[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Friedel–Crafts Cyclization of ω-(α-Naphthyl)-1-alkanesulfonyl Chlorides[1]

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RECEIVED AUGUST 12, 1953

Several ω-(α-naphthyl)-1-alkanesulfonyl chlorides have been converted to cyclic sulfones under Friedel–Crafts conditions 2-(α-Naphthyl)-1-ethanesulfonyl chloride gave a 54% yield of benzo(e)2,3-dihydrothianaphthene-1-dioxide. 3-(α-Naphthyl)-1-propanesulfonyl chloride was converted to benzo(f)thiachroman-1-dioxide in 65% yield. Benzo(g)-homothiachroman-1-dioxide was formed in 16% yield from 4-(α-naphthyl)-1-butanesulfonyl chloride. In these cyclizations none of the isomeric sulfones that might be expected from condensation at the *peri* position were found. α-Naphthylmethanesulfonyl chloride could not be prepared by two different methods, probably because of the inherent instability of this compound.

Although a large volume of work has been reported on the preparation of sulfones by Friedel–Crafts reactions of aromatic sulfonyl chlorides with aromatic hydrocarbons,[3] there are only a few reports of such reactions with aliphatic sulfonyl chlorides. In the presence of an excess of aluminum chloride, methanesulfonyl chloride reacted with benzene to give only a poor yield of methyl phenyl sulfone.[4] Tars were obtained when a mixture of phenylmethanesulfonyl chloride and toluene was treated with aluminum chloride.[5] When hydroquinone dimethyl ether was treated with methanesulfonyl chloride in the presence of zinc chloride, p-anisyl methanesulfonate, rather than a sulfone, was formed.[6] Recent work in this Laboratory has been concerned with the preparation of sulfones by Friedel–Crafts reactions of aliphatic sulfonyl chlorides.[7–9] The reaction of methanesulfonyl chloride with benzene and several substituted benzenes under controlled conditions gave good yields of the corresponding sulfones.[9] Several ω-phenylalkanesulfonyl chlorides were cyclized to the corresponding sulfones in good yields.[7]

The literature contains only a few reports of Friedel–Crafts reactions of sulfonyl chlorides with naphthalene. When naphthalene was treated with benzenesulfonyl chloride in the presence of aluminum chloride, none of the expected sulfone was obtained.[10] A patent has been issued for the preparation of α,β-dinaphthyl sulfone from naphthalene and "naphthalenesulfonyl chloride" using ferric chloride as the catalyst.[11] There appears to be no report in the literature of a Friedel–Crafts reaction involving naphthalene and an aliphatic sulfonyl chloride. The work recorded here is concerned with the internal Friedel–Crafts reaction of three ω-(α-naphthyl)-1-alkanesulfonyl chlorides leading to cyclic sulfones.

Attempts to prepare α-naphthylmethanesulfonyl chloride were largely unsuccessful. Treatment of sodium α-naphthylmethanesulfonate with phosphorus pentachloride resulted in the formation

