Tetrahedron Letters Vol. 21, pp 4711 - 4714
©Pergamon Press Ltd. 1980. Printed in Great Britain

0040-4039/80/1201-4711$02.00/0

# SYNTHESIS WITH BENZENESULFENYL CHLORIDE.
# ON THE STRUCTURE OF A $C_{12}H_{18}$ HYDROCARBON FROM EAST INDIAN SANDALWOOD OIL

Denis HEISSLER (1) and Jean-Jacques RIEHL
Institut de Chimie, Université Louis Pasteur
BP 296/R8 - 67008 STRASBOURG (FRANCE)

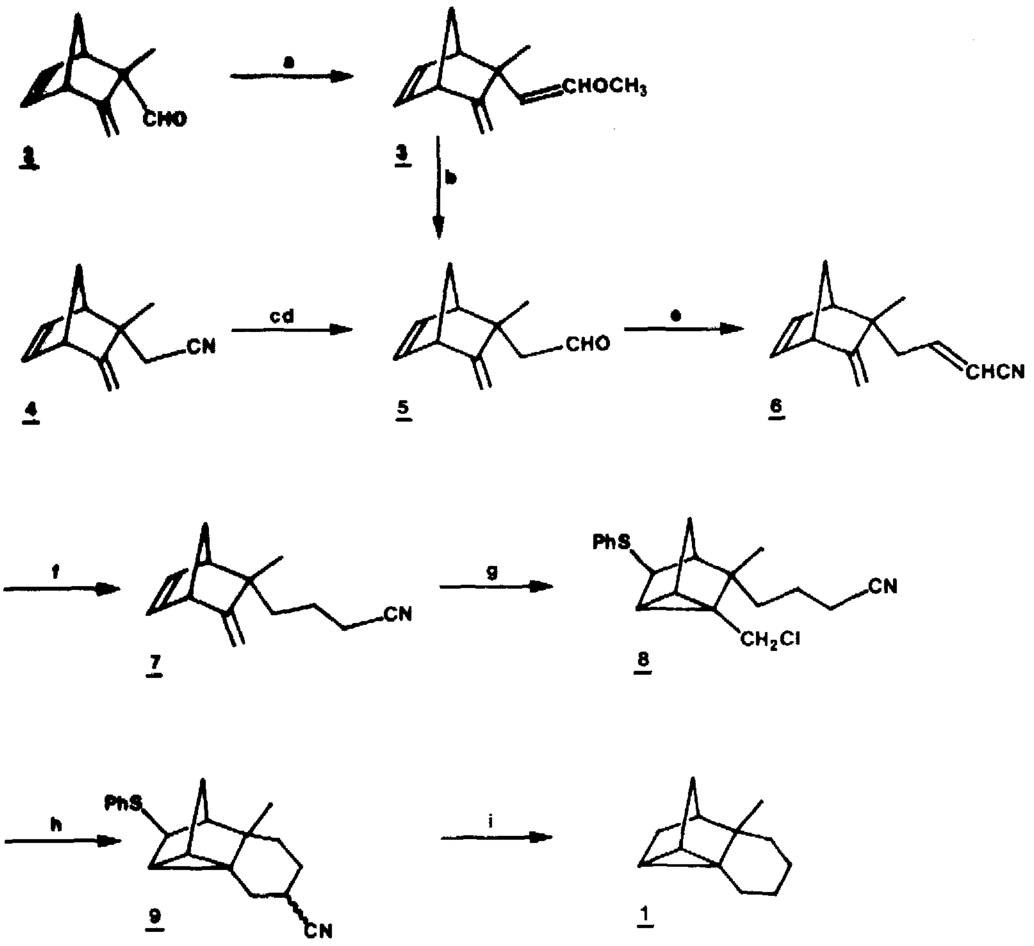
ABSTRACT: *The tetracyclic hydrocarbon 1 was synthesized by means of the electrophilic addition of benzenesulfenyl chloride to an appropriately substituted methylenenorbornene 7. The synthetic methodology used to prepare this latter compound includes a mild enol ether hydrolysis with acidic silica gel.*

In the course of their chemical investigation of the volatile constituents of East Indian sandalwood oil, Demole *et al.* have isolated a $C_{12}H_{18}$ hydrocarbon to which they tentatively assigned the tetracyclic structure 1 on the basis of spectral data (IR, 60 MHz NMR, MS)(2). In order to verify this assignment , we have synthesized the hydrocarbon 1.

