[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, LOYOLA COLLEGE]

On the Olefinic Nature of Anacardic Acid from Indian Cashew Nut Shell Liquid

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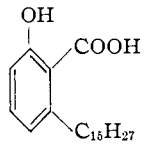
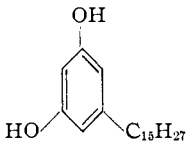
The anacardic acid isolated from the solvent-extracted liquid from Indian cashew nut shells has been separated by low-temperature fractional crystallization into a saturated component and a mono-, di- and triolefin which have been identified by analysis of their permanganate oxidation products, respectively, as 1-hydroxy-2-carboxy-3-pentadecyl benzene, 1-hydroxy-2-carboxy-3-(8′-pentadecenyl)-benzene, 1-hydroxy-2-carboxy-3-(8′11′-pentadecadienyl)-benzene and 1-hydroxy-2-carboxy-3-(8′,11′,14′-pentadecatrienyl)-benzene.

The brown liquid extracted from cashew nut shells by means of organic solvents is known to contain, besides traces of glucoside, gallic acid, etc.,[2] two main phenolic constituents, anacardic acid (90%) and cardol[3] (10%), in which the normal aliphatic side chain was supposed to contain an un-



anacardic acid



cardol

saturation equivalent of two double bonds. The darker liquid obtained, on the other hand, from cashew nut shells by commercial processes involving mostly heat treatment consists mainly of the decarboxylated acid, the monophenol cardanol, a little acid and cardol.

Cardanol, obtained from commercial liquid by low pressure distillation, and having an average of two aliphatic double bonds, has in fact been shown[4,5] to consist of four components, *i.e.*, *m*-pentadecyl-, *m*-(8′-pentadecenyl)-, *m*-(8′,11′-pentadecadienyl)- and *m*-(8′,11′,14′-pentadecatrienyl)-phenols. However, the relative proportions of these components may depend on the type of the commercial heat treatment involved.

As regards anacardic acid itself, the only experimental evidence so far available as to its olefinic heterogeneity was the isolation by Izzo and Dawson[6] of a crystalline monoglycol by molecular distillation of the mixture of glycols from the dimethyl ether ester of anacardic acid, and the fixing of the double bond of the monoölefin between carbon atoms 8 and 9 counting from the nucleus on the basis of heptaldehyde in the oxidation products of the monoglycol.

The present communication deals with the complete separation of all the components of anacardic acid and their olefinic structural determination.

Preliminary attempts to separate the heterogeneous anacardic acid mixture through the fractionation of its bromo derivative and its lead salt were not successful. However, low temperature (0 to −80°) fractional crystallization of the free acid proved effective as described below.

(1) This paper is based on a portion of the thesis submitted by V. J. Paul in 1954 for the Ph.D. degree in chemistry of Madras University.

(2) S. Siddiqui, Om Prakash Bahl Rastogi and V. J. Sarma, *Sci. Ind. Res.*, **8B**, 222 (1949).

(3) Staedeler, *Ann.*, **63**, 137 (1847).

(4) V. J. Paul, M.Sc. Thesis, University of Madras, 1951.

(5) W. Symes and C. R. Dawson, THIS JOURNAL, **75**, 4952 (1953).

(6) P. T. Izzo and C. R. Dawson, *J. Org. Chem.*, **15**, 707 (1950).

The anacardic acid used in this investigation was prepared according to the usual lead salt procedure of Backer and Haack[7,8] and had an unsaturation equivalent of 2.1 double bonds per molecule, as estimated by catalytic hydrogenation.

The progress of the fractionation by crystallization was followed by determining the unsaturation equivalent of each sample by means of iodine number. In the first stage, about 200 g. of anacardic acid was crystallized into four main fractions. Each of these fractions was then subjected to further separations to give finally the pure saturated mono-, di- and triolefinic components. The analytical data on each of the first four fractions (A, B, C and D) are given in Table I.

