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THERMAL CONVERSION OF 2-METHYLPHENYLAZO-COMPOUNDS TO DIARENO-1,2-DIAZEPINES

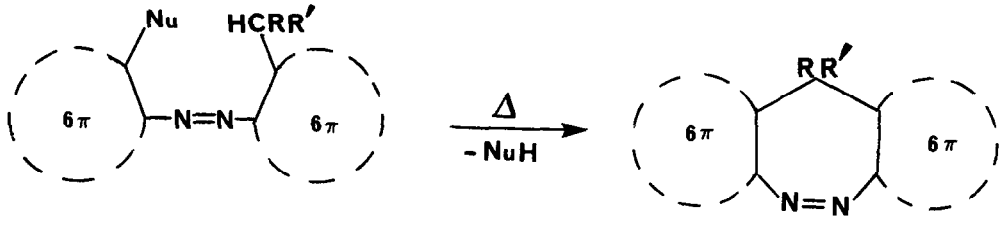
Adam C Alty, [a] Ronald E Banks, [a*] Brian R Fishwick, [b] and A Ronald Thompson [a]

[a] Chemistry Department, The University of Manchester Institute of Science and Technology, Manchester M60 1QD, UK

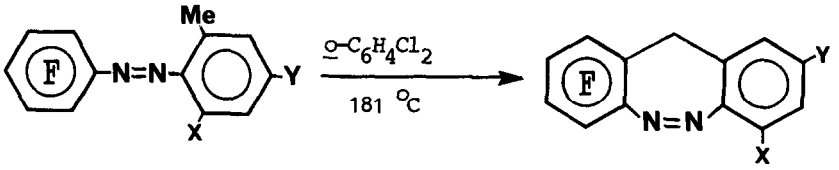
[b] Imperial Chemical Industries PLC, Organics Division, Hexagon House, Blackley, Manchester M9 3DA, UK

Abstract Examples are given of the synthesis of bis-annulated 1,2-diazepines via thermal intramolecular condensation of 2-methylphenylazo-arenes and -heteroarenes carrying an ortho' nucleofugal group.

The discovery,[1] made accidentally whilst comparing anhydrous hydrogen fluoride with 98% sulphuric acid[2] as a diazotisation medium for weakly-basic arylamines, that 2,4,6-trimethylphenylazo-derivatives of perfluorinated aromatic and N-heteroaromatic compounds undergo efficient intramolecular thermal dehydrofluorination to yield novel diareno-1,2-diazepines prompted us to ponder the scope of the basic synthetic stratagem defined in Scheme 1 (Nu = nucleofugal substituent). Thus, other azo-compounds necessarily encountered during the diazotisation study were heated in inert solvents. The results, while far from providing a complete delineation of the method, established beyond doubt the stratagem's importance to those involved with the synthesis of diareno-1,2-diazepines.



SCHEME 1



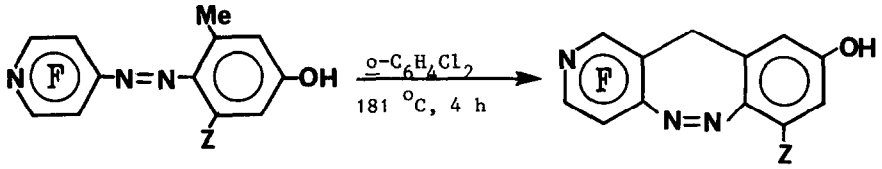
X = Y = H (75 h; 55%; 58%)
X = H, Y = Me (75 h; 52%; 33%)
X = Me, Y = H (8 h; 70%; 90%)

SCHEME 2[a]

[a] The data in parentheses refer, respectively, to duration of reactions, amount of starting material converted, and yield of product based on starting material consumed. The low yields in the cases of the azo-compounds containing only one ortho-methyl group are believed to stem from secondary reactions of the diazepines during the prolonged heating periods.

