ACIDIC ALUMINA- AND $BF_3 \cdot OEt_2$-INDUCED REACTIONS OF 1,2-DIPHENYL-1-AZASPIRO[2.2]PENTANE[1]

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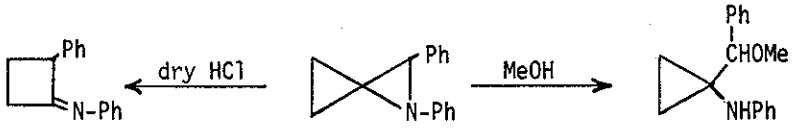
The acidic alumina-induced reaction of 1,2-diphenyl-1-azaspiro-[2.2]pentane (1) afforded 3-phenylindoline-2-spirocyclopropane (2) and 1-anilino-1-hydroxybenzylcyclopropane (3). On treatment with diethyl azodicarboxylate 3 was converted to 2-benzoylquinoline (4). Under the influence of $BF_3 \cdot OEt_2$ 1 gave 2 and a dimer of 1, 1,3,4,6-tetraphenylpiperidine-2,5-bispirocyclopropane (6).

Crandall and Conover[2] have recently reported on the preparation and some chemical properties of the highly strained 1-phenyl-1-azaspiro[2.2]pentanes. 1,2-Diphenylazaspiropentane 1 undergoes two types of reactions under protonic conditions; ring expansion to cyclobutanone anil and the peripheral C-N bond fission of aziridine ring with methanol to anilinocyclopropane derivative.



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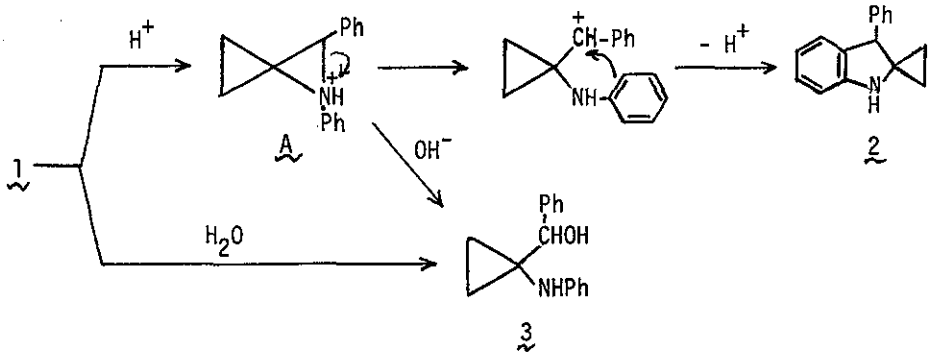
In this communication we wish to report on the acidic alumina- and $BF_3 \cdot OEt_2$

-induced reactions of azaspiropentane 1 which revealed a new type of isomerization of 1.

A solution of azaspiropentane 1 in benzene was allowed to remain over a column of acidic alumina (grade III) (1/alumina=1/80 (wt/wt)) for 2 hr. The eluate of benzene gave 3-phenylindoline-2-spirocyclopropane (2) in 24% yield, and the eluate of benzene-chloroform (3:1) gave 1-anilino-1-hydroxybenzylcyclopropane (3) in 35% yield. Structural elucidation of 2 and 3 was accomplished on the basis of spectral data.[3]

2: reddish yellow oil; ir (neat) 3400 cm^{-1} (NH); nmr (CCl_4) δ 0.5-1.0 (4H, m, cyclopropyl CH_2), 3.55 (1H, br, NH, exchanged with D_2O), 4.75 (1H, s, $\geq CH$), 6.6-7.3 (9H, m, aromatic protons); mass spectrum m/e 221 (M^+).

3: yellow oil; ir (neat) 3580 (OH), 3400 cm^{-1} (NH); nmr (CCl_4) δ 0.5-1.0 (4H, m, cyclopropyl CH_2), 3.75 (2H, br, NH and OH, exchanged with D_2O), 4.85 (1H, s, $\geq CH$), 6.6-7.3 (10H, m, aromatic protons); mass spectrum m/e 239 (M^+).

