Experimental

General Method for the Preparation of the Thiolurethans (Compound 3 as Example).—Three hundred fifty grams of analytically pure dimethylaminoethylthiol[4] (3.3 moles) was dissolved in 2000 cc. of anhydrous pyridine, 781 g. of dicyclohexylcarbamyl chloride,[5] (3.2 moles) was added and the mixture was heated and stirred at 100–105° for 3 hours. The batch was cooled to room temperature, the nearly solid mass was dissolved in 1000 cc. of water and distilled *in vacuo* below 50° to a mush to remove most of the pyridine. The residue was dissolved in 2000 cc. of water, the solution acidified to congo red with concentrated hydrochloric acid and extracted with three 1500-cc. portions of ether which were discarded. The acid solution was made strongly alkaline by adding sodium carbonate and extracted with four 1000-cc. portions of chloroform. The combined chloroform extracts were dried over Drierite, the chloroform was distilled *in vacuo* and the residue held for several hours at 100° (1 mm.) to remove all pyridine; yield, etc. (see Table I).

The Preparation of the Ammonium Iodides.—The urethans were dissolved in 3 to 4 moles of the requisite alkyl iodides, the mixtures were held at 25–35° for 4 hours or longer, cooling in ice as needed. Anhydrous ether was added in excess and the mixtures were allowed to stand overnight at room temperature. The iodides were filtered, washed with anhydrous ether and dried; yields see Table II.

The Ethosulfate Salts.—The urethans (1, 3, 4, 5) were dissolved in ether, 2 moles of ethyl sulfate was added, and on standing one to two days at room temperature the products crystallized out and were filtered and washed with ether. As the ethosulfate of urethan 2, however, did not crystallize, compound 10 of Table II [2-(diamylcarbamylmercapto)-ethyl]-ethyldimethylammonium ethosulfate was obtained as follows:

Fifteen grams of dimethylaminoethylthioldiamylurethan (0.052 mole) was dissolved in 100 cc. of anhydrous ether, 15.4 g. of diethyl sulfate (0.1 mole) was added, and the solution was refluxed for 24 hours. The reaction mixture was extracted with two 25-cc. portions of water and the aqueous extracts were adjusted to a *p*H of 6.5 by adding a little barium hydroxide solution. The turbid solution was clarified by treating with charcoal and filtering through a layer of Supercel. A faint trace of Ba^{++} in the solution was removed by adding a minute amount of ammonium sulfate and filtering. The solution was reduced to a sirup which was air-dried; a sluggish crystallization gradually took place. The soapy masses were frequently broken up, and drying in the air was continued until the weight was constant; yield, etc., see Table II.

Conversion of the Iodides to Sulfates.—As an example, the conversion of iodide 8 to [2-(diamylcarbamylmercapto)-ethyl]-ethyldimethylammonium sulfate (9) was carried out as follows:

Ninety grams of the iodide (0.20 mole) was dissolved in 500 cc. of 50% alcohol, 41 g. of powdered silver sulfate (0.13 mole) was added and the mixture was stirred rapidly until the reaction was completed. The silver salts were filtered and washed with 50% alcohol. The solution was treated with slight excess of hydrogen sulfide to remove a trace of silver, adjusted to *p*H 6.5 by adding barium hydroxide solution, decolorized by treatment with carbon and filtered through a bed of Super-cel. The clear and colorless filtrate was concentrated to a sirup *in vacuo* and the residue was dehydrated by distillation under reduced pressure with ethanol.

Some of the sulfates crystallized in the air and were air-dried to constant weight; others were hygroscopic and were dried *in vacuo* over sulfuric acid to constant weight. For yields, etc., see Table II.

Acknowledgment.—We are indebted to Mr. R. N. Boos and associates for the analyses, and to Mr. E. van Gilder for technical assistance.

Rahway, N. J. Received August 28, 1950

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[4] Gilman, This Journal, **67**, 1845 (1945).

[5] The carbamyl chlorides were prepared from the corresponding amines with excess phosgene in xylene at 0°, in about 90% yields; see Boon, *J. Chem. Soc.*, 313 (1947).

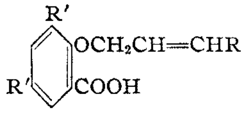
[Contribution from the Department of Chemistry of the University of Rochester]

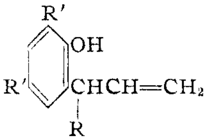
The Effect of Changes in the Allyl Group on the Rearrangement of Allyl Ethers of Salicylic Acids

By William R. Nummy[1] and D. Stanley Tarbell

The synthesis of ethers prepared from 3,5-dichlorosalicylic acid and 3,5-dimethylsalicylic acid, with 3-bromomethylcoumarin and 3-bromomethyl-2,2-dimethylbenzopyran, has been investigated. 2-(3-Coumarinylmethoxy)-3,5-dichlorobenzoic acid yields carbon dioxide, but no crystalline product, upon pyrolysis. An unsaturated phenolic carbinol, 1-*o*-hydroxyphenyl-2,3-dimethylbutene-1-ol-3, has been shown to be an intermediate in the formation of 2,2,3-trimethylbenzopyran from 3-methylcoumarin and methylmagnesium iodide. Measurements of the rate of rearrangement of the allyl and crotyl ethers of 3,5-dimethyl- and 3,5-dichlorosalicylic acid show that the change in nuclear substitution does not affect the rate; the crotyl ethers, however, rearrange several times as rapidly as the allyl ethers in both series, an effect attributed to the inductive effect of the methyl group.

