The Intramolecular Buchner Reaction of Aryl Diazoketones. Substituent Effects and Scope in Synthesis

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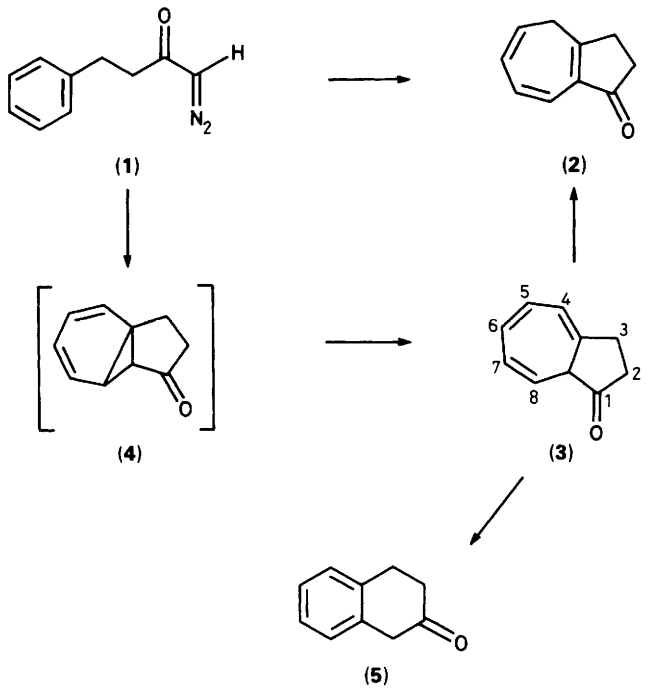
Rhodium(II) acetate-catalysed cyclisation of α-diazoketones derived from 3-arylpropionic acid produces bicyclo[5.3.0]decatrienones or 2-tetralones depending on the substitution pattern of the aryl ring in the precursor; the former products are transformed into the latter catalytically with trifluoroacetic acid. Precursors with methyl, methoxy, and acetoxy substituents have been examined, efficient cyclisation occurring in all cases. When the precursor contains a *meta*-methoxy substituent, 2-tetralones are obtained directly. The efficient conversion of 3-phenylpropionic acid into *trans*-1-methylbicyclo[5.3.0]decan-2-one is also described, partial asymmetric synthesis having been realised through the use of rhodium (*S*)-mandelate as the cyclisation catalyst. Cyclisations of diazoketones derived from 4-phenylbutyric acid and 5-phenylpentanoic acid have also been studied; the former provides a new entry into the bicyclo[5.4.0]undecane system whereas the latter produces a 2,3-disubstituted cyclopentanone *via* C–H insertion. Aspects of the cycloheptatriene–norcaradiene equilibrium in fused ring systems are discussed.

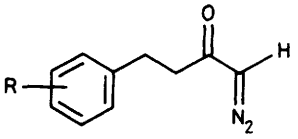
The intramolecular version of the catalysed Buchner reaction of aryl diazoketones is a relatively recent discovery.[1] In 1973 Scott[2,3] found that 1-diazo-4-phenylbutan-2-one (**1**) cyclises in bromobenzene with copper(I) chloride catalysis, furnishing 3,4-dihydroazulen-1(2*H*)-one (**2**) in 50% yield after purification by chromatography over alumina.† Scott surmised correctly that trienone (**2**) was not the primary cyclisation product and obtained evidence from NMR analysis that the less conjugated isomeric trienone (**3**) was first produced but contact with alumina caused it to isomerise to (**2**). Mechanistically, trienone (**3**) is probably the result of cycloaddition of a copper carbenoid onto the benzene ring of (**1**) producing a transient norcaradiene-like intermediate (**4**) which undergoes spontaneous electrocyclic ring opening of the internal cyclopropane bond.[1]

Our interest in the intramolecular Buchner process focussed on the possibility of using it to devise short routes from readily available dihydrocinnamic acids to a range of molecules possessing the bicyclo[5.3.0]decane skeleton characteristic of azulenes and numerous sesquiterpenes, notably the guaianolides and pseudoguaianolides. As a preliminary it was necessary to find out what kinds of functionalised benzenes could be used in the key cyclisation step and observe what directive effects, if any, would be exerted by substituents on the aryl ring. Accordingly, a series of ring-substituted phenyldiazobutanones [(**6**)–(**13**)] were prepared from readily available dihydrocinnamic acids *via* the standard procedure of acyl chloride formation followed by treatment with ethereal diazomethane.

It was already clear when we embarked on this study[4] that certain rhodium(II) catalysts were superior in some instances to the various copper catalysts traditionally used for diazocarbonyl reactions involving carbenoid intermediates,[5] the discovery that rhodium(II) trifluoroacetate[6] is the catalyst of choice for the intermolecular Buchner reaction of benzene with ethyl diazoacetate being particularly relevant. In the event, the more accessible rhodium(II) acetate proved to be an excellent catalyst, one or two milligrams bringing about the nearly quantitative conversion of several hundred milligrams of (**1**) into (**3**) within minutes in hot dichloromethane; NMR analysis confirmed the presence of (**3**), and the absence of (**2**) with about 5% of an unidentified aromatic impurity. Treatment of (**3**) with triethylamine caused the isomerisation to (**2**) which Scott had observed on alumina. Unexpectedly, (**3**) behaved quite differently on contact with silica gel, revealing a new rearrangement to 2-tetralone which may be of general use in synthesis. We were to find later that trienones of type (**3**) are of quite limited stability; attempts at extensive purification led partly to their destruction. In practice treatment of a dichloromethane solution of (**3**) with trifluoroacetic acid (TFA)



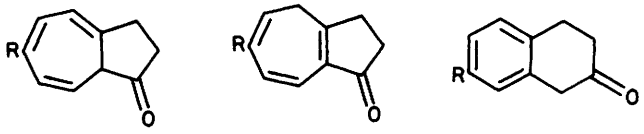
† An earlier catalysed cyclisation of (**1**) has been reported to yield (13%) a bicyclic trienone with a double bond arrangement different from that of either (**2**) or (**3**), presumably as a result of subsequent sigmatropic rearrangements.



(6) R = *p*-Me (10) R = *o*-Me
(7) R = *p*-OMe (11) R = *m*-OMe
(8) R = *p*-OAc (12) R = *m*-OAc
(9) R = *o*-OMe (13) R = *m*-Me

was a more convenient way of bringing about rearrangement and in this way it was possible to cyclise diazoketone (**1**), add TFA, and isolate 2-tetralone (**5**) in 85% yield after purification by distillation.

