[Contribution from the Baker Laboratory of Chemistry of Cornell University]

The Mechanism of the Reaction of N-Nitrosoacetanilide with Methanol[1]

By DeLos F. DeTar

The thermal decomposition of N-nitrosoacetanilide in methanol alone and in methanol containing sodium acetate gives fair yields of benzene. In methanol containing sulfuric acid, the product is largely anisole. It is shown that these reactions and the other reported reactions of N-nitrosoacylamides can be accounted for by means of a reaction scheme which involves a rate-determining rearrangement of the N-nitrosoamide into an aryl diazoacetate. The thermal decomposition in other solvents was examined briefly. In acetic acid, about 50% of phenyl acetate is formed. In acetic anhydride, some benzene was present in the complex mixture of products. The amount of carbon dioxide evolved was found to be small for most of the solvents tried; the largest amount (18%) was obtained in acetic anhydride.

In the course of other work[2] we have become interested in the mechanisms of the reactions of N-nitrosoacylanilides, particularly their thermal decomposition in various solvents. A critical consideration of the evidence presented by Waters[3] shows that contrary to many reviews on the subject there is actually very little cause for preferring a free radical mechanism for the reactions rather than an ionic mechanism. Perhaps the best evidence that free radicals are involved in some reactions of N-nitrosoacylanilides is based on the orienting influence of substituents observed in the formation of biaryls.[4]

Table I

Products Obtained from the Thermal Decomposition of N-Nitrosoacetanilide in Methanol, Acetic Acid and Acetic Anhydride

Solvent (cc.)	Temp., °C.	N-Nitroso-acetanilide mmoles	Acid or base (mmoles)	Products mmoles (per cent.) Benzene	Anisole	Other
Methanol (200)	50	18.3	....	9.94 (54%)	1.06 (6%)	14.1 (77%) HOAc[a]
Methanol (40)	25	3.21	....	0.98 (31)	0.16 (5)	
Methanol (20)	25	1.06	....	.27 (25)	.10 (9)	[b]
Methanol (20)	25	1.06	....	.30 (28)	.13 (12)	[b]
Methanol (20)	25	1.06	$NaOAc \cdot 3H_2O$(1.5)	.41 (39)	.027 (3)	[b]
Methanol (20)	25	1.06	$NaOAc \cdot 3H_2O$(1.5)	.49 (46)	.012 (1)	[b]
Methanol (20)[c]	25	1.06	H_2SO_4 (1)	.018 (2)	.79 (75)	[b]
Methanol (20)[c]	25	1.06	H_2SO_4 (1)	.109 (10)	.58 (55)	[b]
Acetic acid (10)[d]	50	18.3	....	....	....	8.7 (48) PhOAc
Acetic acid (200)[f]	75	18.3	....	.04 (0.2)	....	[b]
Acetic anhydride (400)[e]	60	36.6	....	6.50 (18)	....	45% by wt. of black res.[g]

[a] Formaldehyde polymer was observed when the reaction mixture was distilled to dryness. The presence of formaldehyde in this reaction was demonstrated by Grieve and Hey,[5] who isolated and identified it as the 2,4-dinitrophenylhydrazone. There was 15% of non-volatile residue. [b] Some biphenyl was probably formed in these reactions although conclusive proof of its presence was not obtained. The maximum yield was less than 0.015 mmole (3%), based on measurements of absorption spectra.[4] Grieve and Hey[5] found biphenyl among the products of the reaction in methanol. [c] These experiments were intended as duplicates. However it seems that the amount of sulfuric acid (5 *F*) added was in a critical range and was not duplicated accurately, for the first run resulted in an almost colorless methanol solution when the decomposition was complete while the second of these runs was orange-brown in color although not quite so dark as the first six methanol solutions. [d] Solution very pale yellow orange in color. Only 83–86% of the theoretical amount of nitrogen is obtained in acetic acid (0.03 molar, heated to reflux). [e] Very dark brown solution. [f] The high boiling fraction was tested for the presence of succinic anhydride using aniline to form succinanilic acid, but none was detectable. A control test showed that this method easily detected a few mg. of succinic anhydride. [g] A small amount of phenyl acetate was found, also approximately 1% of biphenyl (spectrophotometrically) and a trace of *p*-acetoxyazobenzene (isolated by chromatography); the test for succinic anhydride was negative.

