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Synthesis and Alkaline Degradation of the Arenesulfonyl Derivatives of α-Menaphthyl- and 1,1-Di-α-menaphthylhydrazine[1]

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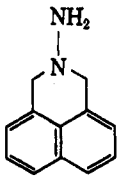
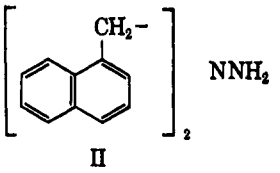
Attempts to prepare 1,1-di-α-menaphthylhydrazine by alkylation of *t*-butyl carbazate by means of 1-chloromethylnaphthalene gave only the monoalkylated product III which was characterized by cleavage to α-menaphthylhydrazine, tosylation of which gave 1-α-menaphthyl-1-*p*-toluenesulfonhydrazide (IV). The structure of IV was established by an alternate synthesis which involved amination of N-α-menaphthyl-*p*-toluenesulfonamide by means of mesitoxyamine. This technique proved to be generally applicable to the amination of a variety of weakly basic amino compounds. Treatment of IV with aqueous ethanolic alkali gave α-methylnaphthalene. Reduction of di-α-menaphthylnitrosamine by means of aluminum amalgam in wet ether gave 1,1-di-α-menaphthylhydrazine, the corresponding *p*-toluenesulfonyl derivative of which with sodium methoxide in ethanol afforded 1,1-di-α-naphthylethane in 87% yield.

Previously it was shown that 2-amino-2,3-dihydro-1H-benz[*de*]isoquinoline (I) was not converted to acenaphthene on oxidation of the free hydrazine or treatment of the corresponding *p*-toluenesulfonyl derivative with aqueous or alcoholic alkali.[2] On the other hand 1,1-dibenzylhydrazine and a variety of



I

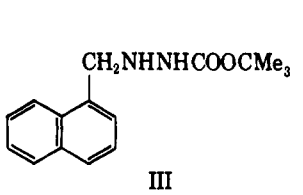


II

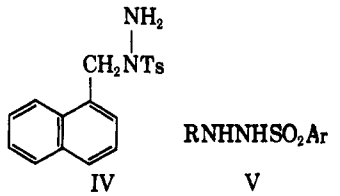
acyclic and cyclic benzylic hydrazines are readily converted to the corresponding dibenzyls under these conditions.[3-6] The abnormal result in the case of I was attributed to electronic or steric effects and a study was initiated to shed more light on this unexpected result and gain a better understanding of the nature of the labile intermediates involved in these reactions.

As part of this study it was necessary to determine whether the nature of the α-naphthylmethyl (α-menaphthyl) grouping itself might not be responsible for this lack of reaction. This possibility has now been eliminated by the preparation and successful conversion of 1,1-di-α-menaphthylhydrazine (II) to 1,2-di-α-naphthylethane.

Initial attempts to prepare II by reaction of *t*-butyl carbazate with excess 1-chloromethylnaphthalene in dimethylformamide in the presence of triethylamine were unsuccessful. Only the monoalkylated carbazate



III



IV V

derivative III could be obtained by this procedure. Cleavage of the carbo-*t*-butoxy group from III by means of hydrogen chloride in nitromethane gave α-menaphthylhydrazine hydrochloride. The free hydrazine was not isolated but was characterized as the *p*-toluenesulfonyl derivative IV. Although the bulk of the α-menaphthyl group is sufficient to prevent further alkylation of III by excess α-menaphthyl chloride, tosylation of α-menaphthylhydrazine occurs on the substituted nitrogen atom with the formation of IV. 1-Substituted 1-arenesulfonhydrazides such as IV appear not to have been described previously in the literature. Presumably the reaction of arenesulfonyl chlorides with simple alkylhydrazines would give other members of this novel class of compounds which are of considerable interest in connection with a comparison of their alkaline degradation with that of the long-known isomeric 2-substituted-1-arenesulfonhydrazides V[7] derived from arylhydrazines and arenesulfonyl

(1) Supported by a grant (G-19506) from the National Science Foundation.