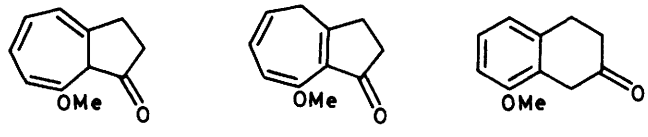
Three *para*-substituted phenyldiazobutanones were included in this series of reactions: *p*-methyl-, *p*-methoxy-, and *p*-acetoxy-, (**6**)–(**8**). All three cyclised smoothly with ring expansion, furnishing trienones (**14**)–(**16**), respectively, in excellent yields.



(14) R = Me (17) R = Me (20) R = Me
(15) R = OMe (18) R = OMe (21) R = OMe
(16) R = OAc (19) R = OAc (22) R = OAc

That the triethylamine-induced bond shift could be brought about in all three products was established with the isolation of conjugated trienones (**17**)–(**19**) whose structures were readily confirmed by their NMR spectra. Furthermore, all three diazoketones gave excellent yields of 2-tetralones, *viz.* (**20**) (85%), (**21**) (88%), and (**22**) (90%), when subjected to the consecutive action of rhodium(II) acetate and TFA. The *para*-substituted series thus provided useful information for future applications inasmuch as we had demonstrated that the cyclisation process was successful with substituents which could be employed in functional group manipulation of the cycloheptyl ring.

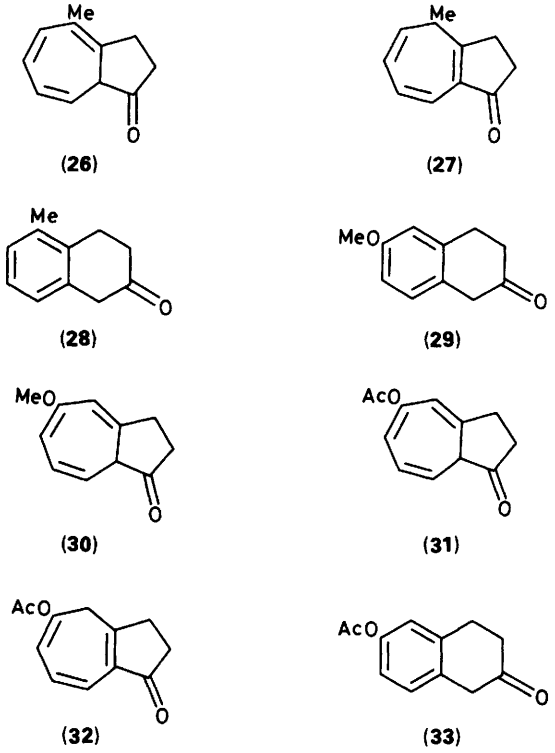
The effect of *ortho*-substitution was next examined. When diazoketone (**9**) was subjected to rhodium(II) acetate catalysis a single cycloheptatrienone (**23**) was obtained in high yield. Comparison of the NMR spectrum of (**23**) with that of its parent (**3**) established the direction of cyclisation of the ketocarbenoid. In particular, proton 8-H, which has a characteristic location at δ 5.0 in (**3**), was missing from the NMR spectrum of (**23**). Furthermore, treatment of (**23**) with triethylamine furnished trienone (**24**) in which the methoxy group remained vinylic



(23) (24) (25)

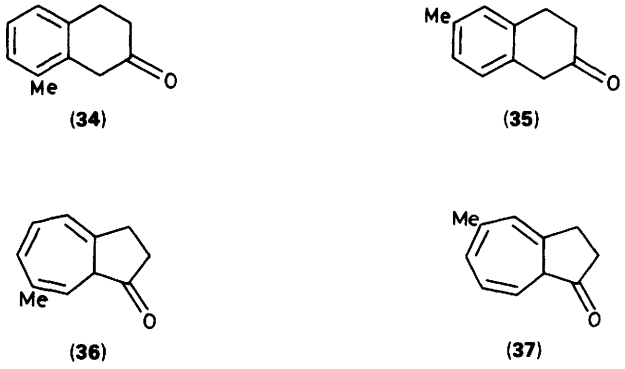
while treatment with TFA produced the known 8-methoxy-2-tetralone (**25**).[7] Thus the ketocarbenoid derived from (**9**) cyclises onto the side of the aromatic ring adjacent to the methoxy substituent. Interestingly, Lewis acid-catalysed cyclisation of diazoketone (**9**) also produces 8-methoxy-2-tetralone, albeit in very low yield.[8] The nature of the attractive effect of the methoxy substituent in the ketocarbenoid cyclisation is unclear. In the intermolecular reaction[6] of ethyl diazoacetate with anisole under rhodium(II) catalysis there is not a preference for attack adjacent to the substituent, though this does not rule out a favourable arrangement in the intramolecular reaction in which the methoxy group participates *via* chelation. The situation with an *ortho*-methyl group was quite the reverse. When diazoketone (**10**) was subjected to the cyclisation conditions a single ring-expanded product was again obtained, but its structure proved to be (**26**), revealing that cyclisation had occurred in the direction away from the *ortho*-methyl group. In the intermolecular reaction of toluene with ethyl diazoacetate little attack occurs adjacent to the methyl group. The structure of (**26**) was assigned on the basis of its NMR spectrum (8-H appearing as a double doublet at δ 5.0), that of the isomeric enone (**27**) produced on triethylamine treatment, and on the formation of 5-methyl-2-tetralone (**28**)[9] on exposure to TFA.

Yet another feature of the cyclisation process emerged when

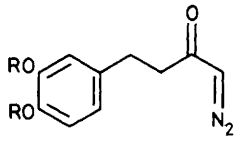


(26) (27) (28) (29) (30) (31) (32) (33)

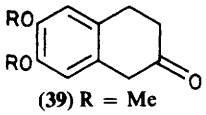
we examined the behaviour of *meta*-substituted diazoketones, for the product isolated from catalysed decomposition of the methoxy derivative (**11**) was 6-methoxy-2-tetralone (**29**)[10] (80%) with no trace of the putative trienone (**30**). The *meta*-acetoxy diazoketone (**12**), on the other hand, did furnish a trienone (**31**) which could be transformed efficiently into its conjugated isomer (**32**) by triethylamine or into tetralone (**33**) by TFA, all three structural assignments being supported by the spectral data. The behaviour of the *meta*-methyl diazoketone



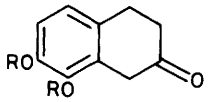
(34) (35) (36) (37)



(38) R = Me



(39) R = Me



(40) R = Me

(41) R–R = CH_2

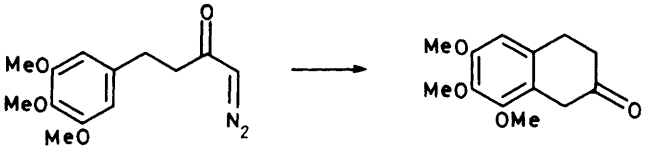
(42) R–R = CH_2

(13) fell between that of its two congeners. The product consisted of two trienones and two tetralones which were not separated as such. Addition of TFA to the mixture had a simplifying effect since after rearrangement it consisted of the tetralones only in a 70:30 ratio (87%). The minor tetralone was isolated by crystallisation and identified as 8-methyl-2-tetralone (**34**)[9]. We concluded that the major tetralone was the 6-methyl isomer (**35**), though it was not isolated as a single compound and that the trienones involved in this sequence were therefore isomers (**36**) and (**37**).