It has been shown that rearrangement of O-crotyl-3,5-dichlorosalicylic acid[2] I takes place with inversion to yield II in which the γ-carbon atom of the crotyl group is attached to the ring.

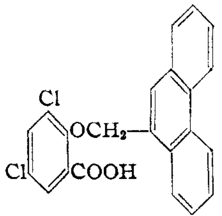




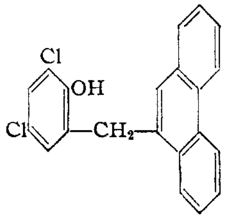
I, R = CH_3, R′ = Cl
III, R = H, R′ = CH_3
V, R = R′ = CH_3
VII, R = H, R′ = Cl

II, R = CH_3, R′ = Cl
IV, R = H, R′ = CH_3
VI, R = R′ = CH_3

The corresponding 9-phenanthrylmethyl ether VIII likewise undergoes rearrangement with loss of carbon dioxide,[3] but the product has been proved by synthesis[4] to be IX; the shift therefore occurs *without* inversion.



VIII



IX

Inversion and other characteristics of the

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[1] Sherman Clarke Fellow, 1949–1950.

[2] Tarbell and Wilson, This Journal, **64**, 607 (1942).

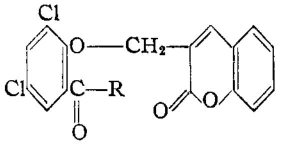
[3] Tarbell and Wystrach, *ibid.*, **65**, 2149 (1943).

[4] Tarbell and Sato, *ibid.*, **68**, 1091 (1946).

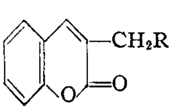
Claisen rearrangement to the ortho position are best explained by the cyclic mechanism.[5] The anomalous behavior of the 9-phenanthrylmethyl ether VIII in this respect may be due to two factors; the first is that the formation of the cyclic transition state may be prevented by spatial interference between the bulky groups involved. The second is that the 9,10-double bond in phenanthrene may have too much aromatic character to allow the necessary electronic displacements to occur.

The object of the present work was to try to choose between the two alternatives, by synthesis of an ether with a less aromatic double bond than VIII, but with a similar degree of steric hindrance.

The 3-coumarinylmethyl ethers seemed the most readily accessible compounds of the type desired, and 2-(3-coumarinylmethoxy)-3,5-dichlorobenzoic acid was prepared by condensation of 3-bromomethylcoumarin[6] (XIII) with 3,5-dichlorosalicylamide,[7] followed by treatment of the resulting amide X with nitrous acid. Pyrolysis of the acid XI yielded some carbon dioxide, but no crystalline material could be isolated from the products, by a variety of procedures.



X, R = NH₂
XI, R = OH
XII, R = OCH₃

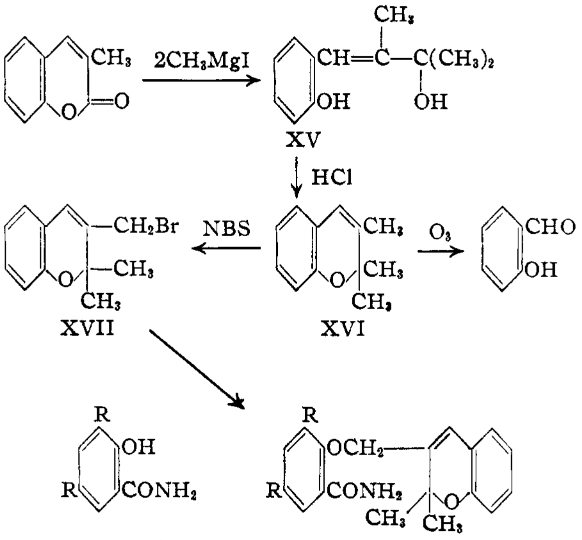


XIII, R = Br
XIV, R = OH

It was thought that the instability of XI might be due to the presence of the lactone ring, and hence the synthesis of the corresponding 3-(2,2-dimethylbenzpyranyl)-methyl ether was investigated. The amide XIX was synthesized successfully as outlined below; treatment of this amide with nitrous acid, or with dilute alkali, with the intention of converting the amide function to a carboxyl group, cleaved the ether linkage instead, and formed 3,5-dichlorosalicylamide (XVIII) as the sole isolatable product.

