Alkylation of Benzene with α-Diazoketones *via* Cycloheptatrienyl Intermediates

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Benzyl ketones can be synthesised efficiently from benzene and α-diazoketones with sequential catalysis by rhodium(ii) trifluoroacetate and trifluoroacetic acid; the process involves cycloheptatrienyl intermediates.

The recent switch from copper to rhodium-based catalysts has produced major improvements in both intermolecular[1] and intramolecular[2] cycloaddition reactions of diazocarbonyl compounds with benzene. Not only are yields of cycloheptatrienes (from intermolecular reaction) and bicyclo[5.3.0]decatrienes (from intramolecular reaction) significantly higher with rhodium catalysts, but the reaction conditions are sufficiently mild to permit isolation of kinetic trienes and not those resulting from subsequent sigmatropic rearrangement. This latter facet of the intramolecular reaction led recently to the discovery of the facile acid-catalysed route from bicyclo[5.3.0]decatrienones to β-tetralones.[2] We now report that the combination of these two catalytic reactions in the intermolecular series provides an efficient means of benzene alkylation, producing a range of alkyl and aryl benzyl ketones in excellent yields in a single operation.

The benzyl ketones (3) summarized in Table 1 were obtained by dropwise addition of the diazoketone (1) (*ca.* 1.4 mmol) in benzene (10 ml) to benzene (20 ml) containing rhodium(ii) trifluoroacetate (*ca.* 2 mg) at room temperature; reactions were complete as monitored by t.l.c. within one hour. The benzene that was in excess was removed and replaced by dichloromethane (30 ml) containing trifluoroacetic acid (*ca.* 0.1 ml). Work up after 2 hours at room

Table 1. Formation of benzyl ketones (3) by alkylation of benzene using α-diazoketones (1).

	Diazoketone[a]		Benzyl ketone (%)[b]
(1a)	$MeCOCHN_2$	(3a)	$MeCOCH_2Ph$ (79)
(1b)	$Me_2CHCOCHN_2$	(3b)	$Me_2CHCOCH_2Ph$ (86)
(1c)	$p\text{-}MeC_6H_4COCHN_2$	(3c)	$p\text{-}MeC_6H_4COCH_2Ph$ (82)
(1d)	$PhCH_2COCHN_2$	(3d)	$PhCH_2COCH_2Ph$ (31) + indan-2-one (49)
(1e)	$N_2CHCO[CH_2]_6COCHN_2$	(3e)	$PhCH_2CO[CH_2]_6COCH_2Ph$ (70)
(1f)	$Cl[CH_2]_3COCHN_2$	(3f)	$Cl[CH_2]_3COCH_2Ph$ (92)
(1g)	$Cl[CH_2]_2COCHN_2$	(3g)	$Cl[CH_2]_2COCH_2Ph$ (80)
(1h)	$ClCH_2COCHN_2$	(3h)	$ClCH_2COCH_2Ph$ (84)
(1i)	$MeCHBrCOCHN_2$	(3i)	$MeCHBrCOCH_2Ph$ (82)
(1j)	$MeOCH_2COCHN_2$	(3j)	$MeOCH_2COCH_2Ph$ (84)
(1k)	$\overline{CH_2CH_2C}HCOCHN_2$	(3k)	$\overline{CH_2CH_2C}HCOCH_2Ph$ (90)

[a] Obtained from the appropriate acyl chloride and diazomethane. [b] Yields based on diazoketone refer to purified products.
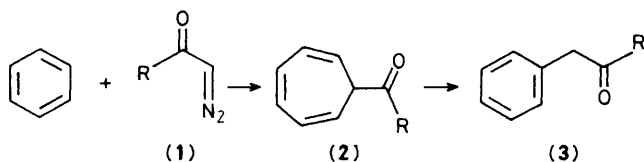
temperature gave benzyl ketones (3) which were purified by distillation, recrystallisation, or chromatography and characterised by n.m.r. spectroscopy. As can be seen from Table 1 benzene alkylation *via* cycloheptatrienyl intermediates proceeds very efficiently not only with simple alkyl and aryl side chains but also with side chains containing reactive halogen and cyclopropyl substituents. Benzyl diazomethyl ketone (1d) is exceptional in that intramolecular cyclisation to indan-2-one competes successfully with intermolecular cycloaddition. Entry (1e) illustrates the application of the method to the synthesis of a symmetrical α,ω-dibenzyl dione.

N.m.r. examination of each reaction product at the cycloheptatriene stage (2) revealed interesting differences in reactivity on varying the substituent R. All diazoketones, with the exception of the α-chloro and α-bromo compounds (1h) and (1i), produced isolable and identifiable cycloheptatrienyl intermediates in essentially quantitative yield; trifluoroacetic

acid treatment was required for the second stage. With (1h) and (1i), however, it was clear that cycloheptatrienyl systems (2h) and (2i) were much less stable and were already undergoing conversion into benzyl ketones in the absence of trifluoroacetic acid. Minor side products accompanying (3i) were eliminated by conducting the reaction in the presence of sodium carbonate. The ease of aromatisation of (2h) and (2i) may be associated with substituent effects on the cycloheptatriene–norcaradiene equilibrium[3] presumed to be involved.

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