(2) L. A. Carpino, *J. Am. Chem. Soc.*, **85**, 2144 (1963).

(3) L. A. Carpino, *ibid.*, **79**, 4427 (1957).

(4) L. A. Carpino, *ibid.*, **84**, 2196 (1962).

(5) L. A. Carpino, A. A. Santilli, and R. W. Murray, *ibid.*, **83**, 2728 (1960).

(6) C. G. Overberger, *Record Chem. Progr.*, **21**, 21 (1960).

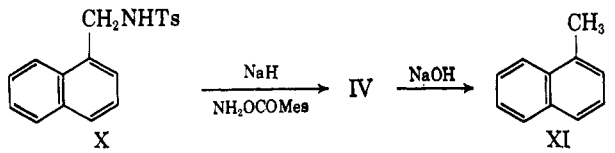
(7) R. Escales, *Ber.*, **18**, 893 (1885).

chlorides. The only alkylhydrazine for which data concerning the reaction with arenesulfonyl chlorides could be found in the literature is the 2-phenyl-2-butyl derivative described by Cram and Bradshaw.[8] In this case also, tosylation occurs on the unsubstituted nitrogen atom, a result which can be attributed to the bulk of the tertiary alkyl group.

The structure of IV was established by its n.m.r. spectrum which, in contrast to that of the compound of Cram and Bradshaw, exhibits only a single NH peak at δ 3.16 (2H), identified by deuterium exchange. Apart from the complex multiplet due to the aromatic protons at δ 7.5, two additional singlets were observed at 2.38 (3H, CH_3) and 4.59 (2H, CH_2). The structural assignment was confirmed by an alternate synthesis. The route used is of interest in connection with recent studies on the reductive deamination of primary amines. Nickon and Hill[9] showed that treatment of an N-substituted sulfonamide with an excess of hydroxylamine-O-sulfonic acid in the presence of aqueous alkali yielded the corresponding hydrocarbon. As has been

$$\underset{\text{VI}}{RNSO_2Ar^-} \xrightarrow[OH^-]{NH_2OSO_3H} \underset{\text{VII}}{RN(NH_2)SO_2Ar} \xrightarrow{OH^-} \underset{\text{VIII}}{[RN{=}NH]} \xrightarrow{-N_2} \underset{\text{IX}}{RH}$$

postulated a logical first step involves the N-amination of the sulfonamide anion VI to yield the N-aminosulfonamide VII. Elimination of benzenesulfinic acid to give the monosubstituted diimide VIII followed by decomposition of the latter would complete the process. However the intermediacy of VII in such reactions had not been established by their isolation under the reaction conditions and it was pointed out[9] that alternative mechanisms do not necessarily require formation of the N-aminosulfonamide as a distinct intermediate. We investigated such reactions while maintaining conditions under which the N-aminosulfonamides would be likely to survive and found that the postulated intermediates (VII) could indeed be isolated. The aminations were carried out using one equivalent of sodium hydride or sodium methoxide in dimethylformamide at 0° and substituting mesitoxyamine[10] for the hydroxylamine-O-sulfonic acid. As an example, IV was obtained in 43% yield from N-α-menaphthyl-*p*-toluenesulfonamide (X). N-benzylbenzenesulfonamide was converted to the corresponding N-amino derivative similarly.



Having available authentic samples of N-aminosulfonamides it was desirable to test the postulations of Nickon[9] and Cram[8] regarding their conversion to hydrocarbons on alkaline degradation. In agreement with these expectations it was shown that IV is converted to α-methylnaphthalene in 58% yield upon treatment with refluxing aqueous ethanolic sodium hydroxide solution.

(8) D. J. Cram and J. S. Bradshaw, *J. Am. Chem. Soc.*, **85**, 1108 (1963).
(9) A. Nickon and A. S. Hill, *ibid.*, **86**, 1152 (1964).
(10) L. A. Carpino, *ibid.*, **82**, 3133 (1960).