of sulfur dioxide and α-chloromethylnaphthalene. When α-naphthylmethyl disulfide was treated with chlorine in the presence of water and glacial acetic acid and the resulting product was added to concentrated ammonium hydroxide solution, a small amount of α-naphthylmethanesulfonamide was produced, the principal product being α-chloromethylnaphthalene. If α-naphthylmethanesulfonyl chloride is an intermediate in these reactions, it apparently breaks down spontaneously to give sulfur dioxide and α-chloromethylnaphthalene. Similarly, phenylmethanesulfonyl chloride is decomposed to sulfur dioxide and benzyl chloride when warmed slightly above its melting point.[12] The probable instability of α-naphthylmethanesulfonyl chloride can be explained by resonance considerations.[9] The hypothetical α-naphthylmethanesulfonyl ion would possess little resonance stabilization while the corresponding carbonium ion would be considerably stabilized by resonance.
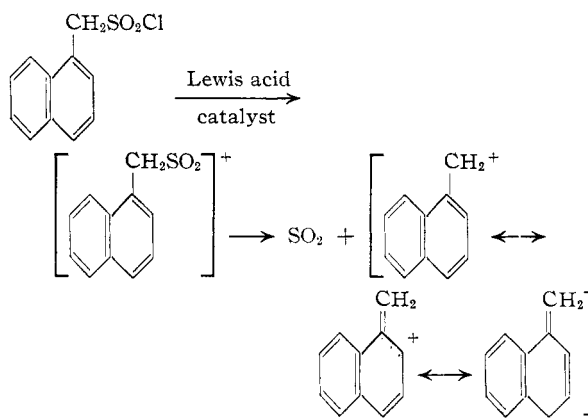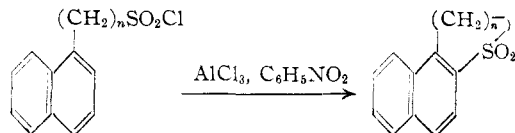

2-(α-Naphthyl)-1-ethanesulfonyl chloride, 3-(α-naphthyl)-1-propanesulfonyl chloride and 4-(α-naphthyl)-1-butanesulfonyl chloride were prepared by the action of phosphorus pentachloride on the corresponding sodium sulfonates. The sodium sulfonates were prepared from the appropriate alcohols by successive treatment with phosphorus tribromide and sodium sulfite. 3-(α-Naphthyl)-1-propanol was prepared by the reaction of 2-(α-naphthyl)-1-ethylmagnesium bromide with formaldehyde. An attempt to prepare 3-(α-naphthyl)-1-propanol, by treating the Grignard reagent of α-chloromethylnaphthalene with ethylene oxide, was not successful. Apparently, rearrangement occurred, because the corresponding sodium sulfonate of the resulting alcohol formed an S-benzylthiuro-

(1) Taken from Mr. Toren's Ph.D. thesis.

(2) Purdue Research Foundation Fellow, 1951–1953.

(3) C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 673–675.

(4) J. Böeseken and H. W. van Ockenburg, *Rec. trav. chim.*, **33**, 320 (1914).

(5) R. Otto, *Ber.*, **13**, 1287 (1880).

(6) H. Burton and E. Hoggarth, *J. Chem. Soc.*, 14 (1945).

(7) W. E. Truce and J. P. Milionis, THIS JOURNAL, **74**, 974 (1952).

(8) W. E. Truce, D. D. Emrick and R. E. Miller, *ibid.*, **75**, 3359 (1953).

(9) W. E. Truce and C. W. Vriesen, *ibid.*, **75**, 5032 (1953).

(10) H. Beckurts and R. Otto, *Ber.*, **11**, 2066 (1878).

(11) J. Huismann, German Patent 701,954; *C. A.*, **36**, 98 (1942).

(12) H. Limpricht, *Ber.*, **6**, 534 (1873).

nium salt, which was different from the same derivative of sodium 3-(α-naphthyl)-1-propanesulfonate prepared in the former way. 4-(α-Naphthyl)-1-butanol was prepared from 2-(α-naphthyl)-1-ethanol by successive treatment with phosphorus tribromide, magnesium and ethylene oxide.

The three sulfonyl chlorides were cyclized by aluminum chloride in nitrobenzene under uniform times, temperatures and concentrations.

Yields: $n = 2$, 54%; $n = 3$, 65%; $n = 4$, 16%.

