ene was maintained at 35° in a nitrogen atmosphere during the 1-hr. addition of a solution of 39 g. (0.2 mole) of diphenylacetonitrile in 100 ml. of toluene. After the addition was complete the reaction mixture was heated under reflux for 3.5 hr., cooled, and 0.7 g. of sodium iodide added. A solution of 2-(4-morpholino)-1-phenethyl chloride [prepared from an aqueous solution of 53 g. (0.2 mole) of the hydrochloride,[6] rendered alkaline with 40% sodium hydroxide, followed by extraction of the liberated base with three 75-ml. portions of toluene which were combined and dried with magnesium sulfate] in toluene was added over 2 hr., maintaining the temperature below 35°. The reaction mixture was heated under reflux for 1.5 hr., cooled to 20°, and treated with 200 ml. of water. At this point some product precipitated and was separated. The toluene layer was separated and the aqueous phase re-extracted with 100 ml. of toluene. The initial precipitate and all toluene fractions were combined and the toluene evaporated. The residue of IIb, triturated with 100 ml. of ethanol, yielded 39 g. (51%).

*1-Piperidino-2,3,3-triphenylhexanimine-4* (IIIc). A solution of ethyl magnesium bromide was prepared from 1.2 g. (0.05 mole) of magnesium and 6.5 g. (0.06 mole) of ethyl bromide in 50 ml. of anhydrous ether and treated while refluxing with a solution of 15.2 g. (0.04 mole) of IIc in 90 ml. of hot tetrahydrofuran (dried over calcium hydride) over 1 hr., followed by 60 ml. of hot xylene. During the addition, the internal temperature was raised to 80–85° by partial distillation and so maintained with stirring for 5 hr. Then 40 ml. of 1:1 hydrochloric acid was added with continued heating over 0.5 hr. Dilution with water and standing afforded the crude, sparingly soluble hydrochloride, 17 g., which was converted to the free base with aqueous sodium hydroxide.

*4-Amino-1-morpholino-2,3,3-triphenylhexane* (IIIb[g], Table I). A refluxing solution of 0.42 g. of lithium aluminum hydride in 50 ml. of ether under nitrogen atmosphere continuously extracted a charge of 4.2 g. (0.01 mole) of IIIb over a period of 20 hr.[23] The cooled, stirred mixture was treated slowly with 35 ml. of 10% aqueous sodium hydroxide, the ether phase decanted, and the aqueous alkaline phase continuously extracted with 100 ml. of ether. The ether extracts were combined, dried over anhydrous magnesium sulfate, filtered, and treated with dry hydrogen chloride, yielding the hydrochloride 2.3 g. (47%), m.p. 188–194°. The hydrochloride was converted to the free base which melted at 64–66°.

The *acetate*[24] was prepared, m.p. 195–197° (hexane–ethyl acetate).

*Attempted hydrolysis of ketimines* (III). Three g. of IIIb hydrochloride was refluxed for 36 hr. with 30 ml. of hydrochloric acid. Solution was never effected and the IIIb hydrochloride was recovered unchanged.

One g. of IIId hydrochloride and 10 ml. of hydrochloric acid in a sealed tube was maintained at 100° for 2 hr. Solution was never complete, and 0.7 g. of IIId hydrochloride was recovered.

One g. of IIId hydrochloride in 2 ml. of acetic acid and 10 ml. of hydrochloric acid in a sealed tube was maintained at 100° for 6 hr. Solution of IIId in the acid mixture was readily obtained, but only the reactant IIId hydrochloride (0.7 g.) could be recovered.

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[21] Data shown in Table I are not reproduced in the Experimental section.

[22] Representative examples are shown for the general procedures used.

[23] W. G. Brown, *Org. Reactions*, VI, 492 (1951).

[24] W. J. Hickinbottom, *Reactions of Organic Compounds*, Longmans, Green and Co., London, 1948, p. 297.

