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CATALYSIS IN FLASH VACUUM PYROLYSIS

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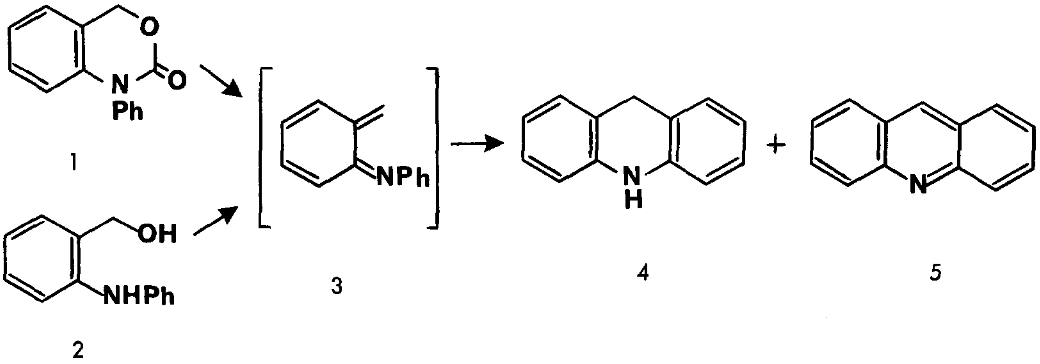
Summary: The temperature required for flash pyrolytic elimination of water from o-aminobenzyl alcohols and of carbon dioxide from dihydrobenzoxazinones to give azaxylylenes is considerably lowered by the presence of alumina and silica gel in the hot zone.

Flash vacuum pyrolysis (FVP) has been widely used to effect thermal rearrangements and fragmentations.[1] The nature of the hot zone surface in these processes has largely been neglected although in principle it could well be very important as the primary site of activation. Isolated reports of FVP over reagents have appeared[2] but the procedure is not generally employed. We now report our observations concerning the flash pyrolytic generation of azaxylylenes which underline the potential advantages of the technique.

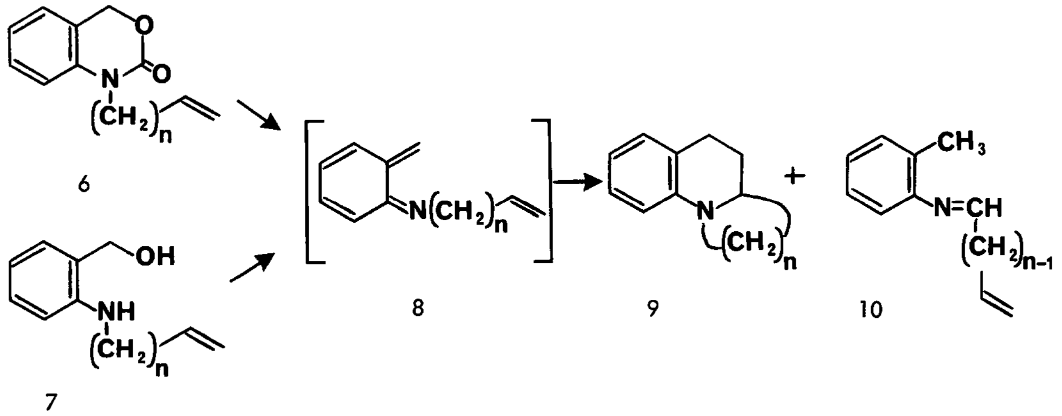
When the azaxylylene (3) is generated by FVP of o-N-phenylaminobenzyl alcohol (2) or 1-phenylbenzoxazinone (1)[3] a minimum temperature of 650° is required for complete dehydration or elimination of CO_2. The azaxylylene produced undergoes electrocyclisation to dihydroacridine, this being accompanied by some dehydrogenation to acridine. The latter process becomes more important as oven temperatures are raised above 650 °C. Introduction of three 5 cm x 8 mm o.d. silica glass tubes coated internally[4] with t.l.c. grade Al_2O_3 or SiO_2 into the pyrolysis tube[5] resulted in a marked lowering of the temperature required for complete generation of the azaxylylene. Thus the N-phenyl alcohol (2) over SiO_2 at 400 °C gives complete conversion to acridine (10%) and dihydroacridine (90%); over Al_2O_3 at 350 °C acridine (70%) and dihydroacridine (30%) are obtained[6]. Introduction of tubes (even when thoroughly etched) uncoated with SiO_2 or Al_2O_3 has no effect. On the other hand passage over molecular sieves(3" boat containing $^1/_{16}$" pellets) at 450° also effects complete conversion giving acridine quantitatively. A similar catalytic effect is observed in the dehydration of the isomeric 2-aminobenzhydrol and in the elimination of CO_2 from the oxazinone (1) (Scheme 1).