This pattern of behaviour in the *meta*-series was also observed in three other cases in which the diazoketone precursor had at least one alkoxy substituent *meta* to the reacting side chain. Thus the 3,4-dimethoxy derivative (**38**) cyclised to afford an 80:20 mixture of tetralones (**39**)[11] and (**40**)[12] (96%), the 3,4-methylenedioxy derivative (**41**) similarly produced the tetralone (**42**) predominantly (97%), and the 3,4,5-trimethoxy derivative (**43**) furnished 6,7,8-trimethoxy-2-tetralone (**44**). The dimethoxytetralones (**39**) and (**40**) were not separated as such and the product ratio was determined by reducing the mixture with lithium aluminium hydride, converting the resulting alcohols to tosylates, and removing the latter reductively with lithium aluminium hydride. This sequence produced a mixture of tetralins (**45**) (64%) and (**46**) (16%), separable by chromatography over silica gel. Although the tetralones produced on cyclisation of the 3,4-methylenedioxy precursor (**41**) were not separated, the similarity of their ^1H and ^{13}C NMR spectra with those of the dimethoxytetralones indicated clearly that (**42**) was the preponderant regioisomer of the mixture. However, the system reverted to the earlier pattern of producing ring-expanded trienones when the *meta*-substituent was acetoxy as in diazoketones (**47**) and (**48**), cyclisation in the presence of rhodium acetate producing trienones (**49**) and (**50**), respectively in >90% yields; addition of TFA completed the synthesis of tetralones (**51**) and (**52**) from these trienones.

In seeking to extend this work to include the synthesis of azulenic bicycles with bridgehead methyl groups, *cf.* the pseudoguaianolide series, we investigated the possibility of introducing this substituent as an integral part of the ketocarbenoid cyclisation. 3-Phenylpropanoyl chloride was treated with ethereal diazoethane to afford diazoketone (**53**). As we have noted elsewhere, rhodium(II) acetate is a rather ineffectual catalyst for aromatic cycloadditions involving disubstituted diazoketones. However, rhodium(II) trifluoroacetate or rhodium(II) mandelate[13] did bring about cyclisation of (**53**), the latter furnished the expected product in quantitative yield. While the spectra of the product did have the general features consistent with structure (**54**), the presence of two IR carbonyl absorptions at 1745 and 1712 cm^{-1}, and the apparent chemical shift (δ 4.31) for the doublet for the vinylic proton (H_A) adjacent to the bridgehead methyl group were considered rather atypical. However, Hannemann's[14] recent analysis of the NMR spectra of cycloheptatrienes in equilibrium with their norcaradiene counterparts has greatly clarified the situation. It seems that structure (**54**) is probably an inadequate representation of this product. The chemical shift for H_A at δ 4.31 is more consistent with its location in the norcaradiene-like tricyclic tautomer (**54a**), there existing a rapid equilibrium between the two with the tricyclic form the dominant partner at room temperature. A very similar situation was encountered with the catalysed decomposition of the *ortho*-tolyl diazoketone (**55**) which we studied to confirm the direction of cyclisation of a disubstituted carbenoid (*cf.* the pseudoguaianolides). The product obtained with rhodium(II) trifluoroacetate was regiochemically homogeneous, its IR spectrum contained carbonyl absorptions at 1745 and 1712 cm^{-1}, and the ^1H NMR spectrum revealed the H_A proton at C-8 as a doublet at δ 3.41. Thus not only is this the product (**56**) of cyclisation in the direction expected from the behaviour of the monosubstituted diazoketone (**10**), but the location of H_A in its NMR spectrum indicates that the tricyclic tautomer (**56a**) is the dominant form at equilibrium.

The use of rhodium(II) mandelate as a catalyst for these diazoketone cyclisations introduces an interesting stereochemical option. In all the bicyclic trienones produced, a single asymmetric centre is created at the bridgehead position adjacent to the carbonyl group of the cyclopentanone. Accordingly, the possibility of catalysed asymmetric synthesis presented itself through the use of mandelate in homochiral form. Diazoketone (**53**) was selected for an initial exploration of this idea. Treatment with rhodium(II) (*S*)-mandelate in the usual way gave trienone (**54**), which had a measurable optical rotation, but which did not respond well to ^1H NMR chiral shift reagents. Reduction of (**54**) with lithium tri-t-butoxyaluminium hydride gave a mixture of epimeric alcohols (**57**) (*ca.* 75:25 ratio) in which we presumed the *cis*-isomer to predominate. The mixture



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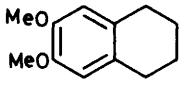
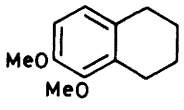
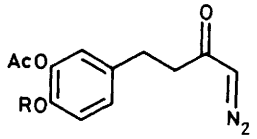
(44)



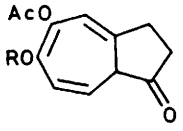
(45)



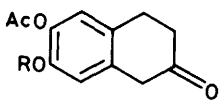
(46)