Ring closure of 2-(α-naphthyl)-1-ethanesulfonyl chloride to the *beta* position and the resulting five-membered ring was surprising. Cyclization was expected to occur at the *peri* position, in view of the much higher yield of the six-membered ring sulfone over its next lower homolog in the benzene series,[7] and in view of the preference for condensation to the *peri* position with the acyl chloride analog.[13] This unexpected result might be at least partially due to a combination of two factors, *i.e.*, greater steric hindrance to attack at the *peri* position and a comparatively high reactivity of the intermediate attacking particle.[9]

Baddeley[14] studied solvent and temperature effects in the aluminum chloride-catalyzed reactions of naphthalene with acetyl chloride and with benzoyl chloride. When nitrobenzene was used as the solvent, reaction occurred almost exclusively at the beta position, while the use of methylene chloride caused the reaction to occur exclusively at the alpha position. The orientation obtained in nitrobenzene was attributed to the formation of a bulky complex involving nitrobenzene, the acid chloride and aluminum chloride, the *peri* position being more sterically hindered than the *beta* position toward attack by this bulky complex. Methylene chloride does not form such a complex; therefore, steric requirements are less pronounced when it is employed as a solvent. A similar factor may be involved in the cyclization of 2-(α-naphthyl)-1-ethanesulfonyl chloride. A three-component complex of the sulfonyl chloride, aluminum chloride and nitrobenzene might be highly subject to steric factors and would accordingly favor cyclization to the beta position over the *peri* position.

Another factor, which may be influencing the course of this cyclization, is based on the observation that in Friedel–Crafts processes aliphatic sulfonyl chlorides appear to be more random in their point of attack than acyl chlorides.[9] Cyclization of 3-(α-naphthyl)-1-propanoyl chloride with aluminum chloride in nitrobenzene occurs principally at the *peri* position; however, an appreciable amount of condensation at the beta position is also observed.[13] Preferential *peri* acylation may be due to a greater reactivity toward electrophilic agents of the *peri* position in comparison with the beta position in α-alkylnaphthalenes. Should an

(13) W. S. Johnson, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 126.

(14) G. Baddeley, *J. Chem. Soc.*, S99 (1949).

appreciable *peri* orienting influence be operative it would be of less importance with sulfonyl chlorides than with acyl chlorides.[9]

Authentic samples of the cyclic sulfones were prepared by way of the corresponding cyclic keto sulfides which were obtained by internal Friedel–Crafts acylation processes. Subsequent oxidation of the sulfide group and reduction of the carbonyl group yielded materials which did not depress the melting points of the products obtained by cyclization of the respective sulfonyl chlorides.

Experimental[15]

Attempted Preparation of α-Naphthylmethanesulfonyl Chloride.—A mixture of 45 g. (0.25 mole) of α-chloromethylnaphthalene[16,17] and a solution of 126 g. (1 mole) of sodium sulfite in 900 ml. of water was refluxed for 18 hours. Upon evaporating the resulting solution to about half its volume and subsequent cooling, sodium α-naphthylmethanesulfonate was precipitated; its S-benzylthiuronium derivative[18] had m.p. 162–162.5°. Equal weights of crude sodium α-naphthylmethanesulfonate, dried at 110°, and powdered phosphorus pentachloride were mixed and the initial vigorous reaction was moderated with an ice-bath. In several runs of this reaction, conditions were varied as follows: 2 hours at ice-bath temperature; room temperature for 2 hours; room temperature for 3 hours; and finally 60–70° for 2 hours. The reaction mixture was poured into a mixture of ice and water and extracted with ether. The ether solution, dried over magnesium sulfate, was evaporated to a residual oil, crude α-chloromethylnaphthalene. A small amount of white crystalline material, m.p. 145–160°, was extracted from this oil with boiling 90–100° petroleum ether. Several recrystallizations of this material from petroleum ether failed to change the melting point. Treatment of the residual oil with aqueous ammonia failed to produce any α-naphthylmethanesulfonamide.

In a second attempt to prepare α-naphthylmethanesulfonyl chloride, α-naphthylmethyl disulfide was prepared by treatment of the Bunte salt, obtained from α-chloromethylnaphthalene and sodium thiosulfate, with iodine[7]; m.p. 106–107° after recrystallization from 90–100° petroleum ether, reported[19] m.p. 108–109°. An excess of chlorine was passed into 13.3 g. (0.04 mole) of the disulfide[7] suspended in 250 ml. of glacial acetic acid containing 2.8 g. (0.16 mole) of water. The odor of sulfur dioxide was observed in the resulting yellow oil, which was found to be principally α-chloromethylnaphthalene. However, with aqueous ammonia, it gave a small amount of α-naphthylmethanesulfonamide, m.p. 172–173° after recrystallization from aqueous alcohol.

