## A Novel Synthesis of Diarylacetylenes from N-Arylmethylheteroarenes and N-Arylmethyleneanilines

Martino Paventi, Edmund Elce, Rebecca J. Jackman and Allan S. Hay\*

Department of Chemistry, McGill University, 801 Sherbrooke St. W., Montreal, Quebec, Canada H3A 2K6

ABSTRACT: Aromatic enamines and diarylacetylenes may be obtained in a novel one-step synthesis involving the condensation of N-arylmethyl heterocycles with aromatic imines in the presence of a strong base. The enamines are isolable intermediates on the route to diarylacetylenes via the elimination of the nitrogen heterocycle.

In dimethylformamide (DMF) in the presence of excess potassium *tert*-butoxide (*t*-BuOK) at 75°C 1*H*-benzylbenzotriazole (1a) reacts with N-phenylmethyleneaniline (2) to yield diphenylacetylene (3), benzotriazole (4a), and aniline (5). Under the same conditions 1*H*-benzylbenzimidazole (1b) and 1*H*-benzyltriazole (1c) also give 3 as the product however the reactions are much slower requiring 5 hours

and 30 minutes, respectively (eq 1). Isolated yields of 3 from the reaction of 1a,b with 2 are around 75 % whereas the yield from 1c and 2 is considerably lower (11%). The heterocycles 4 are readily alkylated with benzyl chloride by heating under reflux equimolar (0.6 mol) quantities of the heterocycle and benzyl chloride in acetonitrile (200 mL) with  $K_2CO_3$  (0.12 mol) for 1h (compound 4b required 3h with 0.4 mol  $K_2CO_3$ ). Reaction of benzyl chloride with 4a,c gives mixtures of 1H- and 2H-isomers in a ratio of about 75:25 (cf ref 1). The mixtures were filtered hot, acetonitrile was removed, and the residues were recrystallized giving, in most cases, the pure and more polar 1H-isomer. The 2H-isomers react in a similar manner to the 1H-isomers and the isomeric mixture may be used in the preparation of the acetylenes. The imine 2 is prepared from benzaldehyde and aniline and since the amines are recovered in the reaction the net result is a new synthesis of diarylacetylenes from arylmethyl halides and araldehydes (eq 2).

$$Ar_1CH_2X + Ar_2 + HX + H_2O$$
 $X = CI, Br$ 
(2)

We have recently shown that N-arylmethyleneanilines react with the methylene groups of tertiary amines to give enamines in the presence of t-BuOK or other strong bases. In the presence of a weaker base or an equimolar amount of t-BuOK the aralkylated heterocycles 1a-c react with an equimolar amount of 2 to give the enamines 7. The enamines can be reacted with 3 equiv of t-BuOK in DMF to give

acetylenes in circa 85% yield by elimination of the heterocycle (eq 3).

1 + 2 
$$\frac{t - \text{BuOK (1 equiv)}}{\text{DMF, 75°C}}$$
  $Y = X$  Ph  $\frac{t - \text{BuOK (3 equiv)}}{\text{DMF, 75°C}}$  3 + 4

Table 1 lists diarylacetylenes that have been prepared by this method.

Table 1. Diarylacetylenes

6	Ar <sub>1</sub>	Ar <sub>2</sub>	Yield <sup>a</sup> (%)	mp <sup>b</sup> (lit mp <sup>3</sup> ) (°C/mmHg)
a	Ph	Ph	75	59-61 (58-61)
b	Ph	4-MeOPh	67	57-8 (58-60)
c	Ph	1-naphthyl	88	51-3 (oil)
d	1-naphthyl	l-naphthyl	67	129 (127-8)
e	2-naphthyl	2-naphthyl	76	225-6 (228-9)
f	4-FPh	4-FPh	50	95-6 (94-5)
Q	3-FPh	3-FPh	30	60-2 (61-2)
g h	Ph	3-pyridyl	80	47-8 (47-8.5)
i	Ph	2-furanyl	90°	oil (74/0.01)

<sup>&</sup>lt;sup>a</sup>After chromatography (PE). <sup>b</sup>Solid recrystallized from MeOH unless stated otherwise. <sup>c</sup>98.5% pure by HPLC. <sup>1</sup>H and <sup>13</sup>C NMR are consistent with its structure.

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## References and Notes

- 1. Claramunt, R. M.; Elguero, J.; Garceran, R. Heterocycles 1985, 23, 2895-2906.
- 2. Paventi, M.; Hay, A. S. Tetrahedron Lett. 1991, 32, 1617-1620.
- 3. 6a: Stephens, R. D.; Casto, C. E. J. Org. Chem. 1963, 28, 3313-3315; 6b: Katritzky, A. R.; Boulton, A. J.; Short, D. J. J. Chem. Soc. 1960, 1519-1523; 6c: Dessy, R. E.; Kandil, S. A. J. Org. Chem. 1965, 30, 3857-3860; 6d,e: Nakasuji, K.; Akiyama, S.; Akashi, K.; Nakagawa, M. Bull. Chem. Soc. Jpn. 1970, 43, 3567-3576; 6f: Gascoyne, J. M.; Mitchell, P. J.; Phillips, L. J. Chem. Soc., Perkin Trans. 2 1977, 1051-1057; 6g: Carpino, L. A.; Chen, H.-W. J. Am. Chem. Soc. 1979, 101, 390-394; 6h: Castro, C. E.; Gaughan, E. J.; Owsley, D. C. J. Org. Chem. 1966, 31, 4071-4078; 6i: Teitei, T.; Collin, P. J.; Sasse, W. H. F. Aust. J. Chem. 1972, 25, 171-182.

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