

very slight at 40°, fair at 70° and rapid (two hours for completion) at 90°.

Acids, obtained by carbonation of the pyrolyzed organosodium compound, are (a) water soluble, unsaturated compounds with more than one carboxyl group to amyl unit; (b) tarry or insoluble acids which are unsaturated and of relatively high molecular weight.

The sole hydrocarbon product was pentane. The solvent, *n*-decane, was not attacked by the organosodium compound under the conditions employed.

The chemical reactions which occur during pyrolysis involve metalation (dismutation) and dehydrogenation.

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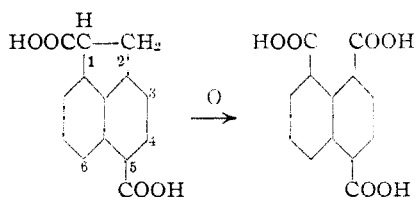
[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 266]

Condensations by Sodium. XXV. Reactions of Amylsodium with Naphthalene, Acenaphthene and Decalin

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Nearly half of the carbonated product obtained from the reaction of amylsodium with naphthalene is di- and tri-substituted, whereas nearly all of the product in the case of benzene is monosubstituted. Octyl- is more active with naphthalene than is amylsodium and the proportion of higher substituted compounds is slightly increased. The α - and β -monoacids, and the 1,3-, 1,8-, and 2,6-dicarboxylic acids were isolated. The tri-substituted compounds were not examined.

Acenaphthene was expected to behave somewhat similarly to toluene. One sodium atom did, in fact, replace a hydrogen atom in a methylene group but a second one entered the ring, giving a dicarboxylic acid, probably the 1,5-compound, in about 50% yield. Oxidation of this diacid with permanganate gave 1,4,5-naphthalene tricarboxylic acid, showing that one carboxyl must have been attached to a methylene, *i. e.*, in the



1-position, and the second was bound to the 5- or 6-position in the aromatic nucleus. The 5-position is considered more likely because (a) in benzene¹ the directing influence of one sodium atom on a second entering one is largely meta; (b) in naphthalene the influence on substitution of another metal in the same ring is meta; and

(c) even in benzylnsodium² a second metalation, when it does occur, is exclusively in the meta position. The 5-position is also in accord with the general principle³ that the introduction of substituents into a bicyclic system containing a meta directing group will take place in the unsubstituted ring. Metalation of acenaphthene by an organo alkali compound, butyllithium, has been observed^{4a} once before but no product was isolated. Horvitz^{4b} also studied the action of amylsodium on acenaphthene but was unable to obtain a product of known purity because of the difficulty in separation.

The action of amylsodium on decalin was most surprising because metalation took place with extreme ease. From a great variety of products a very small amount of a crystalline ester of a tetracarboxylic acid was eventually isolated. It readily formed a dianhydride after being saponified and acidified. The positions of the carboxyl groups are not known but the 1,4,5,8-product is suspected because these positions are reasonably remote from each other, and have the symmetrical arrangement which would increase the tendency of the compound to come out of mixtures in a crystalline form. Moreover, the corresponding acids could easily form a dianhydride of high melting point. The original hope had been that substitution would occur at the tertiary or indented position and that the process would therefore prove to be a new synthetic method in that

(2) Unpublished research.

(3) Grieve and Hey, *J. Chem. Soc.*, 968 (1933).

(4) (a) Gilman and Bebb, *THIS JOURNAL*, **61**, 109 (1939); (b) Horvitz, Ph. D. Thesis, Massachusetts Institute of Technology, 1938.

(1) Morton and Fallwell, *THIS JOURNAL*, **60**, 1924 (1938).

series. The crystalline product isolated, however, could not have had a carbomethoxy group in that location because there was no resistance to saponification under ordinary conditions. Furthermore, alkylation⁵ of decalin by sodium and amyl chloride after the manner employed successfully for toluene, formed products which, though they boiled in the range expected for amyldecalin, yielded an inappreciable quantity of naphthalene and traces only of amyl mercaptan when fused with sulfur. Both of these products would have been expected had alkylation occurred on the tertiary carbon atom. Metalation of decalin is of more than passing interest because it is the first recorded instance of substitution in a hydrocarbon which does not contain an aromatic nucleus.