Experiments with methylated phenylazopentafluorobenzenes (see Scheme 2) showed that the presence of neither a para methyl substituent nor more than the essential ortho methyl group is a prerequisite; ring-closure does proceed faster, however, when a second ortho-methyl is present. This o,o-dimethyl effect, believed to involve conformational preferences in the azo-components, was also noted in work with fluorinated arylazo-pyridines (See Scheme 3) carried out to exemplify pre-positioning of a useful functional group where subsequent modification of a diazepine is concerned.

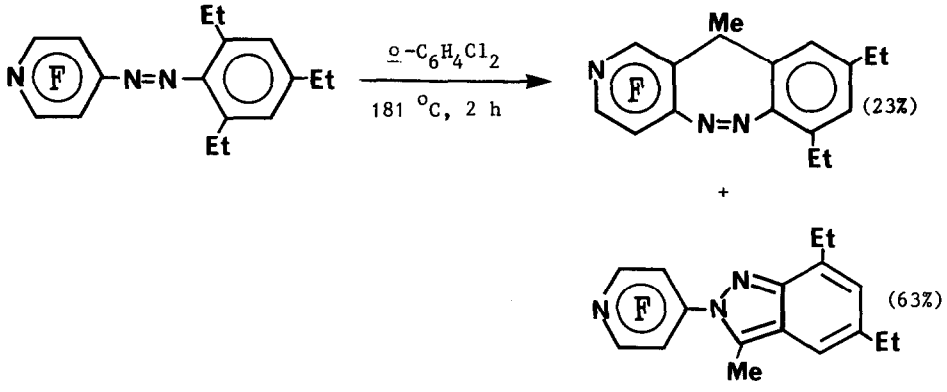
Notionally, direct formation of 11-substituted diareno-1,2-diazepines can be achieved via structural variation at essential ortho-methyl substituents of parent azo-compounds. So far, only a case where the CHRR' group of Scheme 1 is ethyl has been investigated; the reaction proceeded according to plan except that an indazole of the type



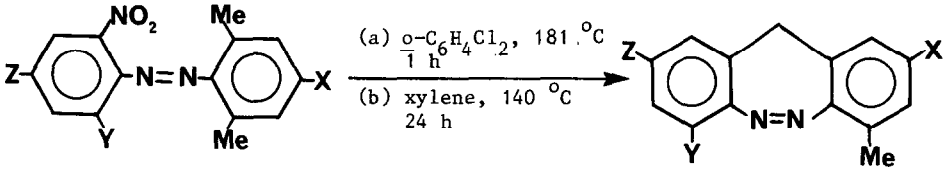
Z = H (12% conv., 72% yield)

Z = Me (46% conv., 79% yield)

SCHEME 3



SCHEME 4



(a) X = Me, Y = Br, Z = NO_2
(100% conv., 60% yield)

(b) X = OEt, Y = NO_2, Z = H
(82% conv., 88% yield)

SCHEME 5

(2-aryl-2H-indazole) procured previously by heating (2-methylphenylazo)benzenes with a nitroso-compound and sodium carbonate[3] was also formed (see Scheme 4).

The most important questions concerning the scope of the synthetic ploy outlined in Scheme 1, however, concern the identities of satisfactory nucleofuges and their structural environments (number and nature of 'auxiliary' substituents, and type of ring to which these are attached). That one can move away from perfluoroaryl or perfluoro-N-heteroaryl[1] moieties has been established (see Scheme 5), and we are continuing to probe this aspect of the work. As yet, we have been unable to effect thermal dehydrogenative ring-close of (2,4,6-trimethylphenylazo)benzene to the corresponding dibenzo-1,2-diazepine.

All the products shown in Schemes 2-5 are new compounds. Their structures were established by elemental analysis (C,H,N and, where appropriate, F) and spectroscopic measurements (i.r., u.v., n.m.r., and mass).

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