Anal. Calcd. for $C_{11}H_{11}NO_2S$: C, 59.70; H, 5.01. Found: C, 59.82; H, 4.92.

2-(α-Naphthyl)-1-ethanesulfonyl Chloride.—2-(α-Naphthyl)-1-ethanol, prepared by the method of Cook and Hewett,[20] was converted to 2-(α-naphthyl)-1-bromoethane by treatment with either phosphorus tribromide[21] (67–70% yield) or 48% hydrobromic acid[22] (50% yield). A mixture of 50 g. (0.28 mole) of this bromide and a solution of 126 g. (1 mole) of sodium sulfite in 900 ml. of water was stirred and refluxed for 18 hours. Upon cooling the resulting solution, sodium 2-(α-naphthyl)-1-ethanesulfonate was precipitated as a white solid, which was filtered and dried at 110°; its S-benzylthiuronium derivative[18] had m.p. 142–143°.

Mixing equal weights of the crude sulfonate and powdered phosphorus pentachloride resulted in a vigorous reaction, which was moderated with an ice-bath. After standing at room temperature for 3 to 4 hours and then for 10 minutes on a steam-cone, the reaction mixture was poured into ice

(15) All melting points are corrected.

(16) A. Cambron, *Can. J. Research*, **17B**, 10 (1939).

(17) O. Grummitt and A. Buck, THIS JOURNAL, **65**, 295 (1943).

(18) W. E. Truce and C. C. Alfieri, *ibid.*, **72**, 2740 (1950).

(19) W. Windus and H. G. Turley, *J. Am. Leather Chem. Assoc.*, **33**, 246 (1938); *C. A.*, **32**, 8823 (1938).

(20) J. W. Cook and C. L. Hewett, *J. Chem. Soc.*, 1098 (1933).

(21) R. L. Shriner and J. H. Young, THIS JOURNAL, **52**, 3332 (1930).

(22) M. S. Newman, *J. Org. Chem.*, **9**, 518 (1944).

and water and the resulting mixture was extracted with diethyl ether. The ether solution was dried over calcium chloride and evaporated to an oil, which was extracted with boiling 60–70° petroleum ether. The chilled extract deposited 2-(α-naphthyl)-1-ethanesulfonyl chloride, m.p. 48–49°. A portion of the sulfonyl chloride was converted with aqueous ammonia to 2-(α-naphthyl)-1-ethanesulfonamide, m.p. 171–173° after two recrystallizations from aqueous ethanol.

Anal. Calcd. for $C_{12}H_{13}NO_2S$: C, 61.25; H, 5.57. Found: C, 61.02; H, 5.43.

