TABLE I

Compd.	Formula	M. p., °C.	Sulfonyl chloride, g.	Yield, %	Deacetylating efficiency, %	Analyses, % Nitrogen Calcd.	Nitrogen Found		Sulfur Calcd.	Sulfur Found	
I	$C_{20}H_{18}O_3N_2S$	237	5	86		7.65	7.58	7.73	8.75	8.88	8.68
II	$C_{18}H_{16}O_2N_2S$	186			80	8.64	8.73	8.69	9.88	9.81	10.04
III	$C_{21}H_{20}O_3N_2S$	208	10	75		7.36	7.41	7.48	8.43	8.52	8.42
IV	$C_{19}H_{18}O_2N_2S$	184			80	8.28	8.36	8.39	9.47	9.47	9.57
V	$C_{20}H_{24}O_3N_2S$	244	8	76		7.52	7.60	7.69	8.61	8.79	8.58
VI	$C_{18}H_{22}O_2N_2S$	219			89	8.48	8.39	8.48	9.70	9.68	9.89
VII	$C_{26}H_{22}O_3N_2S$	250	6	70		6.33	6.40	6.51	7.25	7.22	7.35
VIII	$C_{24}H_{20}O_2N_2S$	216			80	7.00	7.05	6.93	8.00	8.12	8.04
IX	$C_{20}H_{19}O_5N_3S_2$	274	6	80		9.43	9.36	9.46	14.39	14.52	14.55
X	$C_{18}H_{17}O_4N_3S_2$	252d			72	10.42	10.35	10.60	15.89	16.05	16.01
XI	$C_{26}H_{23}O_5N_3S_2$	299	5	90		8.06	8.24	8.06	12.30	12.32	12.18
XII	$C_{24}H_{21}O_4N_3S_2$	277d			87	8.76	8.79	8.85	13.37	13.24	13.40

All compounds were recrystallized to constant melting point as follows: I and II as described; III, V, VII and X from alcohol; IV and IX from 50% alcohol; VI and VIII were dissolved in 8% alcoholic hydrochloric acid and reprecipitated with concd. ammonium hydroxide, then recrystallized once from alcohol; XI was dissolved in dioxane and reprecipitated by adding water; XII was dissolved in 30% alcohol containing 2% hydrochloric acid and reprecipitated with concd. ammonium hydroxide, then recrystallized once from alcohol.

VIII *p*-(*p*-aminophenyl)-benzenesulfon-N-*p*-xenylamide
IX N^4-[*p*-(*p*-acetamidophenyl)-benzenesulfonyl]-sulfanilamide
X N^4-[*p*-(*p*-aminophenyl)-benzenesulfonyl]-sulfanilamide
XI 4-[*p*-(*p*-acetamidophenyl)-benzenesulfonamido]-biphenyl-4′-sulfonamide
XII 4-[*p*-(*p*-aminophenyl)-benzenesulfonamido]-biphenyl-4′-sulfonamide

The molecular formulas, melting points, and results of analyses are given in Table I. All compounds are white and crystallize in short needles.

Summary

p-(*p*-Acetamidophenyl)-benzenesulfonyl chloride has been coupled with the following amino compounds and the resulting compounds deacetylated: aniline, benzylamine, cyclohexylamine, *p*-xenylamine, sulfanilamide, and *p*-(*p*-aminophenyl)-benzenesulfonamide. The new compounds have been analyzed and reported.

PITTSBURGH, PENNA. RECEIVED JANUARY 18, 1941

[CONTRIBUTION NO. 210 FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

Isomerization in the Bouveault and Blanc Reduction of Methyl Hydrogen Camphorates