It may be noted that, like Smith and Ruoff in a similar case,[8] we isolated the unsaturated carbinol XV as an intermediate in the formation of the trimethylbenzopyran XVI. Because of the possibility that the action of the Grignard on 3-methylcoumarin might have led[9] to the 2,3,4-trimethyl derivative instead of the 2,2,3-trimethyl compound XVI, the latter structure was established by ozonization of the compound to salicylaldehyde, identified as the dinitrophenylhydrazone.

Sensitivity to hydrolysis of the ether linkage had proved troublesome in the coumarin series (X and XII) as well as with compound XIX. Thus, no conditions were found which would hydrolyze the methyl ester XII without cleavage of the ether linkage, and 3,5-dichlorosalicylic acid was isolated, usually as the sole product. In one run under mild basic conditions, it was possible to isolate the other product of ether cleavage, 3-coumarinylcarbinol (XIV).



XV

XVII

XVI

XVIII, R = Cl
XX, R = CH₃
XXII, R = CH₃
CONH₂ = COOCH₃

XIX, R = Cl
XXI, R = CH₃

With the idea that the chlorine atoms might be responsible for the unusual sensitivity of the ether linkages, attention was directed to derivatives of 3,5-dimethylsalicylic acid. The ether amide XXI, obtained by alkylation of 3,5-dimethylsalicylamide (XX) with the bromomethylbenzopyran XVII, was not hydrolyzed by refluxing base, but it gave 3,5-dimethylsalicylamide as the sole identifiable product after treatment with nitrous acid.

The rate of alkylation of the phenolic group in methyl 3,5-dimethylsalicylate XXII[10] was found to be very much lower than the corresponding dichlorosalicylate; the allyl and crotyl ethers could be obtained only by alkylation of the sodium salt of XXII in toluene solutions. Attempted alkylation with acetone–potassium carbonate or methanolic alkali gave no ether, apparently because the halides reacted faster in other ways.

The allyl (III) and crotyl (V) ethers of 3,5-dimethylsalicylic acid were prepared, in order to compare their rate of rearrangement with that of the corresponding dichloro compounds.[2] The allyl compound III yielded 2-allyl-4,6-dimethylphenol (IV) and evolved 96% of the calculated amount of carbon dioxide. The crotyl compound yielded a similar amount of gas, and formed 2-(α-methylallyl)-4,6-dimethylphenol (VI), whose structure was proved by isolation of formaldehyde (as the methone derivative) in 23% yield by ozonization.[11]

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[5] (a) Claisen and Tietze, *Ber.*, **58**, 275 (1925); (b) Hurd and Pollack, *J. Org. Chem.*, **3**, 550 (1939); (c) Kincaid and Tarbell, THIS JOURNAL, **61**, 3085 (1939); (d) Cope and Hardy, *ibid.*, **62**, 441 (1940). Recent kinetic evidence (Schuler and Murphy, *ibid.*, **72**, 3155 (1950)) indicates that the gas-phase rearrangement of allyl vinyl ether involves a cyclic transition state.

[6] Molho and Mentzer, *Compt. rend.*, **223**, 1142 (1946).

[7] The material reported by E. J. Smith (*Ber.*, **11**, 1226 (1878)) to be 3,5-dichlorosalicylamide, m.p. 209°, is actually a mixture of the amide and dichlorosalicylic acid; the pure amide, prepared by the action of liquid ammonia on the acid chloride melts at 190° (see below).

[8] Smith and Ruoff, THIS JOURNAL, **62**, 145 (1940).

[9] *Cf.* Shriner and Sharp, *J. Org. Chem.*, **4**, 575 (1939).

[10] This ester was reported by O. Jacobsen (*Ann.*, **195**, 278 (1879)) as an oil giving a negative ferric chloride test; we have obtained it by several methods as a solid, m.p. 73°, giving a blue color with ferric chloride.

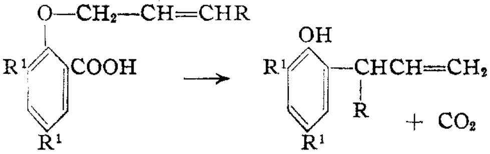
[11] (a) Clemo and MacDonald, *J. Chem. Soc.*, 1294 (1935); (b) Ruzicka, Seidel, Schinz and Tavel, *Helv. Chim. Acta*, **31**, 257 (1948).

This showed that rearrangement occurred with inversion in this case, just as with the dichloro compound.[2]

The comparative rate measurements given in Table I were obtained by following the rate of carbon dioxide evolution. It is apparent that the replacement of methyl by chlorine in the nucleus is virtually without effect on the rate; the replacement of hydrogen by methyl in the allyl group, however, speeds up the reaction several fold in each series. These results provide quantitative support for the ideas previously expressed[2] about the effect on rate of rearrangement of changing from allyl to crotyl, in which the difference was attributed to the inductive effect of the methyl group.