3-(α-Naphthyl)-1-propanesulfonyl Chloride.—The Grignard reagent prepared from 116 g. (0.5 mole) of 2-(α-naphthyl)-1-bromoethane and 12.2 g. (0.5 mole) of magnesium turnings in 600 ml. of anhydrous ether was treated with formaldehyde.[23] The reaction product was hydrolyzed with water and hydrochloric acid and the ether layer was separated, washed with 5% sodium carbonate solution and water, and dried over magnesium sulfate. Distillation gave 60 g. (65%) of 3-(α-naphthyl)-1-propanol, b.p. 144–146° (1–2 mm.), reported[24] b.p. 145° (1 mm.). Treatment of this alcohol with phosphorus tribromide[21] gave 3-(α-naphthyl)-1-bromopropane (81%), b.p. 139–140° (1 mm.), reported[24] b.p. 153–155° (3 mm.). Sodium 3-(α-naphthyl)-1-propanesulfonate was obtained by the action of sodium sulfite on the corresponding bromide using the same procedure employed for sodium 2-(α-naphthyl)-1-ethanesulfonate; its S-benzylthiuronium derivative had m.p. 125–126°. This sodium sulfonate was converted with phosphorus pentachloride to 3-(α-naphthyl)-1-propanesulfonyl chloride. A small amount of the cyclic sulfone, benzo(f)thiachroman-1-dioxide, m.p. 156–156.5°, was obtained as a by-product in this preparation. It was separated from the sulfonyl chloride by extraction and crystallization from 90–100° petroleum ether, in which the sulfone is less soluble. Attempts to purify 3-(α-naphthyl)-1-propanesulfonyl chloride by distillation resulted in decomposition. 3-(α-Naphthyl)-1-propanesulfonamide was prepared in excellent yield by adding the sulfonyl chloride to aqueous ammonia; m.p. 111.5–113° after two crystallizations from aqueous ethanol.

Anal. Calcd. for $C_{13}H_{15}NO_2S$: C, 62.62; H, 6.06. Found: C, 62.60; H, 6.22.

In one attempt to prepare 3-(α-naphthyl)-1-propanol a twofold excess of ethylene oxide was distilled into the Grignard reagent[17] of α-chloromethylnaphthalene chilled by a salt–ice mixture. After the addition was completed, the resulting mixture was kept in the cold-bath for an additional hour followed by 2 hours at room temperature. Slow distillation was started and benzene was added to the reaction mixture until the temperature of the condensing vapors reached 65°. The mixture was refluxed for 10 hours and hydrolyzed with aqueous hydrochloric acid. The benzene–ether layer was separated, washed with water and distilled to give a yellow oil, b.p. 145–148° (1–2 mm.), taken as 3-(α-naphthyl)-1-propanol. Conversion of this alcohol to the corresponding S-benzylthiuronium sulfonate by successive treatment with phosphorus tribromide, sodium sulfite and S-benzylthiuronium chloride gave a derivative, m.p. 96–106°. Recrystallizations from ethanol–water mixtures failed to change the melting point range.

4-(α-Naphthyl)-1-butanesulfonyl Chloride.—A Grignard reagent, prepared from 188 g. (1 mole) of 2-(α-naphthyl)-1-chloroethane,[20] was converted by reaction with ethylene oxide to 4-(α-naphthyl)-1-butanol; yield 100 g. (50%), b.p. 148–149° (1–2 mm.), reported[24] b.p. 150–155° (0.5 mm.). Treatment of this alcohol with phosphorus tribromide[21] gave 4-(α-naphthyl)-1-bromobutane, b.p. 143–145° (1–2 mm.), reported[24] b.p. 160–163° (2 mm.), in 77% yield. Sodium 4-(α-naphthyl)-1-butanesulfonate was obtained by treating the corresponding bromide with sodium sulfite using the procedure employed for the preparation of sodium 2-(α-naphthyl)-1-ethanesulfonate; S-benzylthiuronium derivative,[18] m.p. 152–154°. 4-(α-Naphthyl)-1-butanesulfonyl chloride was obtained by treating the corresponding sodium sulfonate with phosphorus pentachloride, using the procedure employed for the preparation of 2-(α-naphthyl)-1-ethanesulfonyl chloride, m.p. 38–39°.

(23) H. Gilman and W. Catlin, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 188.

(24) R. H. Manske and E. E. Ledingham, *Can. J. Research*, **17B**, 14 (1939).

Anal. Calcd. for $C_{14}H_{15}ClO_2S$: C, 59.46; H, 5.35. Found: C, 59.41; H, 5.42.

4-(α-Naphthyl)-1-butanesulfonamide had m.p. 78–79° after recrystallization from aqueous ethanol.