Experimental

Amyl- or Octyl-sodium with Naphthalene (J. D.).—*n*-Amyl chloride, 18 ml., was added dropwise to 15 g. of sodium sand suspended in a solution of 50 g. of naphthalene in 240 ml. of ligroin maintained at 72° in an atmosphere of nitrogen in the apparatus used for preparing octylsodium.⁶ After carbonating and adding water, the aqueous layer was acidified yielding 4.9 g. of solid product whose neutralization equivalent was 156.2. Ether extraction of the aqueous layer yielded 0.64 g. of acidic material which had a neutralization equivalent equal to 98.5. On the reasonable assumption that the solid precipitate consisted of mono- and di- acids only and that the acids recovered by ether extraction were a mixture of di- and tri-acids, the calculated yields were 14 mono, 10 di, and 2% tri or a total of 26%. From a parallel experiment with *n*-octyl chloride, the yields were 17, 15, and 5%, respectively, or a total of 37%. Separation of pure compounds from the mixture of products was carried out by a series of steps which began with an extraction of the precipitate (4.9 g.) with 4 liters of hot water. The insoluble material was reduced by this treatment to 2.5 g. The aqueous solution, after being cooled, yielded 1.1 g. of precipitate which was fractionally crystallized from a mixture of acetic acid and water. The least soluble portion from the dilute acetic acid was converted to the methyl ester by use of the silver salt and methyl iodide. After being recrystallized from methyl alcohol and then from acetic acid, the methyl ester of the 2,6-di acid (m. p. 189 to 192°) was recovered. The portion moderately soluble (as distinguished from most soluble and least soluble) in dilute acetic acid was sublimed. The sublimate was partially soluble in sodium carbonate. Acidification of the aqueous carbonate fraction gave about 44 mg. of β -naphthoic acid melting 182–184°. The amide melted at 192°. The portion insoluble in sodium carbonate was the anhydride of the 1,8-dicarboxylic acid, melting at 272–275°. The imide melted at 299–300°; the anil at 202–203°. The four liters of aqueous solution from which

the above acids had been precipitated was extracted with ether, from which about 1.2 g. of acid was recovered by evaporation of solvent. This material was fractionally crystallized from water and the moderately soluble portion consisting of 212 mg. was sublimed. The volatile product was crystallized from ligroin yielding a very small amount of α -naphthoic acid, melting 159–160°. The non-volatile portion from the sublimation was recrystallized from water, yielding the 1,3- acid which melted at 264–265°. In all cases the yields were very small because of the many steps involved in separation. The properties of the acids were compared with those recorded by Bradbrook and Linstead.⁷ Examination of the hydrocarbon layer showed little, if any, evidence of alkylation. An experiment⁸ exactly parallel to that between octylsodium and naphthalene but using benzene as the hydrocarbon yielded 33% of benzoic acid with scarcely any phthalic acid. No evidence of alkylation was noted.

Amylsodium and Acenaphthene (T. G.).—*n*-Amyl chloride, 75 ml., was added to 40 g. of fine sodium sand suspended in a solution of 30 g. of acenaphthene in 400 ml. of petroleum ether. The sodium metal was previously activated with 5 ml. of *n*-amyl alcohol. No evidence of any reaction between the metal and acenaphthene was observed. The apparatus was the one used formerly⁸ in this series of studies. The temperature was maintained at below 15° during the forty-five minutes required for addition of the chloride. The color changed progressively from gray to blue to dark green. After four hours the temperature was allowed to rise to 30°, where it remained during the next nineteen hours while stirring was continued. The dark green paste was then heated to 40° for one and a half hours, cooled to 9° and treated with a stream of carbon dioxide. After adding water to remove excess sodium, the aqueous layer was filtered, and acidified with hydrochloric acid. The mixture of gummy yellow precipitated acids was filtered and dried, yielding 54 g. of crude material. This product proved extremely difficult to purify by extraction with organic solvents, gradual acidification of the neutralized salts, conversion to methyl ester with dimethyl sulfate and other conventional methods. Contact with air appeared to cause formation of dark brown tars. The residues, after a considerable number of extractions had been made, were finally combined, the mixture suspended in ether, and treated with diazomethane. After one hour the yellow solution was filtered to remove suspended material and allowed to evaporate. Large yellow needle-like crystals of an ester resulted in a yield of approximately 50% calculated on the original amyl chloride used. After being recrystallized from ether, these crystals were colorless and melted at 112°, were lath-shaped with square ends, had an extinction angle of 10° and showed negative elongation.

