Studies on the Constitution of Shonanic Acid, One of the Two Characteristic Volatile Acids from the Wood of *Libocedrus formosana*, Florin. III. Studies on the Oxidation of Shonanic Acid.

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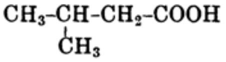
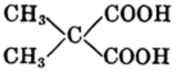
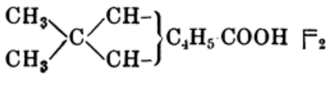
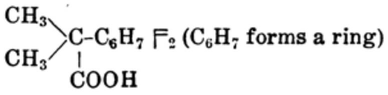
Shonanic acid, when oxidized in cold with dilute potassium permanganate solution, gives a crystalline dibasic acid of the formula $C_5H_8O_4$. The acid purified by sublimation in vacuo melts at 184–186° (with decomp.), its amide melting at 259–260°. There are four possible constitutional formulæ for this acid, viz.,

(1)	$HOOC\text{-}(CH_2)_3\text{-}COOH$	Pyrotartaric acid, m.p. 97°.
(2)	 $CH_3\text{-}CH(CH_3)\text{-}CH_2\text{-}COOH$	Methylsuccinic acid, m.p. 115°, 102°, 112.5°.
(3)	$CH_3\text{-}CH_2\text{-}CH(COOH)_2$	Ethylmalonic acid, m.p. 111.5°.
(4)	 $(CH_3)_2C(COOH)_2$	Dimethylmalonic acid, m.p. 186° (with decomp.).

As the present acid $C_5H_8O_4$, on heating somewhat above its melting point, loses exactly one mol of carbon dioxide and transforms into isobutyric acid, it is obvious that the acid has two carboxyl groups in union with one carbon atom, i.e. it must be dimethylmalonic acid. The formation of dimethylmalonic acid indicates that shonanic acid should be represented by I or II. In case of I the two carboxyl groups (in dimethylmalonic acid) were newly formed as the result of oxidation, while in the latter case one of the carboxyl groups is the originally contained one.



I.



II.

In order to determine the structural feature of the ring-forming nucleus of shonanic acid, the following methods were adopted.

(1) Preparation of hydrocarbon with the same number of carbon atoms as shonanic acid by reducing carboxyl group to methyl group. The resulting hydrocarbon was compared with the known hydrocarbons of the same formula in regard to their physical properties.

(2) Preparation of hydrocarbon with nine carbon atoms by eliminating the carboxyl group on heating the acid with soda-lime.

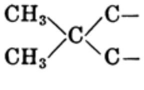
(3) Conversion of shonanic acid into known substances by oxidizing the side chain or substituents in the nucleus of shonanic acid.

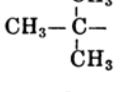
The results of the experiments were as follows.

(1) The hydrocarbon prepared by heating shonanic acid and tetrahydroshonanic acid respectively with hydroiodic acid in a sealed tube showed the following properties:

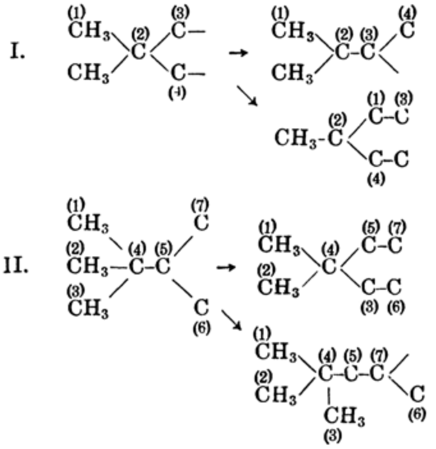
Hydrocarbon from shonanic acid.	Hydrocarbon from tetrahydroshonanic acid.
b.p. 157–158.3°/754 mm.	b.p. 158.5°/765 mm.
d_4^{20} 0.7866	d_4^{20} 0.7872
n_D^{20} 1.4344	n_D^{20} 1.4338

Whether the starting substance be the unsaturated shonanic acid or the saturated tetrahydroshonanic acid, that the product formed by the action of hydroiodic acid should represent the same hydrocarbon is experimentally assured as far as the physical properties are concerned. This hydrocarbon, as should be expected from the known partial structure of the original acid, contains an arrangement I or II, provided that no inversion takes place throughout the reduction by hydroiodic acid.

