

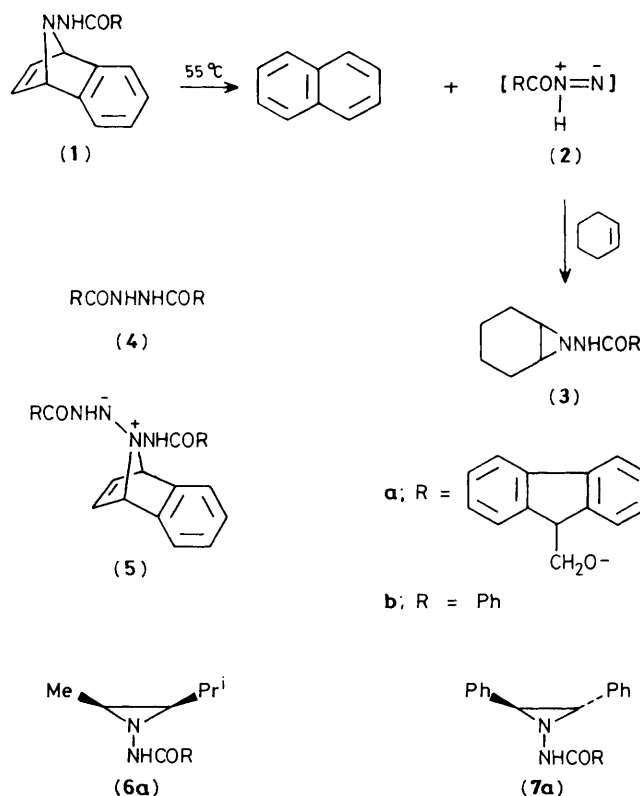
## Monosubstituted Azamines. Generation and Trapping Reactions

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)<sup>†</sup> 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.<sup>1</sup> In the absence of an olefinic trapping agent the major insoluble product along with naphthalene is (4a)<sup>2</sup> (23%) or (4b) (35%). In the latter case the hydrazide (4b) is accompanied by 25% of 1-benzoyl-2-(1-naphthyl)hydrazine,<sup>3</sup> 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



<sup>†</sup> Selected characterization data: (1a): <sup>1</sup>H n.m.r. (CDCl<sub>3</sub>) δ 4.00—4.55 (m, 3H, CHCH<sub>2</sub>), 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): <sup>1</sup>H n.m.r. (CDCl<sub>3</sub>) δ 0.95—1.45 (br m, 4H, CH<sub>2</sub>CH<sub>2</sub>), 1.55—1.95 (br m, 4H, CH<sub>2</sub>) overlapping with following peak, 1.95—2.20 (br m, 2H, CHCH) overlapping with preceding peak, 4.00—4.60 (m, 3H, CHCH<sub>2</sub>), 6.30 (br s, 1H, NH), m.p. 163.5—165 °C; (6a): <sup>1</sup>H n.m.r. (CDCl<sub>3</sub>) δ 0.90 (d, J 6 Hz, 3H, one Me of Pr<sup>i</sup>), 1.10—1.75 (m, 8H, ring Me + 2nd Me of Pr<sup>i</sup> + ring H + CH of Pr<sup>i</sup>), 1.85—2.15 (m, 1H, ring H), 4.10—4.55 (m, 3H, CHCH<sub>2</sub>), 6.20 (br s, 1H, NH), 7.15—7.90 (m, 8H, aromatic), m.p. 153—5 °C (decomp.); (7a): <sup>1</sup>H n.m.r. (CDCl<sub>3</sub>) δ 3.55 (AB, J 5 Hz, 2H, CHCH), 4.00—4.50 (m, 3H, CHCH<sub>2</sub>), 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).<sup>4</sup>

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<sup>5</sup> 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<sup>2</sup> *via* diethylamine in MeCN-CH<sub>2</sub>Cl<sub>2</sub> 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<sup>6</sup> 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<sup>7</sup> 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.<sup>8</sup>

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