above assignment. Here both the chemical shifts and solvent-induced shifts indicate the major isomer to have the *s-trans* conformation about the nitrogen–thiocarbonyl bond. Whereas in formamides the presence of the *t*-butyl group increases only slightly the amount of *s-trans* isomer,[4] the effect here is more profound, and a 2:1 preference for the ordinarily less favorable conformation is shown.

Experimental Section

The thioncarbamates were prepared by reaction of ethyl or methyl isothiocyanate with an alkoxide either in excess of alcohol or in xylene (for the amino alcohols). They were shown to be homogeneous by gas chromatography on Apiezon L at 150° or lower (on-column decomposition occurs at higher temperatures). Infrared spectra on liquid films or Nujol mulls (Beckman IR-12) showed bands at 3250–3285, 1530–1550, 1330–1335, and 1200–1225 cm^{-1}, which are typical of thioncarbamates.[18] Analytical data for previously unreported compounds are in Table III.

S-Ethyl Methylthiocarbamate.—Following a procedure[20] for unsubstituted carbamates a mixture of 3.0 g of O-ethyl methylthiocarbamate and 3.9 g of iodoethane was warmed on the steam bath until gas chromatography indicated that the reaction was complete (1 hr). The mixture was distilled and the product was collected at 104° (0.8 mm). Nmr signals in $CDCl_3$ appeared at δ 2.87 (doublet CH_3N), 5.7 (broad NH), 3.05 (quartet SCH_2), 1.29 (triplet $C\text{-}CH_3$).

Anal. Calcd for C_4H_9NOS: C, 40.31; H, 7.61. Found: C, 40.00; H, 7.55.

2-Dimethylaminoethyl Methyldithiocarbamate.—A solution of 15.0 g (0.105 mole) of 2-dimethylaminoethanethiol hydrochloride in 15 ml of water was neutralized with 210 ml of 1 *N* sodium hydroxide solution and then treated immediately with 8.1 g (0.11 mole) of methyl isothiocyanate dissolved in a few ml of methanol. Following 30 min of stirring at room temperature, the reaction mixture was treated with 105 ml of *N* hydrochloric acid. After 1 hr the solid which had formed was removed by filtration, dried, and recrystallized from benzene–Skellysolve B. The yield was 9.7 g (54%), mp 110–112°.

Anal. Calcd for $C_6H_{14}N_2S_2$: C, 40.41; H, 7.91; N, 15.71. Found: C, 40.53; H, 7.92; N, 15.58.

Registry No.—**1**, 14128-35-9; **2**, 817-73-2; **3**, 14128-37-1; **4**, 14128-38-2; **5**, 14128-39-3; **6**, 14128-40-6; **7**, 14128-41-7; **8**, 14128-42-8; **9**, 14128-43-9; *s*-ethyl methylthiocarbamate, 14128-44-0; 2-dimethylaminoethyl methyldithiocarbamate, 14128-45-1.

Acknowledgment.—The author is indebted to Mr. Michael Camara for assistance in the preparative work and to Mr. Gilbert Suarez for recording the nmr spectra.

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(20) H. L. Wheeler and B. Barnes, *Am. Chem. J.*, **22**, 141 (1899).

The Reaction of 2-(N,N-Dimethylamino)-1,4-diphenyl-1,4-butanediol with Acid. A Novel Tetralone Formation[1a]