TABLE I

TIME IN MINUTES FOR 50% COMPLETION OF REACTION



	R	R¹	100°	125°	140°
VII	H	Cl	...	28.1	7.4
III	H	CH_3	200	28.2	7.3
I	CH_3	Cl	...[a]	4.1	...[b]
V	CH_3	CH_3	...[a]	2.7	...[b]

[a] Below m.p. of compound. [b] Rate too fast to be measured.

Experimental[12]

3,5-Dichlorosalicylamide (XVIII).—The 3,5-dichlorosalicylyl chloride[13] obtained from 26 g. of the acid was introduced without isolation in small portions into 100 cc. of liquid ammonia. Evaporation of the excess ammonia gave a solid yellowish residue which dissolved almost completely in 3 l. of hot water. The filtered and cooled solution was made slightly acid with hydrochloric acid, and the resulting precipitate was collected, washed with water and recrystallized from 700 cc. and 50% ethanol. The yield was 10 g. (37%) of material which melted at 190–190.5°,[7] on further recrystallization from the same solvent.

Anal. Calcd. for $C_7H_5Cl_2NO$: C, 40.77; H, 2.41; N, 6.77. Found: C, 40.93; H, 2.13; N, 6.89.

3-Methylcoumarin was obtained in 55% yield by the Perkin reaction[14] between carefully dried sodium salicylaldehyde and propionic anhydride for seven hours at 170°.

2-(3-Coumarinylmethoxy)-3,5-dichlorobenzamide (X).—To a refluxing mixture of 6.6 g. of 3,5-dichlorosalicylamide, 7.6 g. of 3-bromomethylcoumarin[6] (XIII), 4.6 g. of sodium iodide and 75 cc. of methyl ethyl ketone was added dropwise a solution of 4.6 g. of potassium carbonate in 8 cc. of water. Refluxing and stirring were continued for one hour, the resulting mixture cooled in ice, and the precipitated solid removed by filtration. Recrystallization from dilute acetic acid gave 7.6 g. (65%) of colorless prisms, m.p. 208–209°.

Anal. Calcd. for $C_{17}H_{11}Cl_2NO_4$: C, 56.06; H, 3.04. Found: C, 56.38; H, 2.97.

2-(3-Coumarinylmethoxy-)3,5-dichlorobenzoic Acid (XI).—To a solution of 2.0 g. of the amide X in 160 cc. of glacial acetic acid was added a cold solution of 24 cc. of water and 56 cc. of sulfuric acid. The resulting clear solution was cooled to 0°, and a solution of 2.2 g. of sodium nitrite in 10 cc. of water was added. After mixing thoroughly, the resulting greenish-blue solution was maintained at 0° for one hour and then allowed to come slowly to room temperature. A voluminous precipitate was formed and a colorless gas given off; the solution was diluted with twice its volume of water and the precipitate was collected and washed. Recrystallization from glacial acetic acid gave 1.45 g. (72%) of fluffy, white needles, m.p. 185–187° dec.

Anal. Calcd. for $C_{17}H_{10}Cl_2O_5$: C, 55.96; H, 2.74. Found: C, 55.87; H, 2.61.

Pyrolysis of XI.—Pyrolysis of the above ether acid was carried out in a flask attached to a simple gasometer using brine saturated with carbon dioxide as the leveling liquid. At 235–240°, the gas evolution from a 1-g. sample of XI stopped after 30 minutes, and the volume amounted to 44% of the theoretical. The residue yielded, upon solution in ether and bicarbonate extraction, a 37% yield of 3,5-dichlorosalicylic acid. Extraction of the ether solution with three portions of Claisen alkali, followed by immediate acidification, yielded 58 mg. of amorphous material which decomposed when the purification was attempted. Addition of hydroquinone to the ether solution from another run did not prevent decomposition.

Pyrolysis at 192° for 15 minutes yielded 6% of the theoretical carbon dioxide; only amorphous material was isolated from the residue.

1-*o*-Hydroxyphenyl-2,3-dimethylbutene-1-ol-3 (XV).—To a Grignard solution prepared from 14.6 g. of magnesium, 90 g. of methyl iodide and 150 cc. of ether was added dropwise a solution of 40 g. of 3-methylcoumarin in 800 cc. of ether. Stirring was continued for five hours, and the mixture was then treated with 500 cc. of water containing 110 g. of ammonium chloride and 25 cc. of concentrated hydrochloric acid. The ether layer was separated, the aqueous layer was extracted with 100 cc. of ether, and the combined ether solutions were filtered and dried. Removal of the solvent and recrystallization of the resulting solid from *n*-hexane gave 38 g. (79%) of colorless needles of the carbinol XV, m.p. 79.5–80°.

