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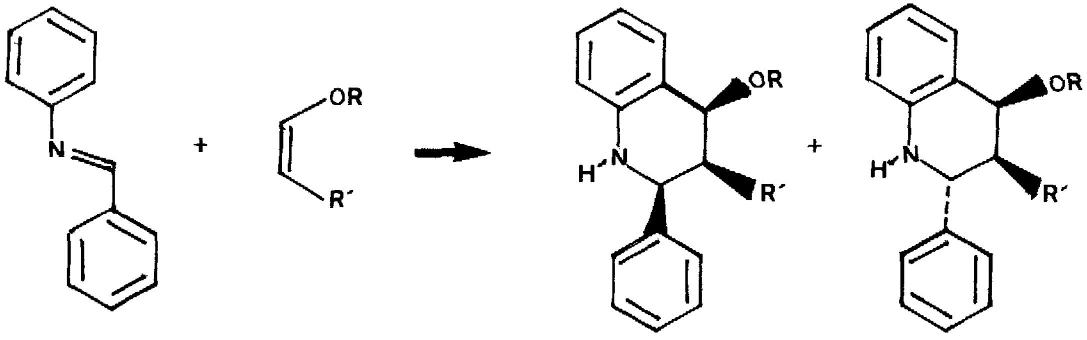
PRODUCT DISTRIBUTION IN DIELS-ALDER ADDITION OF N-BENZYLIDENE ANILINE AND ENOL ETHERS

Jose Cabral and Pierre Laszlo*
Laboratoire de chimie fine, biomimétique, et aux interfaces
Ecole Polytechnique, 91128 Palaiseau, France.

Abstract : The two diastereomeric products, all cis, and trans phenyl, form in highly variable ratio (up to a factor 20), depending on the conditions.

The cycloaddition of N-benzylidene aniline 1 and electron-rich Z vinyl ethers 2 produces the two stereoisomers 3[1] and 4[2,3].



1 2 3 4

While the overall yield is in the range 10-90%, the product distribution depends very much on the conditions (Table).

Reaction conditions import more than substrate structure (entries 9 and 10). The presence of an additional protic source, t-butanol or trifluoroacetic acid, increases significantly the yield enhances the **3**/**4** ratio, in the presence of the K10/Fe^{3+} catalyst[1] (entries 8-10). The best overall yield is achieved with ferric chloride as catalyst and with trifluoroacetic acid as an adjunct (entry 2). By comparison, the heterogeneous K10/Fe^{3+} catalyst decreases the yield somewhat, but improves the selective formation of the all-cis stereoisomer **3** (entries 2 and 9). The Bauld catalyst[4], as an inducer of radical cation formation, does not have a major effect : its influence is compared (entries 1 and 4) with that of a tertiary amine as a free radical trap. The presence of the radical chain carrier tributyltin hydride appears to inhibit the reaction (entries 5 and 6). These results are consistent with two-step ionic mechanisms[5], possibly in concurrence with the concerted pathway. As indicated here, (entries 8-12), the earlier observation of the exclusive formation of the endo adduct 3 in ether[5] must be considered as fortuitous.

Run n°.	Temp.°C	time	solvent	catalyst, mol.eq.	co-factor, mol.eq.	3,%	4,%	3/4
1	25	48	methylene chloride	ferric chloride(0.1)	DABCO[a](0.1)	46,8	24,9	1.9
2	25	71	"	ferric chloride(0.1)	CF_3CO_2H(0.05)	45.1	45.0	1.0
3	25	71	"	-	CF_3CO_2H(0.05)	11.1	56.3	0.2
4	25	4	"	ferric chloride(0.05)	$(BrC_6H_4)_3NSbCl_6$ (0.05)	54.0	33.1	1.6
5	25	48	"	ferric chloride(0.05)	nBu_3SnH(0.05)	18.0	12.0	1.5
6	25	48	"	-	nBu_3SnH(0.05)	12.0	-	-
7	25	2	"	-	$(BrC_6H_4)_3NSbCl_6$ (0.05)	17.0	13.0	1.3
8	37	15	diethyl ether	K10/Fe^{3+} [b]	tBuOH(0.1)	63.4	19.6	3.2
9	37	21	"	"	CF_3CO_2H(0.05)	58.2	16.1	3.6
10[c]	37	21	"	"	CF_3CO_2H(0.05)	55.5	14.5	3.8
11	37	24	"	"	NEt_3(0.1)	19.2	14.1	1.4
12	37	17	"	"	tBuOH(0.1) + NEt_3(0.1)	9.5	-	-
13	78	17	acetonitrile	"	4-tBu-C_6H_4OH(0.1)	50.2	36.1	1.4

[a] diaza-1,4-bicyclo(2.2.2)octane [b] ferric chloride exchange [c] dihydrofuran as dienophile

Table. Cycloadditions Between N-Benzylidene Aniline and Dihydropyran.

References

1. J. Cabral, P. Laszlo, and M.T. Montaufier, Tetrahedron Lett., 29, 547-550.
2. T.L. Gilchrist and A.M. Stannard, Tetrahedron Lett., 29, 3585-3586 (1988).
3. a) We retract the (2+2) structure that we had proposed incorrectly[1]. The presence of an NH resonance[2] had escaped us. The original spectrum (^1H nmr) recorded on too small a sample, did not show this key feature, buried in the noise.
   b) 4 : (pmr, acetone-d_6)δ : 5.26 (bs, 1H, NH); 4.63 (d, 1H, C-2); 4.34 (d, 1H, C-4); ca. 3.92 (dm, 1H); 3.65 (d.t, 1H); 7.4-6.6 (m, 9H, ArH); 1.8-1.4 (cm, 5H); J(Hz) : $J_{2,3}$ = 10.22; $J_{3,4}$ = 2.86
   (cmr, $CDCl_3$) δ : 146.5 (quat.C); 144.06 (quat.C); 131.54; 129.28; 128.64; 128.36; 121.61 (quat.C); 117.00; 114.84; 75.05 (CH); 68.36 (CH_2); 55.8 (CH); 40.0 (CH); 24.97 (CH_2); 23.15 (CH_2).
   Other spectral features as in ref. (1).
4. N.L. Bauld, D.J. Belleville, B. Harirchian, K.T. Lorenz, R.A. Pabon, Jr., D.W. Reynolds, D.D. Wirth, H-S. Chiou, B.K. Marsh, Accounts Chem. Res., 20, 371-378 (1987).
5. T. Kametani, H. Takeda, Y. Suzuki, and T. Honda, Synth. Comm., 15, 499 (1985).

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