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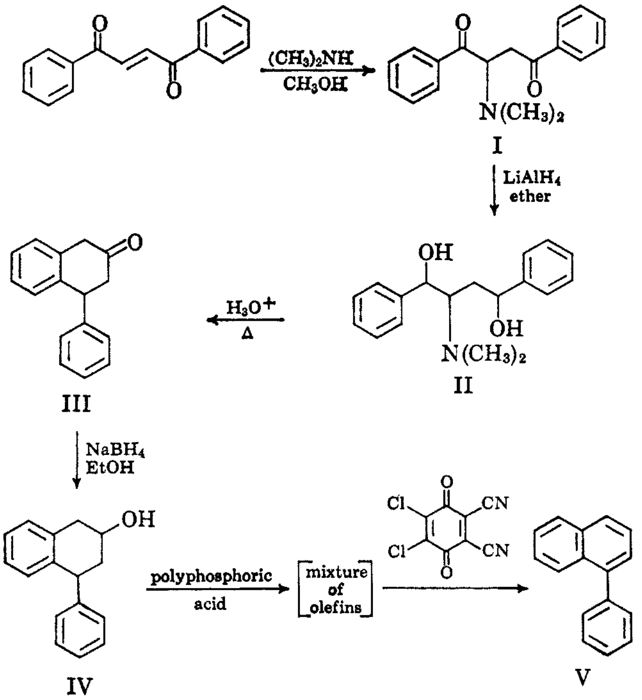
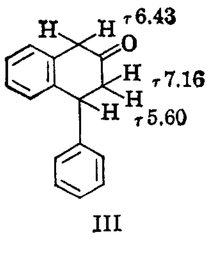
Reduction of 2-(N,N-dimethylamino)-1,4-diphenyl-1,4-butanedione[2] (I) with excess lithium aluminum hydride in ether gave 2-(N,N-dimethylamino)-1,4-diphenyl-1,4-butanediol (II) as a mixture of stereoisomers, mp 89–124° (Scheme I). Treatment of II with refluxing aqueous hydrochloric acid, hydrobromic acid, or sulfuric acid afforded a neutral compound (III) of molecular formula $C_{16}H_{14}O$. Compound III was a colorless liquid: bp 127–128.5° (0.07 mm); $n^{23}D$ 1.6030. The infrared spectrum of a solution of III in carbon tetrachloride showed strong absorption at 5.80 μ, indicating the presence of a nonconjugated ketone. The ultraviolet spectrum of III (λ_{max} 263 mμ, ϵ 1000) suggests the presence of a substituted phenyl group as the only chromophore.

SCHEME I



In order to assign a structure to compound III, it was desirable to convert it into a hydrocarbon having the same carbon skeleton. This was accomplished as follows. Reduction of ketone III with sodium borohydride gave a quantitative yield of alcohol IV, mp 122–123.5°. Treatment of IV with polyphosphoric acid at 95° gave a mixture of two olefins; dehydrogenation of this crude mixture with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in benzene, followed by chromatography of the products on an alumina column, afforded 1-phenylnaphthalene, identified by comparison of physical and spectral properties with an authentic sample. The nmr spectrum of III in $CDCl_3$ showed absorption at τ 2.7–2.9 (complex multiplet, 9 H), 5.60 (triplet, 1 H), 6.43 (singlet, 2 H), and 7.16 (doublet, 2 H). A likely structure for III is therefore 4-phenyl-2-tetralone. The observed nmr splitting pattern is consistent with the suggested structure and the



III

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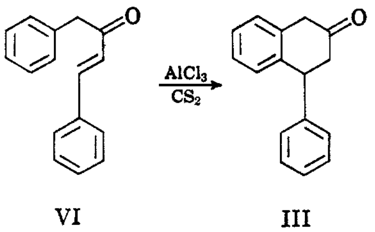
[1] (a) First presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967; (b) to whom inquiries should be addressed.

[2] R. E. Lutz, P. S. Bailey, and N. H. Shearer, Jr., *J. Am. Chem. Soc.*, **68**, 2224 (1946).

assigned τ values are in excellent agreement with those of model compounds.[3]

As final confirmation of the assigned structure, compound III was synthesized independently *via* an intramolecular Friedel–Crafts reaction of 1,4-diphenyl-3-buten-2-one (VI)[4] in carbon disulfide with aluminum chloride. The product was identical in every respect with III obtained by the previous method. The mechanism of tetralone formation is currently under investigation in our laboratories and will be the subject of a future publication.