I. 

II. 

Thus in comparing it with known hydrocarbon, such ones containing a dimethyl or trimethyl group should be adopted, and further more, taking into consideration the ring transformation often effected by hydroiodic acid, the cases of III to VI, viz.:



I. → III. (Transformation into a smaller ring.)

↘ IV. (Transformation into a larger ring.)

II. → V. (Transformation into a larger ring.)

↘ VI. (Transformation into a smaller ring.)

The properties of hydrocarbons $C_{10}H_{20}$ with atom groups mentioned above were tabulated in Table 1. As seen from the table the hydrocarbons $C_{10}H_{20}$ have the general value 0.78–0.81 for the density, 1.43–1.45 for the refractive index. Those with six-membered ring have the boiling points 166–171°, while those with five-membered ring have values lower than 160°. On comparing the physical properties of the hydrocarbon from shonanic acid with those of the known hydrocarbons it is likely that the former possesses a five-membered ring, but this should not at once extended to shonanic acid itself, as the ring transformation might have ensued by the action of hydroiodic acid as in the transformations of benzene to methylcyclopentane and cyclohexyl iodide or cyclohexanol to methylcyclopentane. But judging from its physical properties, it is evident that the hydrocarbon obtained from shonanic acid is either a compound with a five- or six-membered ring system.

(2) With a view to obtain a hydrocarbon C_9H_{18} tetrahydroshonanic acid was heated with soda-lime, when, contrary to the expectation, an unsaturated hydrocarbon C_9H_{16}, which showed the following properties, was obtained. B.p. 145–148°; d_4^{26} 0.8128; n_D^{20} 1.4593.

The attempt to obtain its nitrosochloride or nitrosite in the crystalline state was futile. Next, in order to study the ring system of the hydrocarbon obtained, its physical properties were compared with those of known hydrocarbons of the same formula $C_9H_{16}\ulcorner_1$. For this purpose the following hydrocarbons were chosen (Table 2), taking into consideration the ring transformation or migration of atom groups which might have been accomplished by heating with soda-lime.

Table 1.

Substance	d	nD	B.p.
o-Menthane(1)	0.8135 $\binom{21}{0}$	1.447 (21)	171°
d-*m*-Menthane(2)	0.8116 $\binom{23}{0}$	1.446 (23)	167–168°
l-*m*-Menthane(3)	0.7938- 0.7956 $\binom{20}{0}$	1.4358- 1.4355 (20)	167–168°
i-*m*-Menthane(1)	0.7965 $\binom{24}{0}$	1.440 (24)	166–167°
p-Menthane(4)	0.7974 $\binom{20}{4}$	1.4380 (20)	172°
Hexahydrodurol(5)	0.811 $\binom{20}{4}$	1.4451 (20)	169–170.5°
1,3-Diethyl-cyclohexane(6)	0.7957 $\binom{22}{4}$	1.4388 (20)	169–171°
Butyl-cyclohexane(7)	0.8178 $\binom{20}{4}$	—	178–180°
tert-Butyl-cyclohexane(8)	0.8305 $\binom{16}{4}$	1.4556 (16)	166–167°
1-Methyl-3-propyl-cyclohexane(9)	0.7895 $\binom{21}{4}$	1.4352 (21)	169–170°
1,2-Dimethyl-3-isopropyl-cyclopentane(10)	0.786 $(^{16})$	1.4337 (16)	146–148°
Hydrocarbon from thujane(11)	0.7923 $\binom{20}{0}$	1.4377	157°
Hydrocarbon from shonanic acid	0.7872 $\binom{19}{4}$	1.4338 (19)	158.5°

Table 2.

Substance	d	nD	B.p.
1-Propyl-cyclohene(12)	0.838 $(^{19})$	1.4579 (19)	154–156°
Propyliden-cyclohexane(13)	0.8210 $(^{19})$	1.4631 (19)	157–158°
Δ^1-Tetrahydrocumol(14)	0.8290 $(^{20})$	1.4606 (20)	155–157°
Isopropyliden-cyclohexane(15)	0.836 $(^{20})$	1.4723 (20)	160–161°

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(1) Sabatier and Murat, *Compt. rend.*, **156** (1913), 186.

(2) Sabatier and Murat, *ibid.*, **156** (1913), 187.

