

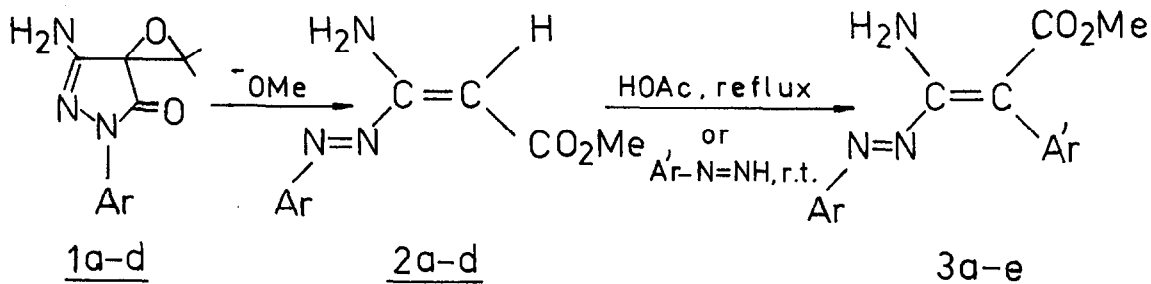
SURPRISING REACTIONS OF SPECIAL AZOOLEFINS - SELF-ARYLATION, INDOLE RING CLOSURE, MILD CHLORINE SUBSTITUTION, AND "TERT. AMINO EFFECT"

K. Kirschke*, A. Möller, E. Schmitz, R. J. Kuban and B. Schulz

Central Institute of Organic Chemistry (K.K., A.M., E.S.) and Central Institute of Physical Chemistry (R.J.K., B.S.) of the Academy of Sciences of the GDR, DDR-1199 Berlin
 German Democratic Republic

Abstract: Azoolefins 2 either decompose or react with aryldiimines with uptake of an aryl group to give compounds 3. The latter can undergo ring closure to *N*-amino-indoles 4. In the 2,4,6-trichloro compound 3b ortho-chlorines are selectively replaced by morpholine under very mild conditions giving 5a, which easily fragments to form the benzimidazole 7.

Spiro-epoxides of the type 1 react with methoxide to form azoolefins 2. On decomposition of 2 in acidic media aryldiimines have been trapped by benzaldehyde and further decomposition products of aryldiimines identified^{1,2}.