TABLE I

FIRST STAGE OF CRYSTALLIZATION OF ANACARDIC ACID

Wt. of anacardic acid, 200 g.; number of double bonds, 2.15

Fraction	Appearance	Yield, g.	$n^{30}D$	Iodine no.	No. of double bonds
A, crystals from acetone at −40°	Brown solid	24	....	134.3	0.82
B, crystals from acetone at −79°	Light brown	40	1.5185	200.6	1.72
C, crystals from methanol at −79°	Light brown	56	1.5223	236.0	2.20
D, filtrate from methanol at −79°	Light brown liq.	80	1.5250	264.9	2.59

Each of these factions was further crystallized to give the results summarized in Table II.

TABLE II

SECOND STAGE OF CRYSTALLIZATION OF ANACARDIC ACID

Fractionation	Appearance	Yield, g.	Iodine no.	No. of double bonds
A_c, crystals from A	Light color solid	13	104.0	0.41
A_f, filtrate from A		10	174.8	1.37
B_c, crystals from B[a]		18	177.0	1.40
C_c, crystals from C	Brown liq.	21	225.0	2.05
C_f, filtrate from C		54	247.1	2.35
D_c, crystals from D	Brown liq.	38	249.4	2.38
D_f, filtrate from D		40	277.4	2.76

[a] The filtrate from B, amounting to 21 g., was added to C and the resulting mixture, 77 g. was crystallized and the crystals are designated C_c and the filtrate C_f.

The increased degree of resolution effected by this second stage of crystallization is clearly indicated by the last column of Table II. The A frac-

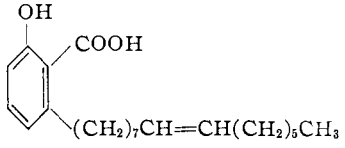
(7) H. J. Backer and N. H. Haack, *Rec. trav. chim.*, **60**, 661 (1941).

(8) Although lead anacardate is reported to be insoluble in alcohol, it was observed in the present investigation that a portion of the lead salt of the higher olefinic anacardic acid was soluble in alcohol, resulting in the loss of a small percentage of the acid along with the soluble cardol portion. (to be published.)

tion of Table I with an unsaturation equivalent of 0.81 double bond is now separated on recrystallization into two fractions: A_c with 0.41 and A_t with 1.37 double bonds. Similar separations were also obtained in the case of the remaining fractions. After this crystallization, fractions having the same degree of unsaturation were grouped together and each group was repeatedly crystallized until the four components were obtained in pure form as judged by physical and chemical criteria.

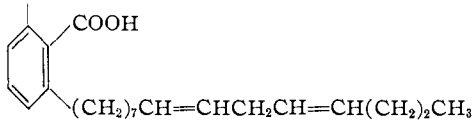
Saturated Component.—The saturated component (m.p. 91.5°) was identified as 2-carboxy-3-pentadecylphenol by carbon–hydrogen analysis and by mixed melting point determination with a pure sample of the compound, obtained by catalytic hydrogenation of anacardic acid.

Monoölefin.—Oxidation of the monoölefin (m.p. 48–49°) with potassium permanganate in acetone gave azelaic, heptylic and oxalic acids. The methyl ether ester of the monoölefin on permanganate oxidation yielded ω-(2-carboxymethyl-3-carboxyphenyl)-caprylic acid and heptylic acid. From these results the structure of the monoölefin was deduced to be 1-hydroxy-2-carboxy-3-(8′-pentadecenyl)-benzene.



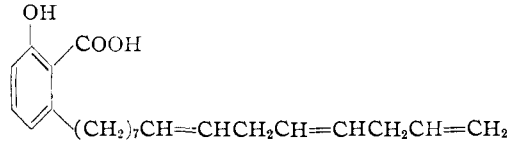
Diolefin.—This component (m.p. 25–26°) on oxidation with permanganate in acetone yielded azelaic, oxalic and butyric acids. The methyl ether ester of the diolefin gave on oxidation ω-(2-carboxymethyl-3-methoxyphenyl)-caprylic acid, and butyric and oxalic acids. The methyl ether of the monophenol from the diolefinic component on oxidation yielded ω-(3-methoxyphenyl)-caprylic acid, and butyric and oxalic acids.