It appeared to us that a continuation of the kinetic studies[5,6] would be helpful in arriving at a better understanding of the reaction. As a preliminary to the study of the effect of acids and bases on the reaction kinetics, we have made a quantitative study of some of the products formed in the decomposition of N-nitrosoacetanilide in methanol in the presence of sodium acetate and of sulfuric acid. The results, summarized in Tables I and II, unexpectedly afford considerable insight into the mechanism. The kinetic studies are still in progress and will be reserved for a future report.

The most obvious feature of the product studies is that under acidic conditions the phenyl group becomes attached to oxygen to form anisole and phenyl acetate while under alkaline conditions the phenyl group picks up a hydrogen atom to form benzene. These results parallel those reported in the literature for diazonium salts (*cf.* ref. 2) and observed directly for benzenediazonium chloride.[7] They indicate that N-nitrosoacetanilide is able to break down by both an ionic process to give phenyl cations (actual or potential) and by a free radical process to give phenyl radicals (actual or potential[8]).

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[1] Presented before the Division of Organic Chemistry at the 118th Meeting of the American Chemical Society, held in Philadelphia, April, 1950.

[2] D. F. DeTar and S. V. Sagmanli, This Journal, **72**, 965 (1950).

[3] W. A. Waters, "The Chemistry of Free Radicals," Oxford University Press, 1946, p. 146.

[4] *Cf.* D. F. DeTar and H. J. Scheifele, This Journal, **73**, 1442 (1951).

[5] W. S. Grieve and D. H. Hey, *J. Chem. Soc.*, 1797 (1934); 689 (1935); E. C. Butterworth and D. H. Hey, *ibid.*, 116 (1938).

[6] R. Huisgen and G. Horeld, *Ann.*, **562**, 137 (1949).

[7] Unpublished results from this Laboratory.

[8] The evidence presented here does not distinguish an ionization (S_N1) or free radical formation process from a direct replacement process in which the indicated direction of bond cleavage occurs only as the new bond is being formed.

TABLE II

THE FORMATION OF CARBON DIOXIDE IN THE THERMAL DECOMPOSITION OF N-NITROSOACETANILIDE IN VARIOUS SOLVENTS[4]

Solvent (cc.)	NA,[a] g.	Temp., °C.	CO_2 formed % yield[b]
Benzene (10)	3.00	50	0.8
n-Heptane (200)[c]	3.00	45	2.1
Dioxane (200)	3.00	50	2.6
Methyl methacrylate (100)	2.00	35	0.8
Acetic anhydride (15)	3.00	45	11.4
Acetic anhydride (200)	3.00	55	17.5
Acetic anhydride (200)	3.00	65	15[d]
Propionic anhydride (100)	2.00	60	5.6
Acetic acid (10)	3.00	55	0.5
Acetic acid (200)	3.00	75	1.7
Methanol (200)	3.00	45	0.0[e]

[a] NA = N-nitrosoacetanilide. [b] Based on a theoretical yield of one mole of CO_2 per mole of NA. [c] Not completely soluble. [d] Incomplete recovery. [e] Same result obtained with a duplicate experiment.

We are able to account for these results, and also for most of the reactions of N-nitrosoacetanilide reported in the literature on the basis of the reaction scheme outlined in Fig. 1. This represents an extension and a clarification of one of the schemes proposed by Huisgen and Horeld.[6]

The evidence is as follows: (1) Step (a) has been proposed by many workers to account for the formation of N-nitrosoacetanilide (I) by nitrosation of acetanilide and its reduction back to acetanilide by means of zinc dust and acetic acid[9] on the one hand, and for the formation of azo dyes on the other. The former reactions require the nitrosoamide structure (I), while the latter requires the benzenediazoacetate form (II).

(2) That step (a) is rate-determining is indicated by two lines of evidence. In the first place Huisgen and Horeld[6] showed that the rate of disappearance of N-nitrosoacetanilide in methanolic solution is independent of the presence or absence of β-naphthol. In the presence of β-naphthol, they obtained a better than 98% yield of benzeneazo-β-naphthol. Our results presented in Table I show that in the absence of β-naphthol considerable benzene is formed. The formation of the dye almost certainly involves an ionic reaction, probably of the benzenediazonium cation (III) itself[10] while the formation of benzene requires a free radical cleavage of benzenediazoacetate (II).

If a cleavage step were the slow step, then step (c) would have to be very much faster than step (b) to account for the high yield of dye formed with β-naphthol, but step (b) would have to be as fast as step (c) in order to explain the kinetic results. One way out of the dilemma is to presume that the rate-determining step is one prior to both (b) and (c), and rearrangement (a) appears to be a reasonable choice of rate-determining step.

