was cooled and filtered. The filtrate was again heated to boiling and 100 ml. of an aqueous, 1 *N* solution of barium acetate added. Digestion and filtration was carried out as before. The filtrate was acidified with a slight excess of 4 *N* sulfuric acid, evaporated to a volume of about 50 ml. and exhaustively extracted with ether. The extracted acids weighed 7 g. Vacuum drying at 90–95° at 1–2 mm. resulted in the sublimation of small amounts of *o*-phthalic acid. The dried product was dissolved in acetone and the solution treated with benzene until it became turbid. After several days of slow evaporation, the precipitated acid was separated by filtration and dried at 100°. The weight of the product was 5.4 g., corresponding to 16% of the original mixture. The equivalent weight was 72 and the molecular weight, by b.p. in acetone, 220. By heating at 230° a readily volatile anhydride (m.p. 166°) was formed.

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[CONTRIBUTION FROM THE POLYCHEMICALS DEPARTMENT, E. I. DU PONT DE NEMOURS AND CO., INC.]

Synthesis of Esters from Olefins, Hydrogen, Carbon Monoxide and Acetic Acid

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RECEIVED NOVEMBER 2, 1951

Ethylene, propylene, diisobutylene, tetrapropylene, triisobutylene and tetraisobutylene have been treated with hydrogen and carbon monoxide at about 250° in the presence of cobalt acetate and acetic acid to give propyl acetate, butyl acetates, nonyl acetates, tridecyl acetates and heptadecyl acetates, respectively. In the case of ethylene and propylene, 2-methylpentyl acetate and octyl acetates have also been obtained. Similar treatment of cyclopentadiene has given cyclopentylmethyl acetate and the diacetates of the glycols formed from cyclopentadiene dimer. Methyl tetrahydrobenzoate has yielded 3- and 4-acetoxymethylcyclohexanecarboxylic acids. Butanols, 2-ethylhexanol, tridecyl alcohols and heptadecyl alcohols have been obtained by alcoholysis of the corresponding acetate esters.

Recent work[1,2] in this country has shown that aldehydes are obtained in good yields by the reaction of olefins with carbon monoxide, hydrogen and cobalt carbonyls in inert solvents. In this Laboratory, investigation of the reaction of olefins with carbon monoxide and hydrogen in the presence of acetic acid and cobalt acetate has shown that esters are obtained by using more drastic conditions.

$$\mathrm{RCH{=}CH_2 + CO + 2\,H_2 + HOAc \longrightarrow}$$
$$\mathrm{RCH_2CH_2CH_2OAc\ (or\ RCH(CH_3)CH_2OAc) + H_2O}$$

The esters are obtained by processing the olefins and acetic acid with 1:1 carbon monoxide–hydrogen gas mixture at 250° and 700 atm. pressure in a stainless steel shaker tube (325-cc. capacity). A soluble cobalt catalyst, such as cobalt acetate, is generally employed in an excess of acetic acid. However, other cobalt salts are operative. The reaction is very exothermic and rapid. Temperatures less than 200° as well as pressures less than 400 atm. give mainly aldehydes. As the pressure drops, additional quantities of carbon monoxide and hydrogen are injected into the tube to maintain a pressure of 700 atm. The catalyst can be recovered by distilling off most of the acetic acid and water in the product at atmospheric pressure. During this distillation the cobalt carbonyls are decomposed as evidenced by evolution of gases and the precipitation of a solid. This solid, probably cobalt acetate, can be filtered off and reused as the catalyst in the reaction. Ethylene, propylene, diisobutylene, tetrapropylene, triisobutylene and tetraisobutylene have been treated with hydrogen and carbon monoxide in the presence of cobalt acetate and acetic acid to give the acetate esters of the alcohols containing one more carbon than the original olefin by this procedure. Alcoholysis of the acetate esters with methanol gave the corresponding alcohols in quantitative yields.

In the case of ethylene or propylene a side reaction, condensation of the intermediate aldehyde, can be made to predominate by increasing the reaction temperature. Thus, a 40% conversion to octyl acetates and 30% conversion to butyl acetates was obtained by processing propylene and acetic acid at 250–270° and 700 atm.

$$\mathrm{2CH_2{=}CHCH_3 + CH_3CO_2H + 2CO + 4H_2 \longrightarrow}$$
$$\mathrm{CH_3CH_2CH_2CH_2CH(C_2H_5)CH_2OOCCH_3 + 2H_2O}$$

Formation of the octyl acetates is believed to occur by aldolization of the intermediate aldehyde, followed by dehydration, hydrogenation and esterification. Alcoholysis of the resulting octyl acetates to octyl alcohols followed by comparison of the mass spectrogram of the octyl alcohols with the mass spectrogram of an authentic sample of 2-ethylhexanol showed that the octyl acetates fraction was essentially 2-ethylhexyl acetate. Ethylene gave propyl acetate and 2-methylpentyl acetate. Higher olefins gave aldehydes that were not as reactive as propionaldehyde or butyraldehyde so that aldolization did not occur as readily. In these cases, the saturated hydrocarbon was the main by-product, conversions being 50–70% to the acetate esters and 20–30% to the hydrocarbon.

Hydroformylation of cyclopentadiene under these conditions yielded cyclopentylmethyl acetate and the diacetates of the glycols formed from the dimerization of cyclopentadiene. A mixture of 3- and 4-acetoxymethylcyclohexanecarboxylic acids was obtained from methyl tetrahydrobenzoate.

Experimental

Acetate Esters.—Hydroformylation of the unsaturated compounds in acetic acid was carried out by processing a 1:2 mole mixture of the unsaturated material and acetic

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(1) W. F. Gresham, R. E. Brooks and W. M. Burner, U. S. Patent 2,437,600.

(2) (a) H. Adkins and G. Krsek, THIS JOURNAL, **70**, 383 (1948). (b) H. Adkins and G. Krsek, *ibid.*, **71**, 3051 (1949).