These oxidation products are completely explained by assigning to the diolefinic component of anacardic acid the structure 1-hydroxy-2-carboxy-3-(8′,11′-pentadecadienyl)-benzene.



It is to be noted, however, that although the oxidation of the group =CH—CH$_2$—CH= should naturally be expected to give malonic acid, actually previous investigations[5,9,10] have definitely established the fact that oxidation of such a group with permanganate leads only to the production of oxalic acid, as in the present case.

Triolefin.—Oxidation of this component with permanganate yielded formic, oxalic and azelaic yields, whereas its methyl ether ester on oxidation gave formic and oxalic and ω-(2-carboxymethyl-3-methoxyphenyl)-caprylic acid. The methyl ether of the monophenol prepared from the triolefinic component yielded formic and oxalic acids, and ω-(3-methoxyphenyl)-caprylic acid. The presence of formed acid in the oxidation products points to the position of one of the double bonds as terminal, *i.e.*, between the 14th and 15th carbon atoms. Also, the production of azelaic acid from free anacardic acid and of ω-(2-carboxymethyl-3-methoxyphenyl)-caprylic acid and ω-(3-methoxyphenyl)-caprylic acid from the corresponding methyl ether ester and methyl ether, respectively, are evidence for the position of another double bond between the 8th and 9th carbon atoms, as in the case of the monoölefin. The third double bond can only be between the 11th and 12th carbon atoms, as explained in the case of the diolefin. Hence, the triolefin is assigned the structure of 1-hydroxy-2-carboxy-3-(8′,11′,14′-pentadecatrienyl)-benzene.



The absence of any conjugated double bonds, as shown by the diene value determination, is further evidence in support of the above structure.

It may be remarked that since the olefinic structure of the various components of solvent-extracted anacardic acid is identical with that of the corresponding components of cardanol from commercial liquid, the heat treatment involved in commercial extraction of cashew nut shell liquid does not induce any shifting of the side chain double bonds.

Experimental

The aliphatic unsaturation of anacardic acid before and after fractional crystallization was determined by the iodine number method developed earlier in this Laboratory,[11] which was found to be rapid and practically as accurate as the catalytic hydrogenation method.

Isolation of **Anacardic Acid.**—Cashew nut shells (1 kg.) cut into small pieces were extracted with 2.5 liters of ether in two 3-liter flasks arranged to serve as a Soxhlet system. The ether extract, anacardic acid, was separated from cardol by the lead salt method; yield 258 g., m.p. 20°.

Hydrogenation and Iodine Number of Anacardic Acid.—A 0.303-g. sample of the acid in 20 cc. of ethyl acetate on hydrogenation over 0.05 g. of 5% palladium-on-charcoal catalyst at 30.5° and 762 mm. absorbed during two hours 55.6 cc. of H_2, corresponding to 2.10 double bonds per mole (mol. wt. 344.5). The hydrogenated product melted without purification at 85–87° (Backer and Haack[7] give m.p. 91–91.5°; Dawson, *et al.*, 89.5–90°).

Anal. Calcd. for $C_{22}H_{36}O_3$: C, 75.8; H, 10.41. Found: C, 75.9; H, 10.31.

The iodine number of the acid was found to be 232.5, and that of the pure hydrogenated sample, 78.0, from which the unsaturated equivalent was calculated to be 2.15 double bonds per mole, in fair agreement with the hydrogenation value.

First Stage.—A solution of 200 g. of acid in 3 liters of acetone (in batches of 200 cc. at a time) was cooled to 40° for ten hours, the crystals removed, washed with acetone at the same temperature and marked as fraction A. The filtrate was diluted to 3.5 liters with acetone and crystallized at −79° for 14 hours, the crystals being designated B. The filtrate was freed of the solvent and the residue, dissolved in 2.5 liters of methanol and crystallized at −79° for 14 hours, and the crystals marked C. The residue from the final filtrate was designated D. The analytical data of these fractions are given in Table I.

Second Stage.—In this stage, each of the above four fractions was subjected to further fractional crystallization in

(9) R. Haworth, *J. Chem. Soc.*, 1458 (1929).