(3) Kishner, *Chem. Zentr.*, **83** (1912), I, 1456.

(4) Smirnow, *Chem. Zentr.*, **81** (1910), I, 740.

(5) Willstätter and Hatt, *Ber.*, **45** (1912), 1473.

(6) Zelinsky and Rudewith, *Ber.*, **28** (1895), 1343.

(7) Douris, *Compt. rend.*, **157** (1913), 57.

(8) Halse, *J. prakt. Chem.*, [2], **92** (1915), 41.

(9) Beilstein, "Handbuch der organischen Chemie," 4. Aufl., Bd. 5, Erstes Ergänzungswerk, 20 (1931).

(10) Godchot and Taboury, *Compt. rend.*, **156** (1913), 472.

(11) Kishner, *Chem. Zentr.*, **83** (1912), I, 1457.

(12) Wallach, Churchill, and Rentschler, *Ann.*, **360** (1908), 58.

(13) Wallach, Churchill, and Rentschler, *Ann.*, **360** (1908), 56.

(14) Wallach and Mallison, *Ann.*, **360** (1908), 69.

(15) Wallach and Mallison, *Ann.*, **360** (1908), 68.

Table 2.—(*Concluded*)

Substance	d	n_D	B.p.
1-Methyl-2-ethyliden-cyclohexane(16)	0.823 $(^{0})$	1.47	158°
1-Methyl-3-ethyliden-cyclohexane(17)	0.813 $(^{0})$	1.4584	153°
1-Methyl-3-ethyl-cyclohexene-(2 or 3)(18)	0.8154 $(^{19}_{0})$	1.4538 (19)	148–149°
1-Methyl-4-ethyl-cyclohexene-(3)(19)	0.8169 $(^{16}_{4})$	1.453 (16)	149°
1-Methyl-4-ethyliden-cyclohexane(20)	0.810 $(^{20})$	1.4571 (20)	152–153°
1,1,2-Trimethyl-cyclohexene-(2)(21)	0.8217 $(^{20})$	1.456 (20)	146.2–147.2°
1,1,3-Trimethyl-cyclohexene-(2)(22)	0.803 $(^{20})$	1.446 (21.5)	139–142°
1,1,4-Trimethyl-cyclohexene-(3)(23)	0.8032 $(^{18.8}_{4})$	1.4415 (23)	139–140°
1,2,3-Trimethyl-cyclohexene-(1)(24)	0.8347 $(^{11.7}_{4})$	1.463 (11.7)	149–150°
1,2,4-Trimethyl-cyclohexene-(4)(25)	0.8078 $(^{16}_{4})$	1.450 (16)	144–146°
1,3,5-Trimethyl-cyclohexene-(1)(26)	0.7965 $(^{21})$	1.4447 (21)	142.5–143.5°
3,5-Dimethyl-1-methylen-cyclohexane(27)	0.7922 $(^{14}_{4})$	1.446 (14)	135–136°
1-Methyl-3-isopropyl-cyclopentene-(1)(28)	0.801 $(^{20})$	1.4478 (20)	144–146°
1-Methyl-3-isopropyl-cyclopentene-(2)(29)	0.791 $(^{22})$	1.4380 (22)	138–139°
Apofenchene(30)	0.794 $(^{21})$	1.4403 (22)	142–143°
1-Methyl-2-isopropyliden-cyclopentane(31)	0.8104 $(^{20}_{0})$	1.4518	149–151°
1-Methyl-2-isopropenyl-cyclopentane(31)	0.8006 $(^{20})$	1.4455	141–143°
Pulegene(32)	0.791 $(^{22})$	1.4380	138–139°
1,1,2-Trimethyl-3-methylen-cyclopentane(33)	—	—	138–140°
1,1,2,5-Tetramethyl-cyclopentene-(3)(34)	0.8034 $(^{20})$	1.44406 (20)	133–135°
Hydrocarbon from tetrahydroshonanic acid	0.8129 $(^{19}_{4})$	1.4595 (19)	145–148°