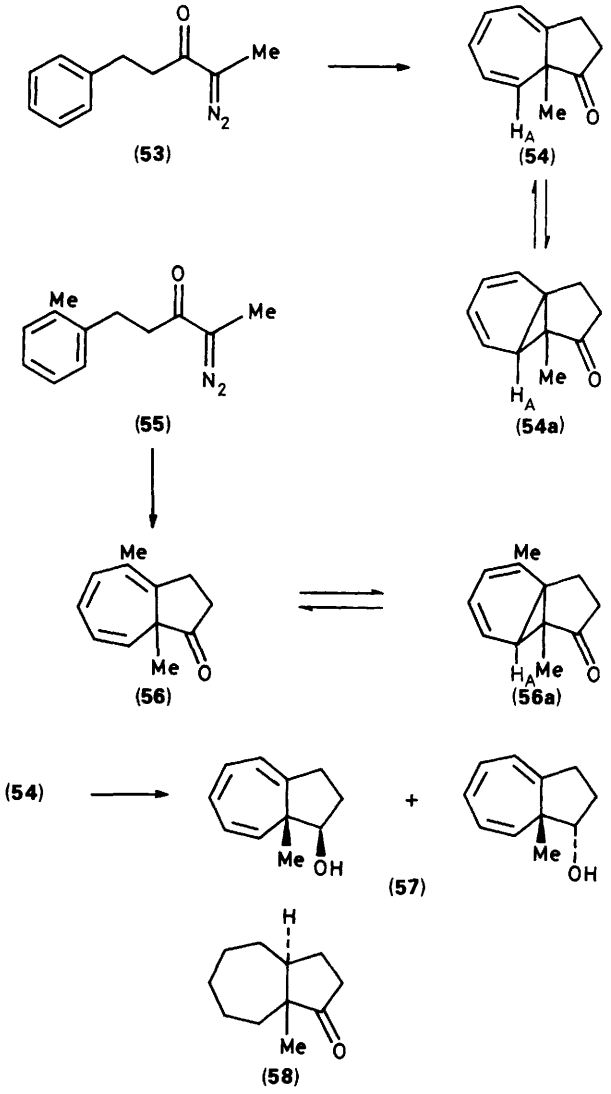
(47) R = Me
(48) R = Ac

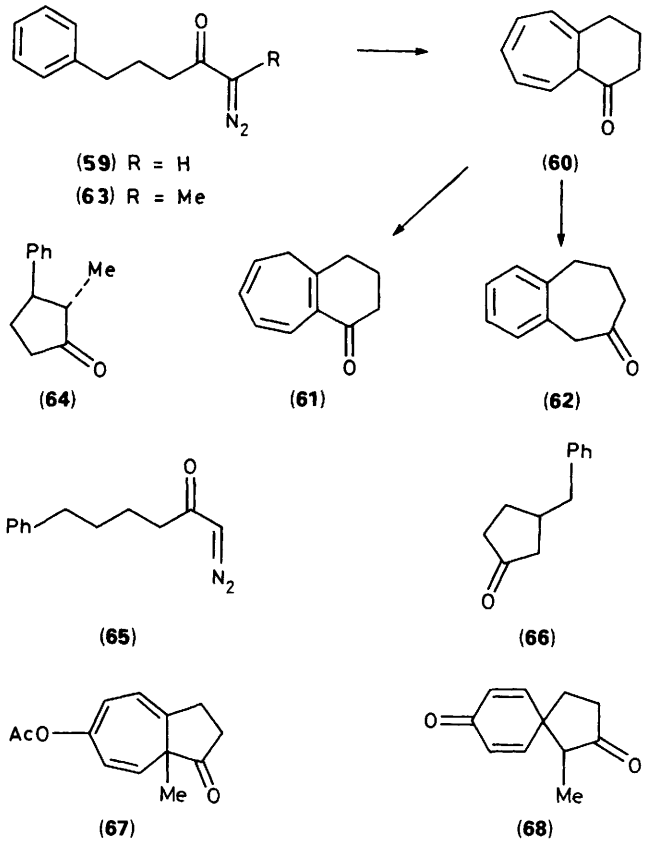


(49) R = Me
(50) R = Ac



(51) R = Me
(52) = Ac





was not separated as such but was subjected to $Eu(tfc)_3$-shifted [tfc = 3-(trifluoromethylhydroxymethylene)camphorato] NMR analysis which showed a clear separation of the epimeric *cis*- and *trans*-alcohols and a further resolution of the enantiomeric forms of the *cis*-isomer which allowed us to assign a 20% enantiomeric excess to the original trienone (**54**). Further experiments are now in hand seeking improvements in these asymmetric cyclisations through the use of new homochiral rhodium catalysts derived from natural α-amino acids. Hydrogenation of (**54**) over 10% palladium on carbon produced the fully saturated ketone (**58**)[15] in 71% yield. This three-step sequence of diazoketone formation, cyclisation, and hydrogenation represents an efficient synthesis of this *trans*-hydroazulenone. We expected that steric approach control of the addition of hydrogen by the angular bridgehead methyl group would favour the formation of the *trans*-product (**58**) and this could be confirmed by comparing the ^1H NMR chemical shift of the methyl group (δ 0.88) with those published for the *cis*- and *trans*-isomers (δ 0.85 and 1.07);[15] none of the *cis*-isomer could be detected in the product. In contrast, catalytic hydrogenation of the alcohol mixture (**57**) followed by chromic acid oxidation of the hydroxy function produced an 80:20 mixture of (**58**) and its *cis*-isomer.

Having now established the scope of the catalysed intramolecular Buchner reaction in the synthesis of the bicyclo[5.3.0]decane system, we next varied the chain length between the aromatic ring and the carbenoid to see if larger bicyclic systems could be similarly constructed. Lengthening the chain by one methylene unit leads to diazoketone (**59**) which was prepared and decomposed with rhodium acetate in the usual way. The reaction proceeded smoothly to give in high yield a single product whose spectral properties left no doubt that it was the ring-expanded bicyclic trienone (**60**). This assignment was confirmed by transforming (**60**) into the more conjugated enone (**61**) (76%) using triethylamine and into 2-benzosuberone (**62**)[16] (89%) using TFA. Thus bicyclo[5.4.0]-undecanones are also accessible by this methodology, though in this case the cyclisation is substituent dependent as we found with the methyl substituted diazoketone (**63**). This precursor and rhodium mandelate furnished *trans*-2-methyl-3-phenylcyclopentanone (**64**)[17] in 46% yield with none of the product of carbenoid attack on the benzene ring. In other words, the reaction pathway has switched from one of cycloaddition to one of C–H insertion. C–H insertion was also observed with diazoketone (**65**), the next higher homologue of (**59**); 3-benzylcyclopentanone (**66**) was the sole product of the reaction.

In summary, our studies demonstrate the efficacy of the intramolecular Buchner reaction for the production of a variety of substituted azulenic bicyclotrienones. The process can be extended to include the efficient synthesis of 2-tetralones. Very recent work by Doyle and his co-workers[18] shows that intramolecular cyclisation of *N*-benzyldiazoacetamides using rhodium(II) acetate is also possible, opening up an efficient route to azabicyclo[5.3.0]decatrienones. In this series, however, the products do not rearomatise under acid catalysis. Oxabicyclic systems are also accessible through the use of aromatic oxadiazoketones though yields are low and mixtures of products are obtained.[19] It seems reasonable to suggest that the mechanism of formation of the trienones and tetralones reported here involves the production of a reactive rhodium carbenoid which cycloadds to the aromatic ring to form a

tricyclic norcaradienone intermediate which, by electrocyclic ring opening and closure, is in rapid equilibrium with a bicyclic trienone. With the exception of the two examples with bridgehead methyl groups, *viz.* (**54**) and (**56**), the bicyclic forms are the dominant components of the equilibrium. The existence of this equilibrium helps also to explain the substituent effects and tetralone formation: in the absence of an electron-donating group at the *meta*-position electrocyclic ring opening produces stable trienones; a *meta*-methoxy group (or to a lesser degree, a *meta*-methyl group), on the other hand, promotes the alternative bond breaking process leading to tetralones; the latter may be catalysed by adventitious acid. The existence of the equilibrium also helps to explain the anomalous behaviour of the acetoxytrienone (**67**) on attempted removal of the ester function by alkaline hydrolysis. The major reaction product (51%) was the spirodienone (**68**).[20]

Experimental

M.p.s were determined on a Thomas Hoover apparatus and are uncorrected. ^{1}H NMR spectra were recorded on an Hitachi Perkin-Elmer R-20A spectrometer at 60 MHz and ^{13}C spectra on a Joel FX60 spectrometer at 15 MHz. Elemental analyses were performed by the Microanalysis Laboratory, University College, Cork. Merck PF_{254} silica gel was used for both PLC and TLC. Magnesium sulphate was employed as the drying agent.