(10) D. T. Mowry, W. R. Brode and J. D. Brown, *J. Biol. Chem.*, **142**, 679 (1942).

(11) V. J. Paul and L. M. Yeddanapalli, *J. Sci. & Ind. Res.*, **12B**, 524 (1953).

appropriate solvents and at different temperatures, and the fractions characterized by iodine value and unsaturation, the data being summarized in Table II.

Third Stage.—The fractions from the previous stage were classified into I containing A_c, II, A_f and B_c, III, C_f and D_c and IV, D_f; each was again recrystallized into the pure components.

Saturated Component.—Fraction I, 12.5 g., was recrystallized thrice from acetone at room temperature, and a pure product, 3 g., melting at 89–89.5°, was identified as 1-hydroxy-2-carboxy-3-pentadecylbenzene and confirmed by mixed m.p. of an authentic sample of tetrahydroanacardic acid (89–90°), obtained by catalytic hydrogenation of a pure sample of acid.

Anal. Calcd. for $C_{22}H_{36}O_3$: C, 75.81; H, 10.42. Found: C, 75.82; H, 10.47.

Monoölefin.—A 27-g. sample of fraction II in 675 cc. of acetone (4% solution) was first cooled to −40° and maintained at this temperature for 8 hours, when a small quantity of crystals that formed was separated. The filtrate was next cooled to −75° for 10 hours. The crystalline fraction (m.p. 42–44°) having 1.12 double bonds and amounting to 18 g. was redissolved in 300 cc. of methanol and cooled to −60° to give crystals melting at 48–49° and possessing 1.04 double bonds. Its purity was confirmed by further crystallization from methanol and petroleum ether, not affecting the m.p. or unsaturation.

Anal. Calcd. for $C_{22}H_{34}O_3$: C, 76.25; H, 9.89. Found: C, 76.20; H, 9.86.

The hydrogenation value (25.7 cc. absorbed by 0.301 g. of the acid at 30° and 758 mm.) was calculated to be 1.0 double bond. The hydrogenated sample melted at 88–89° without any purification.

Diolefin.—Fraction III from the third stage of crystallization was first crystallized from a 10% acetone solution at −75° and the crystals obtained were discarded. The filtrate was evaporated and the acid residue was crystallized from a 4.4% petroleum ether solution at −60° and the crystals obtained were fractionally crystallized from a 4.7% petroleum ether solution at −35, −50 and −75°. The crystals obtained at −50 and −75° were mixed and recrystallized twice from a 5% methanol solution to give the pure diolefin. The final purified sample, 11 g., was a light brown liquid with m.p. 25–26° and $n^{28}D$ 1.5246.

Anal. Calcd. for $C_{22}H_{32}O_3$: C, 76.68; H, 9.36. Found: C, 76.65; H, 9.30.

A 0.4130-g. sample of the acid in 20 cc. of ethyl acetate in the presence of 0.05 g. of 5% Pd-on-charcoal absorbed 71.8 cc. at 30° and 759 mm. corresponding to 2.03 double bonds, in agreement with the value from iodine number 2.04.

Triolefin.—In order to isolate the triolefin, fraction IV was crystallized once at −40° from a 5% petroleum ether solution and thrice at −50° successively from 3, 4 and 7% petroleum ether solution. In each of these above crystallizations the crystals were discarded and from the final filtrate the solvent was evaporated off to give the triolefin. The final product was a light brown liquid with $n^{28}D$ 1.5332 which solidified into a light brown solid at about −30°, without any sharp melting point.

Anal. Calcd. for $C_{22}H_{30}O_3$: C, 77.14; H, 8.73. Found: C, 77.20; H, 8.88.

A 0.3328-g. sample in 20 cc. of ethyl acetate using 0.1 g. of 5% Pd-on-charcoal absorbed 83.5 cc. of hydrogen at 30.5° and 761 mm., corresponding to 2.90 double bonds, the value by iodine number being 2.88. The slightly lower value for double bonds indicates the presence of diolefin, so that the purity of the triolefin sample is about 90%.

