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MOBILE KETO ALLYL SYSTEMS. II.[1] REACTIONS OF 3-BROMO-2-BENZAL-1-INDANONE WITH AMINES

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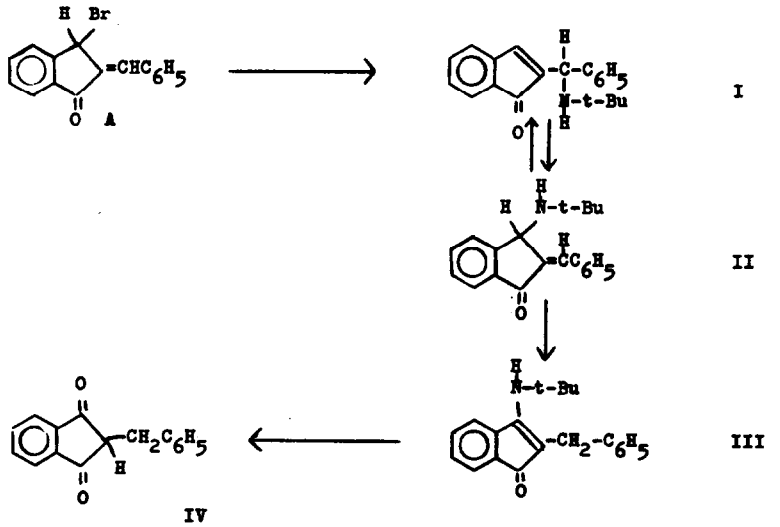
In a previous article[2] it was reported that the allyl system in 3-bromo-2-benzal-1-indanone reacted with secondary amines (piperidine and morpholine) and the primary amine, cyclohexylamine, in the absence of solvent to produce the direct substitution products, the 3-[substituted amino]-2-benzal-1-indanones. A more extensive investigation of these reactions in aprotic solvents and rearrangement-equilibrium studies with the products has now revealed that both aminotropic and prototropic changes in this keto allylamine system take place with ease.



The reaction of two molar equivalents of t-butylamine with 3-bromo-2-benzal-1-indanone (A) in benzene solution at 25°C. gave 2-(α-t-butylaminobenzyl)-1-indenone (I), a product in which the allyl system has been inverted. When the bromide (A) was allowed to react for twenty-four hours with ten equivalents of this primary amine in benzene solution at 25°C, an 81% yield of the non-rearranged product, 3-(t-butylamino)-2-benzal-1-indanone (II) was obtained. It seems probably that II resulted from the rearrangement of the first formed I since such conversion is readily accomplished when I is stored at room temperature with t-butylamine in benzene solution. When I reacted with amine for twenty hours, actually both aminotropic and prototropic changes occured. The components of the resulting mixture were identified by an NMR spectrum as having the following approximate composition.

$$\text{I (29 \%)} \rightleftarrows \text{II (56 \%)} \rightleftarrows \text{III (15 \%)}$$

Treatment of 3-t-butylamino-2-benzal-1-indanone (II) with excess t-butylamine in benzene solution at 25°C for seventy-three hours gave a mixture of 60% of rearranged isomer, 3-t-butylamino-2-benzyl-1-indenone (III), and 40% of unreacted starting material II. When aminoketone II was refluxed with an excess amount of t-butylamine in benzene solution for six and one-half hours, the resulting crude mixture as analysed by its NMR spectrum was indicated to contain 3-t-butylamino-2-benzyl-1-indenone (III) (51%), 2-(α-t-butylaminobenzyl)-1-indenone (I) (18%), and unreacted aminoketone II (31%).

Ultraviolet and infrared spectra, as well as NMR spectra were used to confirm the structural assignments of the aminoketone isomers. The structure of the enaminketone III was further supported by acid hydrolysis to the known 2-benzyl-1,3-indandione (IV)[3].

