A Synthesis of the Indano-[1,2-b]aziridine System

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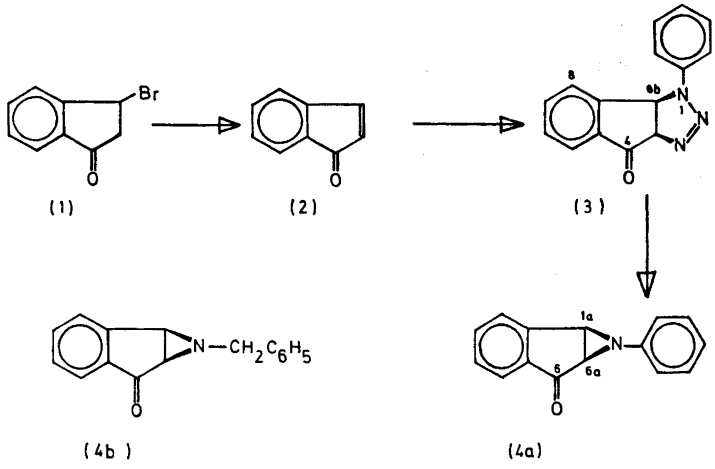
Recently we have reported a synthesis of 1-benzyl-indano[1,2-b]aziridin-6-one (*4b*) for comparison of properties with those of its valence isomeric isoquinolinium-4-oxide.[1] For further studies we required a more convenient synthetic approach to the indano[1,2-b]aziridin-6-one system and a such synthesis is reported in this paper. The key intermediate in the synthesis is an indano[2,1-d]triazoline such as (3) in the scheme below as it is well established that Δ^2-1,2,3-triazolines can be converted photochemically or pyrolytically to aziridines.[2]

This approach requires easy access to indenone (*2*). The older syntheses were deemed less suitable [3-5] while the recent synthesis [6] by reductive acetylation of indane-1,3-dione followed by sodium carbonate treatment proved difficult in larger scale preparations. Slight modifications [1] in the reported [7] procedure for free radical bromination of indanone, however, made 3-bromoindanone (*1*) readily available and therefore suitable as a starting material. HBr elimination from (*1*) was achieved by means of trimethylamine. The use of a tertiary amine prevents Michael addition to the indenone formed, and the relatively low basicity does not initiate polymerisation of the highly reactive indenone molecule. By this procedure (*2*) was obtained in 55 % overall yield from indanone.

Formation of the indano[2,1-d]triazoline (*3*) was thought difficult because of the polymerisation tendency of the indenone molecule. Running the reaction between (*2*) and phenylazide at 0°C in the dark for 3 days, however, gave preparatively a homogeneous product (TLC) with expected spectral properties. Aryl azides react with dipolarophiles according to a concerted 1,3-dipolar cycloaddition mechanism [2,8,9] and a *cis*-adduct is therefore formed from indenone. With unsymmetrically substituted electrophilic double bonds the cycloaddition is regioselective giving a product in agreement with the orientation based on electronic effects [8,10] but a *gem*-substituent to the electron withdrawing group might upset the regioselectivity.[8,11] In the absence of a such *gem*-substituent addition of aryl azides to simple α,β-unsaturated carbonyl compounds and nitriles gives a Δ^2-1,2,3-triazoline which carries the electron withdrawing group in the 4-position.[8,10,11] By analogy the product from indenone is assigned structure (*3*). Triazolines containing an electron withdrawing group in the 4-position are frequently unstable or exist in an equilibrium with the isomeric amino-azo compound.[8,10,11] No such difficulties were experienced from the indenone adduct.



Scheme 1.

Photolysis of (*3*) gave preparatively a homogeneous product with spectral properties in accordance with the desired aziridine. For the photochemical transformation the cold reaction flask was externally illuminated by a 300 watt lamp. Pyrolysis of (*3*) in boiling xylene gave a more heterogeneous product.

The mass spectrum shows characteristic features as reported for (*4b*). The alicyclic indanyl protons in NMR ($CDCl_3$) appear as doublets at 6.62 and 6.09 τ ($J = 3.5$ Hz), the values being similar to those of (*4b*). The lower field signal is a broadened doublet which means that this proton is involved in long-range interannular coupling ($J < 0.5$ Hz) with an aromatic indanyl proton.[12] In the triazoline (*3*) a corresponding broadened doublet is seen at 4.28 τ, the other methine doublet being at 4.54 τ ($J = 9.7$ Hz). The broadened doublets are therefore ascribed to the alicyclic indanyl protons in β-position to the carbonyl group. Since the triazoline (*3*) is thermally unstable its mass spectrum was found to be similar to that of (*4a*).

Experimental. The NMR spectra were recorded on a Varian A-60A spectrophotometer.

Indenone (2). Indanone (10.6 g, 0.08 mol) was brominated by means of *N*-bromosuccinimide as previously described[1] and the crude product dissolved in ether (100 ml). Trimethylamine (11.8 g, 0.20 mol) was added dropwise to the stirred ethereal bromoindanone solution at 0°C. After about 2 h at 0°C the precipitated salt was filtered off, the filtrate evaporated and the residual oil distilled; yield 5.7 g (55 %), b.p. 40–42°C/0.1 mmHg. (Lit.[6] b.p. 61–63°C/0.9 mmHg.)

1-Phenylindano[2,1-d]triazolin-4-one (3). Indenone (2.6 g, 0.02 mol) and phenylazide[13] (2.4 g, 0.02 mol) were mixed and left at 0°C in the dark for 3 days. The original liquid solution had then solidified. The solid was crystallized from chloroform; yield 3.5 g (70 %), m.p. 132°C (decomp.). (Found: C 72.51; H 4.80. Calc. for $C_{15}H_{11}N_3O$: C 72.13; H 4.44.) NMR ($CDCl_3$): 4.54 τ ($H^{3a}(H\alpha)$, d., $J = 9.7$ Hz), 4.28 τ ($H^{3b}(H\beta)$, broadened d.), 2.1–2.8 τ (H-arom., m.). IR (KBr) 1725 cm^{-1} (CO).

1-Phenylindano[1,2-b]aziridin-6-one (4a). *Photolysis:* The triazoline (*3*) (0.9 g, 0.0036 mol) was dissolved in benzene (50 ml) and the solution water-cooled by means of a "cold-finger" immersed in the solution during the illumination. The light source was a 300 watt Philips HP 3202 UV lamp which was placed about 10 cm away from the reaction flask. The illumination was stopped when the evolution of nitrogen had almost ceased (3/4–1 h). The solution was then evaporated at reduced pressure without heating. The residual oil was crystallized from hexane; yield 0.5 g (65 %), m.p. 92°C. (Found: C 81.65; H 5.02. Calc. for $C_{15}H_{11}NO$: C 81.43; H 5.01.) NMR ($CDCl_3$): 6.62 τ ($H^{6a}(H\alpha)$, d, $J = 3.5$ Hz), 6.09 τ ($H^{1a}(H\beta)$, broadened d.), 2.4–3.4 τ (H-arom., m.). IR (Br) 1725 cm^{-1} (CO).

Pyrolysis: Pyrolysis of (*3*) in refluxing xylene gave a heterogeneous product from which (*4a*) was isolated after silica gel column chromatography. The title compound was eluated with hexane:EtOAc (2:1).

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