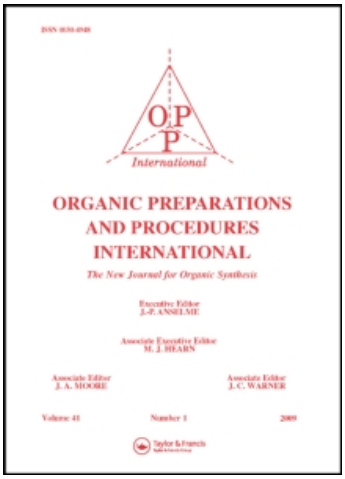

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SYNTHESIS OP 8-HrDROXY-1-NAPHTHALDEHYDE

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REFERENCES

1. E. Taschner, C. Wasilewski, T. Sokolowska and J. F. Biernat, Ann., 646, 127 (1961).

2. R. Camble, R. Purkayastha and G. T. Young, J. Chem. Soc. C, 1219 (1968).
3. E. Taschenr, J. F. Biernat, B. Rzeszotarska and C. Wasilewski, Ann., 646, 123 (1961).

4. E. Schröder and E. Kliegier, ibid., 673, 196 (1964).

5. P. G. Pietta and M. Cavallo, J. Org. Chem., 36, 3966 (1971).

6. G. H. L. Nefkens and R. J. F. Nivard, Rec. Trav. Chim. Pays-Bas, 83, 199 (1964).

7. J. Halstrom, O. Schou, K. Kovacs and K. Brunfeldt, Z. Physiol. Chem., 351, 1576 (1970); CA., 74, 88276f (1971).

8. R. A. Boissonnas, S. Guttmann, P. A. Jaquenoud and J. P. Walter, Helv. Chim. Acta, 38, 1491 (1955).

9. "Organicum. Organisch-Chemisches Grundpraktikum", 15. Auflage VEB Deutscher Verlag der Wissenschaften, Berlin 1981, p. 802.

10. M. Hollosi, M. Kajtar and V. Bruckner, Acta Chim. Acad. Sci. Hung., 62, 305 (1969), CA., 72, 44109h (1970).

SYNTHESIS OF 8-HYDROXY-1-NAPHTHALDEHYDE

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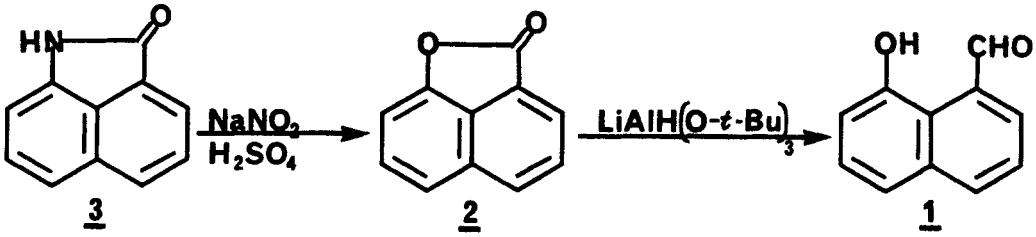
As part of our studies on insect growth inhibition and feeding deterrency involving gossypol and related terpene aldehydes, it was of interest to investigate the least complicated example, 8-hydroxy-1-

naphthaldehyde (1), since many such biologically active substances[1] possess the peri-hydroxy naphthaldehyde configuration. A previous preparation of 1 proceeded from 1,8-naphtholactone by reduction with sodium borohydride to give 8-hydroxymethyl-1-naphthol followed by conversion to the corresponding naphthyl methyl ether which was oxidized with active manganese dioxide to 8-methyl-1-naphthaldehyde.[2] In our hands, however, the requisite removal of the protective methyl group in the final step proved to be erratic and generally led to poor yields of the desired product. It had already been observed that direct reduction of the lactone with a limited amount of sodium borohydride did not give the aldehyde but only an 8-hydroxy-1-napthoate ester of 8-hydroxymethyl-1-naphthol.[2] We have found that the use



3 2 1

of lithium tri-t-butoxyaluminum hydride in stoichiometric amount does provide highly satisfactory yields of 8-hydroxy-1-naphthaldehyde.

