Rhodium(II)-catalysed Cyclisation of Diazoketones derived from Biphenyl; A New Route to Benz[*a*]azulenes and Related Systems

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Cyclisation of 2-diazoacetylbiphenyl with rhodium(II) acetate or mandelate yields the unstable benz[*a*]azulen-10(9a*H*)-one from which benz[*a*]azulene can be obtained by lithium aluminium hydride reduction; similar reactions with the related diazoketones (**2**)—(**5**) yield stable benzobicyclotrienones in high yield.

Diazoketones (**1**)—(**5**) were prepared† and their catalytic reactions‡ with rhodium carboxylates were studied in order to assess the synthetic potential of the intramolecular Buchner reaction in the biphenyl series for the production of polyunsaturated tricyclic systems related to benzazulene and its homologues. Monophenyl diazoketones cyclise very efficiently under rhodium(II) acetate[1,2] or mandelate[3] catalysis giving bicyclodecatrienones, *e.g.* (**6**) → (**7**), which rearomatise to 2-tetralones in trifluoroacetic acid. The intermolecular version of this reaction with benzene is also successful.[4]

Structural considerations suggest that a biphenyl carbenoid of type (**8**) should have three options for intramolecular attack (designated a, b, and c); option c was considered the least likely on steric grounds and in the event was never observed. An earlier study of the decomposition of (**1**) catalysed by copper bronze had identified 9-phenanthrol (**9**) as the sole product in 58% yield.[5] This result established that the direction of attack of the carbenoid is equivalent to pathway b in (**8**). Superficially, it also suggests that either an aromatic C–H insertion or an electrophilic aromatic substitution reaction has occurred.[6]

The n.m.r. spectrum of the crude product of the reaction of diazoketone (**1**) with rhodium(II) acetate in dichloromethane at 20 °C revealed that while 9-phenanthrol (**9**) was indeed present, it was accompanied by a minor product (85 : 15 ratio) which slowly changed into 9-phenanthrol on standing at room temperature. The minor product proved elusive and although it was not isolated as such, sufficient evidence was collected to indicate that it was benz[*a*]azulen-10(9a*H*)-one (**10**). The crude reaction mixture was reduced with lithium aluminium hydride in ether and after separation and purification 9-phenanthrol (48%) and the blue benz[*a*]azulene (**11**) (2%) were isolated. The azulene was identified by its n.m.r. and electronic spectra; its mass spectrum was almost indistinguishable from that of phenanthrene.[7] We presume that the carbonyl group of (**10**) was lost *via* elimination during or after the hydride reduction. The detection of (**10**) in the catalysed cyclisation of (**1**) and its ready aromatisation to 9-phenanthrol suggest that cycloaddition of the ketocarbenoid onto the benzene ring to give a transient cyclopropane is a mechanistic

† Diazoketones (**1**)—(**5**) were obtained from the appropriate acyl chloride and ethereal diazomethane/diazoethane.

‡ Catalysed reactions of (**1**)—(**5**) were performed on a 0.2—9.0 mmol scale.

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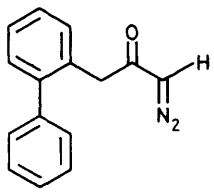
(2) R = Me



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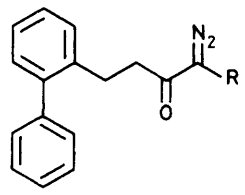

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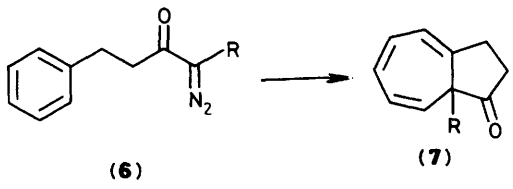
(5) R = Me



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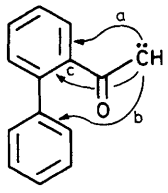

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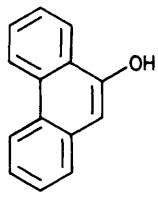

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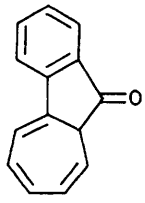

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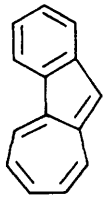

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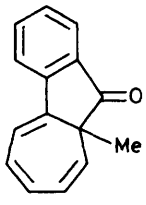

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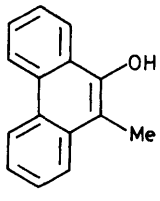

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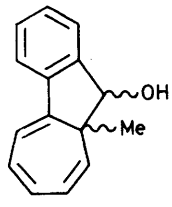

