Tetrahedron Letters No. 25, pp 2213 - 2216, 1978.
0040-4039/78/0615-2213$02.00/0

SYNTHESIS OF NAPHTHALENES FROM ortho-SUBSTITUTED BENZYL SULFONES AND MICHAEL ACCEPTORS

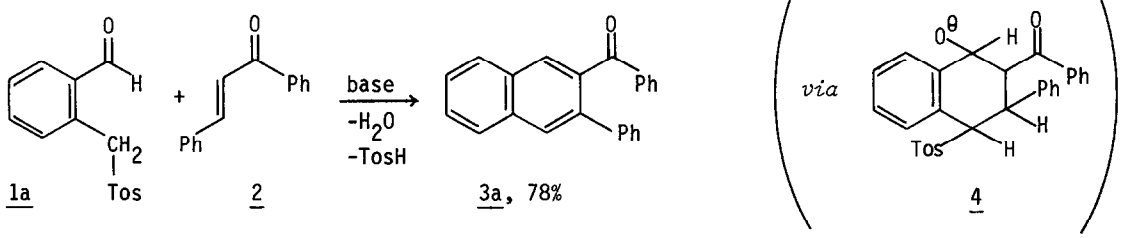
Jurjen Wildeman, Peder C. Borgen, Henk Pluim,
Pieter H.F.M. Rouwette and Albert M. van Leusen*

Department of Organic Chemistry, The University,
Nijenborgh, Groningen, The Netherlands

(Received in UK 10 April 1978; accepted for publication 27 April 1978)

A communication on a closely related subject by Hauser and Rhee[1] prompt us to disclose our preliminary results on a simple synthetic method for the transformation of benzene derivatives to naphthalene ring systems. This novel method[2] is based on the reaction of ortho-substituted benzyl sulfones (1) with Michael acceptors, followed by elimination of water and p-toluenesulfinic acid (TosH), e.g. Scheme I.

SCHEME I



1a 2 3a, 78% 4

When the aldehyde group of o-tosylmethylbenzaldehyde (1a) serves as the electrophilic center for ring closure, the overall process leads to 2,3-disubstituted naphthalenes. Thus, 2-benzoyl-3-phenylnaphthalene (3a) is obtained in good yield from 1a and chalcone (2). This reaction is carried out with 2 to 3 equiv of NaH in 1,2-dimethoxyethane in 2 h, first at room temperature, then at reflux.[3] A Michael addition of the α-sulfonylcarbanion derived from 1a to 2 is followed consecutively by ring closure to 4, elimination of water and TosH (salt). Table I provides further examples, compounds 3a-h.

Analogous to Scheme I, the use of ketones (o-tosylmethylacetophenone 1b or o-tosylmethylbenzophenone 1c, instead of 1a) results in 1,2,3-trisubstituted naphthalenes (3i-k).

An other oxidation state of the ortho-substituent in the sulfonic precursors 1 leads to a different oxidation state of the naphthalene products. In the 1,2,3,-trisubstituted naphthalenes resulting from similar reactions of ethyl o-tosylmethylbenzoate[4] (1d) or o-tosylmethylbenzonitrile (1e) and Michael acceptors the 1-substituent is an OH or a NH_2 group, respectively (Table I, compds 3l,m and 3t,u). Whereas maleic (or fumaric) esters thus give 1-hydroxy- and 1-aminonaphthalene-2,3-dicarboxylates in good yields in a one-pot treatment (3l and 3u, respectively), not all Michael acceptors give 1-hydroxynaphthalenes in the same way. With less

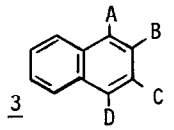


TABLE I. Naphthalenes[5] Synthesized from o-Substituted Benzyl Sulfones 1a-e (or Cyanide 5c)

