Arynic Condensation of αβ-Unsaturated Ketone Enolates

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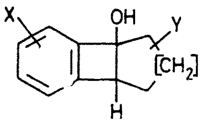
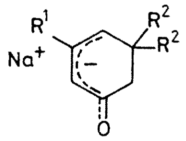
Summary Condensation of αβ-unsaturated ketone enolates with benzyne leads to the new type of cyclobutanols (**3**); ring opening of (**3**) under basic conditions affords the aromatic ketones (**4**) in good yields (75—85%).

We have previously shown[1] that the condensation of ketone enolates with arynes provides a useful method for the synthesis of benzocyclobutenols (**1**).

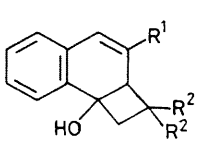
We report here that the αβ-unsaturated ketone enolates (**2**) behave quite differently. Condensation of (**2**) with benzyne (generated from bromobenzene and $NaNH_2$ or $NaNH_2$–Bu^tONa[1]) led, among other products, to the unexpected alcohols (**3**).†



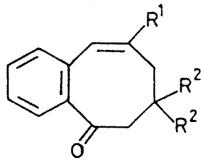
(1)



(2)



(3)



(4)

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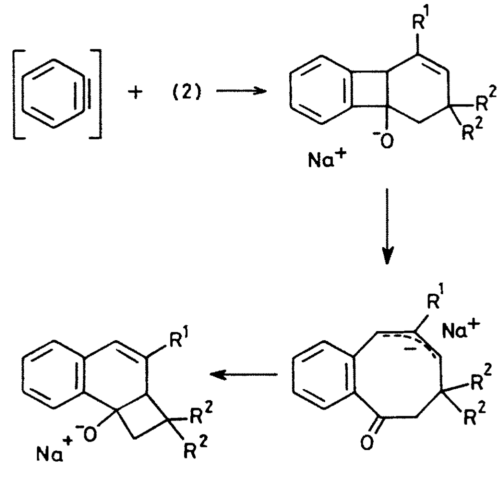
† Satisfactory elemental analyses have been obtained for all compounds (**3**) and (**4**).

Cpds. (2)—(4)	R^1	R^2	% Yield (3) [from PhBr]	% Yield (4) [from (3)]
a	Me	Me	30	85
b	OEt	H	37	75
c	OEt	Me	50	80
d	SEt	Me	20	85

Typically, isophorone (25 mmol) in tetrahydrofuran (THF) was added to the complex base[1] NaNH$_2$ (75 mmol)–Bu^{t}ONa (25 mmol) in THF (30 ml) under nitrogen. The mixture was stirred for 2 h at 45 °C and bromobenzene (1·25 mmol) was added. After 4 h at 45 °C, the mixture was cooled, poured on to ice, extracted with diethyl ether, and dried over MgSO$_4$. The solvent was removed *in vacuo* and the residual oil chromatographed on silica gel column to yield (**3a**)† (30% yield from PhBr), homogeneous by t.l.c. and g.l.c. The structure of (**3a**) was assigned on the basis of its spectroscopic properties:‡ ν (film): 3340—3400 (OH) and 1650 cm^{-1} (C=C). Its u.v. spectrum [λ_{max} (EtOH) (log ε): 304sh (3·06), 293sh (3·27), 276sh (3·78), 267 (3·86), and 258sh nm (3·80)] is quite different from the previously reported[2] spectra of benzocyclobutenols (**1**), and exhibited characteristic absorptions of β-alkyl substituted dihydronaphthalenes.[3] Its n.m.r. spectrum [δ (CCl$_4$): 0·70 (3H, s, Me), 1·27 (3H, s, Me), 1·77 (3H, br.s, vinylic Me), 2·02—2·58 (3H, m, CH$_2$ and OH), 2·67 (1H, br.s, allylic H), 6·11 (1H, br.s, vinylic H), and 6·8—7·4 (4H, m, Ar-H)] was also in agreement with the proposed structure [assignments were confirmed by recording the spectrum in the presence of increasing amounts of the shift reagent Eu(fod)$_3$].

Furthermore treatment of the alcohols (**3**) with sodium hydride in hexamethylphosphoric triamide (HMPA) led to the ketones (**4**) in 75—85% yield.[4] Typically, treatment of (**3a**) (500 mg) with 2 equiv. of NaH in HMPA (30 ml) for 6 h at room temperature afforded (**4a**):† ν (film): 1665 (br.) cm^{-1} (C=O) and (C=C); δ (CCl$_4$): 1·11 (6H, s, 2 × Me), 1·91 2H, s, allylic H), 2·07 (3H, d, *J* 1·5 Hz, vinylic Me), 2·59 (2H, s, CH$_2$, disappears on deuteriation with Na–D$_2$O), 6·62 (1H, m, vinylic H), 6·98—7·43 (3H, m, Ar-H) and 7·92—8·15 (4H, m, Ar-H); double irradiation at δ 6·62 caused the doublet at δ 2·07 to change into a singlet.‡



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Taking into account our previous studies in this field,[1] the formation of the alcohols (**3**) may be rationalized by the mechanism in the Scheme.

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‡ Spectroscopic data for all the alcohols (**3**) were similar to those for (**3a**), and data for all the ketones (**4**) were similar to those for (**4a**). Full details will be published elsewhere.

[1] P. Caubère, *Topics Current Chem.*, 1978, **73**, 72.

[2] P. Caubère, M. S. Mourad, and G. Guillaumet, *Tetrahedron*, 1973, **29**, 1843, and references cited therein.

[3] J. Shabtai, L. H. Klemm, and D. R. Taylor, *J. Org. Chem.*, 1968, **33**, 1489.

[4] A similar ring opening of the benzocyclobutenols (**1**) has been observed previously: P. Caubère, M. S. Mourad, and G. Guillaumet, *Tetrahedron*, 1973, **29**, 1851.