Precursor	Catalyst	Temperature (°C)[7]	Yield[8] 4 +	5 (%)
1	-	650	95	5
1	SiO_2	400	85	15
1	Al_2O_3	400	20	80
2	-	650	100	0
2	SiO_2	400	90	10
2	Al_2O_3	350	30	70
2	Mol.Sieve	450	0	100

SCHEME 1.

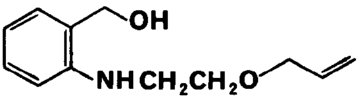
The N-alkylazaxylylenes (8; n = 3 and 4) undergo competitive intramolecular Diels-Alder reaction to give (9; n = 3 and 4) and H-shift to give imines (10; n = 3 and 4)[3] (Scheme 2). When the azaxylylene is generated from the benzoxazinone (6) the minimum working temperature can be lowered from ca. 600 °C to 410-450 °C in the presence of SiO_2 but the ratio of intramolecular adduct to imine remains constant. For the amino alcohols (7; n = 3 and 4) more marked effects are observed and the proportion of intramolecular adduct increases significantly. Thus the pentenyl alcohol (7; n = 3) at 650 °C without catalyst gives adduct (6%) and imine (30%) whereas at 410 °C over SiO_2 the yields are adduct (50%) and imine (40%). The hexenyl alcohol (7; n = 4) gives only imine (60%) at 650 °C without catalyst but at 450 °C over SiO_2 both adduct (5%) and imine (45%) are formed. In the case of allyloxyethyl alcohol (11) only 5% of the analogous intramolecular Diels-Alder adduct is observed at 650 °C without catalyst whereas at 425 °C over SiO_2 this increases to 20%.



Precursor	Catalyst	Temperature (^{0}C)[7]	Yield[9] 9	+ 10 (%)
6 n = 3	-	600	30	30
6 n = 3	SiO_2	450	25	35
6 n = 4	-	600	10	58
6 n = 4	SiO_2	410	10	60
7 n = 3	-	650	6	30
7 n = 3	SiO_2	410	50	40
7 n = 4	-	650	0	60
7 n = 4	SiO_2	450	5	45

SCHEME 2.

Cyclisation of 2-aminobenzophenone to 9-acridone can be accomplished flash pyrolytically, however the yield at 700°C is only 4%. Introduction of SiO_2 into the pyrolysis tube raises this to 60% at the same temperature.



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These preliminary experiments indicate that milder conditions can be used and that both yields and selectivity in flash vacuum pyrolyses can be increased by introduction of supported catalysts in the hot tube and suggest that the technique is worthy of wider consideration.

References and Notes

[1] Pyrolytic Methods in Organic Chemistry, R.F.C. Brown, Academic Press Inc. (London) 1980.

[2] C.M. Buchan, J.I.G. Cadogan, I. Gosney, B.J. Hamill, S.F. Newlands, and D.A. Whan, J.C.S. Chem. Comm., 1983, 725; see also J-C Guillemin and J-M Denis, Angew.Chem. Int.Ed., Engl., 1982, 690; C. Braillon , M.C. Lasne, J.L. Ripoll and J-M. Denis, Nouv. J.Chim., 1982, **6**, 121; J.C. Guillemin, J-M. Denis and A. Lablache-Combier, J.Am.Chem. Soc., 1981, **103**, 468; J-M. Denis, R. Niamayoua M. Vata, and A. Lablache-Combier, Tetrahedron Letters, 1980, 515; O.L. Chapman, C.C. Chang, and N.R. Rosenquist, J.Am. Chem. Soc., 1976, **98**, 261 and J. Boyd and K.H. Overton, J.C.S. Perkin 1, 1972, 2533.

[3] R.D. Bowen, D.E. Davies, C.W.G. Fishwick, T.O. Glasbey, S.J. Noyce, and R.C. Storr, Tetrahedron Letters, 1982, 4501.

[4] The tubes are coated in the same way as glass t.l.c. plates. The pyrolysis apparatus is essentially that described in reference 4 modified in such a way that the hot tube is horizontal. The three coated tubes are stacked together in the centre of the hot tube, the position not being critical.

[5] J.J.A. Campbell, P. Halliwell, and P.W. Manley, Chemistry and Industry, 1978, 842.

[6] At temperatures below 350 °C recovery of pyrolysate falls off sharply due to adsorption on the Al_2O_3 or SiO_2.

[7] Substrates were passed through the pyrolysis tube at the rate of 100mg/h.

[8] Total recovery of pyrolysate was quantitative and the proportions of (4) and (5) were determined by n.m.r. spectroscopy.

[9] The crude pyrolysate was hydrolysed to convert imine (10) to o-toluidine. The amine (9) and o-toluidine were then separated by distillation and preparative t.l.c. No starting material was recovered.

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