Compd	A	B	C	D	% Yield[a]	Mp(°C)	From, and
3a	H	COPh	Ph	H	78	93-94	1a, chalcone
3b	H	COPh	o-C_7H_7	H	76	99-100	1a, o-Me-chalcone
3c	H	C≡N	Ph	H	71	156-157	1a, cinnamonitrile
3d	H	C≡N	o-C_7H_7	H	75	168-170	1a, o-Me-cinnamonitrile
3e	H	COOMe	COOMe	H	75[b]	46-47 (lit.[6] 47)	1a, diMe maleate
3f	H	COOMe	Ph	H	20	c	1a, Me cinnamate
3g	H	COOMe	Me	H	25	180 (0.05 mm)[d,7]	1a, Me crotonate
3h	H	COMe	Me	H	10	c	1a, 3-penten-2-one
3i	Me	C≡N	Ph	H	64	109-110	1b, cinnamonitrile
3j	Ph	C≡N	Me	H	66	113-114	1c, crotononitrile
3k	Ph	C≡N	Ph	H	60	136-137	1c, cinnamonitrile
3l	OH	COOEt	COOEt	H	76	170 (0.1 mm)[d] (lit.[8] 163-4/0.05 mm)	1d, diEt maleate
3m	OH	COPh	COPh	H	71	130-131	1d, 1,2-dibenzoylethene
3n	OMe	COOEt	Me	H	50	55-56	1d, Et acrylate
3o	OMe	COOEt	Ph	H	43	220 (0.1 mm)[d]	1d, Et cinnamate
3p	OMe	COPh	Ph	H	38	161-162	1d, chalcone
3q	OMe	COMe	Me	H	31	56-57	1d, 3-penten-2-one
3r	OMe	C≡N	Ph	H	54	142-143	1d, cinnamonitrile
3s	OMe	C≡N	Me	H	54	68-69	1d, crotononitrile
3t	NH_2	C≡N	Me	H	62	145-146 (lit.[9] 46-7)	1e, crotononitrile
3u	NH_2	COOMe	COOMe	H	80	180 (0.001 mm)[d]	1e, diMe maleate
3v	OH	COOEt	Me	Tos	40[e]	121-122	1d, Et tetrolate
3w	OH	COOEt	H	Tos	23	146-148	1d, Et propiolate
3x	OH	COOEt	Me	C≡N	95	138-141	5c, Et tetrolate
3y	OH	COOEt	H	C≡N	80[e]	89-90 (lit.[10] 92-92.7)	5c, Et propiolate
3z	OH	COOEt	COOEt	C≡N	30[e]	127-128	5c, acetylenedicarboxylate

[a]Isolated yields calc. on 1 (or 5); not always optimized. [b]Contained ca. 25% of naphthalene-2,3-dicarboxylic acid. [c]Not purified. [d]Externally measured bp in bulb-to-bulb distillation. [e]iPr_2NLi used for base.

strongly electronegative substituents in the 3-position of the intermediate 1-hydroxy-4-tosyl-3,4-dihydronaphthalenes,[11] the negative charge of the conjugate 3,4-dihydronaphtholate appears to prevent elimination of TosH. However, after methylation (MeI) of the OH substituent base-induced elimination of TosH (salt) can be effected in a separate step to give 1-methoxynaphthalenes (Table I, 3n-s).

1,2,3,4-Tetrasubstituted naphthalenes are obtained from triple-bond Michael acceptors and 1d (compds 3v,w), and also with ethyl o-cyanomethylbenzoate (5c) to give 3x-z. In these cases, however, no elimination of TosH (or HCN) is involved.

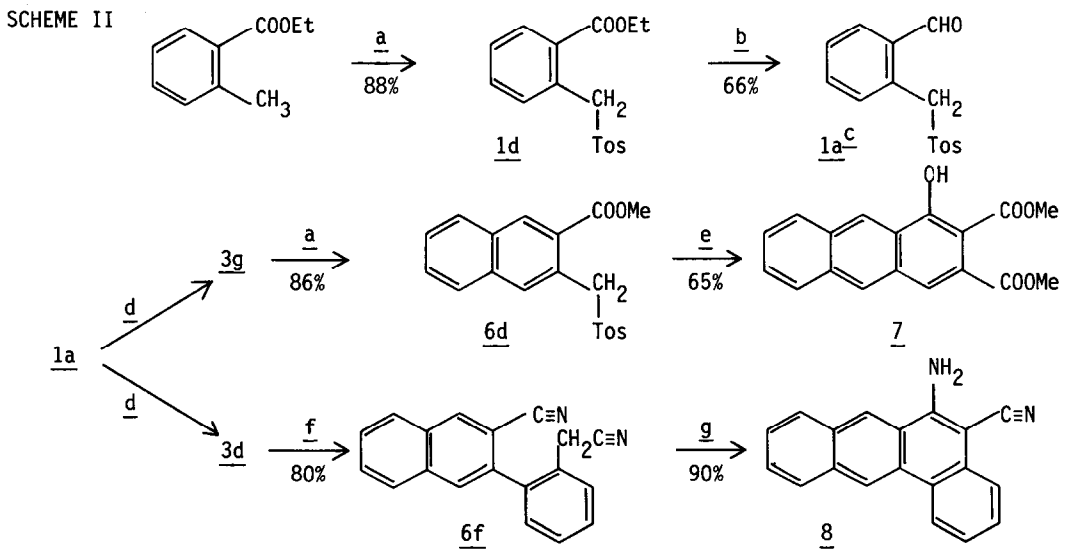
With few exceptions only all naphthalenes 3 in Table I are new compounds, many of which are not easily accessible otherwise.[12] Furthermore the present method has the virtue of being applicable repeatedly, as follows, for example, from the synthesis of 7 and 8 from o-tosylmethylbenzaldehyde (1a, Scheme II).