Another indication that steps (b) and (c) are fast is based on the observation that sodium acetate accelerates the rate of decomposition of benzenediazonium chloride in methanol. At 25° the half-life in pure methanol is about 120 minutes,[7,11] while in the presence of sodium acetate the half-life is of the order of 5 minutes.[7] The rate of decomposition of N-nitrosoacetanilide is qualitatively not very sensitive to the presence of sodium acetate. In the absence of sodium acetate the half-life is about 70 minutes.[7,6] These facts accord well with the scheme given in Fig. 1, but cannot be reconciled with the postulate that either step (b) or step (c) is slow. Since the rate determining step is probably a rearrangement step rather than a cleavage step, the kinetics observed do not provide any evidence for a free radical mechanism as is stated in some reviews.[3]

(3) The scheme accounts for the effect of adding sulfuric acid or sodium acetate. The effect of sulfuric acid is to take acetate ions out of circulation in the form of acetic acid. The benzenediazonium ion then decomposes normally to give anisole. In the presence of sodium acetate the covalent benzenediazoacetate (II) is favored. This is capable of breaking down into free radicals to give benzene.

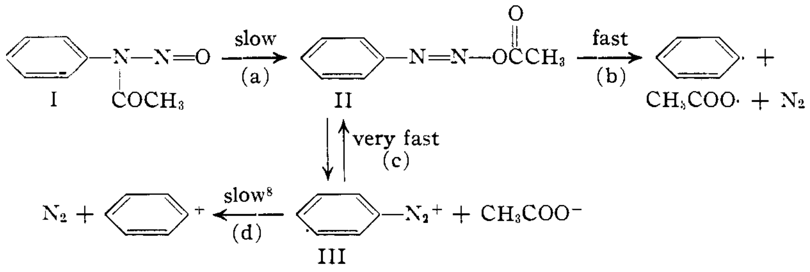

Fig. 1.—Possible mechanism for the decomposition of N-nitrosoacetanilide in solution in methanol.

(4) The conversion of N-nitrosoacetanilide into crystalline benzenediazonium chloride with hydrogen chloride or into sodium benzenediazotate with sodium hydroxide[9] is nicely accounted for as the reaction of these reagents with the benzenediazonium ion (III).

The study of the amount of carbon dioxide formed gave some rather curious results (Table II). A tentative explanation is that the acetoxyl radicals have so short a life in certain solvents such as methanol, benzene and nitrobenzene,[4] that there is insufficient time for them to undergo decarboxylation. Toward other solvents, such as acetic anhydride, the acetoxyl radicals are less reactive, thus permitting a longer average lifetime and a greater amount of decarboxylation. The relative amounts of decarboxylation observed with acetic anhydride and with propionic anhydride accord well with chlorination studies[12] which show that the α-position of acid derivatives is avoided by certain types of radicals. Not much decarboxylation occurs in acetic acid,

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(9) A. Hantzsch and E. Wechsler, *Ann.*, **325**, 226 (1902).

(10) *Cf.* R. Wistar and P. D. Bartlett, THIS JOURNAL, **63**, 413 (1941).

(11) H. A. H. Pray, *J. Phys. Chem.*, **30**, 1477 (1926).

(12) H. C. Brown and Ash, *Rec. Chemical Progress*, **9**, 81 (1948); M. S. Kharasch and H. C. Brown, THIS JOURNAL, **62**, 925 (1940).

for the reaction here seems to be largely ionic (Table I).