The key step of our synthesis is the electrophilic addition of benzenesulfenyl chloride (3) (1.1 equiv., $CH_2Cl_2$, 0°C) to an appropriately substituted methylenenorbornene 7 to afford a quantitative yield of the tricyclenic chloro(phenylthio)nitrile 8(4). By an intramolecular alkylation reaction ($LiNEt_2$, 3:1 THF-HMPA, -78°C)(5), 8 was converted into the epimeric tetracyclic (phenylthio)-nitriles 9 (81 % yield). Treatment of the latter with potassium/HMPA/t-BuOH in ether at 0°C (6) concomitantly resulted in reductive cleavage of the cyano and of the phenylthio groups and gave the hydrocarbon 1 (7) (59 % yield) which was found to be nonidentical with the $C_{12}H_{18}$ hydrocarbon isolated by Demole *et al.*

Compound 7 was prepared either from the aldehyde 2(4) or from the nitrile 4(11) *via* the aldehyde 5. The latter was obtained from 2 by a Wittig reaction ($Ph_3P=CHOCH_3$, DMSO, r.t.)(12, 13) and hydrolysis (acidic silica gel, $CH_2Cl_2$, 48 h)(14), in 73 % yield. It was obtained from 4 by reduction (Diisobutylaluminum hydride, benzene, 1 h) and hydrolysis (10 % aqueous HCl, 20 min)(8) in 89 % yield.

Subjection of the aldehyde 5 to a Horner-Emmons reaction ( $(EtO)_2P(O)CH_2CN$, $CH_3S(O)CH_2Na$, DMSO)(13, 15) gave a mixture of two isomeric α,β-unsaturated nitriles 6 (92 % yield) which were selectively reduced into the nitrile 7 with magnesium in methanol (16) (96 % yield).



a) $Ph_3P{=}CHOCH_3$, DMSO ; b) Acidic silica gel, $CH_2Cl_2$, (2 → 5 : 73 % yield) ; c) $(i\text{-}Bu)_2AlH$, benzene ; d) 10 % aqueous HCl (4 → 5 : 89 %) ; e) $(EtO)_2P(O)CH_2CN$, $CH_3S(O)CH_2Na$, DMSO (92 %) ; f) Mg, MeOH (96 %) ; g) PhSCl, $CH_2Cl_2$ (100 %) ; h) $LiNEt_2$, THF, HMPA, -78°C (81 %) ; i) K, HMPA, t-BuOH, ether, 0°C (59%).

Acknowledgment : We are very grateful to Dr E. Demole (Firmenich S.A., Geneva) for the IR, the NMR and the mass spectra of the $C_{12}H_{18}$ hydrocarbon from East Indian sandalwood oil.

## Spectral and Physical Data

The IR spectra were determined in $CCl_4$ and the NMR spectra (90 MHz) in $CDCl_3$ unless otherwise stated.

Aldehyde 5 : IR : 3080, 2830, 2730, 1725, 1660 $cm^{-1}$ ; NMR $\delta$: 1.33(s,3H,$-CH_3$); 2.37 (m, 2H, $-C\underline{H}_2CHO$) ; 4.72 and 5.03 (s and s, 1H and 1H, $>C=CH_2$) ; 6.17 (m, 2H, -CH=CH-) ; 9.72 (m, 1H, -CHO).

Nitrile 7 : IR : 3075, 2260, 1660 $cm^{-1}$ ; NMR $\delta$ : 1.21 (s, 3H, $-CH_3$) ; 2.32 (t, J = 7 Hz, 2H, $-CH_2CN$); 4.67 and 4.97 (s and s, 1H and 1H, $>C=CH_2$) ; 6.18 (m, 2H, -CH=CH-) ; MS $M^{+\cdot}$ = 187.

Chloro(phenylthio)nitrile 8 : IR : 2260, 1590 $cm^{-1}$ ; NMR (60 MHz) $\delta$: 1.03(s, 3H, $-CH_3$); 2.28 (m, 2H, $-CH_2CN$) ; 3.68 (m, 1H, $>CH-S$) ; 3.72 (s, 2H, $-CH_2Cl$) ; 7.13 - 7.53 (m, 5H, -Ph) ; MS $M^{+\cdot}$ = 331 and 333.