Preparation of Diazoketones.—Diazoketones (**1**), (**6**), (**7**), (**8**), (**9**), (**10**), (**11**), (**12**), (**13**), (**38**), (**41**), (**43**), (**47**), (**48**), (**59**), and (**65**) were all prepared from the appropriate dihydrocinnamic acid *via* the standard procedure of conversion to the acyl chloride with either oxaloyl chloride or thionyl chloride followed by treatment with ethereal diazomethane. The dihydrocinnamic acids were all known compounds; most were commercially available. The diazoketones were obtained in essentially quantitative yield, and generally were of sufficient purity to be suitable for use directly. In some instances small traces of impurities, usually chloromethyl ketones, were removed by chromatography of the diazoketone over silica gel with chloroform as the eluant; pure samples were obtained in 60–70% yield. The following procedure is representative of the diazomethyl ketone series.

1-*Diazo*-4-*phenylbutan*-2-*one* (**1**). An ethereal solution of diazomethane (3.5 equiv.), prepared from *N*-methyl-*N*-nitroso-toluene-*p*-sulphonamide (Diazald) was cooled in an ice–salt bath while a solution of 3-phenylpropanoyl chloride (1.0 equiv.) in dry ether was added dropwise. The mixture was stirred overnight while returning to room temperature. Excess of diazomethane and the solvent were removed using a rotatory evaporator fitted with an acetic acid trap. Diazoketone (**1**) was obtained as an orange-yellow oil; ν_{max}(film) 2 080 and 1 635 cm^{-1}; δ_H(CCl_4) 2.28–2.93 (4 H, m, CH_2CH_2), 5.16 (1 H, s, CHN_2), and 7.10 (5 H, s, ArH).

The following compounds were thus prepared.

1-*Diazo*-4-(4-*methylphenyl*)*butan*-2-*one* (**6**), orange–yellow needles, m.p. 50–52 °C; ν_{max}(KBr) 2 080 and 1 645 cm^{-1}; δ_H($CDCl_3$) 2.26 (3 H, s, Me), 2.45–2.97 (4 H, m, CH_2CH_2), 5.14 (1 H, s, CHN_2), and 7.09 (4 H, s, ArH).

1-*Diazo*-4-(4-*methoxyphenyl*)*butan*-2-*one* (**7**), red–orange oil; ν_{max}(film) 2 100 and 1 640 cm^{-1}; δ_H(CCl_4) 2.42–2.90 (4 H, m, CH_2CH_2), 3.78 (3 H, s, OMe), 5.18 (1 H, s, CHN_2), and 7.10 (4 H, ABq, ArH).

1-*Diazo*-4-(4-*acetoxyphenyl*)*butan*-2-*one* (**8**), yellow crystals, m.p. 95–101 °C (decomp.); ν_{max}(KBr) 2 088, 1 745, and 1 640 cm^{-1}; δ_H($CDCl_3$) 2.27 (3 H, s, Me), 2.50–3.03 (4 H, m, CH_2CH_2), 5.20 (1 H, s, CHN_2), and 7.09 (4 H, ABq, ArH).

1-*Diazo*-4-(2-*methoxyphenyl*)*butan*-2-*one* (**9**), red–orange oil; ν_{max}(film) 2 104 and 1 640 cm^{-1}; δ_H(CCl_4) 2.30–3.00 (4 H, m, CH_2CH_2), 3.77 (3 H, s, Me), 5.03 (1 H, s, CHN_2), and 6.60–7.19 (4 H, m, ArH).

1-*Diazo*-4-(2-*methylphenyl*)*butan*-2-*one* (**10**), orange–yellow oil; ν_{max}(film) 2 080 and 1 645 cm^{-1}; δ_H($CDCl_3$) 2.30 (3 H, s, Me), 2.38–3.07 (4 H, m, CH_2CH_2), 5.17 (1 H, s, CHN_2), and 7.12 (4 H, s, ArH).

1-*Diazo*-4-(3-*methoxyphenyl*)*butan*-2-*one* (**11**), yellow oil; ν_{max}(film) 2 104 and 1 645 cm^{-1}; δ_H(CCl_4) 2.32–2.96 (4 H, m, CH_2CH_2), 3.66 (3 H, s, OMe), 5.12 (1 H, s, CHN_2), and 6.57–7.20 (4 H, m, ArH).

1-*Diazo*-4-(3-*acetoxyphenyl*)*butan*-2-*one* (**12**), yellow oil; ν_{max}(film) 2 105, 1 760, and 1 635 cm^{-1}; δ_H(CCl_4) 2.18 (3 H, s, Me), 2.30–2.99 (4 H, m, CH_2CH_2), 5.11 (1 H, s, CHN_2), and 6.74–7.19 (4 H, m, ArH).

1-*Diazo*-4-(3-*methylphenyl*)*butan*-2-*one* -**13**), yellow oil; ν_{max}(film) 2 100 and 1 640 cm^{-1}; δ_H($CDCl_3$) 2.27 (3 H, s, Me), 2.35–2.95 (4 H, m, CH_2CH_2), 5.10 (1 H, s, CHN_2), and 6.85–7.04 (4 H, m, ArH).

1-*Diazo*-4-(3,4-*dimethoxyphenyl*)*butan*-2-*one* (**38**), yellow solid; ν_{max}(KBr) 2 100 and 1 625 cm^{-1}; δ_H($CDCl_3$) 2.35–3.00 (4 H, m, CH_2CH_2), 3.71 (6 H, s, OMe), 5.47 (1 H, s, CHN_2), and 6.72 (3 H, s, ArH).

1-*Diazo*-4-(3,4-*methylenedioxyphenyl*)*butan*-2-*one* (**41**), yellow solid; ν_{max}(KBr) 2 104 and 1 628 cm^{-1}; δ_H($CDCl_3$) 2.30–3.00 (4 H, m, CH_2CH_2), 5.27 (1 H, s, CHN_2), 5.78 (2 H, s, OCH_2O), and 6.60 (3 H, s, ArH).