Oxidation of Free Monoölefinic Anacardic Acid.—A 1.0-g. sample of the acid in 30 cc. of acetone was slowly oxidized with 7 g. of powdered $KMnO_4$ at 0°. After removal of solvent the residue was digested with 50 cc. of 2% KOH solution and filtered. The filtrate was acidified with dilute H_2SO_4 and steam distilled. The steam distillate, neutralized with KOH solution and evaporated almost to dryness, was acidified with a minimum amount of dilute H_2SO_4 and extracted with ether. Drying and removal of ether gave a colorless liquid fatty acid, b.p. 224°,[12] corresponding to that of heptylic acid (b.p. 223.0°). The mercuric salt of the acid had a melting point 106°,[12] and its amide 95°.

Anal. Calcd. for $CH_3(CH_2)_5CONH_2$: C, 65.10; H, 11.62. Found: C, 65.00; H, 11.55.

The residue from steam distillation was extracted with ether and on removal of the solvent, a yellowish solid was obtained which was purified by recrystallization from hot water to give 0.2 g. of white flaky crystals, m.p. 105.0°; mixed m.p. with a pure sample of azelaic acid,[12] m.p. 105°, was 104°.

Anal. Calcd. for $(CH_2)_7(COOH)_2$: C, 57.40; H, 8.57. Found: C, 57.50; H, 8.50.

The aqueous portion from the above ether extraction was concentrated to dryness and exhaustively extracted with ether. This ether extract gave about 0.20 g. of a white solid which on recrystallization from water was identified as oxalic acid[13] (m.p. 100°).

Methyl Ether Ester of Monoölefinic Anacardic Acid.—A 2.2-g. sample of the acid in 20 cc. of methyl alcohol was methylated with 4.8 g. of dimethyl sulfate according to standard procedure and purified by distillation at 1 mm. to give a colorless liquid (b.p. 212° (1 mm.), $n^{31}D$ 1.4961), yield 1.8 g. A 0.8-g. sample of this ether ester was oxidized in acetone at 0° with 2.6 g. of powdered permanganate, and the resulting mixture was separated as in the previous case to give heptylic acid in the steam-volatile portion and in the steam-non-volatile portion, a reddish oily acid which when purified by distillation under vacuum gave as a main fraction a colorless oily acid setting into a waxy solid at 0°. The analysis as well as the neutralization equivalent of this acid corresponded to the structure ω-(2-carboxymethyl-3-methoxyphenyl)-caprylic acid.

Anal. Calcd. for $C_{17}H_{24}O_5$: C, 66.20; H, 7.87; neut. equiv., 308.40. Found: C, 66.50; H, 7.81; neut. equiv., 307.20.

Glycol of Methyl Ether of Monoölefinic Acid.—The methyl ether ester, 1 g., on saponification in alcoholic NaOH gave 0.8 g. of the ether acid, which was hydroxylated at 0° in 1.2 l. of water containing 0.6 g. of KOH, by addition of 90 cc. of 1% $KMnO_4$ solution. The resulting solid monoglycol was recrystallized three times from ether–petroleum ether mixture to give a pure product (m.p. 96–97°), yield 0.2 g.

Anal. Calcd. for $C_{23}H_{38}O_5$: C, 70.00; H, 9.70. Found: C, 69.90; H, 9.68.

Oxidation of the Methyl Ether of the Monophenol Obtained from the Monoölefinic Acid Component.—A 3.0-g. sample of the acid was heated slowly at 1 mm. up to 200° over an oil-bath and decarboxylated at this temperature for 45 minutes. The resulting monophenol was methylated, and was purified by distillation at 2 mm. (b.p. 192° at 2 mm., $n^{30}D$ 1.4928, yield 2 g.).

A 1.5-g. sample of the ether in 30 cc. of acetone oxidized at 0° with 5 g. of powdered potassium permanganate gave a steam-volatile acid identified as heptylic acid, and a steam-non-volatile acid ω-(3-methoxyphenyl)-caprylic acid (m.p. 51–52°).[5]

Anal. Calcd. for $C_{15}H_{22}O_5$: C, 72.00; H, 8.80; neut. equiv., 251.00. Found: C, 71.70; H, 8.71; neut. equiv., 250.30.