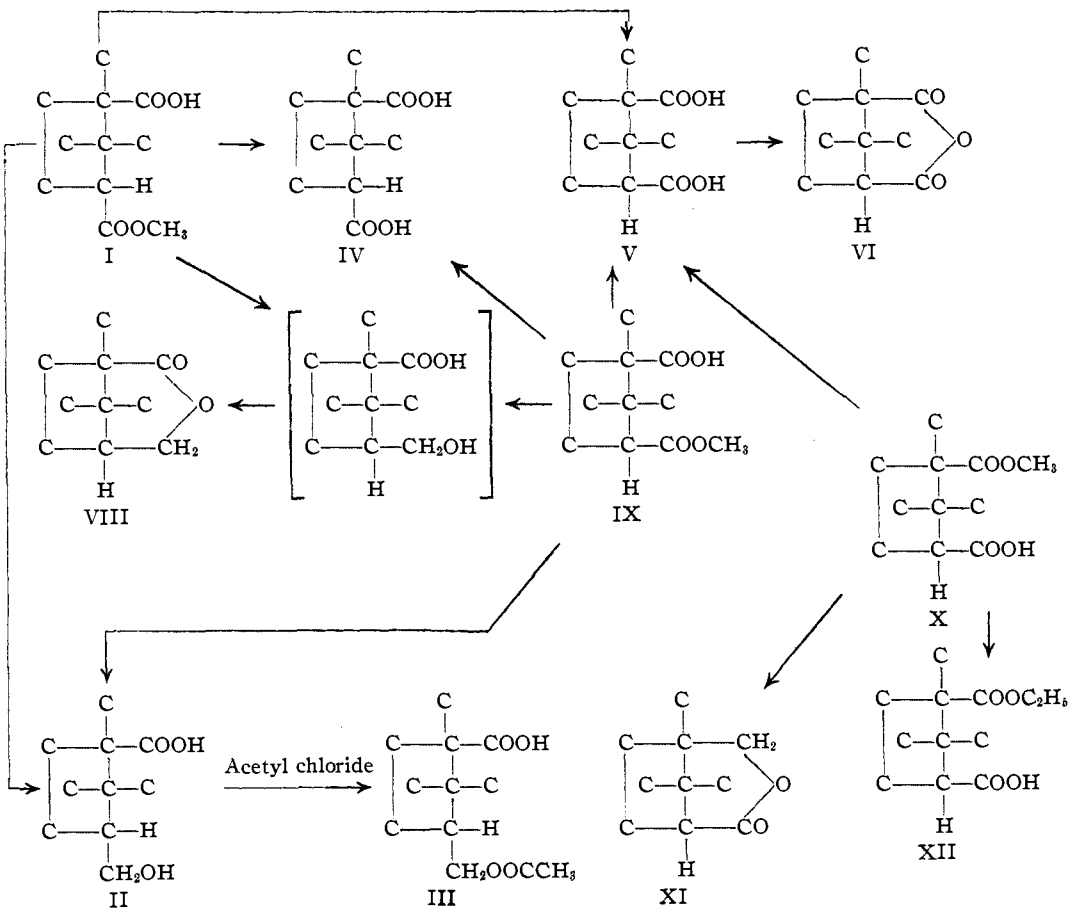
BY W. W. CROUCH AND H. L. LOCHTE

In investigations of the synthesis of certain naphthenic acids need arose for a procedure by which the ortho-methyl hydrogen ester (I) of isocamphoric acid could be reduced to *trans*-hydroxycampholic acid (II). Attempts to reduce this ester by catalytic hydrogenation at 250° and 5000 pounds pressure with copper chromite as catalyst failed. Reduction by sodium in absolute alcohol by the procedure followed by Haller and Blanc[1] in the reduction of *allo*-methyl hydrogen camphorate (X) gave a low yield of reduction product.

The reduction products were separated as a liquid mixture of acids from which not only *trans*-hydroxycampholic acid but also isocamphoric acid (IV), camphoric acid (V) and alpha-campholide (VIII), the lactone of *cis*-hydroxy campholic acid, were isolated.

As isomerization had evidently taken place the ortho-methyl ester of camphoric acid (IX) was treated in similar manner and yielded the same compounds. Since *allo*-methyl hydrogen camphorate (X) has no alpha hydrogen atom through which isomerization should be permitted, its reduction under the same conditions was also carried out. As expected, no *cis–trans* isomerization was observed and a yield of only 3% of beta-campholide (XI) was obtained along with *d*-camphoric acid and *allo*-ethylhydrogen camphorate (XII)

(1) Haller and Blanc, *Compt. rend.*, **141**, 697 (1905).



formed by reaction between sodium ethylate and the methyl ester.