1-*Diazo*-4(3,4,5-*trimethoxyphenyl*)*butan*-2-*one* (**43**), yellow oil, ν_{max}(film) 2 100 and 1 630 cm^{-1}; δ_H($CDCl_3$) 2.50–2.96 (4 H, CH_2CH_2), 3.82 (9 H, s, OMe), 5.27 (1 H, s, CHN_2), and 6.40 (2 H, s, ArH).

1-*Diazo*-4-(3-*acetoxy*-4-*methoxyphenyl*)*butan*-2-*one* (**47**), pale yellow solid; ν_{max}2 110, 1 776, and 1 623 cm^{-1}; δ_H($CDCl_3$) 2.25 (3 H, s, Me), 2.30–3.05 (4 H, m, CH_2CH_2), 3.72 (3 H, s, OMe), 5.24 (1 H, s, CHN_2), and 6.88 (3 H, s, ArH).

1-*Diazo*-4-(3,4-*diacetoxyphenyl*)*butan*-2-*one* (**48**), pale yellow solid; ν_{max} 2 100, 1 760, and 1 628 cm^{-1}; δ_H($CDCl_3$) 2.23 (6 H, s, Me), 2.30–3.10 (4 H, m, CH_2CH_2), 5.21 (1 H, s, CHN_2), and 7.04 (3 H, s, ArH).

1-*Diazo*-5-*phenylpentan*-2-*one* (**59**), yellow oil; ν_{max} 2 105 and 1 640 cm^{-1}; δ_H($CDCl_3$) 1.75–2.50 (2 H, m, CH_2), 2.23 (2 H, m, CH_2), 2.65 (2 H, t, CH_2), 5.15 (1 H, s, CHN_2), and 7.19 (5 H, s, ArH).

1-*Diazo*-6-*phenylhexan*-2-*one* (**65**), yellow oil, ν_{max} 2 100 and 1 635 cm^{-1}; δ_H($CDCl_3$) 1.45–1.70 (4 H, m, CH_2CH_2), 2.20 (2 H, t, CH_2), 2.55 (2 H, t, CH_2), 5.13 (1 H, s, CHN_2), and 7.12 (5 H, s, ArH).

2-*Diazo*-5-*phenylpentan*-3-*one* (**53**). An ethereal solution of diazoethane (80 ml) [prepared from *N*-ethyl-*N*-nitrosourea (21 g)] was cooled to −29 °C and 3-phenylpropanoyl chloride (3.12 g) in ether (15 ml) was added dropwise with stirring over 15 min. The mixture was allowed to come to room temperature and after 10 h the solvent and residual diazoethane were removed under reduced pressure using a rotatory evaporator with an acetic acid trap. The crude product was purified by chromatography (ethyl acetate–hexane) to afford (**53**) as an orange oil (2.82 g, 81%); ν_{max}(film) 2 060 and 1 642 cm^{-1}; δ_H($CDCl_3$) 1.79 (3 H, s, Me), 2.50–3.00 (4 H, m, CH_2CH_2), and 7.31 (5 H, m, ArH).

2-*Diazo*-6-*phenylhexan*-3-*one* (**63**). 4-Phenylbutanoyl chloride [prepared from 4-phenylbutanoic acid (1 g) and oxaloyl chloride (0.8 ml), 45 min, under reflux)] was treated with ethereal diazoethane [from *N*-ethyl-*N*-nitrosourea (7 g)] as just described above for diazoketone (**53**) to afford diazoketone (**63**) as a yellow–green oil (1.15 g, 93%); ν_{max}(film) 2 070 and 1 635 cm^{-1}; δ_H($CDCl_3$) 1.91 (3 H, s, Me), 1.95 (2 H, m, CH_2), 2.50 (4 H, m, CH_2CH_2), and 7.17 (5 H, s, ArH).

Preparation of Trienones.—3,8a-*Dihydroazulen*-1(2H)-*one*

(**3**). A solution of 1-diazo-4-phenylbutan-2-one (**1**) (0.16 g, 0.92 mmol) in dichloromethane (20 ml) was added dropwise with stirring to a solution of rhodium(II) acetate (2 mg, 4.5 μmol) in dichloromethane (50 ml) under reflux. Reaction, which could be monitored by TLC, was complete within 20 min. The cooled solution was washed with water, dried, and concentrated under reduced pressure to afford (**3**) as a yellow oil (0.18 g) which was used in subsequent reactions without purification; ν_{max}(film) 1 745 cm^{-1};$\delta_H(CCl_4)$ 2.32–3.00 (5 H, m, 2-H_2, 3-H_2, and 8a-H), 5.00 (1 H, dd, *J* 9.4 Hz, 8-H), 5.96–6.23 and 6.38–6.48 (4 H, m, 4–7–H), and 7.18 (aromatic impurity, *ca.* 5%).

The above procedure was used to prepare trienones (**14**)–(**16**), (**23**), (**26**), (**31**), (**36**), (**37**), (**49**), and (**50**) all in >95% yield. In each case the trienone was used in subsequent reactions without further purification.

6-*Methyl*-3,8a-*dihydroazulen*-1(2H)-*one* (**14**), yellow oil; ν_{max}-(film) 1 747 cm^{-1}; $\delta_H(CCl_4)$ 1.98 (3 H, s, Me), 2.30–2.80 (5 H, m, 2-H_2, 3-H_2, and 8a-H), 5.00 (1 H, dd, *J* 10.4 Hz, 8-H), 5.92 (1 H, d, *J* 10 Hz, 7-H), 6.06 (1 H, d, *J* 7 Hz, 4-H), 6.17 (1 H, d, *J* 7 Hz, 5-H), and 6.96 (aromatic impurity).

6-*Methoxy*-3,8a-*dihydroazulen*-1(2H)-*one* (**15**), yellow oil; ν_{max}(film) 1 747 cm^{-1}; $\delta_H(CCl_4)$ 2.21–2.93 (5 H, m, 2-H_2, 3-H_2, and 8a-H), 3.54 (3 H, s, Me), 5.12 (1 H, dd, *J* 10.4 Hz, 8-H), 5.56 (1 H, d, *J* 8 Hz, 7-H), 5.81 (1 H, d, *J* Hz, 4-H), and 6.00 (1 H, d, *J* 6 Hz, 5-H).

6-*Acetoxy*-3,8a-*dihydroazulen*-1(2H)-*one* (**16**), yellow oil; ν_{max}-(film) 1 742 and 1 755 cm^{-1}; $\delta_H(CCl_4)$ 2.12 (3 H, s, Me), 2.20–2.92 (5 H, 2-H_2, 3-H_2, and 8a-H), 5.10 (1 H, dd, *J* 9.5 Hz, 8-H), and 5.84–6.10 (3 H, m, 4-, 5-, and 7-H).