(Phenylthio)nitriles 9 : Epimer A : mp = 85.5 - 86.5°C ; IR:2250, 1590 $cm^{-1}$ ; NMR (60 MHz) $\delta$ : 0.94 (s, 3H, $-CH_3$) ; 3.63 (m, 1H, $>CH-S$) ; 7.15 - 7.47 (m, 5H, -Ph) . Epimer B : mp = 100 - 101°C ; IR:2250, 1590 ; NMR (60 MHz) $\delta$ : 0.92 (s, 3H, $-CH_3$) ; 3.00 (m, 1H, $>CHCN$); 3.90 (m, 1H, $>CH-S$), 7.10 - 7.54 (m, 5H, -Ph).

Hydrocarbon 1 : mp = 37-38°C ; IR:3055, 2925, 2880, 2855, 1470, 1445, 1375, 1345, 1325, 1285, 1270, 855 $cm^{-1}$; NMR (60 MHz, $CCl_4$) $\delta$ : 0.73 (m, 1H) ; 0.84 (s, 3H, $-CH_3$) ; 0.85 -2.00 (m, 14 H); MS $M^{+\cdot}$ = 162.

## REFERENCES AND NOTES

1) Centre National de la Recherche Scientifique
2) E. DEMOLE, C. DEMOLE, P. ENGGIST, Helv. Chim. Acta, 59, 737 (1976)
3) Prepared according to F.G. BORDWELL ; M. FIESER and L.F. FIESER, "Reagents for Organic Synthesis " Vol. 5, p. 523 ; John Wiley and Sons, Inc., New York (1975)
4) D. HEISSLER, J.J. RIEHL, Tetrahedron Lett. 3957 (1979)
5) M. LARCHEVEQUE, P. MULOT, T. CUVIGNY, J. Organomet. Chem. 57, C 33 (1973)
6) T. CUVIGNY, M. LARCHEVEQUE, H. NORMANT, Bull. Soc. Chim. Fr. 1174 (1973)
7) The hydrocarbon 1 was also obtained by subjection of compound 9A to reduction (i)diisobutylaluminum hydride, benzene ; ii) 10 % aqueous HCl)(8), desulfurization (Raney nickel, ethanol), oxidation ($CrO_3$- 2py, $CH_2Cl_2$)(9) and decarbonylation ( $(Ph_3P)_3$ RhCl, benzene)(10) (16 % overall yield).
8) L.I. ZAKHARKIN, I.M. KHORLINA, Dokl. Akad. Nauk SSSR 116, 422 (1957) ; Chem. Abst. 52, 8040 f (1958)

9) R. RATCLIFFE, R. RODEHORST, *J. Org. Chem.* **35**, 4000 (1970)

10) J.A. OSBORN, F.H. JARDINE, J.F. YOUNG, G. WILKINSON, *J. Chem. Soc. (A)* 1711 (1966) ; K. OHNO, J. TSUJI, *J. Am. Chem. Soc.* **90**, 99 (1968)

11) D. HEISSLER, J.J. RIEHL preceding paper

12) S.G. LEVINE, *J. Am. Chem. Soc.* **80** , 6150 (1958)

13) R. GREENWALD, M. CHAYKOVSKY, E.J. COREY, *J. Org. Chem.* **28**, 1128 (1963)

14) When performed under the usual conditions (aqueous $HClO_4$, ether) this hydrolysis gave only a 45 % yield of the aldehyde **5**.
The acidic silica gel we used, was prepared according to F. HUET, A. LECHEVALLIER, M.PELLET, J.M. CONIA, *Synthesis* 63 (1978), by treatment of silica gel for column chromatography (Merck, Art. 7734) with 10 % aqueous oxalic acid. The hydrolysis was carried out under nitrogen by stirring 1,5 g of the enol ethers **3** with 10 g of silica gel in 50 ml methylene chloride. After 24 h, the silica gel was neutralized ($NaHCO_3$), filtered off, washed with $CH_2Cl_2$ and the filtrate was treated with fresh silica gel for 24 h.

15) W.S. WADSWORTH, J R., W.D. EMMONS, *J. Am. Chem. Soc.* **83**, 1733 (1961)

16) J.A. PROFITT, D.S. WATT, E.J. COREY, *J. Org. Chem.* **40**, 127 (1975)

(Received in France 1 September 1980)