Separation of the Mixtures Obtained.—The camphoric and isocamphoric acids were separated from the hydroxy acids by fractional extraction of an ether solution of the mixture with aliquots of sodium hydroxide solution. When extracted in 10 such fractions, the first 3 yielded crystalline acid mixtures from which isocamphoric acid and camphoric anhydride were separated by treatment with acetyl chloride.[2]

In the remaining fractions the *cis*-hydroxy acid was separated from the *trans* isomer by the lactonization of the *cis* form to alpha-campholide. *trans*-Hydroxycampholic acid was not lactonized on heating six hours in 1 *N* hydrochloric acid or by treatment with acetyl chloride, which yielded the acetyl derivative (III). This leaves the *trans*-lactone of Noyes and Potter[3] as the only known case in which a *trans*-lactone connected with a five-membered ring has been prepared.

(2) Noyes and Knight, This Journal, **32**, 1669 (1910).
(3) Noyes and Potter, *ibid.*, **34**, 1076 (1912).

trans-Hydroxycampholic acid was purified by vacuum sublimation. From the residue after sublimation a small quantity of another acidic compound was isolated. While not definitely identified, it was synthesized by heating together equivalent quantities of isocamphoric acid and *trans*-hydroxycampholic acid.

Discussion

This type of rearrangement has been observed in the camphoric acids on heating with a mixture of hydrochloric and acetic acids in a closed tube at 180° for several hours or, very slowly, on refluxing with quinoline.[4] These results extend the rearrangement to the esters and to conditions obtaining during reduction by sodium in absolute alcohol.

Experimental

***d*-*o*-Methyl Hydrogen Isocamphorate (I).**—This compound was prepared from isocamphoric acid and methanol by the method of Noyes and Knight.[2]

(4) Aschan, *Ann.*, **316**, 227 (1901).

Attempted Hydrogenation of Methyl Hydrogen Isocamphorate.—Four grams of the acid ester was dissolved in 30 cc. of methylcyclohexane, 0.5 g. of active copper chromite catalyst added, and the mixture heated with hydrogen under 5000 lb. pressure to 250° for three hours. Only the unchanged ester could be isolated from this experiment as from similar ones using dioxane as solvent, the sodium salt with water as solvent, and the ethyl hydrogen ester with methylcyclohexane as solvent.

Reduction of *d-o*-Methyl Hydrogen Isocamphorate.[5]—Sixty grams of sodium cut into 1 cm. cubes was added to a three-neck flask equipped with a dropping funnel and a reflux condenser protected by a drying tube. To this was added 5 g. of the ester dissolved in 100 cc. of dry ethanol followed immediately by another 400 cc. of dry ethanol. The mixture was heated on a hot-plate until the sodium had reacted completely. Water was then added and the solution distilled until the residue began to solidify. The residue was then dissolved in 300 cc. of water and carefully acidified with dilute hydrochloric acid. A viscous oily mixture of acids separated.

Fractional Extraction of the Acid Mixture.—The mixture of acids dissolved in 1 liter of ether was extracted with 10 portions of 50 cc. each of 4% sodium hydroxide solution. Each portion of the base was thoroughly stirred with the ether layer for two hours before separation. The water layer was washed once with ether, boiled a few minutes to remove dissolved ether, and then acidified with dilute hydrochloric acid. The precipitate from fractions 1–3 crystallized on standing but the other seven remained liquid.

Separation of Camphoric (V) and Isocamphoric Acids (IV).—Twenty grams of the crystalline material was treated with an equal weight of acetyl chloride and the mixture left at room temperature for four hours during which the acid chloride evaporated. The crystals remaining were powdered and shaken with an excess of sodium bicarbonate solution to remove isocamphoric acid from camphoric anhydride formed by the acid chloride. The insoluble camphoric anhydride was recrystallized from alcohol: m. p. 225°; mixed m. p. 225°.

α-Campholide (VIII).—The acid mixture from the reduction of 25 g. of methyl hydrogen camphorate was heated for six hours in contact with 1 *N* hydrochloric acid. Organic compounds were extracted with ether and the ether layer extracted twice with a 10% sodium carbonate solution to remove acids. The ether was then evaporated leaving 4 g. of crystals. Recrystallized twice from petroleum ether, it melted at 213°. Rupe and Jaggi[6] report 210–212°.