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(16) Murat, *Ann. chim.*, [8], **16** (1909), 125.
(17) Wallach and Evans, *Ann.*, **360** (1908), 51.
(18) Zelinsky and Gutt, *Ber.*, **35** (1902), 2140; Zelinsky and Zelikow, *Ber.*, **34** (1901), 3255
(19) Sabatier and Mailhe, *Compt. rend.*, **142** (1906), 439.
(20) Wallach and Rentschler, *Ann.*, **365** (1909), 271.
(21) v. Auwers and Lange, *Ann.*, **409** (1915), 174.
(22) Tiemann, *Ber.*, **33** (1900), 3711.
(23) v. Auwers and Lange, *Ann.*, **409** (1915), 167.
(24) v. Auwers and Krollpfeiffer, *Ber.*, **48** (1915), 1231.
(25) v. Auwers, *Ann.*, **420** (1919), 105.
(26) v. Auwers, Hinterseber, and Treppmann, *Ann.*, **410** (1915), 270.
(27) v. Auwers, Hinterseber, and Treppmann, *Ann.*, **410** (1915), 272.
(28) Semmler, *Ber.*, **37** (1904), 237.
(29) Wallach, Collmann, and Thede, *Ann.*, **327** (1903), 131.
(30) Wallach, *Ann.*, **369** (1909), 83.
(31) Kishner, *Chem. Zentr.*, **83** (1912), II, 1925.
(32) Wallach, Collmann, and Thede, *Chem. Zentr.*, **73** (1902), I, 1925.
(33) Bouveault and Blanc, *Compt. rend.*, **136** (1903), 1461.
(34) Tiemann, *Ber.*, **30** (1897), 595.

As seen from Table 2, the hydrocarbons with six-membered ring system have values 0.80–0.83 for density while those with five-membered ring 0.79–0.81. Thus it can not be decided by comparing the densities whether the hydrocarbon under investigation is of five- or six-membered ring. Viewed from refractive indices, hydrocarbon of six-membered ring system have values 1.44–1.47 while those of five-membered ring system values 1.43–1.45. The actual hydrocarbon has $n_D^{20} = 1.4595$ and consequently is likely to be one with six-membered ring system, but it should not be strongly taken into account, as its boiling point is found to be 145–148° which is close to those of hydrocarbons with five-membered ring as well as with six-membered ring.

(3) The attempt to obtain some known derivatives from shonanic acid by oxidation at last succeeded by the use of dilute nitric acid as oxidant. When shonanic acid was heated with dilute nitric acid for some hours *o*-dinitrobenzene was obtained with a fairly good yield. Though it can not easily be elucidated under what mechanism the acid was converted into *o*-dinitrobenzene, the formation of it may be taken as an evidence for the presence of six-membered ring in shonanic acid molecule, unless other data appear which are rigorously against the above reasoning.

Experimental.

I. Oxidation of shonanic acid with potassium permanganate. 600 c.c. of 4% potassium permanganate solution was added drop by drop to a well-cooled solution of the acid (5 g. of the acid in 500 c.c. of 7% Na_2CO_3 solution) with vigorous stirring. After all the permanganate solution has been added the reaction mixture was warmed on the water-bath at 40–50° for 30 minutes and filtered while hot in order to remove manganese dioxide precipitated. The filtrate was then evaporated nearly to dryness, acidified with dilute sulphuric acid and extracted with ether. On distilling off the solvent there remained about 3.5 g. of reddish yellow sticky substance, which on standing at the ordinary temperature for 7–10 days nearly half of the contents solidified to a crystalline mass. The crystalline substance thus obtained was filtered and spread over a porous plate to remove liquid matter.

(1) *The crystalline portion.* The crystalline substance thus separated was soluble in ether, alcohol and ethyl acetate but difficultly soluble in benzene, chloroform and petroleum ether. The substance was acidic and readily soluble in alkali, from which the original acid could be recovered by acidification. The test for aldehydic substance with Schiff's reagent and Tollens' solution proved negative. The substance melted at 178–180° when precipitated in prismatic needles from ethereal solution by addition of light petroleum. The melting point after purifications by sublimation at 115–120° under 5 mm. could be raised up to 184–186° (with decomp.).

The substance did not decolourise bromine or permanganate in cold showing the saturated nature of the substance. The acid was found to be dibasic by the electrolytic conductivity method. The difference of the equivalent conductivities of N/32 and N/1024 sodium salt solutions was found 10×2.21. From the value 2.21 the substance under investigation must be dibasic. Acid value 844.3 (0.0810 g. of the sample required 39.08 c.c. of N/32 NaOH), calculated for $C_5H_8O_4$ 848.4. (Found: C, 45.53; H, 6.09. Calculated for $C_5H_8O_4$: C, 45.45; H, 6.06%. Analysis of the silver salt: Ag, 62.37. Calculated for $C_5H_6O_4Ag_2$ 62.42%.)