The (potential) precursors to naphthalenes, anthracenes, phenanthrenes, etcetera, used in this investigation are new compounds by themselves. The ones studied thus far are collected in Table II. They are readily accessible by standard reactions from commercially available starting materials; examples of such reactions can be drawn from Scheme II (compds 1a, 1d, 6d and 6f).

o-Tosylmethylphenyl isocyanide (1f, a vinylogue of tosylmethyl isocyanide, TosMIC[13]) does not give 7-membered ring systems with Michael acceptors and base, nor with other unsaturated substrates (aldehydes, acyl chlorides, imines). In all cases the only product was 3-tosylindole (mp 172-173°C) formed by intramolecular ring closure of the conjugate α-sulfonyl carbanion. This result is in line with previous observations with TosMIC.[13c]

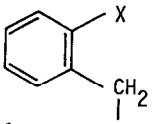
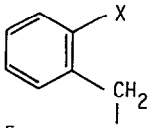
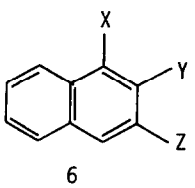
Full details of the above reactions of compounds 1, 5 and 6, as well as reaction with other unsaturated substrates will be published elsewhere.

SCHEME II



a 1) NBS, 2) TosNa. b 1) $LiAlH_4$, 2) $C_5H_5NHCrO_3Cl$. c We have prepared 1a by other routes as well. d See Table I. e With diMe fumarate, t-BuOK, 20°C, 100 min, cf Scheme I. f 1) NBS, 2) NaC≡N. g 0.1 Equiv of t-BuOK, 20°C, 30 min.

TABLE II.[5]

	Compd	X	Y	Z	Mp (°C)
 1	1a	CHO			116-118
	1b	COMe			137-139
	1c	COPh			185-189
	1d	COOEt			90-91
	1e	C≡N			159-161
	1f	N=C			143-145
 5	5a	COMe	C≡N		bp. 116 (0.2 mm)
	5b	COMe	$SOC_7H_7(p)$		138-140
	5c	COOEt	C≡N		27-29[14]
 6	6a	H	COOMe	CH_2Tos	161-163
	6b	Ph	C≡N	CH_2Tos	189-192
	6c	C≡N	CH_2Tos	H	191-192
	6d	COOMe	CH_2Tos	H	131-132
	6e	CH_2Tos	C≡N	Ph	203-205
	6f	H	C≡N	$C_6H_4(CH_2CN)(o)$	126-128

References and Notes

1. F.M. Hauser and R.P. Rhee, J. Org. Chem., 43, 178 (1978).
2. Presented for the Organic Division of the Royal Dutch Chemical Society (KNCV) at Leyden, February, 13, (1978).
3. Actually, an equimolar solution of 1a and 2 was stirred at room temperature with 2.5 equiv of NaH for 100 min, then some MeOH was added and the mixture was refluxed for 20 min. Similar results were obtained with 2 equiv of t-BuOK.
4. At this point the interference of Hauser's work with ours is strongest: Hauser et al.[1] have similarly prepared 1-hydroxy-2-B,3-C-naphthalenes from the corresponding sulfoxide (o-phenylsulfinylmethylbenzoate) using thermal elimination of sulfenic acid for aromatization. Furthermore they have synthetized 1,2,3,4-tetra-substituted naphthalenes from 1-H-2-benzofuran-1-one 3-(phenyl sulfone) which may be regarded as an internal ester of o-(phenylsulfonylmethyl)-benzoic acid.
5. Satisfactory elemental microanalyses, and IR and PMR spectra were obtained for all new compounds, with the exception of elemental analyses for 2f,h,u.
6. E.F. Bradbrook and R.P. Linstead, J. Chem. Soc., 1936, 1739.
7. J. Rigaudy and M. Maumy, Bull. Soc. Chim. France, 1972, 3936.
8. Z. Horii, T. Katagi, Y. Tamura, and T. Tanaka, Chem. Pharm. Bull., 10, 887 (1962).
9. E. Campaigne, D.R. Maulding, and W.L. Roelofs, J. Org. Chem., 29, 1543 (1964).
10. R.K. Hill, C.E. Glassick, and L.J. FLiedner, J. Am. Chem. Soc., 81, 737 (1959).
11. For example, in the case of 3n the precursor 2-ethoxycarbonyl-3-methyl-4-tosyl-3,4-dihydro-1-naphthol, mp 121-122°C, was obtained in 82%.
12. Cf. ref. 6-10.
13. Leading references: (a) O. Possel, D. van Leusen, and A.M. van Leusen, Tetrahedron Lett., 1977, 4229, 4233; (b) O.H. Oldenziel, D. van Leusen and A.M. van Leusen, J. Org. Chem., 42, 3114 (1977); (c) A.M. van Leusen, J. Wildeman, and O.H. Oldenziel, J. Org. Chem., 42, 1153 (1977).
14. Bp. found 130-134°C (10 mm); lit. 170-170.5°C (16 mm): C.C. Price, F.M. Lewis, and M. Meister, J. Am. Chem. Soc., 61, 2760 (1939).