***trans*-Hydroxycamphoric Acid (II).**—Fractions 7–9 of the extraction series were dried with sodium sulfate and sublimed at 175° in vacuum. The sublimate was dissolved in ether and the ether solution extracted with 100 cc. of 10% sodium carbonate solution. Acidification of the basic layer yielded 8 g. of material that solidified on cooling. Recrystallized four times from a benzene–petroleum ether mixture, it melted at 112–113°.

Anal. Calcd. for $C_{10}H_{18}O_3$: C, 64.50; H, 9.74. Found: C, 64.26; H, 9.86.

Acetylation of the *trans*-Hydroxy Acid.—One gram of the hydroxy acid was treated, at room temperature, with an equal weight of acetyl chloride and the excess of the acid chloride evaporated at room temperature. The residue was washed with water and recrystallized from petroleum ether, m. p. 55–56°.

Anal. Calcd. for $C_{12}H_{20}O_4$: C, 63.13; H, 8.83. Found: C, 63.12; H, 8.73.

Reduction of *o*-Methyl Hydrogen Camphorate (IX).—This ester was prepared from camphoric anhydride and sodium methylate by the method of Walker.[7] Reduction by the procedure used with the isocamphorate yielded 22 g. of α-campholide from 115 g. of the ester. The liquid residue was extracted with 11 portions of 4% sodium hydroxide solution and the first 9 fractions were now found to solidify. From 45 g. of combined solid fractions, 9 g. of isocamphoric acid was separated, m. p. 171–172°. Treatment with methanol and hydrogen chloride yielded the ortho-methyl hydrogen ester, m. p. 87°.

Investigation of the Sublimation Residue.—Fractions 10 and 11 of the above series were sublimed in vacuum at 175°. The residue was dissolved in ether and the ether solution extracted with 10% sodium carbonate solution. Acidification of the water layer gave an acid melting at 218–219° after three recrystallizations from an alcohol–water mixture. The neutralization equivalent now was 189. The residue from the sublimation of *trans*-hydroxy campholic acid proved to be the same compound. Two hundred milligrams of isocamphoric acid and 180 mg. of *trans*-hydroxy campholic acids were heated for five hours at 175°; the pressure was then reduced to permit the more volatile part to sublime. The residue after purification showed a melting and mixed melting point of 217–218°. The compound was insoluble in water, benzene, and petroleum ether, and raised the melting point of camphor.

Reduction of *allo*-Methyl Hydrogen Camphorate (X).—The method of Walker[7] was used to prepare 110 g. of this acid ester which was reduced by sodium and absolute ethanol as before. The sodium hydroxide solution formed after adding water was heated for three hours before acidification. The ether solution of the acids was extracted with 11 portions of sodium hydroxide solution as before. Fractions 1–7 turned solid and proved to be *d*-camphoric acid melting at 187° after one recrystallization from alcohol. Treated with acetyl chloride at room temperature 5 g. of this material yielded 4.5 g. of camphoric anhydride with no acid residue.

From the remaining fractions and the ether solution there was isolated, by the method described for alpha-campholide, 3 g. of beta-campholide, m. p. 220°. The acid residue from fractions 8–11 solidified after distillation. The melting point of 57° and neutralization equivalent of 226 showed it to be *allo*-ethyl hydrogen camphorate, formed by reaction of sodium ethylate with the methyl ester.

Summary

1. The reduction of the ortho methyl hydrogen esters of both camphoric and isocamphoric acids by sodium in absolute alcohol yields mixtures of

(5) Bouveault and Blanc, *Bull. soc. chim.*, [3] **31**, 666 (1904); Goheen, *Ind. Eng. Chem.*, **32**, 504 (1940).

(6) Rupe and Jaggi, *Helv. Chim. Acta*, **3**, 654 (1920).

(7) Walker, *J. Chem. Soc.*, **61**, 1089 (1892).

cis- and *trans*-hydroxy acids and of camphoric and isocamphoric acids.