8-*Methoxy*-3,8a-*dihydroazulen*-1(2H)-*one* (**23**), yellow oil, a mixture with its conjugated isomer (**24**); ν_{max}(film) 1 705–1 745 cm^{-1} (br); $\delta_H(CCl_4)$ 2.05–2.95 (4 H, m, 2-H_2, 3-H_2, and 8a-H), 3.57 and 3.61 (3 H, s × s 1.5:1, Me), 5.30 and 5.46–6.27 (4 H, m, 4–7-H), and 6.95 (aromatic impurity).

4-*Methyl*-3,8a-*dihydroazulen*-1(2H)-*one* (**26**), yellow oil; ν_{max}-(film) 1 745 cm^{-1}; $\delta_H(CCl_4)$ 1.86 (3 H, s, Me), 2.28–2.82 (5 H, m, 2-H_2, 3-H_2, and 8a-H), 5.00 (1 H, dd, *J* 10.5 Hz, 8-H), 5.84–6.32 (3 H, m, 5–7-H) and 7.00 (aromatic impurity).

5-*Acetoxy*-3,8a-*dihydroazulen*-1(2H)-*one* (**31**), yellow oil; ν_{max}(film) 1 750 cm^{-1} (br); $\delta_H(CCl_4)$ 2.12 (3 H, s, Me), 2.26–2.88 (5 H, m, 2-H_2, 3-H_2, and 8a-H), 4.94 (1 H, dd, *J* 10.5 Hz, 8-H), and 5.92–6.24 (3 H, m, 4-, 6-, and 7-H).

Reaction of the diazoketone (**13**) *with rhodium*(II) *acetate.* Treatment of (**13**) with the catalyst as described for diazoketone (**1**) yielded a mixture of unconjugated trienones (**36**) and (**37**) and tetralones (**34**) and (**35**) as judged by NMR analysis. The conversion of trienones into tetralones and the isolation of tetralone (**34**) is described below.

5-*Acetoxy*-6-*methoxy*-3,8a-*dihydroazulen*-1(2H)-*one* (**49**), yellow oil; ν_{max}(film) 1 755 and 1 705 cm^{-1}; $\delta_H(CDCl_3)$ 2.00 (3 H, s, Me), 2.10–3.00 (5 H, m, 2-H_2, 3-H_2, and 8a-H), 3.40 (3 H, s, Me), 4.80–5.45 (1 H, m), and 5.65–6.10 (2 H, m).

5,6-*Diacetoxy*-3,8a-*dihydroazulen*-1(2H)-*one* (**50**), yellow oil after 5 min reaction time; longer reaction times resulted in partial or complete isomerisation of the product into the conjugated isomer; ν_{max}(film) 1 750 and 1 710 cm^{-1}; $\delta_H(CDCl_3)$ 2.18 (6 H, s, Me), 2.30–3.20 (5 H, m, 2-H_2, 3-H_2, and 8a-H), 5.00–5.25 (1 H, m), and 5.90–6.20 (2 H, m).

Preparation of Conjugated Enones.—3,4-*Dihydroazulen*-1(2H)-*one* (**2**). The diazoketone (**1**) (0.50 g) was cyclised with rhodium acetate (2 mg) as described above to afford a dichloromethane solution of (**3**). The cooled solution was treated with triethylamine (0.2 ml) and after stirring at room temperature for 30 min the solution was washed with cold 1% hydrochloric acid (10 ml) and water (3 × 50 ml), and dried. Removal of the solvent furnished an oil which on purification by PLC (EtOAc–hexane, 15:85) furnished the trienone (**2**) as a yellow oil (0.36 g, 90%); ν_{max}(film) 1 690 and 1 620 cm^{-1}; the NMR data agreed closely with those quoted by Scott.[2] The trienone (**2**) formed a semicarbazone, m.p. 236–238 °C (from ethanol).

The above one-pot procedure was used to prepare each of the following conjugated enones from the appropriate diazoketone.

6-*Methyl*-3,4-*dihydroazulen*-1(2H)-*one* (**17**). The diazoketone (**6**) furnished the *ketone* (**17**) as an oil (69%) after purification by PLC (chloroform) (Found: C, 82.2; H, 7.1. $C_{11}H_{12}O$ requires C, 82.5; H, 7.55%); *m*/*z* 160 (M^+); ν_{max}(film) 1 692 and 1 625 cm^{-1}; $\delta_H(CDCl_3)$ 1.87 (3 H, s, Me), 2.43–2.78 (6 H, m, 2–4-H_2), 5.20 (1 H, t, *J* 6 Hz, 5-H), 6.40 (1 H, d, *J* 12 Hz, 7-H), and 6.69 (1 H, d, *J* 12 Hz, 8-H); $\delta_C(CDCl_3)$ 32.35 (q), 29.76 (t), 30.67 (t), 35.74 (t), 117.41 (d), 121.56 (d), 134.17 (d), 136.58 (s), 136.71 (s), 168.28 (s), and 205.64 (s).

6-*Methoxy*-3,4-*dihydroazulen*-1(2H)-*one* (**18**). The diazoketone (**7**) furnished the *methoxyazulene* (**18**) (80%) as crystals, m.p. 105–106 °C (from ether) (Found: C, 75.45; H, 6.8. $C_{11}H_{12}O_2$ requires C, 75.0; H, 6.8%); *m*/*z* 176 (M^+);ν_{max}(film) 1 625 and 1 685 cm^{-1}; $\delta_H(CDCl_3)$ 2.45–2.84 (6 H, 2–4-H_2), 3.50 (3 H, s, Me), 4.57 (1 H, t, *J* 6 Hz 5-H), 6.35 (1 H, d, *J* 12 Hz, 7-H), and 6.73 (1 H, d, *J* 12 Hz, 8-H); $\delta_C(CDCl_3)$ 27.09 (t), 29.89 (t), 35.61 (t), 55.55 (q), 92.13 (d), 123.38 (d), 128.45 (d), 136.58 (s), 156.65 (s), 171.59 (s), and 205.18 (s).

6-*Acetoxy*-3,4-*dihydroazulen*-1(2H)-*one* (**19**). The diazoketone (**8**) furnished the *acetoxy compound* (**19**) (76%) as crystals, m.p. 92–93 °C (from ether) (Found: C, 70.7; H, 5.9. $C_{12}H_{12}O_3$ requires C, 70.6; H, 5.9%); *m*/*z* 204 (M^+); ν_{max}(film) 1 750, 1 695, and 1 625 cm^{-1}; $\delta_H(CDCl_3)$ 2.10 (3 H, s, Me), 2.39–2.70 (4 H, m, 2- and 3-H_2), 2.87 (2 H, d, *J* 6.5 Hz, 4-H_2), 5.14 (1 H, t, *J* 5 Hz, 5-H), 6.13 (1 H, d, *J* 12 Hz, 7-H), and 6.68 (1 H, d, *J* 12 Hz, 8-H); $\delta_C(CDCl_3)$ 20.68 (q), 27.35 (t), 30.34 (t), 35.54 (t), 110.33 (d), 124.03 (d), 126.96 (d), 129.309 s), 136.97 (s), 140.01 (s), 169.32 (s), and 204.92 (s).

