Tetrahedron Letters, Vol.27, No.6, pp 703-704, 1986 0040-4039/86 $3.00 + .00
Printed in Great Britain

DIENAMINES AS DIELS-ALDER DIENES. A NOVEL BENZANNULATION SEQUENCE.

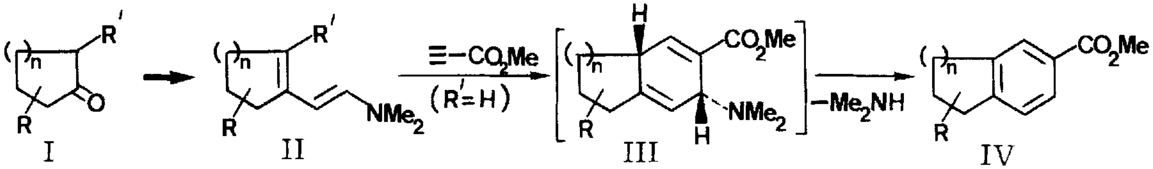
Roger L. Snowden* and Manfred Wüst

Firmenich SA, Research Laboratories, 1211 Geneva 8, Switzerland

Abstract: Diels-Alder reaction between (E)-dienamines 1 - 7 and methyl propiolate followed by elimination of Me_2NH from the intermediate cycloadducts III affords the aromatic methyl esters 8 - 14 in good yield.

The preceding Letter[1] describes an efficient sequence for the cyclohexannulation of cycloalkanones I using, as the key step, a *Diels-Alder* reaction between (E)-dienamines II and methyl acrylate. We now report an analogous benzannulation sequence, I → IV[2], which involves the regioselective [4+2]cycloaddition of II (R'=H) with methyl propiolate and subsequent elimination of Me_2NH from the intermediate cycloadduct III[3] (*cf. Scheme*). Accordingly, reaction of dienamines 1 - 7 with methyl propiolate (1.5 mole equiv.) in toluene (10% solution) at 25° or 50° (*cf. Table*) followed by treatment with silica gel at 60° during 2 h afforded the methyl esters 8 - 14 in good yield. This one-pot procedure thus allows the efficient construction of aromatic carboxylic esters IV from (E)-dienamines II with complete regiochemical control[4].

Scheme



References and Notes

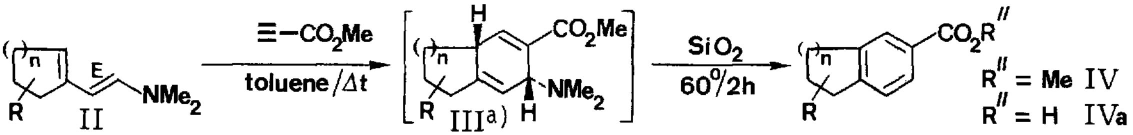
[1] See preceding paper.

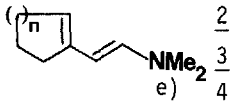
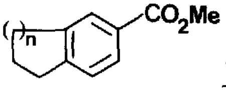
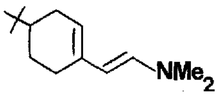
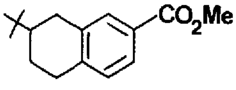
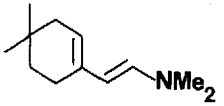
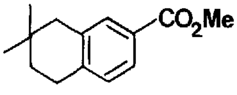
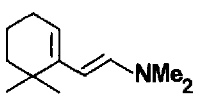
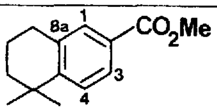
[2] For examples of previous benzannulation methods, see: J.B.Dickenson & W.Reusch, *Syn.Comm.* 13(4), 303 (1983); M.A.Tius & A.Thurkauf, *J.Org.Chem.*48, 3839 (1983); D.L.Boger & M.D.Mullican, *Tetrahedron Lett.*24, 4939 (1983); K.Takaki, M.Ohsugi, M.Okada, M.Yasumura & K.Negoro, *J.Chem.Soc. Perkin I*, 741 (1984); G.Singh, H.Ila & H.Junjappa, *Tetrahedron Lett.* 25, 5095 (1984); R.K.Dieker & Y.J.Lin, *ibid* 26, 39 (1985) and references cited therein..

