Tetrahedron Letters,Vol.24,No.6,pp 609-612,1983
Printed in Great Britain

0040-4039/83/060609-04$03.00/0

FORMATION OF 1-CHLOROBENZOCYCLOBUTENE, ANTHRACENE OR BENZOFURAN BY FLASH VACUUM PYROLYSIS

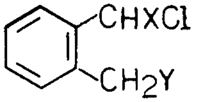
Amjad Hussain and John Parrick*
Department of Chemistry, Brunel University
Uxbridge, Middlesex, UB8 3PH, England

Abstract: pyrolysis of o-substituted benzylidene chlorides is shown to be a useful route to 1-chloro-benzocyclobutene, anthracene or benzofurans; evidence is given for a carbene intermediate in the pyrolysis of o-methoxybenzylidene chloride.

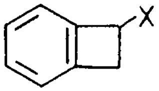
As an extension of our work on pyrolysis reactions,[1] we have investigated the flash vacuum pyrolysis (f.v.p.) of some o-substituted benzylidene chlorides. This was of interest since such compounds might be formed as intermediates in the pyrolysis of benzene derivatives with chloroform[1] and also because the reports[2] of the f.v.p. of o-methylbenzyl chloride (1) to give benzocyclobutene (4) seemed to offer promise of a useful preparative route to 1-substituted benzocyclobutenes. We have been prompted to report our findings by the very recent report of related work by P. Schiess and co-workers.[3a,b]

All the o-substituted dichloromethylarenes used in our work were obtained by reaction of the corresponding aldehyde with thionyl chloride in the presence of DMF.[4] (Table).

F.v.p. of o-methylbenzylidene chloride (2) at 700°C in our apparatus[5] gave 1-chlorobenzocyclobutene (5) (89% yield). The high yield and ready accessibility of the starting material makes this a convenient route to (5) and a more efficient method than the related alternative procedure[2] (yield 53%) from commercially available α,α'-dichloro-o-xylene (3). These results are in general agreement with those reported by Schiess.[3b]

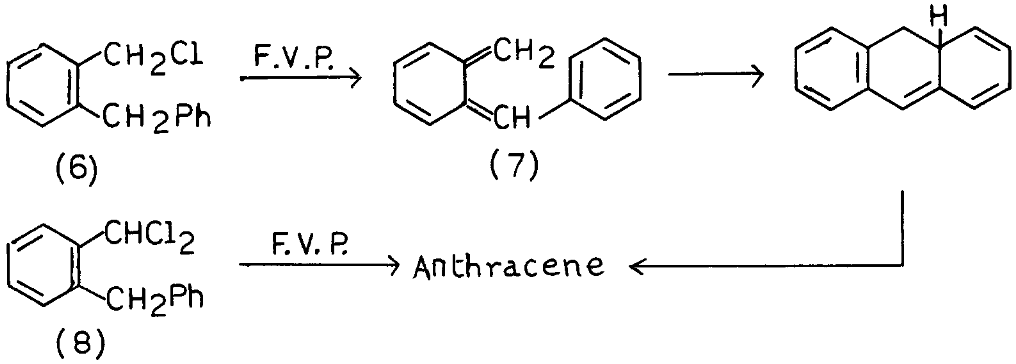


(1) X = Y = H
(2) X = Cl, Y = H
(3) X = H, Y = Cl



(4) X = H
(5) X = Cl

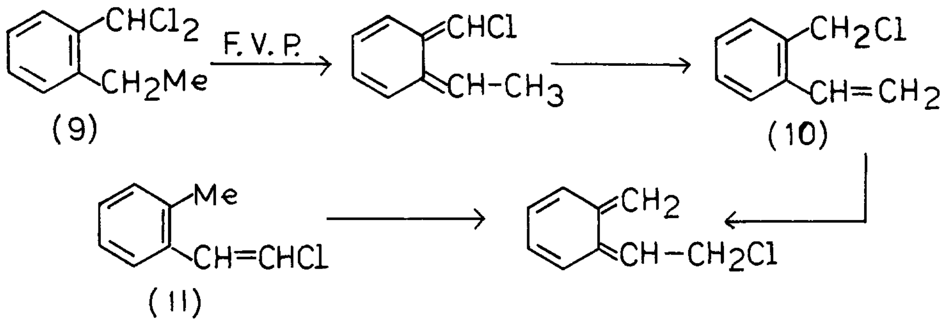
We have also studied the f.v.p. of benzylidene chlorides having o-benzyl, o-ethyl or o-alkoxy groups. Either o-benzylbenzylidene chloride (8) or o-benzylbenzyl chloride (6) gave a high yield of anthracene. This appears to be an attractive route to certain polycyclic homo- and hetero-aromatic compounds. Probably the reaction of (6) proceeds by trapping of the intermediate o-quinodimethene[2] intermediate (7) through an electrocyclisation reaction followed by either 1,2- or 1,4-elimination after a 1,3-sigmatropic shift of hydrogen in the latter case.



A similar process followed by loss of hydrogen, probably by 1,4-elimination,[6] would yield anthracene from *o*-benzylbenzyl chloride.

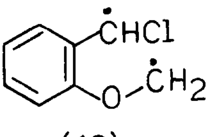
o-Ethylbenzylidene chloride (9) gave a product containing four components of which three were identified as indene, a 2-*o*-tolylethenyl chloride (11) and *o*-chloromethylstyrene (10) (Table). The fourth component is isomeric with (10) and (11) and is possibly the geometrical isomer of (11) but we were unable to obtain it pure. The formation of the styrene derivatives are thought to arise by the sequence of steps in Scheme 1.