From the composition of the silver salt the molecular weight and the molecular formula of the acid were determined: molecular weight, 132.9; molecular formula, $C_5H_8O_4$.

We find among dibasic acids of the formula $C_5H_8O_4$, dimethylmalonic acid melting at 186° (with decomp.) whose identity with the actual substance was proved as follows.

(*a*) *Preparation of the amide.* The acid chloride prepared from 1.2 g. of the acid and 4 g. of phosphorus pentachloride was added to cold aqueous ammonia. Yellowish crystalline diamide was obtained, which after recrystallization from water furnished colourless scales melting at 262°, in good accordance with the melting point of dimethylmalonic diamide. (Found: N, 21.64. Calculated for $C_5H_{10}O_2N_2$: N, 21.54%.)

(*b*) *Conversion into isobutyric acid by elimination of carbon dioxide.* That the acid $C_5H_8O_4$ is dimethylmalonic acid was also proved by conversion into isobutyric acid by elimination of one mol of carbon dioxide from the original molecule. The acid, when heated somewhat above its melting point, loses readily one mol of carbon dioxide, the amount of which was quantitatively estimated by absorbing it in soda-lime. (Sample 2.2563 g. evolved 0.7518 g. of CO_2, calculated for $C_5H_8O_4$ 0.7521 g.) The resulted substance had the following properties: b.p. 153–153.5°/761 mm.; d_4^{20} 0.9505; n_D^{20} 1.3933; M.R. obs. 22.11, calculated for $C_4H_8O_2$ 22.21.

The substance has acidic properties and does not decolourize bromine and permanganate in cold. Acid value 636.4 (0.2033 g. of the sample required 24.32 c.c. of 0.095N NaOH), calculated for $C_4H_8O_2$ 636.3. (Found: C, 54.38; H, 9.15. Calculated for $C_4H_8O_2$: C, 54.55; H, 9.09. Analysis of the silver salt: Ag, 55.58. Calculated for $C_4H_7O_2Ag$: Ag, 55.31%.) The substance was proved to be identical with isobutyric acid by preparing its acid chloride and amide.

Isobutyryl chloride. A mixture of 1 g. of the acid and 1 g. of phosphorus trichloride was heated to gentle boiling for a few minutes. The acid chloride obtained showed the following properties: b.p. 90–93°; d_4^{20} 1.1079; n_D^{20} 1.4081. These constants are in good accordance with those of isobutyryl chloride (b.p. 92°; d_4^{20} 1.0174; n_D^{20} 1.40789) reported by Brühl(35).

Isobutyryl amide. The acid chloride was added drop by drop to well-cooled aqueous ammonia, when colourless glistening leaflets were obtained. It melted at 116–123° without purification, which was separated into two portions, namely, prismatic needles melting at 170–173° (separated at first) and glistening scaly crystals melting at 124–128°, by recrystallization from water. The substance melting at 170–173° might have been crude diisobutyryl amide, a by-product obtained by Hoffmann(36) in this reaction, but owing to the scarcity of the substance its confirmation could not be attained. The substance melting at 124–128° was once more recrystallized

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(35) Brühl, *Ann.*, **203** (1880), 20.
(36) Hoffmann, *Ber.*, **15** (1882), 981.

from benzene, when it melted at 127–128° alone and in admixture with a specimen of isobutyryl amide.

(2) *Liquid portion.* The amount of liquid portion obtained after removal of dimethylmalonic acid was nearly the same with that of the latter. It showed acidic characteristics as well as those of aldehyde. The substance decolourized bromine in cold showing the unsaturated nature, and on oxidation with 4% potassium permanganate another crop of dimethylmalonic acid was obtained.