The successful amination of sulfonamide anions by means of mesitoxyamine suggested that this reagent might be generally useful in the amination of those amino compounds which can easily be converted to the corresponding anions by treatment with alkali. This has now been shown to be the case for amides (N-benzylbenzamide[11]), imides (naphthalimide[11] and *t*-butyl iminodicarboxylate[12]), and pyrroles (2,5-diphenylpyrrole,[13] 2,3,4,5-tetraphenylpyrrole,[13] and carbazole[11]).

Since bis alkylation of *t*-butyl carbazate could not be achieved, the synthesis of II was carried out by an alternate standard sequence involving reduction of the nitrosamine by means of aluminum amalgam in moist ether. The *p*-toluenesulfonyl derivative of II upon treatment with alcoholic sodium methoxide, gave 1,2-di-α-naphthylethane in 87% yield. Aqueous sodium hydroxide proved to be ineffective in this case probably because of the insolubility of the hydrazide and/or its sodium salt in the aqueous medium.

Experimental[14-16]

***t*-Butyl 2-(α-Menaphthyl)carbazate.**—A solution of 100 g. of 1-chloromethylnaphthalene, 82.8 g. of *t*-butyl carbazate,[17] and 110 ml. of triethylamine in 280 ml. of dimethylformamide was warmed to an internal temperature of 60° and then let stand at room temperature for 24 hr. The mixture was diluted with 1.4 l. of water, acidified with 170 ml. of 2·*N* hydrochloric acid, stored in a refrigerator for 24 hr., and filtered. The crude solid was dried in air and recrystallized from ligroin (b.p. 88–98°). There was obtained 54 g. (35%) of white powdery solid, m.p. 123–127°. An analytical sample had m.p. 126.5–128.5°.

Anal. Calcd. for $C_{16}H_{20}N_2O_2$: C, 70.56; H, 7.40; N, 10.29. Found: C, 70.25; H, 7.64; N, 10.50.

α-Menaphthylhydrazine Hydrochloride.—Cleavage of *t*-butyl 2-(α-menaphthyl)carbazate in nitromethane by passage of hydrogen chloride gas in the usual manner[2,3,5] gave 70% of the hydrochloride which was recrystallized from ethanol and ethanol–ether: m.p. 187–191° (lit.[18] m.p. 189–190°).

Anal. Calcd. for $C_{11}H_{13}ClN_2$: C, 63.30; H, 6.28; N, 13.43. Found: C, 63.41; H, 6.32; N, 13.74.

1-(α-Menaphthyl)-1-*p*-toluenesulfonylhydrazine.—Treatment of α-menaphthylhydrazine hydrochloride with *p*-toluenesulfonyl chloride and triethylamine in dimethylformamide in the usual manner[3] gave the sulfonyl derivative, m.p. 109–111° dec. (ethanol), in 30% yield. There was considerable loss on recrystallization, presumably because of decomposition in the warm solvent. Subsequently methanol was shown to be a better recrystallization solvent (see below).

Anal. Calcd. for $C_{18}H_{18}N_2O_2S$: C, 66.24; H, 5.56; N, 8.58. Found: C, 66.25; H, 5.57; N, 8.56.

The **benzal derivative** had m.p. 144–145° (ethanol).

Anal. Calcd. for $C_{25}H_{22}N_2O_2S$: C, 72.45; H, 5.35; N, 6.76. Found: C, 72.53; H, 5.48; N, 7.07.