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.98; H, 8.38. Found: C, 75.14; H, 8.51.

2,2,3-Trimethylbenzopyran (XVI).—1-*o*-Hydroxyphenyl-2,3-dimethylbutene-1-ol-3 (XV) (43 g.) was dropped slowly into 50 cc. of concentrated hydrochloric acid at 0°. After standing for three hours in an ice-bath with occasional shaking, the resulting light purplish oil was extracted with ether, dried and distilled *in vacuo*, yielding 22 g. (56%) of colorless liquid and some resinous residue. The liquid had the following properties: b.p. 83° (1 mm.), n^{25} 1.5525, d^{25} 1.0278.

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.76; H, 8.04; M_D, 54.42.[15] Found: C, 82.74; H, 8.05; M_D, 54.34.

Ozonization.—A solution of 4 g. of the pyran XVI in 15 cc. of dry carbon tetrachloride was ozonized[9] and the 2,4-dinitrophenylhydrazone of m.p. 254–254.5°, obtained from the product, was shown to be that of salicylaldehyde by a mixed m.p. with an authentic sample.[16] The dinitrophenylhydrazone of *o*-hydroxyacetophenone, which has not been reported, was prepared, because this ketone would be the other possible ozonization product. The derivative melted after recrystallization from glacial acetic acid, at 212–213°.

Anal. Calcd. for $C_{14}H_{12}N_4O_5$: C, 53.16; H, 3.83. Found: C, 53.55; H, 3.95.

3-Bromomethyl-2,2-dimethylbenzopyran (XVII).—A solution of 27 g. of 2,2,3-trimethylbenzopyran (XVI) in 300 cc. of dry carbon tetrachloride was refluxed in a 1-l. flask with 32.2 g. of freshly ground recrystallized N-bromosuccinimide,[17] with a pinch of benzoyl peroxide as initiator. After six and a half hours, all of the solid present was floating on top, indicating that the reagent had been converted to succinimide. The mixture was cooled, the succinimide removed, and the solvent was evaporated; recrystallization of the residue from 50 cc. of hexane gave 21.7 g. (54%) of colorless rhombic crystals, m.p. 69–70°. The material is best kept under mother liquor in the refrigerator.

Anal. Calcd. for $C_{12}H_{13}BrO$: C, 56.91; H, 5.18. Found: C, 57.13; H, 5.26.

2-(3-(2,2-Dimethylbenzopyranyl)-methoxy)-3,5-dichlorobenzamide (XIX).—To a refluxing mixture of 1.0 g. of 3,5-dichlorosalicylamide, 1.2 g. of the bromomethylbenzopyran XVII and 15 cc. of methyl ethyl ketone, was added

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(12) Melting points are uncorrected; analyses by Micro-Tech Laboratories, Mrs. G. Sauvage and W. R. Nummy.

(13) Earle and Jackson, THIS JOURNAL, **28**, 109 (1906).

(14) Perkin, *J. Chem. Soc.*, **28**, 12 (1875).

(15) Using the values of Shriner and Sharp.[9]

(16) The reported m.p. is 252° (Campbell, *Analyst*, **61**, 392 (1936)).

(17) Ziegler, *Ann.*, **551**, 80 (1942); Djerassi, *Chem. Revs.*, **43**, 271 (1948).

0.7 g. of anhydrous potassium carbonate. After ten minutes, a brownish color began to develop, the mixture was cooled and the solid residue removed by filtration. The ketone layer yielded 0.55 g. (30%) of product when it was chilled in an ice–salt mixture; the material formed colorless needles, m.p. 142–143°, when it was crystallized from hexane–chloroform.

Anal. Calcd. for $C_{19}H_{17}Cl_2NO_3$: C, 60.34; H, 4.56. Found: C, 60.61; H, 4.67.

Hydrolysis Experiments.—To a solution of 0.15 g. of the above amide XIX in 10 cc. of glacial acetic acid was added 1 cc. of 70% sulfuric acid. The solution was supercooled to 6° and a solution of 0.2 g. of sodium nitrite in 0.7 cc. of water was added. The resulting dark red solution evolved gas as it warmed up. Dilution with water gave a light greenish color and a slight precipitate. Extraction with chloroform and subsequent extraction of this separated layer with 5% sodium bicarbonate gave some 3,5-dichlorosalicylamide which was identified by mixed m.p. and positive phenol test. A second attempt with exactly the same amounts of material was made. In this case the sulfuric acid was added to a cooled mixture of XIX solution containing the required sodium nitrite. The same results as above were observed on working up the product. A solution of 0.25 g. of the amide XIX in 10 cc. of 60% methanol was warmed with 0.2 cc. of Claisen alkali, which gave a clear orange solution. 3,5-Dichlorobenzamide was recovered on working up the mixture.