10 g. of the liquid substance was dissolved in 500 c.c. of 4% sodium bicarbonate solution and dilute permanganate solution (4%) was added drop by drop with stirring till the solution acquired permanent reddish colour, left over night at the ordinary temperature and manganese dioxide precipitated was filtered off. The filtrate after being saturated with carbon dioxide was evaporated to dryness, acidified by dilute hydrochloric acid and the oily substance thus set free was extracted with ether. The residue after removal of the solvent crystallized to a soft mass, from which a crystalline substance was separated by filtration. It proved to be dimethylmalonic acid. The liquid portion was then treated with a mixture of ether and light petroleum ether (1:1) in which dimethylmalonic acid was insoluble, and thus could be separated from the liquid portion. The filtered crystals were purified by reprecipitation from ethereal solution by adding light petroleum ether when it exhibited every characteristic property of dimethylmalonic acid.

Identification of formic acid. The ether–petroleum ether solution obtained above was then shaken vigorously with water for an hour in order to separate water-soluble acids. The aqueous layer was separated, neutralized with dilute ammonia and evaporated to smaller volume. The neutral solution produced an irritating odour on acidification with 5N sulphuric acid, while a quantity of the silver salt was precipitated on adding silver nitrate solution which immediately turned into bright grayish colour. It precipitates calomel from mercuric chloride solution. From these results it follows that the liquid portion contained formic acid.

II. Preparation of hydrocarbon from shonanic acid. (1) *By Rosenmund and Zetzche's method*(37) ($R{\cdot}COOH \rightarrow R{\cdot}CO{\cdot}Cl \rightarrow R{\cdot}CHO \rightarrow R{\cdot}CH_3$). By applying this method to the reduction of shonanic acid, the yield of aldehyde was very poor and almost all of the reaction product was a resinous matter, so that only the properties and the derivatives of the aldehyde were studied.

When shonanic acid chloride (freshly prepared) in benzene solution was treated with hydrogen in presence of palladium on barium sulphate as catalyser, the vigorous evolution of hydrochloric acid gas was observed. After the evolution of HCl gas was over, the reaction mixture was filtered from the catalyser and the yellowish matter which remained after removal of the solvent was distilled under reduced pressure. Most of the substance remained undistilled even on heating to 280° under 3 mm., and only a few drops of colourless mobile liquid (0.3 g.) of the following properties was obtained. B.p. 73°/5 mm.; d_4^{20} 0.935; n_D^{20} 1.4630; M.R. obs. 46.78, calculated for $C_{10}H_{18}O$ 46.50.

The substance showed aldehydic nature on testing with Schiff's reagent and Tollens' solution and gave a crystalline semicarbazone.

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(37) *Ber.*, **51** (1918), 585, 594.

Semicarbazone. The semicarbazone was prepared from 0.22 g. of the sample, 0.14 g. of sodium bicarbonate and 0.15 g. of semicarbazide hydrochloride. Recrystallization from ethyl alcohol furnished a colourless scales melting at 165°. (Found: N, 20.03. Calculated for $C_{11}H_{21}ON_3$: N, 19.9%.) Thus it is clear that the substance obtained was the aldehyde corresponding to tetrahydroshonanic acid ($C_{10}H_{18}O_2$).

(2) *Preparation of hydrocarbon from shonanic acid by reduction with hydroiodic acid.* 5 g. of shonanic acid was heated with 10 g. of hydroiodic acid ($d = 1.7$) together with 1.6 g. of red phosphorus in a sealed tube as in the case of reduction of succinic,(38) palmitic(39) and hexahydro-*m*-xylic acid(40) for 5 hours at 220–225°, then another 4 hours at 240° with the further addition of 0.5 g. of red phosphorus, then 4 hours more at 250–270° with a third addition of 0.5 g. of red phosphorus and 0.7 c.c. of water. The contents of the sealed tube were then poured into 200 c.c. of water, shaken with 5% sodium hydroxide solution to remove acidic substance, dried over anhydrous sodium sulphate and then ether was distilled off. The light mobile oil remaining behind was rectified twice under the ordinary pressure over metallic sodium and in this manner a hydrocarbon of the following properties was obtained. (Yield 1.3 g.) B.p. 157–158.5°/754 mm.; d_4^{20} 0.7866; n_D^{20} 1.4344; M.R. obs. 46.37, calculated for $C_{10}H_{20}$ 46.18. The substance does not decolourize either bromine or permanganate showing that the substance is saturated. (Found: C, 85.62; H, 14.37; molecular weight in phenol, 144.7. Calculated for $C_{10}H_{20}$: C, 85.7; H, 14.3%; molecular weight, 140.2.)