Friedel–Crafts Cyclization of the Sulfonyl Chlorides.—The sulfonyl chloride, dissolved in nitrobenzene, was chilled and added with stirring to a cold solution of anhydrous aluminum chloride in nitrobenzene. The ice-bath was removed and the reaction was allowed to proceed at room temperature for 2.5 hours and then at 65–70° for 2 hours. The reaction mixture was allowed to cool for 30 minutes before it was poured into a mixture of ice-water and hydrochloric acid. Vigorous agitation was necessary to decompose the addition complex. The nitrobenzene layer was washed several times with water and then steam distilled to remove the nitrobenzene. The residual material in the distillation pot was extracted with boiling benzene, decolorized with Norite, evaporated to reduce the volume of benzene and added to a large excess of 90–100° petroleum ether to precipitate the sulfone, which was subsequently recrystallized from methanol.

Using this procedure with 14 g. (0.052 mole) of 2-(α-naphthyl)-1-ethanesulfonyl chloride and 8 g. (0.06 mole) of anhydrous aluminum chloride in 120 g. of nitrobenzene gave 6 g. (54%) of the crude sulfone, benzo(e)-2,3-dihydrothianaphthene-1-dioxide, m.p. 177–178°.

Anal. Calcd. for $C_{12}H_{10}O_2S$: C, 66.03; H, 4.62. Found: C, 65.74; H, 4.73.

Treatment of 9 g. (0.035 mole) of 3-(α-naphthyl)-1-propanesulfonyl chloride with 4.7 g. (0.037 mole) of anhydrous aluminum chloride in 75 g. of nitrobenzene gave 6 g. (65%) of the crude sulfone, benzo(f)thiachroman-1-dioxide, m.p. 156–156.5°.

Anal. Calcd. for $C_{13}H_{12}O_2S$: C, 67.21; H, 5.21. Found: C, 67.38; H, 4.97.

Treatment of 4.2 g. (0.02 mole) of 4-(α-naphthyl)-1-butanesulfonyl chloride with 2.5 g. (0.021 mole) of anhydrous aluminum chloride in 40 g. of nitrobenzene gave 0.8 g. (16%) of the crude sulfone, benzo(g)homothiachroman-1-dioxide, m.p. 134–135°.

Anal. Calcd. for $C_{14}H_{14}O_2S$: C, 68.26; H, 5.73. Found: C, 68.39; H, 5.91.

Independent Synthesis of Benzo(e)2,3-dihydrothianaphthene-1-dioxide.—β-Naphthylmercaptoacetyl chloride was obtained by treatment of 24 g. (0.11 mole) of the corresponding acid[25] with phosphorus pentachloride in chloroform. After stripping off the chloroform and phosphorus oxychloride under reduced pressure, the crude acid chloride was taken up in 150 ml. of chlorobenzene, chilled in an ice-bath and treated with 30 g. (0.224 mole) of anhydrous aluminum chloride at ice-bath temperature for 10 hours, room temperature for 10 hours, and at 40° for 5 hours. The resulting mixture was poured into ice and water containing an excess of hydrochloric acid and allowed to stand overnight. The chlorobenzene layer was then steam distilled to remove solvents and the residual material was extracted with 90–100° petroleum ether. Benzo(g)-3-thia-1-hydrindone was obtained, 14 g. (64%), as yellow plates from the petroleum ether extracts, m.p. 119–121°, reported[25] m.p. 122°.

Reduction of 7 g. (0.035 mole) of this ketone by a modified Wolff–Kishner[26] procedure gave 6 g. (92%) of benzo(e)-2,3-dihydrothianaphthene, m.p. 88–89° after recrystallization from a methanol–water mixture. The reduction procedure was further modified in that the potassium hydroxide was added to the reaction mixture after the hydrazone was formed and the temperature was raised to 195°.

A solution of 1.3 g. of benzo(e)2,3-dihydrothianaphthene, 35 ml. of glacial acetic acid and 5 ml. of 30% hydrogen peroxide was refluxed for 2 hours. The mixture was cooled, poured on ice, and the sulfone, benzo(e)2,3-dihydrothianaphthene-1-dioxide, was filtered off and recrystallized from methanol, m.p. 177–178°.