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# 5-Phthalimido-2-tetralone[1]

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Reported here is the preparation of 5-phthalimido-2-tetralone. Some synthetic paths leading to tricyclic diterpenes and related compounds using this tetralone were initiated. Unfortunately, that work was interrputed and no further efforts in that area are now contemplated by us. However, there is continued interest and activity in such synthetic problems by other workers. We believe this tetralone and its method of preparation may be of use to others; apparently it is the only 2-tetralone carrying an amino (or potential amino) group so far prepared.

2-Methoxy-5-naphthylamine[2] (I) was reduced with sodium and alcohol in liquid ammonia. The resulting dihydro compound (enol ether) could be isolated and purified, but for convenience and obtaining maximum yield of the desired ketone, the amine was not isolated, but converted to a phthalimide derivative and subsequently to the 2-tetralone. The resulting 5-phthalimido-2-tetralone was thus obtained in 63% yield from I. The free amino group apparently is not compatible with the keto group; cleavage of the enol ether without blocking the amino group or reduction of the corresponding amino phenol with sodium and alcohol in liquid ammonia gave what appeared to be a polymeric material. The amino group could be converted to an acetamide, but the yield was not as satisfactory as with the phthalimide protecting group.

## EXPERIMENTAL[3]

*5-Phthalimido-2-tetralone.* Sodium (35 g.) was added slowly over a period of 1.5 hr. to a solution of 6-methoxy-1-naphthylamine[2] (100 g.) in liquid ammonia (900 ml.) and 95% ethanol (130 ml.). Water (1 l.) was then added and the mixture extracted with four portions of benzene (total vol., 1 l.). The benzene extract was washed with water and then added to a solution of phthalic anhydride (100 g.) in hot benzene (1.5 l.) which resulted in an immediate precipitate of the phthalamic acid. This crude acid (164 g., m.p. 147–150° dec.) was not purified, but was converted directly to the phthalimide by refluxing a solution of it in glacial acetic acid (500 ml.) for 2 hr. To the hot acetic acid solution was added 5% hydrochloric acid (100 ml.) and after 2 min. the mixture was poured onto ice (2.5 kg.).[4] The precipitated tetralone was separated by filtration, dried (wt., 137 g.), ground to a fine powder, and stirred for 24 hr. with a solution of sodium bisulfite (665 g.) in water (1.2 l.) and 95% ethanol (300 ml.). The addition product was separated by filtration, dried, washed with chloroform, suspended in

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[1] Taken from part of the Ph.D. thesis by Ross C. Terrell, 1954, Columbia University.

[2] (a) A. Butenandt and G. Schramm, *Ber.*, 68, 2083 (1935); (b) L. F. Fieser and B. Riegel, *J. Am. Chem. Soc.*, 59, 2561 (1937).

[3] Melting points for analytical samples are corrected; other melting points are uncorrected.

water (3 l.), and finally decomposed with solid sodium carbonate to regenerate the ketone. This was isolated by filtration, washed with water and very dilute acid, dried, and recrystallized from benzene. 5-Phthalimido-2-tetralone, 105 g., 63% yield, was obtained as colorless prisms, m.p. 200–202°. These crystals tenaciously retained traces of the benzene solvent. The analytical sample was recrystallized from a mixture of chloroform and methanol as colorless needles, m.p. 202–204°.

*Anal.* Calcd. for $C_{18}H_{13}O_3N$: C, 74.21; H, 4.50; N, 4.81. Found: C, 74.48; H, 4.35; N, 4.64.

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(4) In this sequence, the period of refluxing for conversion of the phthalamic acid to the phthalimide is not critical, but the time required for cleavage of the enol ether is. The acetic acid solution may be refluxed indefinitely beyond the 2 hour period suggested without impairment of yield. For the aqueous hydrochloric acid treatment, however, the yield of 5-phthalimido-2-tetralone falls off fairly rapidly with periods appreciably more than 2 minutes, and with shorter periods cleavage of the enol ether is not complete.

