[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

The Pinacol Rearrangement of *cis*- and *trans*-1,2-Di-*o*-tolyl- and Di-*p*-tolylacenaphthenediols-1,2[1]

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cis- and *trans*-1,2-di-*o*-tolyl- and di-*p*-tolylacenaphthenediols were prepared and caused to rearrange to the corresponding pinacolones in acetic acid with sulfuric acid as the catalyst. In methanol as the solvent, either the *cis*- or *trans*-*p*-tolylpinacol rearranged to give the dimethyl acetal of the pinacolone, even at room temperature, and the *cis*-monomethyl ether could not be isolated from short runs at room temperature. Either *cis*- or *trans*-*o*-tolylpinacol gave only the pinacolone under all conditions in methanol as solvent. Since there is reason to expect the epoxide as a product in this case, the product was shown to be a ketone by alkaline cleavage. The presence of the ortho-methyl group in the *o*-tolylpinacols should hinder migration. However, models show that the center of charge in a carbonium ion intermediate is protected front and back from external reagents by the ortho-methyl groups and the only possibilities for reaction are rearrangement or epoxide formation. The results are in harmony with a carbonium ion mechanism proposed earlier by us.

Since previous work[2] has indicated the importance of steric factors in the pinacol rearrangement of *cis*- and *trans*-1,2-diphenylacenaphthenediols in acetic acid or in alcoholic solvents, it seemed of interest to investigate the effect of ortho substituents in the migrating phenyl group. It is well known[3] that, in the symmetrical benzpinacols, a group such as methoxy, which in the para position enhances migratory aptitude, will, in the ortho position, depress the migratory aptitude. In this Laboratory, as a working hypothesis, it has been assumed that the presence of an ortho group will interfere in the formation of a transition state for migration because of steric hindrance between the ortho group and the groups remaining attached to the reactive centers (Fig. 1).[4] Thus, Bachmann[3] had difficulty in completing those rearrangements in which ortho substituents were present. This idea is similar to that advanced by Pollak and Curtin[5] that the transition state in which the large groups on the ring are in a *trans* configuration will be favored over that in which the large groups are in a *cis* configuration. In applying this concept to the acenaphthenepinacol systems, it is apparent that if one used the methyl group in the ortho position, then the ion formed from either *cis*- or *trans*-1,2-di-*o*-tolylacenaphthenediol-1,2 (*o*-Ic or *o*-It) would be less likely to exist as a carbocyclic ion than in the phenyl or *p*-tolyl cases (*p*-Ic or *p*-It). In fact, one might reason that only ethers would be formed in acidic methanol solutions. But the construction of a model (Fisher–Hirschfelder–Taylor) showed that the ortho-methyl groups are disposed in such a manner as to block access to the center of charge in the carbonium ion by an external reagent (Fig. 2). On this basis, the ion must rearrange, or form the epoxide. However, because of the extra length of the C_1–C_2 bond in acenaphthene, the ortho-methyl may not prove to be as effective in blocking rearrangement as might be supposed from Bachmann's work with the benzpinacols.

To test these ideas, *cis*- and *trans*-1,2-di-*o*-tolyl- and di-*p*-tolylacenaphthenediols-1,2 were prepared and rearranged under various conditions. As was expected, the *p*-tolylpinacols reacted as did the phenylpinacols[2] except for the extra reactivity to be anticipated from the electronic effects of the methyl groups from the para position. Both *p*-Ic and *p*-It were converted smoothly and rapidly to the pinacolone in acetic acid with sulfuric acid as the catalyst. In methanol, with sulfuric acid catalyst, the dimethyl acetal of the pinacolone was the major product either at the temperature of reflux or at room temperature. The latter reaction was quite fast, being almost complete within 24 hours. The *cis*-monomethyl ether could not be isolated from the complex reaction mixture even after very short reaction times at room temperature. The *o*-tolylpinacols rearranged nicely in acetic acid–sulfuric acid to the pinacolone. That this was not the epoxide was shown by alkaline cleavage of the ketone to give 8-(di-*o*-tolylmethyl)-1-naphthoic acid. In methanol, at room temperature or at the boiling point, sulfuric acid catalyst, either of the *o*-tolylpinacols yielded only the pinacolone, regardless of the length of time of reaction.

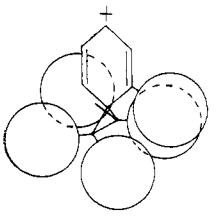

Fig. 1.

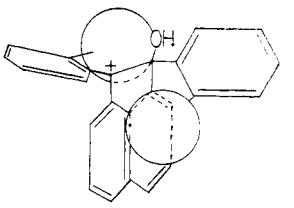

Fig. 2.