VI III

Experimental Section[5]

2-(N,N-Dimethylamino)-1,4-diphenyl-1,4-butanediol (II).—2-(N,N-dimethylamino)-1,4-diphenyl-1,4-butanedione (I) was prepared from dibenzoylethylene and dimethylamine according to the method of Lutz, *et al.*[2] A solution of the dione (47.7 g, 0.170 mole) in 250 ml of anhydrous ether was added dropwise to a stirred suspension of lithium aluminum hydride (18.2 g, 0.48 mole) in 150 ml of anhydrous ether. After stirring 24 hr at room temperature, a solution of ethyl acetate (50 ml) in ether (50 ml) was added dropwise, followed by cautious addition of water (50 ml). The resulting mixture was filtered and the solid washed thoroughly with ether. The combined filtrates were washed with water and dried over magnesium sulfate. Distillation gave a colorless gum, bp 162° (0.01 mm). Recrystallization from benzene-*n*-hexane (1:2) gave 31.0 g (0.115 mole, 64%) of a white crystalline substance, mp 89–124°. The infrared spectrum showed absorption at 2.78 (sharp, unassociated OH) and at 2.93 μ (broad, associated OH); there was no absorption in the carbonyl region.

Anal. Calcd for $C_{18}H_{23}NO_2$: C, 75.82; H, 8.13; N, 4.92. Found: C, 75.89; H, 8.29; N, 5.12.

Reaction of 2-(N,N-Dimethylamino-1,4-diphenyl-1,4-butanediol with Hydrochloric Acid (Formation of III).—A solution of 2-(N,N-dimethylamino)-1,4-diphenyl-1,4-butanediol (20 g, 0.074 mole) in concentrated hydrochloric acid (500 ml) was refluxed for 3 hr. The appearance of an insoluble orange oil soon became obvious. The cooled mixture was extracted three times with ether. The combined ether extracts were washed twice with water, 10% sodium carbonate solution, and again with water. The dried organic layer was evaporated under reduced pressure. The crude product (12.6 g of orange oil) was vacuum distilled to yield 9.0 g (0.041 mole, 58%) of a colorless liquid: bp 127–128.5° (0.07 mm); $n^{23}{}_D$ 1.6030. Thin layer chromatography and vapor phase chromatography indicated that the liquid was a single, pure compound.

Anal. Calcd for $C_{16}H_{14}O$: C, 85.70; H, 6.35; mol wt, 222. Found: C, 85.95; H, 6.37; mol wt, 230 ± 10 (osmometry).

Reduction of 4-Phenyl-2-tetralone (III) with Sodium Borohydride.—Sodium borohydride (273 mg, 7.20 mmoles) was added to a stirred solution of 4-phenyl-2-tetralone (3.00 g, 13.5 mmoles, prepared as above) in absolute ethanol (30 ml). A mildly exothermic reaction occurred. After stirring 10–15 min, 36 ml of water was added. The solution was boiled for a few minutes and filtered while hot. Upon cooling to room temperature white needles were deposited in the filtrate. After further cooling (0.5 hr) in a refrigerator, the product was collected by suction, washed with 30 ml of cold ethanol–water (1:1), and air dried: yield, 3.06 g (13.6 mmoles, 100%); mp 122–123.5°. The structure 4-phenyl-2-tetralol (IV) was assigned on the basis of the infrared spectrum (2.78 μ, sharp; 2.91 μ, broad; no carbonyl absorption) and elemental analysis.

Anal. Calcd for $C_{16}H_{16}O$: C, 85.67; H, 7.19. Found: C, 85.59; H, 7.30.

Dehydration and Aromatization of 4-Phenyl-2-tetralol (IV). Generation of 1-Phenylnaphthalene.—A rapidly stirred mixture of 4-phenyl-2-tetralol (5.45 g, 24.3 mmoles, prepared as above) and polyphosphoric acid (125 ml) was heated on the steam bath for 1 hr. The reaction mixture was poured onto ice and extracted with ether. Washing of the ether extract with 5% sodium bicarbonate and water followed by drying and evaporation of solvent left a light-yellow gum (4.97 g). The infrared spectrum of the crude product revealed no significant OH absorption. The ultraviolet spectrum of a solution of the crude product in *n*-hexane showed adsorption maxima at 253 and 277 mμ, suggesting the presence of a conjugated olefin. Thin layer chromatography showed two components to be present.