Experimental

N-Nitrosoacetanilide.—Previous descriptions[13] give little information about handling this rather unstable substance. The following method of preparation and purification has been found to give a product of better than 99% purity (based on elementary analysis): Acetanilide (13.5 g., 0.100 mole), 15 g. (0.16 mole) of potassium acetate, 35 ml. of glacial acetic acid and 15 ml. of acetic anhydride were placed in a flask equipped with a strong sweep stirrer,[14] a thermometer and a dropping funnel. The solids were dissolved by heating and reprecipitated in finely divided form by stirring and cooling. A 25–30% solution of nitrosyl chloride[15] in acetic anhydride was added over a period of 10 to 15 minutes, the temperature being maintained at about 5–10°, until a slight excess was present, as determined by a rather weak spot test with moistened starch–iodide paper or by the appearance of a slight orange color in the solution. The mixture was poured with stirring into 400 ml. of water containing ice, causing separation of the N-nitrosoacetanilide as a pale yellow granular solid (75–85% yield). This material can be preserved for several hours if kept at about 0°, and the filtered, wet solid, containing about 50% of N-nitrosoacetanilide, can be preserved for several weeks at Dry Ice temperatures. A sample of this moist material can be dried to constant weight in about 1 hour if it is spread thinly on a blotter and placed in a draft, but every sample of crude material which we have dried in this fashion has had a tan color indicating some decomposition. A convenient method for purifying the N-nitrosoacetanilide was mentioned by Otto Fischer.[13] The method works satisfactorily only for samples which have not undergone partial decomposition, however. An 18.5-g. sample of wet material containing 10 g. dry weight of N-nitrosoacetanilide was dissolved in 40 ml. of glacial acetic acid at 15°, the solution filtered, and 40 ml. of water added. The product thus obtained was air-dried on a sheet of paper, giving 4.0 g. (40%) of pale yellow needles with a strong orange fluorescence. Dilution of the mother liquor with 150 ml. of water gave another 3.6 g. of equally good product. A Dumas analysis[16] for nitrogen showed that the material was quite pure.

Anal. Calcd. for $C_8H_8N_2O_2$: N, 17.07. Found: N, 17.27.

Within 4 hours at about 25° the solid material had darkened to a tan color, and within 24 hours it had become a dark brown tar. Though not so stable as the moist material, purified and dried samples can also be preserved for several days at the temperature of Dry Ice without serious darkening. Recrystallization from other solvents seems less satisfactory. Hey[5] observed that samples recrystallized from ether or petroleum ether did not keep well, and we have found that a mixture of methylene chloride and pentane does not work too well because of the fairly rapid decomposition which occurs both in solution and during evaporation of solvent from the crystals. (The rate of decomposition in acetic acid is about one-tenth that in most other solvents.)

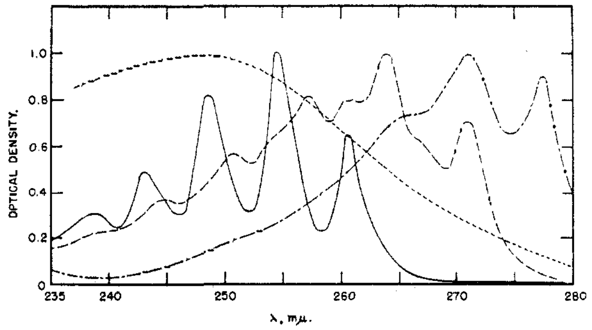

Fig. 2.—Ultraviolet absorption spectra of anisole (60 mg./l.) — - —-, benzene (404 mg./l.); ———, chlorobenzene (535 mg./l.); - - - -, biphenyl (9.2 mg./l.) - - - - - -, solvent used was methanol.

We investigated the possibility of measuring quantitatively the nitrogen evolved from solutions of N-nitrosoacetanilide in acetic acid in order to determine the purity of various samples of the material. However, only about 85% of the theoretical amount of nitrogen was obtained and the yellow color of the solution of decomposition products gave evidence of the presence of azo compounds. The evolution of nitrogen is not quantitative in other solvents[5] either.

Solvents.—For the determination of carbon dioxide and for the larger scale experiments reported in Table I good commercial grades of benzene and methanol were used. The methanol in small scale experiments and for the spectroscopic solvent was of reagent grade, as also were the acetic acid, and the acetic anhydride. The *n*-heptane was designated as "Pure Grade"[17] and the dioxane was a purified sample suitable for hydrogenation.

Determination of Benzene, Anisole and Phenyl Acetate.—These substances were determined spectrophotometrically with the Beckmann model DU ultraviolet spectrophotometer, making use of the optical density at the following wave lengths (Å.): 2430, 2485, 2520, 2545, 2585, 2605, 2640, 2710, 2750, 2775. The use of the large number of wave lengths increased the accuracy of the determinations. The absorption spectra given in Fig. 2 show the significance of the wave lengths chosen for the analysis.[18]

Two methods were used for calculation of concentrations from the optical density data, an analytical procedure described by Tunnicliff, Brattain and Zumwalt,[19] and a second method involving approximations. In Table III are given the results obtained for three synthetic mixtures as calculated by the analytical method.