Anal. Calcd. for $C_{18}H_{14}O_4$: C, 71.2; H, 5.2; sapon. equiv., 135. Found: C, 71.1; H, 5.5; sapon. equiv., 131, 134.

This diester was very soluble in cold methanol, acetone, methyl cellosolve, and carbon tetrachloride, moderately soluble in ether, and sparingly soluble in petroleum ether.

The dicarboxylic acid recovered after saponification was

(5) Morton and Fallwell, Jr., *THIS JOURNAL*, **60**, 1429 (1938); Morton, Richardson and Hallowell, *ibid.*, **63**, 327 (1941).

(6) Morton, Davidson and Best, *ibid.*, **64**, 2239 (1942).

(7) Bradbrook and Linstead, *J. Chem. Soc.*, 1739 (1936).

(8) Morton, Fallwell and Palmer, *THIS JOURNAL*, **60**, 1426 (1938).

moderately soluble in carbitol, cellosolve, and *t*-butyl alcohol, sparingly soluble in cold acetone, dioxane, and ether, almost insoluble in chloroform, and water, and insoluble in carbon tetrachloride, benzene and xylene; melting point 292–294°.

Anal. Calcd. for $C_{14}H_{10}O_4$: C, 69.4; H, 4.1. Found: C, 69.4; H, 4.3.

When heated (280°) with an equal weight of lime and copper bronze, the mixture gave acenaphthene as a sublimate; heated in the absence of these agents, it yielded two products which proved to be acenaphthene and an acid melting at 215° (acenaphthene 5-carboxylic acid melts at 217°).

One-tenth gram of the acid was oxidized by excess permanganate solution (2.2%) at 50–60° with stirring. At the end of an hour the solution was decolorized with alcohol, and filtered. A white precipitate was obtained after the filtrate was acidified. This material was redissolved in aqueous alkali, reprecipitated with acid and then crystallized from ether; m. p. 266–268°. The neutralization equivalent was 86, agreeing with the value for a naphthalene tricarboxylic acid. The acid readily changed on drying to the anhydride which melted at 273–275° (cor.).

Anal. Calcd. for $C_{18}H_{10}O_6$: C, 64.4; H, 2.48. Found: C, 64.3; H, 2.58.

When mixed with an authentic sample⁹ of naphthalene-1,4,5-tricarboxylic acid anhydride, no depression of the melting point was obtained.

The mono methyl ester anhydride was also prepared according to the directions of Fieser and Peters⁷ and had the properties described by these workers.

Amylsodium and Decalin (E. L., E. C., and A. G.).—Numerous experiments were made in an endeavor to obtain a pure compound readily from the carbonation of the product of amylosodium and decalin. Some of these involved tests with pure *cis* and *trans* decalin but isolation of pure materials was not apparently simplified by such means. The following account is of two experiments employing the method which finally proved successful. Amylosodium was prepared in the usual manner from 100 g. of *n*-amyl chloride and 48 g. of sodium sand in 400 ml. of petroleum ether contained in a 1-liter creased flask. Two hours were required for addition of the chloride at 15 to 20°. Decalin (59.1 g. in one experiment and 119 g. in the other) was then added quickly, and the mixture heated to 49 and 53°, respectively, for two hours. The contents were then cooled to room temperature and treated with a stream of carbon dioxide. Toward the end of the two hour carbonation process the mixture was again heated to a refluxing temperature. Subsequently the excess sodium sand was removed by water and the aqueous layer acidified with hydrochloric acid. The aqueous layer was first extracted with petroleum ether, then saturated with salt and extracted with ethyl ether. The ethyl ether extract was twice esterified with methyl alcohol and hydrochloric acid. This method of esterification was expected to effect a separation of those acids in which the carboxyl group was sterically hindered by being in the indented position. The ester from this step was freed from all acid by washing with