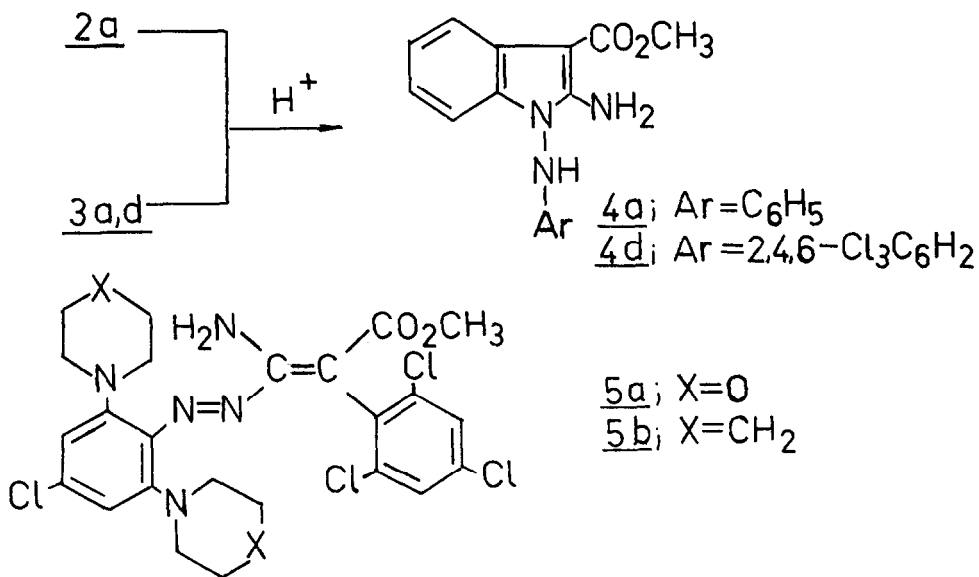


1,2 Ar: a=C₆H₅, b=2,4,6-Cl₃C₆H₂, c=2,5-Cl₂C₆H₃, d=4-NO₂C₆H₄

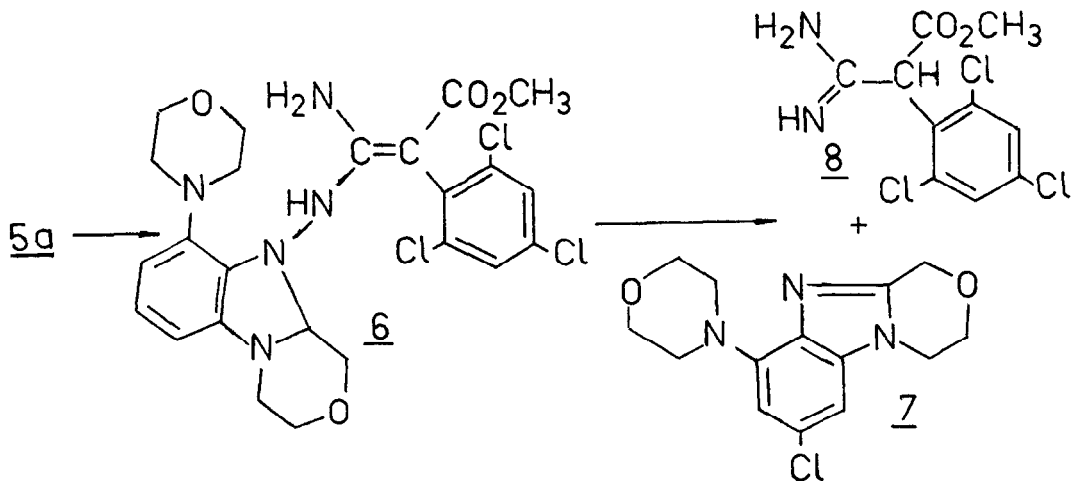
<u>3</u>	<u>a</u>	<u>b</u>	<u>c</u>	<u>d</u>	<u>e</u>
Ar	C ₆ H ₅	2,4,6-Cl ₃ C ₆ H ₂	2,5-Cl ₂ C ₆ H ₃	2,4,6-Cl ₃ C ₆ H ₂	2,4,6-Cl ₃ C ₆ H ₂
Ar'	C ₆ H ₅	2,4,6-Cl ₃ C ₆ H ₂	2,5-Cl ₂ C ₆ H ₃	C ₆ H ₅	4-NO ₂ -C ₆ H ₄

In anhydrous acetic acid³ a new azo compound 3b is formed from 2b with uptake of an aryl group. The same arylation yields 3a - e when azo compounds 2 are reacted with aryldiimine, formed in situ by saponification of aryl-benzoyl-diazene^{4,5}. Details are given in the Table. An arylation by aryl radicals is plausible. An *E*-configuration of 3 is indicated by

X-ray analysis of 3a. In boiling acetic acid 2a forms the N-amino-indole 4a. The reaction proceeds via the arylation step to give 3a, which subsequently cyclizes to 4a, since in another experiment 4a is obtained from 3a under the same conditions. The compound 3d reacts analogously to form 4d by action of acids^{6,7}.

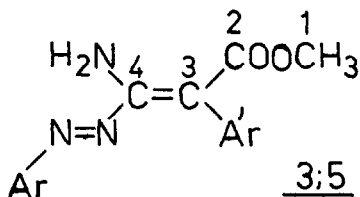


Two ortho-chlorine atoms in 3b are unexpectedly mobile and are replaced by morpholine and by piperidine even at room temperature, the para-chlorines being untouched, leading to 5a and 5b, respectively⁸. Cleavage of the N=N-double bond of 5a to 7 and 8 takes place on attempted recrystallization from ethyl acetate. The empirical formula of 7 and 8 add up to the empirical