2. Isomerization does not occur in the reduction of *allo*-methyl hydrogen camphorate under these conditions.

AUSTIN, TEXAS RECEIVED DECEMBER 23, 1940

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The Synthesis of Symmetrical Diaryl Ethylenes*

BY J. H. WOOD, J. A. BACON, A. W. MEIBOHM, W. H. THROCKMORTON AND G. P. TURNER

Trithiobenzaldehyde upon being heated above its melting point alone or with copper powder gives considerable stilbene.[1] The desirability of using this reaction as a method for preparing substituted stilbenes as well as their analogs in the naphthalene, anthracene, and phenanthrene series has been made the subject of this investigation.

The starting polymeric thioaldehydes are made in good yields by passing hydrogen chloride and hydrogen sulfide into solutions of the oxo-aldehydes. The thioaldehydes are then decomposed by heating in the presence of very finely divided copper powder. This method is applicable to unsubstituted or alkoxy substituted aryl thioaldehydes and although the yields in most cases are not especially good the method offers promise because of its simplicity and the ready availability of starting materials. When freshly reduced copper powder is not used in the pyrolysis of the thioaldehydes, sulfur-containing compounds in addition to the ethylene compounds result. For instance, trithiobenzaldehyde when heated alone forms tetraphenylthiophene as well as stilbene.

1,2-Di-(3-phenanthryl)-ethylene, 1,2-di-(2-methoxy-1-phenanthryl)-ethylene, and 1,2-di-(9-anthryl)-ethylene have not been heretofore prepared. The method followed in their preparation is indicative of their structure. Upon mild oxidation, the ethylene double bond is broken with the formation of known acids which were isolated to further substantiate the structure of these ethylene compounds. The dibromide was made of each known ethylene compound as a means of identification. The heretofore unknown dibromide of 1,2-di-(9-anthryl)-ethylene was also made. That the bromine added to the ethylene double bond was proved by oxidation to anthraquinone.

2-Methoxyphenanthrene-1-aldehyde was prepared by an adaptation of the method of Kalischer, Keller and Scheyer[2] in which the aldehyde group is introduced directly by phosphorus oxychloride and N-methylformanilide. An 80% yield was obtained.

Experimental

Preparation of the Ethylene Compounds.—The thioaldehyde was ground to a fine powder and then intimately mixed with 3 to 4 times the theoretical amount of freshly reduced copper powder. The mixture was heated for thirty minutes in a small flask by means of an oil-bath to the temperature indicated in Table I. After cooling and breaking up the fused mass, the ethylene compound was extracted with boiling benzene. 1,2-Di-(9-anthryl)-ethylene proved to be only slightly soluble in benzene and several extractions with large quantities of benzene were necessary in this case. The benzene solutions were then concentrated to bring about crystallization. Frequently, treatment with Norit was required to remove color from the ethylene compound and generally one to two recrystallizations from benzene (or alcohol in the case of the more soluble ones) were required to obtain a pure product. The yields in Table I are in terms of pure compound.

1,2-Di-(3-phenanthryl)-ethylene.—This compound crystallized from benzene as very small, light-yellow crystals, m. p. 289° (cor.), which exhibited a greenish-blue fluorescence in ultraviolet light.

Anal. Calcd. for $C_{30}H_{20}$: C, 94.70; H, 5.30; mol. wt., 380. Found: C, 94.52; H, 5.60; mol. wt. determination (Rast camphor method), 354 and 390.

The compound was oxidized with a slight excess of chromic anhydride in glacial acetic acid to the known phenanthraquinone-3-carboxylic acid.

1,2-Di-(2-methoxy-1-phenanthryl)-ethylene.—This compound crystallized from benzene as light-cream colored needles, m. p. 277° (cor.), which exhibited a greenish blue fluorescence in ultraviolet light.

Anal. Calcd. for $C_{32}H_{24}O_2$: C, 87.24; H, 5.49; mol. wt., 441; methoxyl, 2. Found: C, 87.16; H, 5.59; mol. wt. determination (Rast camphor method), 453 and 429; methoxy, 1.96.

Upon oxidation with excess 3% sodium hypochlorite at reflux temperature the known 2-methoxyphenanthroic-1-acid resulted.

* Presented at the 101st meeting of the American Chemical Society, St. Louis, Mo., April, 1941.

(1) H. Klinger, *Ber.*, **9**, 1893 (1876).

(2) G. Kalischer, K. Keller and H. Scheyer, U. S. Patent 1,807,693, June, 1931.