The crude product (3.69 g) was dissolved in 20 ml of dry benzene. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone[6] was added and the mixture refluxed 4 hr under nitrogen. The mixture was poured into 100 ml of petroleum ether (bp 30–60°) and filtered, leaving 4.56 g of 2,3-dichloro-5,6-dicyanohydroquinone. The filtrate was reduced to 10 ml in volume and a portion chromatographed on an alumina column using *n*-pentane as eluent. A colorless liquid isolated from intermediate fractions had infrared and ultraviolet spectra identical with those of an authentic sample of 1-phenylnaphthalene.

1,4-Diphenyl-3-buten-2-one (VI).—The method of Southwick[4] did not produce satisfactory yields in our hands; so the following modification was employed. A solution of sodium hydroxide (1.50 g) in water (800 ml) was heated to 55°. Benzaldehyde (20.4 g, 0.192 mole) and phenyl-2-propanone (25 g, 0.186 mole) were added and the mixture was stirred rapidly during the next hour and allowed to remain at 68–70° during the next 2 hr. The stirred mixture was then kept at 58° for a total reaction time of 21 hr. Stirring was discontinued, the mixture cooled slowly to room temperature, and water was decanted from the yellow crystalline cake. The crude product was washed with water, air dried, and recrystallized from methanol, affording 25.2 g (0.112 mole, 61%) of pale yellow crystals, mp 73–76° (lit.[4] mp 68–70°).

Independent Synthesis of 4-Phenyl-2-tetralone by Intramolecular Friedel–Crafts Reaction.—A solution of 1,4-diphenyl-3-buten-2-one (20.0 g, 0.090 mole) in reagent grade carbon disulfide (200 ml) was added under nitrogen over 30 min to a vigorously stirred suspension of anhydrous aluminum–chloride (24.0 g, 0.180 mole) in carbon disulfide (300 ml). After 10 min at room temperature, the mixture was refluxed on the steam bath for 2 hr or until evolution of HCl had ceased. The dark red solution was poured onto a stirred mixture of ice and concentrated hydrochloric acid. The organic layer was separated and washed with water. The solvent was evaporated under reduced pressure; the residual oil was dissolved in ether and extracted three times with 10% sodium hydroxide solution. The ether layer was dried and then evaporated. Distillation of the dark oil afforded 6.46 g (0.029 mole, 32%) of 4-phenyl-2-tetralone as a colorless oil, bp 132–136° (0.12 mm). The infrared spectrum of the product was superimposable with that of a sample prepared by the previous method. A portion of the product was reduced with sodium borohyride to yield 4-phenyl-2-tetralol which was identical in all respects with the alcohol obtained by the previous method.

Registry No.—II, 14195-36-9; III, 14195-35-8; IV, 14195-34-7; VI, 5409-59-6.

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(3) NMR Spectra Catalogs, Varian Associates, Palo Alto, Calif.

(4) P. L. Southwick and D. I. Sapper, *J. Org. Chem.*, **19**, 1926 (1954.

(5) Infrared spectra were taken on a Beckman IR-8 recording spectrophotometer and were determined as chloroform solutions unless otherwise noted. Ultraviolet spectra were recorded on a Bausch and Lomb Spectronic 505 instrument in methanol solutions. Proton nmr spectra were recorded on a Varian Associates A-60 instrument in deuteriochloroform. Osmometric molecular weights were determined in benzene solution using a Mechrolab Model 301a vapor pressure osmometer; calibration was against benzil solutions. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

(6) E. A. Braude, A. G. Brook, and R. P. Linstead, *J. Chem. Soc.*, 3569 (1954).