1-(α-Menaphthyl)-1-*p*-toluenesulfonylhydrazine by Amination of N-α-Menaphthyl-*p*-toluenesulfonamide.—To a solution of 3.11 g. of N-α-menaphthyl-*p*-toluenesulfonamide in 40 ml. of dry dimethylformamide there was added 0.72 g. of 50% sodium hydride–oil dispersion. The mixture was stirred magnetically in a water bath at 90–95° for 10 hr. and then was cooled in an ice bath; 3.6 g. of mesitoxyamine was added over 2–3 min. The mixture was allowed to stir in the ice bath for 1 hr. and at

(11) See Experimental.
(12) L. A. Carpino, *J. Org. Chem.*, **29**, 2820 (1964).
(13) L. A. Carpino, *ibid.*, in press.
(14) All melting points and boiling points are uncorrected.
(15) Elemental analyses were by Dr. A. Bernhardt, Mülheim (Ruhr), Germany.
(16) Unless otherwise noted n.m.r. spectra were recorded in deuteriochloroform on a Varian A-60 instrument using tetramethylsilane as internal standard. Infrared spectra were recorded on a Perkin-Elmer 237B grating spectrophotometer.
(17) L. A. Carpino, *J. Org. Chem.*, **28**, 1909 (1963); *J. Am. Chem. Soc.*, **82**, 2725 (1960).
(18) A. L. Green, *Biochem. J.*, **84**, 217 (1962).

room temperature for 2 hr. Dilution with water to 250 ml. gave an orange-colored viscous material. Decantation of the water followed by trituration with methanol gave a solid which was recrystallized as rapidly as possible from methanol. Cooling in an ice bath gave 1.4 g. (43%) of the hydrazide as yellow-orange crystals, m.p. 110–113° (gas), identified by infrared spectral comparison with a sample prepared by treatment of α-menaphthylhydrazine hydrochloride with *p*-toluenesulfonyl chloride.

1-Benzyl-1-benzenesulfonylhydrazine.—A stirred solution of 2.47 g. of N-benzylbenzenesulfonamide in 25 ml. of dry dimethylformamide was treated with 1.35 g. of sodium methoxide. After 5 min. at room temperature the mixture was cooled in an ice bath; 3.23 g. of mesitoxyamine hydrochloride[19] was added over 5–7 min. The mixture was stirred in the ice bath for 2 hr. and diluted to 250 ml. with water. An oil separated which solidified on cooling. Recrystallization from ethanol gave 1.5 g. (57%) of the N-amino compound as white crystals, m.p. 85–90°. A second recrystallization from ligroin (60–70°)–benzene gave 0.5 g. (19%) of white crystals, m.p. 110–112° dec.

Anal. Calcd. for $C_{13}H_{14}N_2O_2S$: C, 59.54; H, 5.38. Found: C, 59.89; H, 5.22.

Conversion of 1-(α-Menaphthyl)-1-*p*-toluenesulfonhydrazide to α-Methylnaphthalene.—To a solution prepared from 8 g. of sodium hydroxide dissolved in 90 ml. of water and 50 ml. of ethanol there was added 7.5 g. of IV and the mixture refluxed for 4.5 hr. The solid dissolved in 10–15 min. with effervescence. Dilution with water to 500 ml. followed by extraction with ether gave 1.9 g. (58%) of α-methylnaphthalene, b.p. 122–124° (24 mm.). The infrared spectrum was identical with that of an authentic sample.

N-Aminonaphthalimide.—Amination of naphthalimide by the method described for IV gave 81% of the N-amino derivative, m.p. 265–268° (lit.[20] m.p. 262°), identified by infrared spectral comparison with a sample prepared from naphthalic anhydride and hydrazine.[5]

1-Benzyl-1-benzoylhydrazine.—Amination of N-benzylbenzamide by the method described for IV gave 20% of the N-amino compound, m.p. 68.5–70.5° (lit.[5] m.p. 69–70°), identified by infrared spectral comparison with an authentic sample.[5]

N-Aminocarbazole.—Amination of carbazole by the method described for IV gave 60% of the N-amino derivative, m.p. 150–151° (lit.[21] m.p. 151°), identified by infrared comparison with an authentic sample kindly provided by Dr. J. L. Ferrari which had been prepared by aluminum amalgam reduction[5] of the N-nitroso compound in wet ether.