Methyl 2-(3-Coumarinylmethoxy)-3,5-dichlorobenzoate (XII).—To a refluxing mixture of 19.8 g. of methyl 3,5-dichlorosalicylate,[17a] 22.5 g. of 3-bromomethylcoumarin,[6] 13.5 g. of sodium iodide and 225 cc. of methyl ethyl ketone, was added dropwise with stirring a solution of 13.8 g. of potassium carbonate in 24 cc. of water. After stirring and refluxing for five hours, the mixture was cooled, and the solid collected by filtration was recrystallized from glacial acetic acid. An 86% yield (10.3 g.) of fluffy white needles, m.p. 171°, was obtained.

Anal. Calcd. for $C_{17}H_{10}Cl_2O_5$: C, 57.27; H, 3.19. Found: C, 57.22; H, 3.21.

Hydrolysis Experiments.—(1) A sample of the above ester XII (3 g.) yielded, after refluxing with 25 cc. of Claisen alkali for 15 minutes followed by acidification, 1.4 g. of 3,5-dichlorosalicylic acid.

(2) The ester XII (1 g.) dissolved rapidly in 10 cc. of concentrated sulfuric acid, and the solution was poured onto 100 cc. of ice. The resulting solid was collected, was recrystallized from alcohol and the product (0.5 g.) was shown to be methyl 3,5-dichlorosalicylate by a mixed m.p. No other product could be isolated.

(3) After standing for four months in the cold, a mixture of 0.5 g. of the ester XII, 0.5 g. of sodium bicarbonate, 10 cc. of water and 15 cc. of methanol gave a small amount of 3,5-dichlorosalicylic acid on acidification. Dilution of the resulting alcoholic solution gave an oil which crystallized to a yellowish solid. This material could be recrystallized from 40% ethanol and melted at 186–187°. An analytical sample, prepared by sublimation under reduced pressure, had the composition calculated for the second cleavage product, **3-coumarinylcarbinol** (XIV).

Anal. Calcd. for $C_{10}H_8O_3$: C, 68.18; H, 4.58. Found: C, 68.43; H, 4.82.

3,5-Dimethylsalicylic Acid.—2.4-Dimethylphenol (80.3 g.) was added to a solution of 16.1 g. of sodium in 350 cc. of absolute alcohol, the alcohol was replaced by xylene and the sodium salt was collected and dried in a vacuum oven at 105°; the yield was 80 g.

In the liner of a 1-l. high pressure hydrogenation bomb was placed 38 g. of this salt and 125 g. of Dry Ice. The apparatus was rapidly sealed and heated to 150°, which gave a gage pressure of 800 lb.; after five hours at this temperature, the product was removed from the bomb and dissolved in 1 l. of hot water. Acidification gave 35 g. (80%) of acid which melted at 178–180°; this is the reported m.p.[18]

3,5-Dimethylsalicylyl Chloride.—3,5-Dimethylsalicylic acid (10 g.) was heated with 14 g. of phosphorus pentachloride at 60–70° for one hour. The mixture was dissolved in 50 cc. of hexane, from which crystalline material precipitated on cooling in an ice–salt mixture. This acyl halide rapidly decomposed in moist air and hence was usually used directly in the next step. The analytical sample was prepared by sublimation *in vacuo*, and melted at 75–76°.

Anal. Calcd. for $C_9H_9ClO_2$: C, 58.54; H, 4.91. Found: C, 58.13; H, 4.57.

Hydrolysis of the hexane filtrate gave 4.4 g. of starting material.

3,5-Dimethylsalicylamide (XX).—The 3,5-dimethylsalicylyl chloride obtained in the above procedure was added cautiously to 100 cc. of liquid ammonia. Upon evaporation of the excess ammonia, a yellowish solid remained, which was readily soluble in 500 ml. of hot water. The yield of material obtained on acidification and cooling of this solution was 3.9 g. (69%, based on unrecovered starting material) of white solid. This material was best recrystallized from an ethyl acetate–hexane mixture. An analytical sample was prepared by sublimation *in vacuo*, with the m.p. 161–161.5°.

Anal. Calcd. for $C_9H_{11}NO_2$: C, 65.43; H, 6.71. Found: C, 65.40; H, 6.60.

2-(3-(2,2-Dimethylbenzpyranyl)-methoxy)-3,5-dimethylbenzamide (XXI).—This product was prepared in the same manner as described above for the dichloro analog XIX, except that the mixture was refluxed for 4 hours. The yield was 26% of material which melted, after crystallization from ethyl acetate–hexane, at 167.5–168.5°.

Anal. Calcd. for $C_{21}H_{23}NO_3$: C, 74.74; H, 6.87. Found: C, 74.53; H, 6.60.

Attempted hydrolysis with butyl nitrite, sulfuric acid and ethanol yielded a small amount of 3,5-dimethylsalicylic acid. Basic hydrolysis with Claisen alkali evolved some ammonia, but the only solid product obtained was an unidentified neutral material.