aqueous sodium carbonate. The combined esters from both experiments were then fractionated through an 8-plate Podbielniak type column at 2 mm. About 5 ml. of methyl butylmalonate was collected at 64–89°, and 15 cc. of another liquid at 84 to 112°. Crystals then clogged the condenser system. The viscous red oily residue, after standing a week, also formed a mass of crystalline material which had the appearance of a fine mold-like growth over the surface. The crystals from both sources were identical with each other. After being recrystallized from methyl alcohol and water, they melted at 61–62°. The saponification value of 92 was that calculated for the methyl ester of a decalyl tetracarboxylic acid. The molecular weight (Rast) was 374 as compared with a calculated value of 368. The compound proved difficult to burn for analysis.

The product recovered after being saponified and acidified was a white solid which melted near 300° with sublimation. The neutralization equivalent of this material agreed with that calculated for a dianhydride.

Anal. Calcd. for $C_{14}H_{10}O_6$: C, 60.87; H, 4.35. Found: C, 60.8; H, 4.58.

The remaining acids and esters were liquids whose neutralization and saponification equivalents did not agree with any calculated for a mono-, di- or tri-acid, although the scheme of separation by solvent extraction, methylation by both methyl alcohol and acid and by diazomethane (of the difficultly esterified portion) and fractionation was carried to completion. Out of 87.9 g. of total ester (all of the acids were eventually esterified) from both experiments, only 0.15 g. of the methyl decalyltetracarboxylate was obtained. One of the fractions from a methylation by diazomethane had an unusually low saponification equivalent, indicating the presence of even more than four carboxyl groups per decalin unit.

Alkylation of Decalin (E. L.).—*n*-Amyl chloride (200 g.) in 100 ml. of decalin was added gradually to 300 ml. of decalin in which was suspended 96 g. of sodium sand which had been activated by addition of 8.4 ml. of *n*-amyl alcohol. The temperature was maintained at 72 to 80° in expectation that decalin would be converted to amyldecalin in the same manner as toluene was changed to hexylbenzene.⁸ The reaction proceeded smoothly at first but after all but 60 ml. of the diluted amyl chloride had been added, the mixture became too solid to stir. The material was allowed to stand overnight under nitrogen, and then treated with a stream of carbon dioxide and reheated for about an hour and a half. The mixture was then allowed to cool. Water was added as usual to remove excess sodium. Much of the metal had agglomerated together in large lumps which were eventually lifted from the mixture with forceps. This agglomeration of sodium particles had been noticed only in the case of some of the experiments with decalin. The hydrocarbon fraction was dried over calcium chloride and fractionated carefully through a packed column of about fourteen plates, in order to remove low-boiling compounds, decane, and decalin. The residue boiling above 194° consisted of about 60 ml. which was then fractionated at 10 mm. through a Podbielniak type column of about eight plates. A portion (2.3 g.) of the fraction (6 cc.) boiling from 124–137° at 10 mm. was mixed with 1.9 g. of sulfur and heated for three hours at 230°. The product was then extracted with small portions

(9) The authors are greatly indebted to Professor L. F. Fieser of Harvard University for his courtesy in furnishing this sample. See Fieser and Peters, *THIS JOURNAL*, 54, 4352 (1932).

(200 ml. in all) of ethyl ether. The combined ether extracts were fractionated (final temperature 230°). Since no principal fraction boiling at 126°, the boiling point of *n*-amyl mercaptan, was found, the combined distillate was extracted with sodium hydroxide, the alkali solution then acidified and extracted with ether. The ether was evaporated and the residual foul-smelling liquid treated with 2,4-dinitrochlorobenzene, which produced a few crystals of the *n*-amyl 2,4-dinitrophenyl thioether melting at 80–81° (recorded¹⁰ value 80°). The material left after extraction with alkali was treated with picric acid in hot alcoholic solution. A few yellow crystals melting from 268–273° were obtained. Had the amyl group been substituted in the indented position, the product should have been naphthalene picrate, melting at 149–150°. Several experiments using decalin showed that the above process would give good yields of naphthalene and naphthalene picrate.