TABLE III

THE SPECTROPHOTOMETRIC ANALYSIS OF SYNTHETIC MIXTURES OF BENZENE, CHLOROBENZENE AND ANISOLE USING THE ANALYTICAL CALCULATION OF RESULTS

	C_6H_6, mg.	C_6H_5Cl, mg.	$C_6H_5OCH_3$, mg.	$C_6H_5C_6H_5$, mg.
Taken	310	22.7	15.3	0.0
Found	324	24.5	14.6	− .4
Taken	70.9	63.5	93.6	.0
Found	74.8	66.1	93.8	.0
Taken	10.2	10.0	156	.0
Found	14.4	7.9	153	− .1

It should be noted that it is relatively easier to determine small amounts of anisole in the presence of benzene than it is to determine small amounts of benzene in the presence of anisole.

The second method of treating the data was based on a series of approximations in which the concentration of one component was estimated by use of some feature peculiar to the component. Thus the optical densities at 2710, 2750 and 2775 Å. are due primarily to anisole, and a first estimation of its concentration can be made. By calculating the optical density that this estimated concentration of anisole would have at each of the measured wave lengths and subtracting each of these values from the observed densities of the solution, anisole can be arithmetically eliminated. From the residual densities it is possible to estimate the concentration of a second component, then a third and so on. A second approximation for the concentration of anisole can be made by subtracting the small contribution to the density of the solution at 2710, 2750 and 2775 Å., due to the benzene, the chlorobenzene, etc. A second approximation

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[13] O. Fischer, *Ber.*, **9**, 463 (1876); H. France, I. M. Heilbron and D. H. Hey, *J. Chem. Soc.*, 369 (1940).

[14] Hershberg type, "Organic Syntheses," Coll. Vol. 2, p. 117.

[15] We are greatly indebted to the Solvay Process Division of the Allied Chemical and Dye Corporation for the nitrosyl chloride.

[16] Analysis by Mrs. M. Liebowitz.

[17] Specified as not less than 99 mole per cent., obtained from Phillips Petroleum Company, Bartlesville, Oklahoma.

[18] *Cf.* also curves published by Nat. Bureau Stds., API Project 44, Ser. Nos. 300 (chlorobenzene), 325 (anisole), 94 (biphenyl), 1 (benzene).

[19] D. D. Tunnicliff, R. R. Brattain and L. R. Zumwalt, *Anal. Chem.*, **21**, 890 (1949).

for the other substances is made similarly. At the end of the process a series of final residuals is obtained by subtracting the optical densities due to all of the known components from the measured optical densities of the solution. These final residuals will approximate to zero if no interfering impurities are present. Interfering impurities show up as a series of final residuals which form a smooth curve when plotted, but obviously this curve must not show any tendency of being an absorption curve (positive or negative) for one of the known compounds already estimated. For the compounds listed in Table III this second method seems to be as reliable as the analytical method.

Decomposition of N-Nitrosoacetanilide in Methanol.—In a 50-ml. distilling flask were placed 20 ml. of reagent grade methanol and 174 mg. of N-nitrosoacetanilide. The mixture was allowed to stand for more than 12 hours. Then 0.20 ml. of 5 *N* NaOH solution was added to convert the liberated acetic acid into non-volatile sodium acetate and the reaction mixture was distilled on the steam-bath. The distillate was collected in a 50-ml. volumetric flask. When all of the methanol had distilled, methanol was run into the flask from a dropping funnel at the same rate as it distilled, the flask remaining nearly dry during the distillation. When the first volumetric flask was nearly full, a second one was put in place and the distillation continued. All of the benzene and at least 70% of the anisole came over in the first 50 ml. of distillate.

For the acetic acid and acetic anhydride solutions an extraction technique was developed. A 5-ml. aliquot of distillate was transferred to a 50-ml. volumetric flask, hydrolyzed with water, then the mixture was cooled and made alkaline with 5 *N* NaOH solution. Water was added to bring the liquid level just to the neck of the flask and the aqueous solution was extracted in the volumetric flask with four 2.5-ml. portions of 2,2,4-trimethylpentane of spectroscopic grade. The hydrocarbon layer was removed from the neck with a pipet and transferred to another volumetric flask for dilution with methanol. The extinction coefficients obtained in methanolic solution were used for estimating the concentration of benzene and of anisole. The errors introduced should not be very great since the solution used for determination of optical density contained only 20% of the isoöctane.