Benzyl 3,5-Dimethylsalicylate.—This compound was prepared with the idea that the ester group might saponify more rapidly than the methyl ester, and hence be suitable for preparation of the desired ether. Sodium 3,5-dimethylsalicylate (11 g.) was heated with 8 g. of benzyl chloride and ten drops of diethylamine for 16 hours at 135°.[19] The mixture was dissolved in benzene, filtered and steam distilled, to remove excess benzyl chloride and solvent. The solid which remained after cooling was crystallized from 90% acetic acid to give 13.3 g. (89%) of colorless needles. The analytical sample, m.p. 57.8–58°, was prepared by sublimation *in vacuo*.

Anal. Calcd. for $C_{16}H_{16}O_3$: C, 75.57; H, 6.34. Found: C, 75.53; H, 6.37.

Methyl 3,5-Dimethylsalicylate.—Benzyl 3,5-dimethylsalicylate (3 g.) was refluxed overnight with a solution of 0.2 g. of sodium in 200 cc. of dry methanol; dilution and acidification of the solution yielded a white solid, which, after crystallization from 60% alcohol, gave 1.6 g. (76%) of colorless plates. The analytical sample, prepared by sublimation *in vacuo*, melted at 73°.

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.64; H, 6.71. Found: C, 66.63; H, 6.64.

The ester was also obtained by treatment of 3,5-dimethylsalicylic acid with methyl sulfate in bicarbonate solution, and by alkylation of the dry salt of the acid with methyl sulfate and a trace of diethylamine for 20 hours at 125°.

2-Allyloxy-3,5-dimethylbenzoic Acid (III).—A solution of 3.4 g. of methyl 3,5-dimethylsalicylate in 100 cc. of dry toluene was added to a solution of 0.42 g. of sodium in 100 cc. of dry methanol. The methanol–toluene azeotrope was distilled off, with addition of toluene, until the b.p. had reached 110°, and the simultaneous addition and distillation of toluene was continued for 30 minutes to ensure complete removal of the methanol. Allyl bromide (7 g.) was added to the heavy yellow gel of the sodium salt, and the mixture was refluxed with stirring for 20 hours. The mixture was cooled, and the separated salt was collected and washed with ether. The combined organic layer gave a slightly positive phenol test with ferric chloride solution. It was washed with three 100-cc. portions of Claisen alkali followed by three 100-cc. portions of brine, separated, and dried; this material gave a negative phenol test.

The solvents were evaporated under reduced pressure. Treatment of the residue on the steam-bath with 20 cc. of Claisen alkali for 20 minutes and subsequent addition of 80 cc. of water gave a clear solution. The buff-colored pre-

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[17a] Claisen and Eisleb, *Ann.*, **418**, 85 (1918).

[18] O. Jacobsen, *Ber.*, **14**, 44 (1881).

[19] *Cf.* Volwiler and Vliet, THIS JOURNAL, **43**, 1672 (1921).

cipitate which formed on acidification of this material was dissolved in 50 cc. of 5% sodium bicarbonate solution, treated with charcoal and filtered. Acidification of this solution gave 2.1 g. (55%) of the acid. Recrystallization from hexane gave fine colorless needles, m.p. 78.5–79.0°.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 70.08; H, 6.93.

2-Crotyloxy-3,5-dimethylbenzoic Acid (V).—This acid was prepared by essentially the above procedure from the sodium salt of 5.0 g. of methyl 3,5-dimethylsalicylate and 8.5 g. of crotyl bromide.[20] The product was obtained in 37% yield which melted at 103.5–104° after crystallization from hexane.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.88; H, 7.32. Found: C, 71.14; H, 7.58.

2-α-Methylallyl-4,6-dimethylphenol (VI).—2-Crotyloxy-3,5-dimethylbenzoic acid (2.6 g.) was heated for 30 minutes at 125° under nitrogen. The resulting light yellowish oil was combined with three small batches resulting from rate runs and dissolved in benzene. The solution was washed with 5% sodium bicarbonate solution to remove acidic material, and then extracted with a total of 60 cc. of Claisen alkali in three portions. The combined Claisen alkali extracts were acidified and extracted with a benzene-ether mixture. The organic layer was separated and dried. Evaporation of solvent and distillation under diminished pressure gave 2.1 g. of pale yellowish oil, which was redistilled to give a colorless oil, b.p. 126.5° (17.5 mm.).

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.56; H, 9.22.

The phenylurethan, recrystallized from ligroin, formed colorless needles, m.p. 100.0–100.5°.

Anal. Calcd. for $C_{19}H_{21}NO_2$: C, 77.25; H, 7.17. Found: C, 77.26; H, 7.05.

The α-naphthylurethan, prepared similarly, melted at 144.5–145.5°.