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## The Mesomorphic State. Phototropy of *p-n*-Nonoxybenzalphenylhydrazone and *p-n*-Decyloxybenzalphenylhydrazone

GLENN H. BROWN AND WILFRID G. SHAW

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It is well known that a large number of organic compounds are mesomorphic in character. Even though it is not the purpose of this report to emphasize that the phenylhydrazones described here are mesomorphic, it might be mentioned that no phenylhydrazones with this property appear to have been described in the literature previously. An extensive review of the structure and the properties of the mesomorphic state may be found in a recent article by Brown and Shaw.[1]

Phototropic character of a number of both inorganic and organic compounds is also well established. Marckwald[2] gave the name "phototropy" to the phenomenon in which a solid changes color when exposed to light but reverts to its original color in the dark. Chalkley[3] reviewed the subject of phototropy a number of years ago. A number of phenylhydrazones have been described in the literature as phototropic and those described before 1928 are cited in Chalkley's review.[3] Gheorghiu and Matei[4] found the *α*-phenylhydrazones of 1-benzylidene-2-propanone, 1-benzylidene-2-pentanone, and 4-methyl-1-piperonylidene-2-pentanone are all phototropic but these compounds were not described as mesomorphic in character. Matei[5] reported the phototropic character of the *α*-phenylhydrazones of 1-benzylidene-2-butanone and of 1-benzylidene-2-pentanone but they were not described as showing mesomorphism.

The purpose of this preliminary report is to record two compounds which exhibit the properties of both mesomorphism and phototropism. No such compounds appear to have been described in the literature previously.

In the progress of research on the mesomorphic properties of a series of phenylhydrazones, it was found that *p-n*-nonoxybenzalhydrazone and *p-n*-decyloxybenzalphenylhydrazone both exhibit phototropy and mesomorphism. *p-n*-Nonoxybenzalphenylhydrazone has a crystalline-nematic point of 94–95° and a nematic-liquid point at 97–98°. It gives white flakes on crystallization from ethanol; these white flakes turn pink on exposure to direct sunlight. The compound was recrystallized from ethanol until it showed constant transition points.

*Anal.* Calcd. for $C_{22}H_{30}ON_2$: C, 78.06; H, 8.93. Found: C, 77.86; H, 8.72.

The color change from white to pink is rapid, taking place in less than five minutes. The reverse process, pink to white, takes place in about two hours. *p-n*-Decyloxybenzalphenylhydrazone crystallizes from ethanol to give white flakes which turn red on exposure to sunlight; the reverse process also takes place but is much slower than the rate of excitation. The time change on color transitions for this compound are comparable to those of *p-n*-nonoxybenzalphenylhydrazone. *p-n*-Decyloxybenzalphenylhydrazone has a crystalline-nematic point of 91–92° and a nematic-liquid point of 93–94°. The compound was recrystallized from ethanol until it showed constant transition points.

*Anal.* Calcd. for $C_{23}H_{32}ON_2$: C, 78.36, H, 9.15. Found: C, 78.11; H, 9.02.

The phototropic process for both compounds can be repeated again and again. No study has been made whether or not the compounds fatigue.

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[1] G. H. Brown and W. G. Shaw, *Chem. Revs.*, 57, 1049 (1957).

[2] W. Marckwald, *Z. physik. chem.*, 30, 140 (1899).

[3] L. Chalkley, *Chem Revs.*, 6, 217 (1929).

[4] C. V. Gheorghiu and V. Matei, *Bull. soc. chim. France*, [5] 6, 1324 (1939).

[5] V. Matei, *Ann. sci. univ. Jassy, I* 29, 17 (1943); *Chem. Abstr.*, 42, 3743 (1948).

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## Action of Grignard Reagents on Triphenylacetyl Chloride

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In an attempt to prepare methyl trityl ketone by the addition of methylmagnesium iodide to