Photoenolization of Some Photochromic Ketones. The Scope and Mechanism of the Reaction

K. R. Huffman, M. Loy, and Edwin F. Ullman

The text below was inadvertently omitted from the end of the Experimental Section of the article published on pp. 5417–5423 (1965).

3-Benzoyl-2-(phenylsulfonylmethyl)chromone (*XVIII*). The crude oily bromo derivative (0.34 g.) and 0.21 g. of sodium benzenesulfinate dihydrate were mixed in 15 ml. of acetone and refluxed for 2 hr. The filtered solution was evaporated to an oil which crystallized on addition of ether to give 0.14 g. of white crystals, m.p. 172–177°. After one recrystallization from ethanol–water the melting point was 175–178° (see Table I).

3-Benzoyl-2-benzyl-4(1H)-quinolone (*XIX*). Ethyl 4-phenylacetoacetate[40] was converted to ethyl 3-anilino-4-phenylcrotonate by the literature method.[41]

To a cold, stirred suspension of 4.8 g. of sodium hydride (50% dispersion in mineral oil) in 80 ml. of toluene was added dropwise a solution of 28.1 g. (0.10 mole) of ethyl 3-anilino-4-phenylcrotonate in 125 ml. of toluene. After the addition, stirring was continued for 4 hr. and 14.1 g. (0.10 mole) of benzoyl chloride in 25 ml. of toluene was added dropwise. The mixture was heated on the steam bath with stirring for 2 hr. and then allowed to stand overnight. Dilute hydrochloric acid was added and the toluene layer was separated and washed with saturated sodium bicarbonate solution and then with water. The solution was dried over magnesium sulfate and evaporated. Addition of ether caused crystallization of some benzanilide, which was removed by filtration. The filtrate was evaporated and the residual oil was extracted several times with boiling petroleum ether. The combined extracts were then evaporated to give the desired *ethyl 3-anilino-2-benzoyl-4-phenylcrotonate* as a crude oil.

The above oil was added with stirring to 250 ml. of diphenyl ether which had been preheated to 230° in an oil bath. The solution was then refluxed for 15 min., allowed to cool, and diluted with petroleum ether. The residual gum was crystallized with methanol and then recrystallized from dilute ethanol to give 9.0 g. (27%) of the quinolone, m.p. 258–261°.

Anal. Calcd. for $C_{23}H_{17}NO_2$: C, 81.39; H, 5.05; N, 4.13. Found: C, 81.30; H, 5.21; N, 4.46.

3-Benzoyl-2-benzyl-1-methyl-4(1H)-quinolone (*XXI*). Powdered 3-benzoyl-2-benzyl-4(1H)-quinolone (2.10 g., 0.0062 mole) was added to a solution of 0.0062 mole of sodium methoxide in 25 ml. of methanol under nitrogen and the mixture was stirred for about 1 hr. until a clear solution had formed. The solvent was then removed *in vacuo*, dry 1,2-dimethoxyethane was added, and the solution again was evaporated to dryness *in vacuo* to remove any residual methanol.

The resulting sodium salt then was dissolved in 25 ml. of dry 1,2-dimethoxyethane, and this solution was added dropwise with stirring under nitrogen to 8 ml. of iodomethane in 20 ml. of dimethoxyethane at 60°. The solution was refluxed for 1 hr. and evaporated to dryness. The residue was taken up in benzene and filtered to remove the inorganic salt which was washed with several portions of fresh benzene. The combined benzene solutions were evaporated and the oily residue was crystallized from ethanol to give 1.65 g. (75%) of colorless prisms, m.p. 177–178°.

Anal. Calcd. for $C_{24}H_{19}NO_2$: C, 81.56, H, 5.42; N, 3.96; mol. wt., 353. Found: C, 80.22, 80.48; H, 5.35, 5.39; N, 4.32; *m/e* (parent), 353.

Despite consistently low carbon analyses the n.m.r. spectrum showed signals corresponding to aromatic H (multiplet τ 1.46–2.76), CH_2 (τ 5.88), and NCH_3 (τ 6.40) with integral ratios very close to the theoretical 14:2:3. The mass spectrum confirms the empirical formula.

3-Benzoyl-2-(1-phenylethyl)-1-methyl-4(1H)-quinolone (*XXII*). A suspension of 2.0 g. (0.0059 mole) of 3-benzoyl-2-benzyl-4(1H)-quinolone in 75 ml. of dry 1,2-dimethoxyethane was added dropwise to a stirred suspension of 0.65 g. (0.0135 mole) of 50% sodium hydride dispersion in 25 ml. of the same solvent. The mixture was stirred for 1 hr. under nitrogen. About 4 ml. of iodomethane was added and the mixture was refluxed for 2 hr. and then evaporated *in vacuo*. The resulting solid was triturated once with petroleum ether and once with water and then recrystallized twice from methanol–water using charcoal to give 1.0 g. (46%) of colorless solid, m.p. 171–172°.

Anal. Calcd. for $C_{25}H_{21}NO_2$: C, 81.72; H, 5.76; N, 3.81; mol. wt., 367. Found: C, 81.02, 81.09; H, 5.78, 5.82; N, 3.95, 4.21; *m/e* (parent), 367.

Despite consistently low carbon analyses, the n.m.r. integrals for aromatic H (τ 1.48–2.71), *t*-H (τ 5.51, quartet), NCH_3 (τ 6.58, singlet), and CCH_3 (τ 8.23, doublet) were very close to the theoretical 14:1:3:3 ratio. The mass spectrum confirms the empirical formula.

3-Benzoyl-2-benzyl-4-methoxyquinolone (*XX*). A suspension of 0.50 g. of 3-benzoyl-2-benzyl-4(1H)-quinolone (XIX) in 75 ml. of methanol was stirred magnetically in an ice bath while an excess of ethereal diazomethane was added slowly. The mixture was stirred in an open flask overnight and the resulting colorless solution was evaporated. Addition of ether caused crystallization of 0.15 g. of starting material which was removed by filtration. The ethereal filtrate was evaporated and the residual oil was crystallized from ethanol to give 0.15 g. of XX, m.p. 92.5–93.5°. Recrystallization from ethanol raised the melting point to 93–94°.

Anal. Calcd. for $C_{24}H_{19}NO_2$: C, 81.56; H, 5.42; N, 3.96. Found: C, 81.62; H, 5.65; N, 4.21.

Acknowledgment. We are indebted to Dr. J. E. Lancaster and Mrs. M. Neglia for the n.m.r. spectra, to Mr. T. E. Mead for mass spectral measurements and to Dr. J. Deonarine and his staff for microanalyses.

---

(40) G. W. Anderson, I. F. Halverstadt, W. H. Miller, and R. O. Roblin, *J. Am. Chem. Soc.*, **67**, 2197 (1945).

(41) A. K. Kiang, F. G. Mann, A. F. Prior, and A. Topham, *J. Chem. Soc.*, 1319 (1956).