Anal. Calcd. for $C_{23}H_{23}NO_2$: C, 79.97; H, 6.71. Found: C, 80.02; H, 6.84.

Ozonization of VI.[11]—A solution of 0.2981 g. of 2-α-methylallyl-4,6-dimethylphenol (VI) in 15 cc. of dry carbon tetrachloride was ozonized for an hour, the exit gases being passed through two water absorption tubes. The tubes were then washed into 50 cc. of 1% aqueous methone solution at 100°. The mixture was cooled to 70°, and the crystalline methone derivative isolated; it weighed 0.1092 g. (22.6%) and melted at 187–188°, which is the reported[21] m.p. for the methone derivative of formaldehyde.

2-Allyl-4,6-dimethylphenol (IV) was formed by heating 2-allyloxy-3,5-dimethylbenzoic acid (III) under nitrogen at 140° for 30 minutes. The product boiled at 121–122° (22 mm.) and its phenylurethan melted at 108.5–109°; the reported[22] m.p. is 109°.

Determination of Rate of Rearrangement.—The apparatus used was a simple gasometer comprised of an inverted buret and a brine-filled leveling bulb. The buret was attached by glass and rubber tubing to a standard size test-tube in which the rearrangements were carried out. The tubes were immersed about one-quarter of their length in a wax-bath maintained at the desired temperature; temperature control within 0.5° was possible using an electric heating element connected with a Varitran. All rubber to glass joints in the system were sealed with varnish and the system tested for leaks under a slight negative pressure before each run. Approximately 0.2 g. of acid was used each time, which gave convenient amounts of carbon dioxide for measurement. Buret readings were recorded at suitable intervals as the rearrangements proceeded.

Readings taken at room temperature before and after completion of the reaction gave the total amount of carbon dioxide evolved. Since the same portion of the system was heated throughout the procedure, the initial room temperature volume could be corrected to reaction temperature by applying the difference between the final readings at reaction temperature and room temperature. The volume of gas evolved for any given reading was then obtained by subtraction from the corrected initial volume. The percentage completion of the reaction was calculated by dividing the total volume evolved into the volume evolved at the time of the reading.

The 2-allyloxy- and 2-crotyloxy-3,5-dichlorobenzoic acids were samples which had been prepared by Dr. J. W. Wilson.[2]

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[20] Young and Lane, THIS JOURNAL, **59**, 2051 (1937). The crotyl alcohol was obtained readily by lithium aluminum hydride reduction of crotonaldehyde (Nystrom and Brown, *ibid.*, **69**, 1197 (1949)).

[21] Vorländer, *Z. anal. Chem.*, **77**, 247 (1929).

[22] Claisen and Tietze, *Ann.*, **449**, 81 (1926).

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The *cis*-Decahydro-2-naphthoic Acids and their Relationship to the *cis*-2-Decalols and *cis*-2-Decalylamines

BY WILLIAM G. DAUBEN AND EARL HOERGER

The two *cis*-decahydro-2-naphthoic acids and their amides have been prepared in pure form. Each acid has been degraded, with stereochemical retention, to a *cis*-2-decalol and a *cis*-2-decalylamine. The steric relationship postulated by Hückel for these latter compounds has been found to be inverted.

The preparation of the isomeric decahydro-2-naphthoic acids and their derivatives has been reported by various workers over the past twenty-five years. The results of such investigations are tabulated in Table I. Kay and Stuart[1] isolated the four possible isomers, as the amides, by the reduction of 5,6,7,8-tetrahydro-2-naphthoic acid. The amides of acids obtained by sodium and ethanol reduction were assigned a *cis*-decalin configuration whereas the products isolated when the reduction was conducted in amyl alcohol were given the *trans*-decalin structure. The ring-juncture configuration of one of the *cis* amides and of one of the *trans* amides has been established by the preparation of the acids (and their amides) from known *cis*- and *trans*-decalins[2] or decalols.[3]

TABLE I

Ring config.	Acid m.p., °C.	Amide m.p., °C.	Method of preparation	Ref.
cis	80–90	171	Reduction[a]	1
cis		140	Reduction[a]	1
cis	98	168	Grignard[c]	2, 3
cis	81	145	Hydrogenation	4, 5
trans	65–75	174	Reduction[b]	1
trans		196	Reduction[b]	1
trans	109	201	Grignard[c]	2, 3

[a] Sodium and ethanol. [b] Sodium and amyl alcohol. [c] The starting *cis*- and *trans*-chlorodecalins were prepared from the corresponding decalins and decalols.

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[1] F. W. Kay and N. Stuart, *J. Chem. Soc.*, 3038 (1926).

[2] W. Borsche and E. Lange, *Ann.*, **434**, 219 (1923).

[3] G. Tsatsas, *Ann. chim.*, **19**, 217 (1944).

[4] V. Ipatieff, *Ber.*, **42**, 2097 (1909).