EXPERIMENTAL SECTION

Lithium tri-t-butoxyaluminum hydride was obtained from Alfa products, 1,8-naphtholactam (Benz[c,d]indol-2(1H)-one) from Aldrich Chemicals, silica gel from Bio-Rad Laboratories and TLC plates from E. Merck Co., IR spectra were taken on a Perkin-Elmer Model 727-B Spectrophotometer and NMR spectra were obtained at 90 MHz using a Varian EM 390 Spectrometer. Reference to a company and/or product named by the Department is only for purposes of information and does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

1,8-Naphtholactone (2)[3].- To 400 ml of 0.5 N sodium hydroxide solution was added 8.45 g (50 mmoles) of 1,8-naphtholactam (3), and the resulting suspension was boiled 45 min to achieve complete homogeneity. This mixture was cooled to 0° and 3.50 g (50 mmoles) of sodium nitrite added. The resulting solution was added over 15 min to a mixture of 55 ml H_2SO_4 in

1000 ml of ice water; after the addition was complete, the acidic mixture was warmed gradually. At 40° gas evolution occurred with separation of a sticky solid; after the temperature had risen to 70°, the suspension was then cooled to 0°, and the brownish solid was collected. The damp product was dissolved in 50 ml benzene, dried over sodium sulfate and passed through a column of silica gel (30 mm x 70 mm dia.) and eluted with an additional 150 ml of benzene. Evaporation gave 7.16 g (85%) of nearly colorless lactone, mp. 105-107°, lit.[3] 99-101°. IR ($CHCl_3$): 1785 cm^{-1}, ^1H NMR ($CDCl_3$, TMS): δ 7.1-8.2 (complex). The lactone was used in the next step without further purification.

8-Hydroxy-1-naphthaldehyde (1).- A mixture of 7.16 g (42 mmoles) of 1,8-naphtholactone in 100 ml of THF was cooled to 0° under an inert atmosphere. A solution of 11.4 g (45 mmoles) of lithium tri-t-butoxyaluminum hydride in 100 ml THF was then added over 10 min during which the temperature remained below 5°. The reaction mixture was allowed to warm to ambient temperature and at the end of 16 hrs had changed in color from pale-yellow to deep orange. The mixture was diluted with 100 ml of 1N HCl and the layers were separated. The aqueous layer was shaken with 100 ml of ether after which the combined organic phases were extracted with three 100 ml portions of 1N aqueous sodium hydroxide. The basic extract was washed with ether (2 x 100 ml) and then acidified to give a suspension which was extracted into ether, (2 x 100 ml). Drying over sodium sulfate followed by evaporation gave 7.2 g of crude product which was taken up in 35 ml of chloroform and passed through silica gel (250 mm x 50 mm) and eluted with an additional 450 ml of chloroform to yield 6.6 g of 8-hydroxy-1-naphthaldehyde (1) whose TLC (SI-60, benzene, R_f = 0.25) showed one material. Crystallization from 250 ml hexane gave 5.42 g (75%) of orange crystals, mp. 97-99°, lit.[2] 92-96°. IR ($CHCl_3$): 1665 cm^{-1}; ^1H NMR ($CDCl_3$, TMS): δ 7.16 (1H, dd, J = 9 and 2 Hz);

7.3-7.6 (3H, complex); 8.00 (1H, dd, J = 8 and 1.5 Hz); 8.10 (1H, dd, J = 9 and 1.5 Hz); 9.84 (1 H, s); 11.64 (1H, s).

REFERENCES

1. R. Adams, T. A. Geissman and J. D. Edwards, Chem. Rev., 60, 555 (1960); R. D. Stipanovic, A. A. Bell and M. J. Lukefahr, "Chemical Basis for Host Plant Resistance to Pests", pp. 197-214. P. A. Hedin, Ed., ACS Symposium Series 62, American Chemical Society, Washington, D. C., 1977; A. Manmade, P. Herlihy, J. Quick, R. P. Duffley, M. Burgos and A. P. Hoffer, Experientia, 39, 1276 (1983).
2. D. Berry and D. C. C. Smith, J. Chem. Soc. Perkin I, 699 (1972).
3. A. J. Birch, M. Salahud-Din and D. C. C. Smith, J. Chem. Soc. (C), 523 (1966).

OXIDATION OF 2,3-DICHLORO-5,6-DICYANOHYDROQUINONE TO 2,3-DICHLORO-5,6-DICYANOBENZOQUINONE

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2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ) has been widely used in dehydrogenation experiments. The oxidation of the resulting 2,3-dichloro-