This not unexpected result supports the mechanism proposed earlier[2] in which a carbonium ion was postulated as an intermediate rather than a carbocyclic ion although the latter still is not excluded entirely. We propose to continue the work by preparing the corresponding mesitylpinacols in which, both ortho positions being occupied, rearrangement might be impossible. It is possible now to study the kinetics of rearrangement of the *o*-tolylpinacols without having the complication of isomerization of the *trans*- to the *cis*-form as occurs in the phenylpinacols.[6] It is interesting to note that an epoxide evidently is not involved as an intermediate or alternate path of rearrangement here

(1) Presented at the American Chemical Society Meeting, Los Angeles, March, 1953.

(2) R. F. Brown, THIS JOURNAL, **74**, 428 (1952); R. F. Brown, J. B. Nordmann and M. Madoff, *ibid.*, **74**, 432 (1952).

(3) W. E. Bachmann and F. H. Moser, *ibid.*, **54**, 1124 (1932).

(4) See C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 478, for an alternative viewpoint.

(5) P. I. Pollak and D. Y. Curtin, THIS JOURNAL, **72**, 961 (1950).

(6) P. D. Bartlett and R. F. Brown, *ibid.*, **62**, 2927 (1940).

as has been demonstrated so elegantly recently by Adams and Gebhart[7] in the benzpinacol rearrangement.

Experimental[8]

All solvents and reagents used were of ordinary quality unless otherwise noted. Details of preparation of the pinacols are given since they differ somewhat from those presented previously.[6,9]

trans-1,2-Ditolylacenaphthenediol-1,2, either ortho or para, was prepared by the addition of 18.2 g. (0.1 mole) of dry finely powdered acenaphthoquinone to an ice-cold solution of the Grignard reagent prepared from 7.2 g. (0.3 mole) of magnesium and 36.1 ml. (51.3 g., 0.3 mole) of the appropriate bromotoluene under nitrogen in 150 ml. of dry ether. Dry benzene, 300 ml., was added immediately, and the mixture, stirred vigorously, brought to a boil on the steam-bath. Approximately 200–250 ml. of the solvent was removed by distillation, and the mixture heated under reflux until the total period of heating was 3–4 hours. After hydrolysis of the mixture with excess dilute hydrochloric acid and ice (more ether was usually necessary), the ether layer was washed with 5% sodium hydroxide solution until no more blue solid was formed. After a short drying period, most of the solvent was removed, and replaced by isopropyl alcohol from which the products crystallize nicely. The yield of crude *o*-tolylpinacol was 22.0–24.0 g. (60–66%), which after one recrystallization gave 20.0–22.0 g. of material of m.p. 162.5–163.5°. An analytical sample had m.p. 164–165°, lit. m.p. 164°.[10] The yield of crude *p*-tolylpinacol was 25.0–27.0 g. (68–74%), which after recrystallization gave 23.0–25.0 g. of material of m.p. 185.0–185.5°, lit. m.p. 182.0–182.5°.[9]

1,8-Ditoluoylnaphthalene, either ortho or para, was prepared by the oxidation of the corresponding *trans*-pinacol, 18.3 g. (0.05 mole) in 150 ml. of boiling acetic acid with 5.0 g. (0.017 mole) of potassium dichromate added all at once (chromic oxide causes considerable rearrangement to occur). The temperature was maintained for 10–15 minutes, and 300 ml. of water added gradually while the mixture was stirred. After standing overnight, the product was collected by filtration, dried and used directly in the next step. Yields were 17.9–18.2 g. (98–99%) of crude product. Recrystallization from carbon tetrachloride gave tiny needles, m.p. 242–243°, lit. m.p. 238°,[10] of 1,8-di-*o*-toluoylnaphthalene. Recrystallization from isopropyl alcohol gave flat needles, m.p. 183–184°, lit. m.p. 181.5–182.5°,[9] of 1,8-di-*p*-toluoylnaphthalene.