The phenyl acetate absorption spectrum has poorly defined maxima at 2590 and 2650 Å. and a slight minimum at 2640 Å. It is unsuitable for the determination of phenyl acetate in the presence of other materials. The phenyl acetate formed in acetic acid solution was isolated by neutralization of the acetic acid, extraction of the phenyl acetate with methylene chloride followed by drying and distillation, b.p. 77° at 9 mm., odor similar to that of an authentic sample, b.p. 76° at 8 mm.

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[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT BRANCH, OFFICE OF SYNTHETIC LIQUID FUELS, U. S. BUREAU OF MINES]

The Anomalous Reaction of 1-Tetralone with *o*-Tolylmagnesium Bromide[1]

BY MILTON ORCHIN, LESLIE REGGEL AND R. A. FRIEDEL

The reaction of 1-tetralone with *o*-tolylmagnesium bromide gives, in addition to the expected 1-(*o*-tolyl)-1-hydroxy-1,2,3,4-tetrahydronaphthalene (I) and 1-(*o*-tolyl)-3,4-dihydronaphthalene (II) a 19% yield of a substance which is believed to be 1-(*o*-tolyl)-1,1′-dihydroxy-1,2,3,4,1′,2′,3′,4′-octahydro-2,1′-dinaphthyl (III). Dehydrogenation of III with palladium-on-charcoal gives 1-(*o*-tolyl)-2-(1′-naphthyl)-naphthalene (V). Treatment of III with formic acid gives two isomeric hydrocarbons; one of these is shown to be 1-(*o*-tolyl)-2-(3′,4′-dihydro-1′-naphthyl)-3,4-dihydronaphthalene (IX). The second hydrocarbon is believed to have a spiro-3,4-benzfluorene structure (AII) arising from a cyclodehydration. 1-(*o*-Tolyl)-2-(1′-naphthyl)-naphthalene (V) has been synthesized from *o*-tolyllithium and 1-keto-2-(1′,2′,3′,4′-tetrahydro-1′-naphthyl)-1,2,3,4-tetrahydronaphthalene (VI), followed by dehydration and dehydrogenation.

The most direct route to 1-(*o*-tolyl)-naphthalene would appear to be reaction of *o*-tolylmagnesium bromide with 1-tetralone, followed by dehydration and dehydrogenation of the intermediate tertiary carbinol. Although this series of reactions has been shown to provide some of the desired hydrocarbon,[2] the formation of an unusual product during the Grignard addition has prompted us to investigate the reaction in detail. We have found that four products are obtained: 1-(*o*-tolyl)-1-hydroxy-1,2,3,4-tetrahydronaphthalene (I); 1-(*o*-tolyl)-3,4-dihydronaphthalene (II); a high-boiling, viscous gum, of unknown composition; and a colorless, crystalline compound, $C_{27}H_{28}O_2$, m.p. 173.5–176.0°, whose study constitutes the major portion of the present investigation.

The structure of I follows from its analysis, from the presence of a hydroxyl group (as shown by its infrared absorption spectrum) and from its conversion to the known 1-(*o*-tolyl)-naphthalene (IV). The structure of II is established by its analysis, by its conversion to IV, and by its ultraviolet absorption spectrum (Fig. 3), which is that of a substituted 1,2-dihydronaphthalene.

We have assigned the structure of 1-(*o*-tolyl)-1,1′-dihydroxy - 1,2,3,4,1′,2′,3′,4′ - octahydro - 2,1′-dinaphthyl (III) to the crystalline compound $C_{27}H_{28}O_2$. Compound III, the "diol," is obtained in 19% yield when the Grignard reaction mixture is decomposed with ammonium chloride, the ether layer separated and the ether evaporated; the diol precipitates as a white solid and is obtained analytically pure by filtration and washing with petroleum ether. It melts, without obvious decomposition, over a fairly small temperature range, with some dependence upon the rate of heating. When it is recrystallized from ether, ethanol or petroleum ether, the melting point is lowered, extends over a wider range, and gas is evolved on melting; the analysis is unchanged. It is possible that the diol is not a stereochemically pure individual, but is a mixture of two or more of the four possible racemates having the structure III. If the diol is such a mixture, the change in melting point after recrystallization might be explicable, although the gas evolution on melting seems unusual.

The structure of the diol follows from its analysis; from the presence of two active hydrogen (hydroxyl) atoms in the Zerewitinoff determination; from the ultraviolet spectrum (Fig. 3), which indicates substituted phenyl groups only; and from catalytic dehydration–dehydrogenation to

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(1) Not subject to copyright.

(2) R. A. Friedel, M. Orchin and L. Reggel, THIS JOURNAL, **70**, 199 (1948).