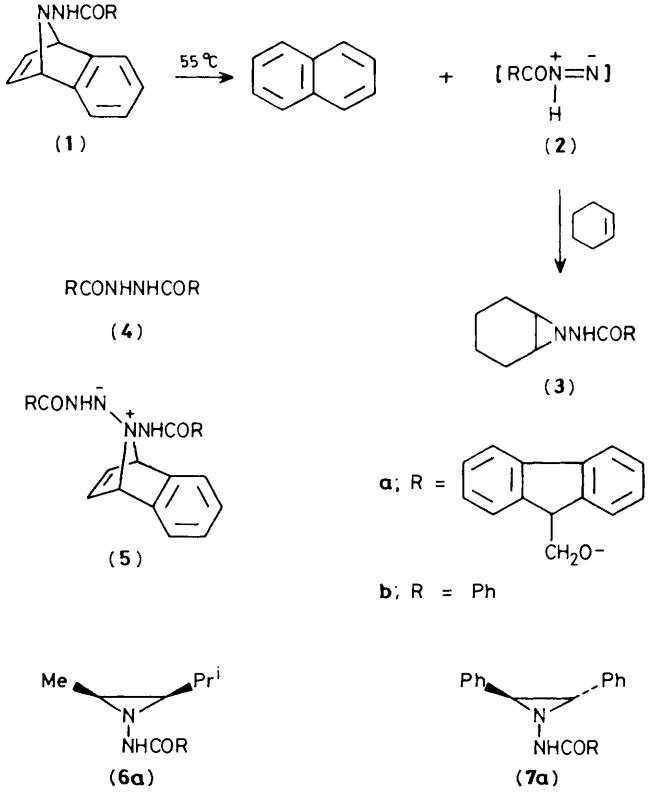
Monosubstituted Azamines. Generation and Trapping Reactions

Louis A. Carpino* and Robert E. Padykula

Department of Chemistry, University of Massachusetts, Amherst, MA 01003, U.S.A.

Thermolysis of 7-acylamino-7-azabenzonorbornadienes and 1-(acylamino)-2,3-diphenylaziridines leads to the generation of monosubstituted azamines as shown by trapping reactions.

We report the first examples of the generation and capture by olefins of monosubstituted azamines (aminonitrenes, 1,1-diazenes) (**2**). Thermolysis of (**1a**)† in cyclohexene at 55 °C led to the isolation of (**3a**) in 44% yield [(**3b**), 18%]. These results show that under these conditions (**2**) does not suffer 1,2-hydrogen migration to the corresponding monosubstituted diimide.[1] In the absence of an olefinic trapping agent the major insoluble product along with naphthalene is (**4a**)[2] (23%) or (**4b**) (35%). In the latter case the hydrazide (**4b**) is accompanied by 25% of 1-benzoyl-2-(1-naphthyl)hydrazine,[3] a product which must arise *via* simple ring-opening of the strained azabicyclic ring system. Hydrazide (**4**) may arise *via* interception of (**2**) by (**1**) to give (**5**) followed by thermolysis of



† Selected characterization data: (**1a**): ^{1}H n.m.r. ($CDCl_3$) δ 4.00—4.55 (m, 3H, $CHCH_2$), 4.70 (t, major) and 4.90 (br s, minor) [totalling 2H, bridgehead protons of two invertomers], 5.80 (br s, major) and 6.50 (br s, minor) [totalling 1H, NH of two invertomers], 6.75—7.90 (m, 14H, olefinic + aromatic), m.p. 84 °C (decomp.); (**3a**): ^{1}H n.m.r. ($CDCl_3$) δ 0.95—1.45 (br m, 4H, CH_2CH_2), 1.55—1.95 (br m, 4H, CH_2) overlapping with following peak, 1.95—2.20 (br m, 2H, CHCH) overlapping with preceding peak, 4.00—4.60 (m, 3H, $CHCH_2$), 6.30 (br s, 1H, NH), m.p. 163.5—165 °C; (**6a**): ^{1}H n.m.r. ($CDCl_3$) δ 0.90 (d, *J* 6 Hz, 3H, one Me of Pr^i), 1.10—1.75 (m, 8H, ring Me + 2nd Me of Pr^i + ring H + CH of Pr^i), 1.85—2.15 (m, 1H, ring H), 4.10—4.55 (m, 3H, $CHCH_2$), 6.20 (br s, 1H, NH), 7.15—7.90 (m, 8H, aromatic), m.p. 153—5 °C (decomp.); (**7a**): ^{1}H n.m.r. ($CDCl_3$) δ 3.55 (AB, *J* 5 Hz, 2H, CHCH), 4.00—4.50 (m, 3H, $CHCH_2$), 5.73 (br s, 1H, NH), 7.00—7.90 (m, 18H, aromatic), m.p. 99—100.5 °C (decomp.) All new compounds gave satisfactory elemental analyses.