cis-1,2-Ditolylacenaphthenediol-1,2, either ortho or para, was prepared by the addition of 18.2 g. (0.05 mole) of the corresponding 1,8-ditoluoylnaphthalene to an ice-cold mixture in 100 ml. of dry ether of magnesium plus magnesium iodide made by the addition all at once of 12.7 g. (0.05 mole) of iodine to 2.4 g. (0.1 mole) of magnesium, under nitrogen, with vigorous stirring, until the iodine color had completely disappeared. Dry benzene, 300 ml., was added, stirring resumed, the mixture heated to boiling, and 100–125 ml. of the solvent distilled. The mixture was heated under reflux until the total period of heating was 3–4 hours when the mixture was cooled and hydrolyzed in the usual manner to give 16.5 g. (90%) of the *o*-tolylpinacol, m.p. 199–203°, or 16.1 g. (88%) of the *p*-tolylpinacol, m.p. 144–148°. Recrystallization from isopropyl alcohol gave 15.2 g. of hexagonal plates, m.p. 206–207°, of *cis*-1,2-di-*o*-tolylacenaphthenediol-1,2. *Anal.*[11] Calcd. for $C_{26}H_{22}O_2$: C, 85.22; H, 6.05. Found: C, 85.43; H, 6.15. Recrystallization from carbon tetrachloride–Skellysolve B gave 14.1 g. of tiny needles, m.p. 155–156°, lit. m.p. 154.3–155.3°,[9] of *cis*-1,2-di-*p*-tolylacenaphthenediol-1,2.

The pinacolones were obtained as described previously.[6,9] Curiously, both 2,2-di-*o*-tolylacenaphthenone and 2,2-di-*p*-tolylacenaphthenone have the same m.p., 135.5–136.5° (lit. m.p. for the latter 128.5–129.5°).[9] The *o*-pinacolone, 1.0 g., was cleaved to 8-(di-*o*-tolylmethyl)-1-naphthoic acid by boiling with 2.0 g. of potassium hydroxide in 20 ml. of ethanol for 3 hours. Then 50 ml. of water was added, the alcohol removed by distillation, and the acid precipitated from the cooled solution by the addition of 20 ml. of 3 *N* hydrochloric acid. Crystallization from benzene, and recrystallization from ethanol gave 0.4 g. of colorless needles, m.p. 247–248°. *Anal.*[11] Calcd. for $C_{26}H_{22}O_2$: C, 85.22; H, 6.05. Found: C, 84.98; H, 5.92.

The reactions in methanol were carried out as described previously.[2] The dimethyl acetal of the *p*-tolylpinacolone, 2,2-di-*p*-tolyl-1,1-dimethoxyacenaphthene, colorless prisms from isopropyl alcohol, m.p. 172–173°. *Anal.*[11] Calcd. for $C_{28}H_{26}O_2$: C, 85.24; H, 6.64; CH_3O, 15.73. Found: C, 85.43; H, 6.34; CH_3O, 15.39.

(7) K. H. Adams and H. J. Gebhart, Jr., Organic Division, American Chemical Society Meeting, Atlantic City, New Jersey, September 14–19, 1952.

(8) All melting points are uncorrected.

(9) W. E. Bachmann and E. J. Chu, THIS JOURNAL, **58**, 1118 (1936).

(10) E. Clar, H. Wallenstein and R. Avenarius, *Ber.*, **62**, 950 (1929).

(11) Analysis by Mr. Joseph Pirie.

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Substituted Long Chain Fatty Acid Hydrazones of 5-Nitrofurfural

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Methods have been developed for a generalized procedure of preparation of derivatives of branched, long chain acid hydrazides which contain a substituted quaternary ammonium group.

Bacteriological tests[2] on certain members of a series of 5-nitrofurfurylidene derivatives of quaternary ammonium acethydrazones[3] indicated that these compounds have about the same level of antibacterial activity, *in vitro*, against a spectrum of selected organisms as does Furacin (5-nitrofurfural semicarbazone). It was thought that lengthening and branching of the acid chain might enhance the desired type of action.

In a previous study[4] of quaternary ammonium salts of branched chain fatty acid hydrazides, the preparative procedure employed permitted substitution of an alkyl group in the position beta to the carboxyl function. The present investigation was undertaken to develop methods whereby it would be possible to obtain a branched alkyl grouping at other places along the chain, as well as to incorporate the 5-nitrofurfurylidene radical into the compound.

The synthetic scheme employed should lead to structures of the general formula

$$[R_3N(CH_2)_x\ CHR'(CH_2)_y\ CONHN{=}CHR'']^+Br^-$$

(1) Abstracted in part from a thesis submitted by M. S. Cohen to the Graduate College of the University of Missouri, 1952, in partial fulfillment of the requirements for the Ph.D. degree.

(2) E. C. Heath, H. S. Goldberg and M. N. Green, *Bact. Proc.*, 142 (1950).

(3) Norman Rabjohn and M. S. Cohen, unpublished work.

(4) Norman Rabjohn and P. D. Strickler, THIS JOURNAL, **75**, 3852 (1953).