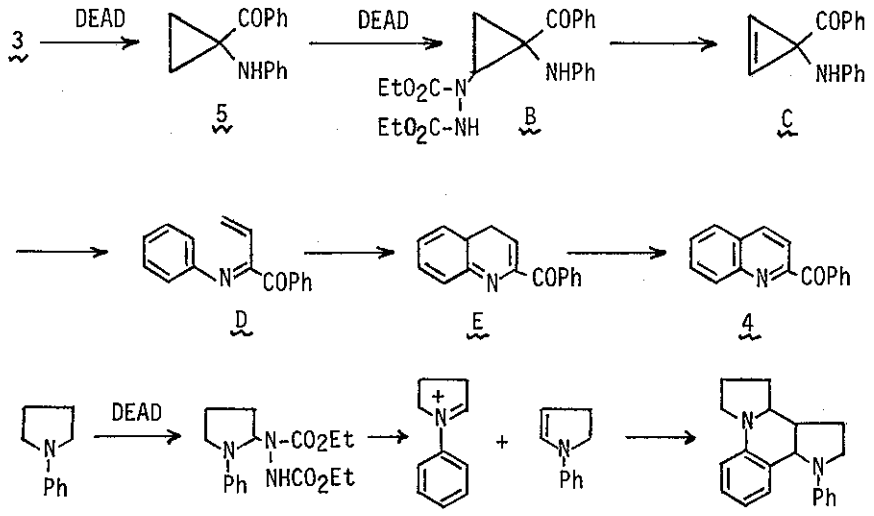


Scheme 1

Compound 2 might form via a protonated intermediate A, followed by ring opening and subsequent cyclization with concurrent deprotonation as shown in Scheme 1. The formation of 3 can be interpreted by the peripheral C-N bond fission of aziridine ring with water or by the attack of hydroxide ion on A

with concurrent ring opening.

Treatment of 3 with diethyl azodicarboxylate (DEAD) in boiling benzene for 10 hr afforded 2-benzoylquinoline (4) in 54% yield [4: mp 110-111°C (lit.[4] mp 111°C); ir (KBr) 1660 cm^{-1} (CO); mass spectrum m/e 233 (M^+)]. A plausible pathway for the formation of 4 is illustrated in Scheme 2. 1-Anilino-1-benzoylcyclopropane (5) and then cyclopropene intermediate C are formed by dehydrogenation with DEAD. Subsequent ring opening of C yields a diene intermediate D which undergoes an electrocyclic reaction to give E. Dehydrogenation of E gives the final product 4. This pathway is supported by the following evidence. Treatment of 3 with pyridine 1-oxide in boiling benzene for 8 hr gave 5, mp 142-143°C, in 10% yield [5: ir (KBr) 3400 (NH), 1660 cm^{-1} (CO); nmr ($CDCl_3$) δ 1.22, 1.73 (each 2H, m, cyclopropyl CH_2), 4.52 (1H, br, NH, exchanged with D_2O), 6.5-7.9 (10H, m, aromatic protons); mass spectrum m/e 237 (M^+), 236, 132 (M^+ - PhCO)]. When 5 was heated with DEAD in boiling benzene for 6 hr, 4 was obtained in 60%

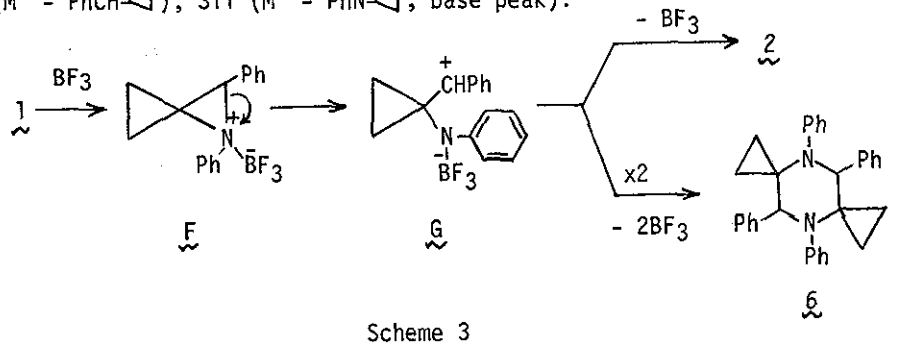


DEAD: diethyl azodicarboxylate

Scheme 2

yield. A good analogy exists for this type of reaction in the interaction of 1-phenylpyrrolidine and DEAD to form the adduct which on thermolysis forms a mixture of isomeric dimers of 1-phenylpyrroline (Scheme 2).[5]

When azaspiropentane 1 was treated with 0.5 molar $BF_3 \cdot OEt_2$ in ethyl ether at 0°C, under nitrogen for 1 hr, 2 and a dimer 6 were obtained in 45 and 5% yields respectively. The same reaction at room temperature for 18 hr resulted only in the formation of 2 in 63% yield. On the basis of spectral data, the dimer was assigned to be 1,3,4,6-tetraphenylpiperidine-2,5-bispirocyclopropane (6). 6: mp 293-295°C; nmr ($CDCl_3$) δ 0.57-1.58 (8H, m, cyclopropyl CH_2), 5.28 (2H, s, ≥CH), 6.5-7.4 (20H, m, aromatic protons); mass spectrum m/e 442 (M^+), 312 (M^+ - PhCH=◁), 311 (M^+ - PhN=◁, base peak).



Scheme 3

The potential pathway for the formation of 2 and 6 is depicted in Scheme 3. In analogy with the above alumina-induced reaction, 2 would be formed via G, which was generated by ring opening of complex F. Dimerization of G with concurrent elimination of BF_3 would give dimer 6.

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Received, 2nd October, 1976