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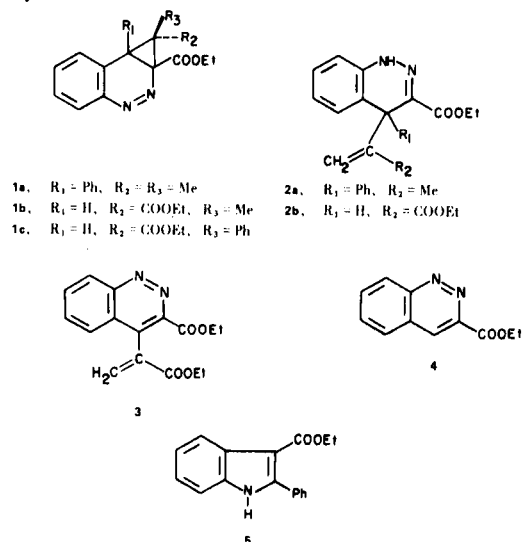
Heating of **1a, b** in boiling xylene resulted in the rearranged products **2a, b**, probably through concerted ring cleavage and 1,5-hydrogen shift. Under the same conditions, **1c** reacted slowly to give a mixture from which the fragmentation products **4** and **5** were obtained.

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While thermal and photo induced reactions of diazonorcaradienes have been the object of extensive investigation (1-3), there is no report on the behaviour of the corresponding benzo fused derivatives. Since 1a,7b-dihydro-1H-cyclopropa[c]cinnolines (4,5-diaza-2,3-benzonorcaradienes) have been shown to be accessible starting from properly *ortho*-substituted phenylhydrazoyl chlorides (4), we were interested in possible rearrangements of this new class of strained molecules. The present communication deals with the results obtained by heating compounds **1a-c** in an inert solvent.

Compounds **1a, b** underwent in boiling xylene a rather clean rearrangement reaction leading to the 1,4-dihydrocinnoline derivatives **2a, b** in 64 and 60% yield respectively. The structures of the products are consistent with elemental analyses, molecular weights determined by mass spectrometry, and ir and nmr spectra (see Experimental). Treatment of **2b** with palladised charcoal afforded the aromatised compound **3**, thus providing chemical support to the assigned structure.

Contrary to what was observed in the case of **1a, b**, compound **1c** reacted very slowly in boiling xylene to originate a complex, tarry mixture, from which the chromatographic separation gave **4** (28%) and **5** (7%) as the only characterizable products. The latter compounds were identified on comparison of their physical and spectral data with those of authentic samples prepared by independent synthesis.



The results so far described appear to be of interest and merit some comments.

The formation of **2a, b**, which involves opening of the cyclopropane ring and 1,5-hydrogen shift from carbon to heteroatom, can be related to the known thermal isomerization of 1-acyl-2-methylcyclopropanes to γ -enones (5). In the present case, the electron withdrawing character of the -N=N- group probably facilitates the observed rearrangement. A concerted mechanism is plausible in view of the molecular geometry of the substrates, both of which possess a methyl group in the *endo* position. The absence of a suitable hydrogen for the migration in compound **1c** may prevent a similar reaction, accounting for the much greater stability of **1c** in comparison with **1a, b**. Actually, this lack of reactivity is a strong argument against a stepwise mechanism for the formation of **2a, b**, in which ring cleavage is prior to the hydrogen transfer (6).

Little can be said about the fragmentation processes occurring when **1c** is heated for a prolonged time. The one leading to **4** could be formulated as a reverse cheletropic reaction, which is well preceded in the photochemistry of 2,3-benzonorcaradienes (7-9).

EXPERIMENTAL

Melting points were taken on a Büchi apparatus and are uncorrected. Nmr spectra were recorded on a Varian A-60A instrument in deuteriochloroform solution with tetramethylsilane as internal standard. Ir spectra were obtained on a Perkin-Elmer Model 377 spectrophotometer. Mass spectra were determined on a Varian MAT 112 spectrometer at 70 eV.

Compounds **1a-c** were prepared as previously reported (4).

Thermal Reaction of **1a**.

A solution of **1a** (0.14 g.) in dry xylene (18 ml.) was refluxed for 6 hours. The solvent was removed under reduced pressure and the residue was recrystallized from light petroleum to afford 3-carbethoxy-4-phenyl-4-(propen-2-yl)-1,4-dihydrocinnoline (**2a**) (0.090 g.), m.p. 169°; ir (Nujol): 3300 (NH) and 1710 cm^{-1} (CO); nmr: δ 1.22 (3H, t, CH_2CH_3), 1.82 (3H, s, CH_3), 4.23 (2H, q, CH_2CH_3), 4.67, 5.25 (1H each, signals with long range coupling, $\text{CH}_2=$), 6.75-7.45 (9H, m, aromatics), 8.7 (1H, broad s, NH); ms: m/e (relative intensity) 320 (4.5%), 280 (21), 279 (100), 251 (17), 243 (7), 206 (20).