Oxidation of the Diolefinic Component.—Careful oxidation of 2.0 g. of the acid in 50 cc. of acetone with 16 g. of powdered permanganate at −20° yielded a steam-volatile acid (b.p. 165°, $n^{29}D$ 1.3930[13]) identified as butyric acid (0.3 g.) from its amide[13] (m.p. 114°; mixed melting point, the same); and a non-volatile acid mixture, oxalic and azelaic acids[13] (0.4 g.) as in the case of the monoölefin.

Anal. Calcd. for C_4H_9NO: C, 55.20; H, 10.40. Found: C, 55.10; H, 10.20.

The Dimethyl Ether Ester of the Diolefinic Component.—It was prepared by the same procedure as in the case of the monoölefinic acid and had the following physical constants, b.p. 212.0° (1 mm.) and $n^{31}D$ 1.5058. On oxidation with powdered potassium permanganate at 0°, it gave butyric, oxalic and ω-(2-carboxymethyl-3-methoxyphenyl)-caprylic acid.

Anal. Calcd. for $C_{17}H_{24}O_5$: C, 66.12; H, 7.87. Found: C, 66.30; H, 7.89.

The quantitative estimation of oxalic acid was done by its precipitation from the oxidized products of the ether ester as calcium salt from which the acid was regenerated for ti-

(12) E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1946.

tration with $KMnO_4$. The titer value corresponded to 0.286 g. of the oxalic acid per 1.5 g. of the ether ester, so that on molar basis 0.00405 mole of the ether ester gave 0.00227 mole of oxalic acid (yield 56%).

Glycol of the Methyl Ether of the Diolefinic Component.—The methyl ether ester (1 g.) was saponified to give 1-methoxy-2-carboxy-3-pentadecadienylbenzene (yield 0.7 g.). This on hydroxylation as in the case of the monoölefin yielded a sirupy liquid (0.5 g.) which, when kept at 0° for a day, set to a yellow waxy solid and on further purification with ether–petroleum ether mixture gave 0.40 g. of a yellowish amorphous solid without a sharp m.p.

Anal. Calcd. for $C_6H_3(OCH_3)(COOH)C_{15}H_{27}(OH)_4$: C, 64.80; H, 8.99. Found: C, 64.80; H, 9.01.

On decarboxylation, the diolefinic acid gave the corresponding monophenol whose methyl ether (b.p. 186° (1 mm.), $n^{30}D$ 1.5028) on oxidation with permanganate in acetone at 0° gave butyric, oxalic and ω-(3-methoxyphenyl)-caprylic acids.

Oxidation of the Triolefinic Component.—A 2-g. sample of the acid was oxidized with 21 g. of powdered permanganate at −20°. The steam-volatile portion gave a qualitative test for formic acid. The non-volatile portion gave azelaic (0.4 g.) and oxalic acids as in the previous case. A separate oxidation was conducted in order to estimate formic acid quantitatively by its conversion into CO_2 by mercuric acetate[13] and absorption of the gas by standard alkali. A 1-g. sample of the triolefin gave CO_2 corresponding to 0.0177 g. or 0.00038 mole of formic acid (yield, 13%).

Dimethyl Ether Ester of the Triolefinic Component.—Prepared according to the previously described method, the ether had boiling point 214° (1 mm.) and $n^{31}D$ 1.5132. Oxidation of the ether ester, 2 g. in 50 cc. of acetone at −20° with 8 g. powdered permanganate gave formic, oxalic and ω-(2-carboxymethyl-3-methoxyphenyl)-caprylic acids.

Anal. Calcd. for $C_{17}H_{24}O_5$: C, 66.12; H, 7.87. Found: C, 66.30; H, 7.79.

Oxalic acid quantitatively estimated here as in the case of the diolefinic component was found to be 0.0058 mole of acid per 0.00537 mole of the ether ester. It may be noted that this molar proportion of oxalic acid is twice that in the case of the diolefinic acid.

Diene Value Determination.—A 0.5781-g. sample of the ether ester when heated in a sealed tube with 10 cc. of a 2% maleic anhydride solution in acetone at 90° for 20 hours, according to the procedure of Priest and Von Mikusch,[14] gave no evidence for the presence of conjugated double bonds.