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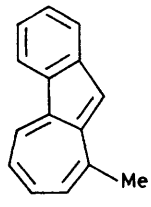

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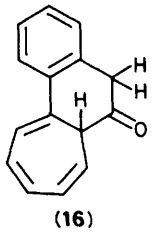

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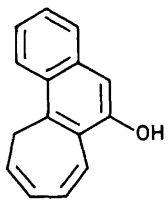

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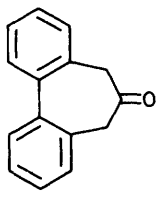

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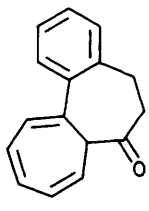

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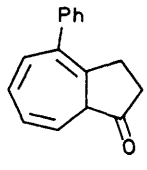

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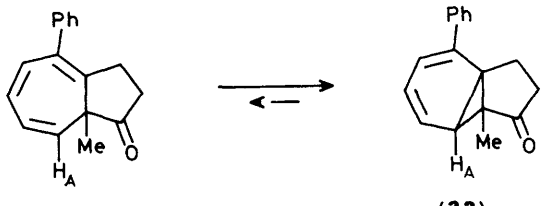

(21) (22)

alternative to aromatic C–H insertion or electrophilic aromatic substitution.

A major change of behaviour was observed when a methyl group was added to the diazo carbon atom in (**1**) for when diazoketone (**2**) was decomposed catalytically the only product isolated was the stable azulenone (**12**) (89% yield); in this cyclisation rhodium(II) mandelate was a much more efficient catalyst than rhodium(II) acetate. Furthermore, azulenone (**12**) did not re-aromatise easily, requiring treatment with trifluoroacetic acid in hot toluene to bring about conversion to 10-methyl-9-phenanthrol[8] (**13**) (60% yield). Conversion of (**12**) into a benzazulene, on the other hand, required a shift of the methyl group. This was readily brought about by sodium borohydride reduction to alcohol (**14**) (66%) which was then heated with trifluoroacetic acid in dichloromethane to afford a single methylbenz[*a*]azulene, m.p. 90—92 °C, in 89% yield. The new location of the methyl group was established by n.m.r. analysis. In particular, in the nuclear Overhauser enhancement (n.O.e.) difference spectrum irradiation of the methyl resonance clearly demonstrated the existence of a non-coupled proton resonance at δ 7.60, confirming that the product was (**15**). The methyl group had, therefore, migrated into the seven-membered ring rather than the five-membered ring.

Diazoketone (**3**) is a simple homologue of (**1**) with a longer side chain. Cyclisation pathways a and b both appeared

accessible to the ketocarbenoid, the former leading to a phenylindanone (possibly *via* electrophilic aromatic substitution, and the latter to a cycloheptatrienone *via* cycloaddition). Treatment of (**3**) with rhodium(II) acetate in dichloromethane gave a single stable product in 95% yield whose spectroscopic properties were entirely consistent with trienone (**16**). The ^{1}H n.m.r. spectrum contained a doublet at δ 2.72 for the unique bridgehead hydrogen atom and an AB system at δ 5.53 and 5.68 (*J* 6 Hz) for the unique methylene group. Treatment of (**16**) with triethylamine produced a double bond shift and enolisation, furnishing the phenol (**17**) (characterised as the tosylate) whereas an alternative aromatisation, to (**18**),[9] occurred in trifluoroacetic acid.

To complete this investigation of a- *vs.* b-type cyclisations of ketocarbenoids (**8**) we studied the catalysed decomposition of the next homologue, diazoketone (**4**). Type b cyclisation in this case was of particular interest since it should lead to the benzodicycloheptyl system (**19**) characteristic of colchicine. In fact, reaction of (**4**) with rhodium(II) acetate gave a single product in almost quantitative yield whose spectral data pointed clearly to the phenylazulenone system (**20**). Thus the distal benzene ring in (**4**) acts as a substituent rather than as a site for ketocarbenoid attack and the product is that of type a cyclisation. This was also the case when the diazocarbon atom was disubstituted, diazoketone (**5**) with rhodium mandelate furnishing a phenylazulenone in excellent yield. The n.m.r. spectra of this product were unusual in that the chemical shifts were more consistent with the norcaradiene structure (**22**) than with the cycloheptatriene structure(**21**). Typical norcaradiene resonances for bridgehead protons occur in the δ 2.8—3.5 range. Thus the H_A proton doublet at δ 3.00 indicated that (**22**) was the dominant element of the (**21**)/(**22**) equilibrium.[10]

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