Anal. Calcd. for $C_{12}H_{10}O_2S$: C, 66.03; H, 4.62. Found: C, 65.80; H, 4.61.

Independent Synthesis of Benzo(f)thiachroman-1-dioxide. —4-Benzo(f)thioachromanone[27] was reduced in 67% yield to benzo(f)thiachroman by the modified Wolff–Kishner proce-

(25) P. Friedlander and N. Woroshzow, *Ann.*, **388**, 1 (1911).

(26) Huang-Minlon, THIS JOURNAL, **68**, 2487 (1946).

(27) G. B. Bachman and H. A. Levine, *ibid.*, **69**, 2341 (1947).

dure described above. Attempts to reduce[28] 4-benzo(f)-thiachromanone in both acid and basic media gave very low yields of benzo(f)thiachroman. Benzo(f)thiachroman was recrystallized from methanol, m.p. 91–92°.

Anal. Calcd. for $C_{13}H_{12}S$: C, 77.95; H, 6.04. Found: C, 78.24; H, 5.92.

Oxidation of benzo(f)thiachroman in glacial acetic acid with 30% hydrogen peroxide gave the sulfone, benzo(f)-thiachroman-1-dioxide. Recrystallization from methanol gave white needles, m.p. 155–156°.

Anal. Calcd. for $C_{13}H_{12}O_2S$: C, 67.21; H, 5.21. Found: C, 66.98; H, 5.22.

Independent Synthesis of Benzo(g)homothiachroman-1-dioxide.—4-(β-Naphthylmercapto)-butanenitrile was prepared from 34 g. (0.23 mole) of 4-bromobutanenitrile[29] and 36 g. (0.23 mole) of 2-naphthalenethiol (74%) by the method employed for the preparation of the analogous phenyl compound[7]; b.p. 184–186° (1 mm.), 227–230° (6–7 mm.). This nitrile, 38 g. (0.167 mole), was hydrolyzed[7] to give 39 g. (94%) of 4-(β-naphthylmercapto)-butanoic acid. Recrystallization from 90–100° petroleum ether gave white needles, m.p. 86–87°.

Anal. Calcd. for $C_{14}H_{14}O_2S$: C, 68.26; H, 5.73. Found: C, 68.61; H, 5.42.

4-(β-Naphthylmercapto)-butanoyl chloride (amide, m.p. 150–151°) was prepared from 10 g. (0.04 mole) of the corresponding acid by treatment with phosphorus pentachloride in benzene (1 hour at room temperature, then 10

(28) E. L. Martin, *ibid.*, **58**, 1438 (1936).

(29) A. A. Goldberg and W. Kelly, *J. Chem. Soc.*, 1369 (1947).

minutes on a steam-cone). The reaction mixture was chilled on an ice-bath and a solution of 22 g. (0.08 mole) of stannic chloride and 15 ml. of dry benzene was added. The resulting mixture was agitated occasionally, allowed to stand for 16 hours, and then it was hydrolyzed with ice-water and hydrochloric acid. The resulting yellow organic layer was evaporated and the residual material was recrystallized from methanol to give 6 g. (65%) of 5-benzo-(g)homothiachromanone, white plates, m.p. 78–79°.

Anal. Calcd. for $C_{14}H_{12}OS$: C, 73.64; H, 5.30. Found: C, 73.85; H, 5.20.

Several attempts to cyclize 4-(β-naphthylmercapto)-butanoyl chloride, obtained by treatment of the corresponding acid with thionyl chloride, with either anhydrous aluminum chloride or ferric chloride in carbon disulfide were unsuccessful.

5-Benzo(g)homothiachromanone was oxidized with 30% hydrogen peroxide in glacial acetic acid to give 5-benzo(g)-homothiachromanone-1-dioxide. Recrystallization of the crude product from ethanol gave white needles, m.p. 176–177°.