Oxidation of the Methyl Ether of the Triolefinic Component.—The decarboxylated acid on methylation as before gave a liquid (b.p. 187° (1 mm.), $n^{28}D$ 1.5120). A 2-g. sample of this ether on oxidation with 11 g. of powdered potassium permanganate in acetone at −20° gave formic, oxalic and ω-(3-methoxyphenyl)-caprylic acids.

Acknowledgment.—The authors wish to express their sincere thanks to Professor Charles R. Dawson, Chemistry Department, Columbia University, for help in the revision of the manuscript of this paper; and to the Ministry of Education, Government of India, for a senior research scholarship to one of the authors (V. J. P.).

(13) J. D. Reid and H. D. Weihe, *Ind. Eng. Chem., Anal. Ed.*, **10**, 271 (1938).

(14) G. W. Priest and J. D. von Mikusch, *Ind. Eng. Chem.*, **32**, 1314 (1940).

MADRAS, INDIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF DELAWARE]

The Products of Addition of Sulfenyl Halides to Norbornene[1,2]

BY HAROLD KWART AND ROBERT K. MILLER

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2,4-Dinitrobenzenesulfenyl chloride and bromide and *p*-toluenesulfenyl chloride have been treated with norbornene. The products of reaction have been identified by various degradative procedures. An effect on the product composition due to solvent medium of reaction has been observed. A general interpretation is proposed to explain the differences between sulfenyl halide addition and other addition reactions of the bicyclic double bond which have been studied previously.

Introduction.—The addition of several sulfenyl halides to norbornene (I) has been undertaken in extension of previous work[1] in this Laboratory investigating the nature of addition reactions of bicyclic olefins. Kharasch and his co-workers have studied[3] the addition of this class of double bond reagents and have observed normal *trans* addition in the case of aliphatic and alicyclic olefins. They have demonstrated,[4] further, that the addition proceeds predominantly according to Markownikov's rule when conducted in glacial acetic acid and that the results are consistent with a three-membered cyclic cationic intermediate formed by addition of 2,4-dinitrobenzenesulfenyl cation to the double bond. Further aspects of the stereospecificity of this reaction have been emphasized in the work of Kharasch and Havlik[5] and of Cram.[5]

In our previous work we have investigated and interpreted the unusual course (rearrangement) taken by such comparatively simple reactions as halogenation and hydroxylation in the bicyclic system. The present objective was to determine the influence of the reagent on the course of addition to bicyclic olefins.[6] The aromatic sulfenyl halides seemed to be ideal reagents from this point of view because of the considerably greater size and highly polar nature of addition fragments.

2,4-Dinitrobenzenesulfenyl Chloride.—The addition of 2,4-dinitrobenzenesulfenyl chloride (II) to norbornene in a variety of solvents yielded predominantly two products: a 1:1 adduct III and a

(1) Paper VI in this series; for previous papers see THIS JOURNAL, **76**, 5400 (1954).

(2) Revised nomenclature reported by A. M. Patterson, *Chem. Eng. News*, **30**, 930 (1952).

(3) W. I. Orr and N. Kharasch, THIS JOURNAL, **78**, 1201 (1956), is paper XXIII in a series on sulfenyl halide chemistry and contains references to prior contributions.

(4) N. Kharasch and C. M. Buess, *ibid.*, **71**, 2724 (1949).

(5) (a) N. Kharasch and A. J. Havlik, *ibid.*, **75**, 3734 (1953), A. J. Havlik and N. Kharasch, *ibid.*, **78**, 1207 (1956); (b) D. J. Cram, *ibid.*, **71**, 3884 (1949).

(6) While our work was under way we became aware (through personal communication with Dr. S. J. Cristol) of a similar study being undertaken at the University of Colorado laboratories. These results have now been disclosed (see S. J. Cristol and G. D. Brindell, Abstracts of Papers, Am. Chem. Soc. Meeting, Cincinnati, Ohio, March 29–April 7, 1955, p. 35N).