Comp.	Yield %	M.p. °C (crystallizing)	Spectroscopic data ^{x)}
<u>3a</u>	51 ⁵	115 - 7 (EtOH)	δ_{H} : 3,74(s,3H), 6,90(s,2H), 7,27-7,62(m,10H); δ_{C} : 51,6(C-1), 170,6(C-2), 107,2(C-3), 157,2(C-4)
<u>3b</u>	22 ³	196 - 8 (EtOH)	δ_{H} : 3,69(s,3H), 6,80(s,2H), 7,25(s,2H), 7,28(s,2H); δ_{C} : 52,0(C-1), 168,6(C-2), 103,3(C-3), 157,3(C-4); λ_{max} (MeOH) 417(log ϵ : 3,92)
<u>3c</u>	5 ³	134 - 6 (iPrOH)	δ_{H} : 3,72(s,3H), 6,85(s,2H), 7,00-7,44(m,6H); m/z: 417/419/421/423, 419(53%), 382(65), 244(100)
<u>3d</u>	58 ⁵	158 - 9 (MeOH)	δ_{H} : 3,74(s,3H), 6,80(s,2H), 7,22-7,29(m,7H); δ_{C} : 51,9(C-1), 170,6(C-2), 110,2(C-3), 157,2(C-4)
<u>3e</u>	57 ⁵	198 - 9 (MeOH)	δ_{H} : 3,76(s,3H), 6,92(s,2H), 7,32(s,2H), 7,73(4H, $J_{\text{A,B}}$ 8Hz); δ_{C} : 52,1(C-1), 169,4(C-2), 107,6(C-3), 157,1(C-4)
<u>4a</u>	10 ³ 90 ⁶	211 - 3 (Toluene)	δ_{H} : 3,69(s,3H), 6,65(s,2H), 6,33-7,55(m,9H), 8,84(s,1H); m/z: 281(40%), 189(55), 157(100), 93(59)
<u>4d</u>	90	210 - 2 (iPrOH)	δ_{H} : 3,84(s,3H), 6,31(s,2H), 6,52-7,74(m,6H), 7,26(s,2H); m/z: 383/385/387/389, 383(11%), 189(79), 157(100)
<u>5a</u>	83	157 (EtOH)	δ_{H} : 2,87(m,8H), 3,56(m,8H), 6,50(s,2H), 7,34(s,2H); δ_{C} : 51,4(C-1), 169,1(C-2), 96,3(C-3), 159,8(C-4); λ_{max} (MeOH) 444(log ϵ : 3,15)
<u>5b</u>	31	154 - 6 (EtOH)	δ_{H} : 1,50(m,12H), 282(m,8H), 3,60(s,3H), 6,23(s,2H), 7,32(s,2H); m/z: 583/585/587/589
<u>6</u>	5	208 - 9 (Toluene)	m/z: 587/589/591/593, 589(8%), 294(100)
<u>7</u>	70	236 - 7 (EtOAc)	δ_{H} : 3,41-3,50(m,4H), 3,84-3,92(m,6H), 4,02-4,17(m,2H), 4,92(s,2H), 6,54(d,1H, J 2Hz), 6,85(d,1H, J 2Hz); m/z: 293/295, 293(36%), 259(100)
<u>8</u>		213 - 5 (Benzene)	m/z: 294/296/298/300, 294(48%), 259(100)

x) ¹H-NMR: 100MHz, HMDS, CDCl₃ (3a-e, 4d, 5a, b, 7), DMSO-d₆ (4a), ¹³C-NMR: CFT-20 Varian, CDCl₃; all elemental analyses are correct (±0,3%)



formula of 5a. A benzimidazole structure could be assigned to 7 on the basis of spectral data (Table), and the amidine structure 8 to the second product. An intermediate 6 is formed when the decomposition of 5a is carried out in ethanol^{9,10}.

The smooth formation of the cyclization product 6 is explained by an 1,5-H-shift based on the so-called "tert. amino effect"¹⁰.

References and Notes:

- 1) K.Kirschke, A.Möller, and E.Schmitz, *J.Prakt.Chem.* **327**,893(1985).
- 2) 2d was prepared analogously to lit.¹: Yield 49 %, m.p. 122-4 °C, ¹H-NMR (100 MHz, CDCl₃,HMDS): 3,76(s,3H), 5,74(s,1H), 6,40(s,2H), 7,95 and 8,33 (J_{A,B}9,5 Hz).
- 3) 2b (32 mmol) in acetic acid (20 ml) was heated under reflux for 45 min. 3b crystallized on cooling. 2c was converted to 3c analogously and isolated by addition of water, extraction with ether, evaporation and extraction of the residue with petroleum ether (Table).
- 4) H.Bock, E.Baltin, and J.Kroner, *Chem.Ber.* **99**,3337(1966).
- 5) Aryl-benzoyl-diazene (30 mmol) was added in portions to a boiling solution of 2 (5 mmol) and 1M-NaOMe (3 ml) in methanol (50 ml). After 0.5 h the solvent was distilled off, methyl benzoate was removed by steam distillation under slightly reduced pressure, the residue was extracted with ether to yield 3 on filtration and evaporation (Table).
- 6) 3a or 3d (2 mmol) was boiled in acetic acid (20 ml) for 10 min. Dilution with water, extraction with ethyl acetate, evaporation and recrystallization yielded 4.
- 7) H.H.Wasserman and H.R.Nettleton, *Tetrahedron Letters* **1960**,33.
- 8) 3b (2 mmol) was dissolved in morpholine (5 ml) or piperidine (5 ml). After 1 h at room temperature the solution was diluted with ether, extracted with 2M-HCl and then with water and concentrated (Table).
- 9) 5a (1.7 mmol) was boiled in ethanol for 1 h and stored overnight. Crystallization gave > 5 % 6. The filtrate was concentrated and the residue recrystallized from ethyl acetate to give 7 (70 %). 8 was isolated from the mother liquor (Table). 6 was cleaved by a small amount of concentrated HCl to 7 and 8.
- 10) M.Verboom, M.R.J.Hamzik, D.N.Reinhoudt and R.Visser, *Tetrahedron Letters* **1984**,4308; O.Meth-Cohn and H.Suschitzky, *Adv. in Heterocyclic Chemistry* **14**,212(1972).

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