Di-α-menaphthylamine Hydrochloride and Di-α-menaphthylnitrosamine.—A stirred suspension of 3.06 g. of lithium aluminum hydride in 300 ml. of dry ether was heated to reflux temperature, the source of heat was removed, and 41 g. of the imine[22] prepared from α-naphthaldehyde and α-menaphthylamine was added through a solids addition tube over a period of about 10 min. at a rate to maintain gentle refluxing. The deep green-blue mixture was refluxed for 15 hr., cooled in an ice bath, and decomposed by the dropwise addition of water. The complex salts were filtered and washed with ether; the dried ether solution was treated with a stream of hydrogen chloride gas which precipitated 40 g. (86%) of the hydrochloride as a green-white powder, m.p. 230–235° dec. (lit.[23] m.p. 239°).

The N-nitroso derivative was obtained in 65% yield as yellow flakes, m.p. 147.5–149.5° (lit.[23] m.p. 147°), by nitrosation of the hydrochloride in acetic acid by the addition of solid sodium nitrite.

1,1-Di-α-menaphthylhydrazine Hydrochloride.—Over a period of 1 hr. 2.7 g. of water was added to a stirred suspension of 4.5 g. of aluminum amalgam and 13.8 g. of N-nitrosobis(α-menaphthyl)-amine in 300 ml. of water-saturated ether at reflux temperature. The mixture was refluxed for 9 hr., whereupon the nitroso compound gradually dissolved. The alumina sludge and ether were decanted from the aluminum amalgam into a solution of 40 g. of sodium hydroxide in 200 ml. of water. After thorough mixing, the ether layer was dried (magnesium sulfate) and treated with a stream of hydrogen chloride gas. The initially precipitated viscous oil solidified on continued passage of the gas. There was obtained 9 g. (61%) of cream-colored solid, m.p. 215–225°. An analytical sample was obtained by recrystallization from ethanol–ether and ethanol–nitromethane which gave snow-white needles, m.p. 228–233°.

Anal. Calcd. for $C_{22}H_{21}ClN_2$: C, 75.74; H, 6.07; Cl, 10.16; N, 8.03. Found: C, 75.67; H, 6.26; Cl, 10.03; N, 8.20.

The *p*-toluenesulfonyl derivative was prepared in the usual manner[3] in dimethylformamide solution in 52% yield: m.p. 153–154° dec. (ethanol–nitromethane).

Anal. Calcd. for $C_{29}H_{26}N_2O_2S$: C, 74.65; H, 5.62; N, 6.01. Found: C, 74.33; H, 5.63; N, 6.25.

Conversion of 1,1-Bis(α-menaphthyl)-2-*p*-toluenesulfonylhydrazine to 1,2-Di-α-naphthylethane.—A solution of 0.63 g. of the sulfonhydrazide and 1 g. of sodium methoxide in 25 ml. of 95% ethanol was refluxed for 10 hr. and diluted with water to 80 ml. The mixture was filtered after several hours to give 0.33 g. (87%) of the hydrocarbon, m.p. 155–159°. Recrystallization from benzene gave white crystals, m.p. 164–165° (lit.[24] m.p. 161–162°). The infrared spectrum was identical with that of an authentic sample prepared by reaction of 1-chloromethylnaphthalene with magnesium in ether.

(19) Since mesitoxyamine is stored as the more stable hydrochloride it is often convenient to use the hydrochloride directly in the amination reactions by employing a second mole of alkali. However, in a number of cases in which the free base was used successfully the hydrochloride was not effective.

(20) A. Bistrzycki and J. Risi, *Helv. Chim. Acta*, **8**, 810 (1925).

(21) A. V. Blom, *J. prakt. Chem.*, [2] **24**, 77 (1916).

(22) H. Dahn, U. Solms, and P. Zoller [*Helv. Chim. Acta*, **35**, 2117 (1952)] employed catalytic hydrogenation (Raney nickel) to reduce the imine.

(23) J. v. Braun, G. Blessung, and F. Zobel, *Ber.*, **56**, 1988 (1923).

(24) F. Mayer and A. Sieglitz, *ibid.*, **55**, 1835 (1922).