The UV spectrum (isooctane) of I, m.p. 83-85°, showed λmax. 238, 244 mμ (ε, 41,470, 42,930). The IR spectrum showed νc=o (CCl_4), 1715 cm.$^{-1}$ (V.S.), νAr, 1610cm. (M.). The NMR spectrum (CCl_4) showed nine aromatic protons and the vinylic proton represented by a multiplet in the range 2.42-3.25τ, a benzyl proton as a doublet at 5.20τ (J=0.5 c.p.s.) and ten protons of the t-butylamino group as a singlet at 8.95τ.

Anal. Calcd. for $C_{20}H_{21}NO$: C, 82.44; H, 7.26; N, 4.52. Found: C, 82.00; H, 7.24; N, 4.81.

The UV spectrum (isooctane) of II, m.p. 91-94°, showed λmax. 238, 245 (sh), 310 mμ (ε, 14.400, 13,600, 24,200). The IR spectrum showed νNH (CCl_4), 3380 cm.$^{-1}$ (W); νc=o, 1705 cm.$^{-1}$ (V.S.); νc=c, 1631 cm.$^{-1}$ (S); νAr, 1607 cm.$^{-1}$ (M). The NMR spectrum (CCl_4) showed one methine proton as a doublet at 4.63τ (J=2 c.p.s.), ten protons of the t-butylamino group as a singlet at 9.11τ, ten protons of aromatic and vinylic type in the range 2.0-2.76τ.

Anal. Calcd. for $C_{20}H_{21}NO$: C, 82.44; H, 7.26; N, 4.52. Found: C, 82.12; H, 7.22; N, 4.66.

The UV spectrum (methanol) of III, m.p. 145-147°, showed λ max. 218, 255 (sh), 264, 312 (sh), 430 mμ (broad band), (ε, 15.500, 18,200, 20,000, 1,200, 1,900). The IR spectrum ($CHCl_3$) showed νNH, 3450 cm.$^{-1}$ (W); νc=o, 1670 cm.$^{-1}$ (S); νAr, 1608 cm.$^{-1}$ (S). The NMR spectrum ($CDCl_3$) showed two benzyl protons as a singlet at 6.33τ, ten protons of t-butylamino group as a singlet at 8.62τ, and nine aromatic protons in the range 2.50-2.84τ.

Anal. Calcd. for $C_{20}H_{21}NO$: C, 82.44; H, 7.26; N, 4.52. Found: C, 82.54; H, 7.54; N, 4.81.

The UV spectrum of IV, m.p. 104-105° (lit. m.p. 95-97°)[3], showed λmax. (isooctane) 222, 233, 240 mμ (ϵ, 12,800, 2,880, 3,120). The IR spectrum showed γc=o (CCl_4), 1745 cm.$^{-1}$ (S), 1710 cm.$^{-1}$ (V.S.), and a broad band in the range 1600-1500 cm.$^{-1}$. The NMR spectrum (CCl_4) showed five aromatic protons at 2.90τ, four aromatic protons in the range 2.03-2.42τ, and three protons as a multiplet at 6.7τ.

Anal. Calcd. for $C_{16}H_{12}O_2$; C, 81.31; H, 5.08. Found: C, 81.38 H, 5.08.

The initial reaction of 3-bromo-2-benzal-1-indanone with t-butylamine in benzene probably proceeds by an abnormal bi-molecular substitution (SN2') to produce I. The conversion of I by t-butylamine to the thermodynamically favored II undoubtedly involves a bimolecular, intermolecular aminotropic rearrangement. The prototropic rearrangement of II to the highly conjugated β-amino-α, β-unsaturated ketone III is energetically favored since III is thermodynamically the most stable of the three isomeric t-butylamino ketones.

In the earlier investigation of the β-keto allyl system in α-bromo-methyl chalcone an abnormal substitution with t-butylamine was also observed. The kinetically favored α-t-butylaminobenzylacrylophenone readily underwent either an intra or intermolecular aminotropic rearrangement to produce the thermodynamically favored α-[t-butylaminomethyl]-chalcone, depending on the presence or absence of excess t-butylamine.

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