the latter and loss of nitrogen. Even in the presence of cyclohexene, (**4b**) is the major product (47%) from (**1b**). As expected for the labile intermediacy of (**2a**), when thermolysis is conducted in *cis*-4-methylpent-3-ene only *cis*-aziridine (**6a**) is observable (*cis* : *trans* ratio >95 : 5).[4]

Novel techniques were developed for the synthesis of the 7-amino-7-azabenzonorbornadienes. The parent hydrazine (**1**; COR = H) was generated from the corresponding amine by direct amination *via* *O*-mesitylenesulphonylhydroxylamine[5] at −10 °C followed by immediate acylation with fluoren-9-ylmethyl chloroformate or benzoyl chloride. In view of the instability of the parent hydrazine it was conveniently stored as the fluoren-9-ylmethoxycarbonyl derivative (**1a**) from which the free hydrazine could be quickly regenerated by deblocking[2] *via* diethylamine in MeCN–CH_2Cl_2 at 0 °C. Although of significant theoretical interest, this route to (**2**) is somewhat tedious for preparative purposes. A more practical route involves the readily-available[6] aziridine (**7a**) which in cyclohexene (*cis*-4-methylpent-2-ene) at 55 °C for 5.5 h gives 58% (**3a**) [76%, (**6a**)].Thermolysis of the free hydrazine (**1**; COR = H) will be described separately. Schultz and co-workers[7] have reported the extrusion of azamine fragments from a variety of *N*-di-, mono-, and un-substituted 7-amino-7-azanorbornadienes. In the case of the *N*-monosubstituted derivatives, the fate of the extruded fragment was not specifically considered. The thermolysis of arenesulphenyl analogues of (**1**) was also reported recently.[8]

We thank the National Science Foundation and the American Chemical Society for support. Thanks are also due to J. G. Krause and R. Dufresne for preliminary studies on the synthesis of (**1**).

Received, 13th January 1986; Com. 053

References

1 *Cf.* A. P. Sylwester and P. B. Dervan, *J. Am. Chem. Soc.*, 1984, **106**, 4648.
2 L. A. Carpino and G. Y. Han, *J. Org. Chem.*, 1972, **37**, 3404.
3 M. Freund, *Chem. Ber.*, 1891, **24**, 4178.
4 *Cf.* T. L. Gilchrist, C. W. Rees, and E. Stanton, *J. Chem. Soc.* (*C*), 1971, 988.
5 L. A. Carpino, *J. Am. Chem. Soc.*, 1960, **82**, 3133; J. G. Krause, *Synthesis*, 1972, 140.
6 L. A. Carpino and R. K. Kirkley, *J. Am. Chem. Soc.*, 1970, **92**, 1784; D. Felix, R. K. Muller, U. Horn, R. Joos, J. Schreiber, and A. Eschenmoser, *Helv. Chim. Acta*, 1972, **55**, 1276.
7 A. G. Schultz and M. Shen, *Tetrahedron Lett.*, 1979, 2969; A. G. Schultz, M. Shen, and R. Ravichandran, *ibid.*, 1981, 1767; M. Shen and A. G. Schultz, *ibid.*, 1981, 3347.
8 R. S. Atkinson, M. Lee, and J. R. Malpass, *J. Chem. Soc., Chem. Commun.*, 1984, 919.