[3] For an analogous *Diels-Alder* reaction of acyclic dienamines, see: S.Tanimoto, Y.Matsumura, T.Sugimoto & M.Okano, *Tetrahedron Lett.*, 2899 (1977).

[4] The influence of the dimethylamino group on the rate and regioselectivity of the *Diels-Alder*

Table

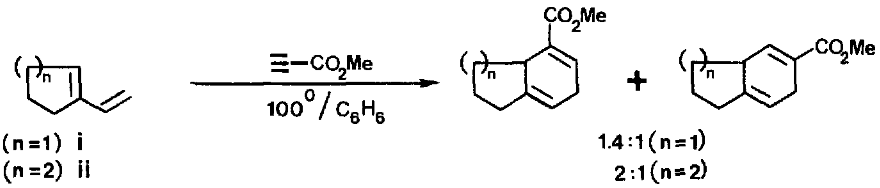


Entry	b) DIENAMINE		D.-A. React. Cond.	PRODUCT c)		Yield d) %	IVa m.p.(°C)
1		1 (n=1)	25°/5h		8[8] (n=1)	89	180 - 182°[5]
2		2 (n=2)	25°/24h		9[6] (n=2)	76	152 - 153°[6]
3		3 (n=3)	25°/5h		10 (n=3)	78	174 - 175°[7]
4		e) 4 (n=8)	50°/24h		(m.p. 113-5°) 11 (n=8)	52	181 - 182°
5		5	50°/5h		12	81	203 - 205°
6		6	50°/24h		13	83	144 - 146°
7		7	25°/24h		14 (m.p. 31-3°)	82	179 - 181°

a) The presumed stereochemistry of III is consistent with the ^{1}H-NMR(360 MHz, CDCl$_3$) spectral data, e.g. entry 7: δ1.06, 1.15 (2 *s*, CH$_3$); 1.00 - 2.10 (6 H); 2.24 (*s*, N(CH$_3$)$_2$); 2.88 (*m*, H-C(8a)); 3.76 (*s*, CO$_2$CH$_3$); 4.21 (*dd*, *J* = 4, 4 Hz, H-C(3)); 5.54 (*d*, *J* = 4 Hz, H-C(4)); 6.82 (*d*, *J* = 4 Hz, H-C(1)); b) for the preparations of 1, 2, 3, 6 and 7 *cf.* reference 1; 4 and 5 were prepared from cyclododecanone and 4-*t* butylcyclohexanone resp. (*cf.* Method A[1]); c) all new compounds have been fully characterised spectroscopically *e.g.* 14: IR(film): 1718, 1284, 1196, 762 cm^{-1}; UV(EtOH): λmax. 242 (ε 13,700); ^{1}H-NMR(CDCl$_3$): δ1.30 (*s*, 6 H); 1.60 - 1.90 (4 H); 2.81 (*t*, *J* = 7 Hz, 2 H); 3.89 (*s*, 3 H); 7.38 (*d*, *J* = 8 Hz, H-C(4)); 7.74 (br.*s*, H-C(1)); 7.78 (br.*d*, *J* = 8 Hz, H-C(3)); MS: 218 (19, M$^+$), 203 (100), 171 (25), 144 (15), 129 (18); d) yields refer to chromatographically pure, distilled products; e) 1:1 mixture of E/Z-1'-cyclododecenyl double bond isomers

---

reactions of 1 and 2 is demonstrated by comparison with the dienes i and ii, see: J.H.Markgraf, E.W.Greeno, M.D.Miller, W.J.Zaks & G.A.Lee, *Tetrahedron Lett.* 24, 241 (1983).



[5] J.Lindner, F.Schmitt & B.Zaunbauer, *Monatsh.* 72, 216 (1939).
[6] M.S.Newman & H.V.Zahm, *J.Am.Chem.Soc.* 65, 1097 (1943).
[7] R.H.Wightman, D.E.Laycock & H.W.Avdovich, *J.Org.Chem.* 43, 2167 (1978).
[8] I.M.Hunsberger, D.Lednicer, H.Girtowsky, D.Bunker & P.Taussig, *J.Am.Chem.Soc.* 2466 (1955).

(Received in France 5 December 1985)