Scheme 1

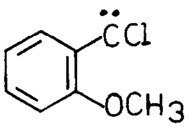


Our attention now turned to *o*-alkoxybenzylidene chlorides. F.v.p. of *o*-methoxybenzylidene chloride gave a useful yield of benzofuran (62%) with benzyl chloride (3%) as a minor impurity. This route to annelated furans was further exemplified by the formation of 2-methylbenzofuran (71%) and naphtho[2,1-*b*]furan from *o*-ethoxybenzylidene chloride and 1-dichloromethyl-2-methoxynaphthalene. This route to furan derivatives complements the pyrolytic formation of 2,3-dihydrobenzofurans from *o*-alkoxybenzaldehyde *p*-toluenesulphonylhydrazones.[7]

A diradical, e.g. (12), or carbene, e.g. (13), intermediate seemed likely. In order to obtain



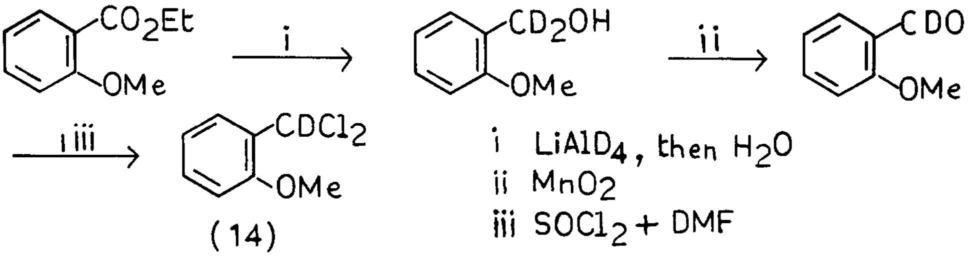
(12)



(13)

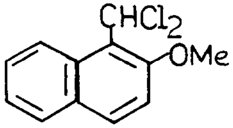
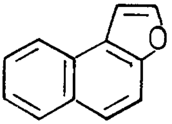
more evidence, o-methoxybenzaldehyde-d_1 was prepared from ethyl o-methoxybenzoic acid by the route in Scheme 2.

Scheme 2



The finding that f.v.p. of (14) gave unlabelled benzofuran is evidence in support of the carbene intermediate. This is in line with the formation of 2-methylbenzofuran rather than a benzopyran from o-ethoxybenzylidene chloride since o-ethoxyphenylcarbene is known to strongly favour formation of a five-membered rather than a six-membered ring.[7] Accordingly, the f.v.p. of o-methoxybenzyl chloride gave benzofuran, but in lower yield than that obtained from the corresponding benzylidene chloride, together with monocyclic byproducts (Table). This

Table o-Substituted-benzylidene and -benzyl chlorides and their flash vacuum pyrolysis products

Starting material o-$R^1C_6H_4R^2$	Yield (%) from aldehyde	Average pyrolysis temp. (°C)	Products (% yield)
$R^1 = CHCl_2$, $R^2 = Me$	81	700	1-chlorobenzocyclobutene (89)
$R^1 = CHCl_2$, $R^2 = CH_2Ph$	90	475	anthracene (91)
$R^1 = CH_2Cl$, $R^2 = CH_2Ph$		575	anthracene (90)
$R^1 = CHCl_2$, $R^2 = Et$	80	675	indene (34), 2-o-tolylethenyl chloride (36), o-chloromethylstyrene (14), unidentified (15)
$R^1 = CHCl_2$, $R^2 = OMe$	82	600	benzofuran (65)
$R^1 = CH_2Cl$, $R^2 = OMe$		550	benzofuran (31), styrene (20), toluene (9), ethylbenzene (6), benzene (4)
$R^1 = CHCl_2$, $R^2 = OEt$	83	675	2-methylbenzofuran (71)
	64	600	 (68)

complex mixture may reflect the less ready α-elimination from the chloromethyl group compared with the more crowded dichloromethyl substituent. This result contrasts with that obtained with the chloromethyl (6) and dichloromethyl (8) compounds, where essentially identical high yields were obtained and an initial 1,4-elimination of HCl probably occurred in each case.

Acknowledgement

We thank the Ministry of Education of the Pakistan Government for financial support to A.H.

Notes and References

1. R.E. Busby, S.M. Hussain, M. Mohamed, J. Parrick, C.J.G. Shaw, I.A. Bhatti and A.B. Shirazi, J. Chem. Res. (S), 408; (M) 4935 (1980), and references therein.
2. M.J. Morello and W.S. Trahanovsky, Tetrahedron Lett., 4435 (1979).
3. (a) P. Schiess, S. Rutschmann and V.V. Toan, Tetrahedron Lett., 23 3665 (1982).
   (b) Idem ibid 23, 3669 (1982).
4. M. S. Newman and P.K. Sujeeth, J. Org. Chem., 43, 4367 (1978).
5. The apparatus consisted of a quartz tube (55 cm long, 17 mm i.d.) packed with quartz rings for 30 cm of its length. The packed volume was heated in a furnace at the quoted temperatures. The sample, contained in a flask connected to one end of the quartz tube, was vapourised by a secondary furnace into the reaction zone. The pressure was 0.1 Torr in each case and the pyrolysate was collected in traps cooled with liquid N_2.
6. R.F.C. Brown, G.E. Gream, D.E. Peters and R.K. Solly, Aust. J. Chem., 21, 2223 (1968).
7, W.D. Crow and H. McNab, Aust. J. Chem., 32, 99 (1979).

(Received in UK 17 November 1982)