Summary

A series of studies on the reaction of amyl-

(10) Bost, Turner and Norton, *THIS JOURNAL*, **54**, 1986 (1932).

sodium with bicyclic compounds showed that metalation occurred readily in a considerable number of places. The positions of attack were shown by examination of the products of carbonation.

The end-products from naphthalene were both mono-carboxylic acids, at least three dicarboxylic acids, and some tricarboxylic acid.

Acenaphthene was attacked readily; the only product which could be isolated was a dicarboxylic acid, either 1,6- or probably 1,5.

Decalin was attacked very easily and a considerable variety of products was formed. A small amount of the dianhydride of a tetracarboxylic acid was separated. The tertiary hydrogen atom in decalin may be attacked but does not appear to be a favored position.

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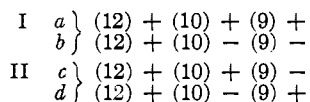
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[CONTRIBUTION FROM THE OIL AND PROTEIN DIVISION, NORTHERN REGIONAL RESEARCH LABORATORY¹]

The Diastereoisomerism of the 9,10,12-Trihydroxystearic Acids and the Geometric Configurations of Ricinoleic and Ricinelaic Acids

BY J. P. KASS AND S. B. RADLOVE

In the course of an investigation of the dehydration of ricinoleic and ricinelaic acids to isomeric linoleic acids, it became necessary to identify the parent 12-hydroxy-9,10-octadecenoic acids by means of their partial oxidation to the 9,10,12-trihydroxystearic acids. Theoretical considerations^{2,3,4} indicate that each of the geometrically isomeric, dextrorotatory monohydroxy acids should yield two diastereoisomeric trihydroxystearic acids, with the following configurations of the initially dextrorotatory twelfth carbon atom and the newly asymmetric ninth and tenth carbon atoms



Moreover, assuming that no inversion occurs during oxidation, the pairs of the derivatives should be

(1) The Northern Regional Research Laboratory is one of four regional laboratories authorized by Congress in the Agricultural Adjustment Act of 1938 for the purpose of conducting research to develop new uses and outlets for agricultural commodities. These laboratories are administered by the Bureau of Agricultural Chemistry and Engineering of the U. S. Department of Agriculture. (Not subject to copyright.)

(2) Mangold, *Monatsh.*, **13**, 326 (1892).

(3) Walden, *Ber.*, **27**, 3471 (1894).

(4) Smit, *Rec. trav. chim.*, **49**, 675 (1930).

related in such a manner that the products of the *cis*-hydroxylation of one of the unsaturated acids must correspond to the products of the *trans*-addition to its geometric isomer; specifically, the mild alkaline permanganate oxidation of ricinoleic acid should yield two trihydroxystearic acids identical with the pair resulting from the oxidation of ricinelaic acid with acid hydrogen peroxide, and *vice versa*. This relationship has been shown to obtain uniformly in the monoethenoid^{5,6} and linoleic acid⁷ series.

The older literature⁸ reports the preparation of three of the trihydroxystearic acids under consideration, and intimates the existence of the fourth isomer. The oxidation of ricinoleic acid with cold alkaline permanganate was first shown by Hazura and Grüssner⁹ to produce two trihydroxystearic acids, m. p. 110–111° and 140–142°, for which Dieff¹⁰ later reported m. p. of 100–114° and 137–140°. From similarly treated ricinelaic

(5) Hilditch, *J. Chem. Soc.*, 1828 (1926).

(6) Braun, *THIS JOURNAL*, **51**, 228 (1929).

(7) Kass and Burr, *ibid.*, **61**, 1062 (1939).

(8) Cf. Lewkowitch and Warburton, "The Chemical Technology and Analysis of Oils, Fats and Waxes," 6th ed., Vol. I, The Macmillan Co., London, 1938, p. 236.

(9) Hazura and Grüssner, *Monatsh.*, **9**, 475 (1888).

(10) Dieff, *J. prakt. Chem.*, [2] **39**, 339 (1889).