Anal. Calcd. for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_2$: C, 74.97; H, 6.29; N, 8.74. Found: C, 74.91; H, 6.10; N, 8.80.

Thermal Reaction of **1b**.

A solution of **1b** (0.25 g.) in dry xylene (30 ml.) was refluxed

for 8 hours. Evaporation of the solvent under reduced pressure and recrystallization from diisopropyl ether gave 3-carbethoxy-4-(1-carbethoxyvinyl)-1,4-dihydrocinnoline (**2b**) (0.15 g.), m.p. 83°; ir (Nujol): 3320 (NH) and 1725 cm⁻¹ (CO); nmr: δ 1.30, 1.35 (6H, two t, CH₂CH₃), 4.24, 4.33 (4H, two q, CH₂CH₃), 5.32, 5.51, 6.24 (1H each, signals with long range coupling, CH₂=C-CH-), 6.7-7.5 (4H, m, aromatics), 8.8 (1H, broad s, NH); ms: m/e (relative intensity) 302 (13%), 273 (4), 256 (12), 228 (23), 203 (11), 200 (29), 199 (100), 175 (21), 155 (28).

Anal. Calcd. for C₁₆H₁₈N₂O₄: C, 63.56; H, 6.00; N, 9.27. Found: C, 63.32; H, 6.04; N, 9.00.

Thermal Reaction of **1c**.

A solution of **1c** (2.0 g.) in dry xylene (220 ml.) was refluxed for 120 hours. The solvent was removed under reduced pressure and the residue was adsorbed on a silica gel column (200 g.). Elution with light petroleum-diethyl ether 5/1 gave **4** (0.32 g.) and **5** (0.10 g.) as the only characterizable products. Both compounds **4** and **5** showed melting points and nmr spectra identical with those of authentic samples prepared as follows

3-Carbethoxycinnoline (**4**).

This compound was prepared according to the literature method (10); m.p. 96° (lit. 97-97.5°); nmr: δ 1.53 (3H, t, CH₂CH₃), 4.60 (2H, q, CH₂CH₃), 7.7-8.8 (5H, m, aromatics).

3-Carbethoxy-2-phenylindole (**5**).

A solution of 2-phenylindole (2.0 g.) in anhydrous ether (10 ml.) was added dropwise to an ethereal solution of methylmagnesium iodide prepared from 0.32 g. of magnesium and 1.85 g. of methyl iodide. Ethyl chloroformate (1.30 g.) in anhydrous ether (10 ml.) was then added dropwise under stirring and ice-cooling. The mixture was stirred for 90 minutes at room temperature, poured into 5% aqueous hydrochloric acid, and extracted with ether. The organic solution was dried over sodium sulphate, the solvent evaporated, and the residue chromatographed on a silica gel column (100 g.) with light petroleum-diethyl ether 1/1 as eluent to give **5** (1.4 g.), m.p. 152-153° [lit. (11) 153-155°]; nmr: δ 1.26 (3H, t, CH₂CH₃), 4.24 (2H, q, CH₂CH₃), 7.1-8.3 (9H, m, aromatics), 8.8 (1H, broad s, NH).

Treatment of **2b** with Palladised Charcoal.

A solution of **2b** (0.16 g.) in dry xylene (15 ml.) was treated with 5% palladised charcoal (0.10 g.) and refluxed for 30 hours. The catalyst was filtered off and the solution was evaporated under reduced pressure. Recrystallization of the residue from diisopropyl ether gave 3-carbethoxy-4-(1-carbethoxyvinyl)cinnoline (**3**) (0.085 g.), yellow crystals m.p. 69°; ir (Nujol): 1725 cm⁻¹ (CO); nmr: δ 1.18, 1.44 (6H, two t, CH₂CH₃), 4.21, 4.50 (4H, two q, CH₂CH₃), 5.79, 6.91 (1H each, two d, J ca. 1 Hz, CH₂=), 7.7-8.7 (4H, m, aromatics).

Anal. Calcd. for C₁₆H₁₆N₂O₄: C, 63.99; H, 5.37; N, 9.33. Found: C, 63.61; H, 5.18; N, 9.34.

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