Anal. Calcd. for $C_{14}H_{12}O_3S$: C, 64.59; H, 4.69. Found: C, 64.37; H, 4.67.

Reduction of 5-benzo(g)homothiachromanone-1-dioxide by the modified Wolff–Kishner procedure described above gave the sulfone, benzo(g)homothiachroman-1-dioxide. Recrystallization from methanol gave white needles, m.p. 134–135°.

Anal. Calcd. for $C_{14}H_{14}O_2S$: C, 68.26; H, 5.73. Found: C, 68.21; H, 5.86.

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p-Nitrophenylmaleic Anhydride in the Diels–Alder Reaction[1]

By Leonard E. Miller and Charles J. Strickler[2]

p-Nitrophenylmaleic anhydride has been prepared by the reaction of p-nitrophenylsuccinic anhydride with N-bromosuccinimide in the presence of cumene hydroperoxide. That this compound does participate in the Diels–Alder reaction as a dienophile has been demonstrated by its adduct formation with 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, isoprene, 2-ethyl-1,3-butadiene, 2-isopropyl-1,3-butadiene, cyclopentadiene and anthracene. A single product was obtained in each case. The adducts with the unsymmetrical dienes have been shown to be 1-p-nitrophenyl-4-alkyl-4-cyclohexene-1,2-dicarboxylic acids. This compound plays the role of a diene in its reaction with 1-vinylnaphthalene to give a derivative of 1,1'-binaphthyl.

Since it has been demonstrated that phenylmaleic anhydride can participate in the Diels–Alder reaction as either dienophile[3a] or diene,[3b] p-nitrophenylmaleic anhydride has been prepared in order to observe the influence of a strongly polar group, which is sterically removed from the reactive centers, upon the course of this reaction.

p-Nitrophenylmaleic anhydride was synthesized by modifications of the method used for the preparation of phenylmaleic anhydride.[4] The starting material, p-nitrophenylsuccinic acid, was prepared by the nitration[5] of phenylsuccinic acid.[6] The p-nitro acid was, in turn, converted to the corresponding anhydride by treatment with acetyl

(1) Presented before the Division of Organic Chemistry at the 121st Meeting of the American Chemical Society, Milwaukee, Wisconsin, March 31 to April 2, 1952.

(2) From portions of a thesis submitted by Charles J. Strickler to the Graduate College of the University of Illinois, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) (a) L. E. Miller and D. J. Mann, This Journal, **72**, 1484 (1950); (b) **73**, 45 (1951).

(4) L. E. Miller, H. B. Staley and D. J. Mann, *ibid.*, **71**, 374 (1949).

(5) Fr. Fischter and O. Walter, *Ber.*, **42** [4], 4312 (1909).

(6) *Org. Syntheses*, **30**, 83 (1950).

chloride.[7] The resulting oil was used directly in the dehydrogenation with N-bromosuccinimide to give p-nitrophenylmaleic anhydride. During the first attempts to carry out this dehydrogenation, it was observed that the red color of bromine which developed in solution would disappear as the reaction proceeded. However, under these conditions, only an uncrystallizable oil which gave a positive test for a vicinal dihalide[8] could be isolated. To avoid this difficulty the bromine was distilled from the reaction mixture in an azeotrope with carbon tetrachloride as the reaction proceeded.

It was found, further, that cumene hydroperoxide was superior to benzoyl peroxide as a catalyst, although under the best conditions found the yield was but 34% of the theoretical amount.

When an attempt was made to prepare p-nitro-

(7) M. A. Wali, A. K. Khalil, R. L. Bhatia and S. S. Ahmad, *Proc. Indian Acad. Sci.*, **14A**, 139 (1941), have reported this preparation and the isolation of the anhydride by crystallization from "ether." All of our efforts to duplicate their crystallization from all available solvents were unsuccessful.

(8) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, New York, N. Y., 1948, p. 141.