(3) *Preparation of hydrocarbon from tetrahydroshonanic acid by reduction with hydroiodic acid.* Next, exactly the same method as in the case of (2) was applied to tetrahydroshonanic acid taking 16 g. of the acid and the product showed the following properties: b.p. 158.5°/765 mm.; d_4^{20} 0.7872; n_D^{20} 1.4338; M.R. obs. 46.34, calculated for $C_{10}H_{20}$ 46.18. Inert against bromine and permanganate. (Found: C, 85.49; H, 14.36. Calculated for $C_{10}H_{20}$: C, 85.7; H, 14.3%.)

(4) *Preparation of hydrocarbon* $C_9H_{16}\ \ulcorner\!\!=_1$ *by the dry distillation of tetrahydroshonanic acid with soda-lime.* Tetrahydroshonanic acid (10 g.) was heated with soda-lime (30 g.) under ordinary pressure. A little oily matter began to distil over at 134° which ceased at 150°. Yield 6.0 c.c. It was fractionally distilled over metallic sodium and was separated into three portions as shown in Table 3. The fraction (3) was again subjected to another fractional distillation under ordinary pressure and the following fractions were obtained (Table 4).

Table 3.

Fr. No.	B.p./753 mm.	Vol. (c.c.)
1	75–138°	0.8
2	138–141°	1.0
3	141–149°	3.8

Table 4.

Fr. No.	B.p./755 mm.	Vol. (c.c.)
a	142–145°	0.4
b	145–148°	3.1
c	148–149°	0.2

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(38) Berthelot, *Ann.*, **147** (1868), 376.

(39) Kraft, *Ber.*, **15** (1882), 1689, 1711.

(40) Aschan, *Ber.*, **24** (1891), 2718.

The main fraction b was once more rectified and 2.7 g. of hydrocarbon with the following properties was obtained. B.p. 144.5–145°/757 mm.; d_4^{19} 0.8129; n_D^{19} 1.4595; M.R. obs. 41.12, calculated for $C_9H_{16}\overline{\Gamma}_1$ 41.07. The hydrocarbon obtained absorbs bromine readily and decolourizes permanganate in cold. Bromine value 1236 (0.2403 g. absorbed 0.297 g. bromine), calculated for $C_9H_{16}\overline{\Gamma}_1$ 1290. (Found: C, 86.95; H, 12.60. Calculated for C_9H_{16}: C, 87.1; H, 12.90%.) The attempt to obtain its nitrosochloride or nitrosite in the crystalline state was not successful.

III. Preparation of *o*-dinitrobenzene from shonanic acid. 5 g. of shonanic acid was heated on the water-bath with 50 c.c. of nitric acid ($d = 1.12$) with constant stirring. A brisk reaction took place at first, which soon subsided but the heating was continued for 5 hours. On standing over night long needle crystals appeared, which were filtered off and recrystallized from water. It melted at 117–118°. The filtrate bore an odour reminding of nitrobenzene and on evaporating another crop of crystals was obtained, which proved to be the same substance as the main product. The substance was neutral and the presence of nitrogen was recognized by the evolution of ammonia on heating with soda-lime. (Found: C, 42.75; H, 2.38; N, 16.67. Calculated for $C_6H_4O_4N_2$: C, 42.86; H, 2.38; N, 16.67%.)

The empirical formula of the substance calculated from the experimental data is $C_3H_2O_2N$ while among the substances corresponding to this empirical formula *o*-dinitrobenzene melts at 117.5°. The substance showed no depression of the melting point in admixture with *o*-dinitrobenzene, thus the identity of these two substances being proved.

Summary.

(1) Dimethylmalonic acid and formic acid were obtained by the oxidation of shonanic acid.

(2) A hydrocarbon $C_{10}H_{20}$ was obtained by the reduction of shonanic and tetrahydroshonanic acid with hydroiodic acid.

(3) A hydrocarbon $C_9H_{16}\overline{\Gamma}_1$ was obtained by the dry distillation of shonanic acid with soda-lime.

(4) The attempt to determine the ring structure of shonanic acid by comparing the properties of these hydrocarbons with those of known hydrocarbons gave no reliable results.

(5) The formation of *o*-dinitrobenzene from shonanic acid by treating it with dilute nitric acid may be taken as an evidence for the presence of six-membered ring system in its molecule.

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