8-*Methoxy*-3,4-*dihydroazulen*-1(2H)-*one* (**24**). The diazoketone (**9**) furnished the *methoxy compound* (**23**) (70%) as an oil, b.p. 98–105 °C at 0.05–0.07 mmHg (Found: C, 75.2; H, 7.2. $C_{11}H_{12}O_2$ requires C, 75.0; H, 6.9%); *m*/*z* 176 (M^+); ν_{max}(film) 1 620 and 1 700 cm^{-1}; $\delta_H(CDCl_3)$ 2.49–2.91 (6 H, m, 2–4-H_2), 3.76 (3 H, s, Me), 5.36 (1 H, m, 5-H), 5.81 (1 H, d, *J* 6.5 Hz, 7-H), and 6.18 (1 H, dd, *J* 7.5 Hz, 6-H); $\delta_C(CDCl_3)$ 29.43 (t), 31.25 (t), 36.65 (t), 55.23 (q), 103.96 (d), 117.54 (d), 127.54 (d), 130.14 (s), 155.29 (s), 170.55 (s), and 203.69 (s).

4-*Methyl*-3,4-*dihydroazulen*-1(2H)-*one* (**27**). The diazoketone (**10**) furnished (**27**) as an oil (65%) after purification by PLC (chloroform); *m*/*z* 160 (M^+); ν_{max}(film) 1 690 and 1 610 cm^{-1}; $\delta_H(CDCl_3)$ 1.31 (3 H, d, Me), 2.30–2.90 (5 H, m, 2–4-H_2), 5.27 (1 H, dd, *J* 10.5 Hz, 5-H), 6.16 (1 H, dd, *J* 7 Hz, 6-H), 6.62 (1 H, dd, *J* 9 Hz, 7-H) and 6.96 (1 H, d, *J* 12 Hz, 8-H); $\delta_C(CDCl_3)$ 14.68 (q), 26.96 (t), 35.35 (t), 35.74 (d), 122.34 (d), 126.76 (d), 128.13 (d), 130.40 (d), 135.60 (s), 169.84 (s), and 205.51 (s). The trienone (**27**) formed a *semicarbazone*, m.p. 202–203 °C (from ethanol) (Found: C, 66.8; H, 7.1; N, 19.5; $C_{12}H_{15}N_3O$ requires C, 66.3; H, 6.95; N, 19.3%).

5-*Acetoxy*-3,4-*dihydroazulen*-1(2H)-*one* (**32**). The diazoketone (**12**) furnished the *acetoxy compound* (**32**) as crystals (78%), m.p. 74–75 °C (Found: C, 70.4; H, 6.2. $C_{12}H_{12}O_3$ requires C, 70.6; H, 5.9%); *m*/*z* 204 (M^+); ν_{max}(film) 1 750, 1 690, and 1 620 cm^{-1}; $\delta_H(CDCl_3)$ 2.14 (3 H, s, Me), 2.37–2.85 (4 H, m, 2- and 3-H_2), 3.00 (2 H, s, 4-H_2), 5.88 (1 H, d, *J* 6 Hz, 6-H), 6.25 (1 H, dd, *J* 10 Hz, 7-H), and 6.65 (1 H, d, *J* 10 Hz, 8-H); $\delta_C(CDCl_3)$ 20.73 (q), 30.15 (t), 35.28 (t), 35.87 (t), 115.13 (d), 121.56 (d), 126.31 (d), 137.49 (s), 140.08 (s), 164.77 (s), 169.13 (s), and 205.44 (s).

Preparation of Tetralones.—2-*Tetralone* (**5**). The diazoketone (**1**) (0.5 g) was cyclised with rhodium acetate (2 mg) as described above to afford a dichloromethane solution of (**3**) to which was then added at room temperature trifluoroacetic acid (0.2 ml) with stirring. After 30 min the solution was washed with 2%

aqueous sodium hydrogen carbonate and water, and dried. Removal of the solvent furnished an oil which on distillation yielded 2-tetralone (**5**) (0.39 g, 86%), b.p. 70–75 °C at 0.05–0.07 mmHg. The spectral data were identical with those of an authentic sample.

The above one-pot procedure was used to prepare the following tetralones from the diazoketone precursors.

7-*Methyl*-2-*tetralone* (**20**). The diazoketone (**6**) furnished (**20**) in 85% yield, m.p. 59–60 °C (lit.,[9] 57–59 °C).

7-*Methoxy*-2-*tetralone* (**21**). The diazoketone (**7**) furnished (**21**) in 88% yield, b.p. 90–100 °C at 0.02–0.03 mmHg; the spectral data were in close agreement with those published.[7,12]

7-*Acetoxy*-2-*tetralone* (**22**). The diazoketone (**8**) furnished the *acetoxy compound* (**22**) in 90% yield, b.p. 130–140 °C at 0.02–0.04 mmHg (Found: C, 69.9; H, 6.15. $C_{12}H_{12}O_3$ requires C, 70.6; H, 5.9%); *m/z* 204 (M^+); ν_{max}(film) 1 755, 1 715, and 1 615 cm^{-1}; $\delta_H(CDCl_3)$ 2.21 (3 H, s, Me), 2.41 (2 H, t, *J* 6 Hz, 3-H_2), 2.94 (2 H, t, *J* 6 Hz, 4-H_2), 3.45 (2 H, s, 1-H_2), 6.79 (1 H, s, 8-H), 6.92 (1 H, d, *J* 9.0 Hz, 6-H), and 7.15 (1 H, d, *J* 9.0 Hz, 5-H); $\delta_C(CDCl_3)$ 20.99 (q), 27.74 (t), 37.94 (t), 44.83 (t), 119.87 (d), 121.24 (d), 128.52 (d), 128.52 (d), 134.24 (s), 134.76 (s), 149.44 (s), 169.51 (s), and 209.54 (s).

8-*Methoxy*-2-*tetralone* (**25**). The diazoketone (**9**) furnished (**25**) in 84% yield, b.p. 100–110 °C at 0.25 mmHg; the spectral data were in close agreement with those published.[7,8]

5-*Methyl*-2-*tetralone* (**28**). The diazoketone (**10**) furnished (**28**) in 86% yield, b.p. 80–90 °C at 0.03–0.05 mmHg; the spectral data were in close agreement with those published.[9]

6-*Methoxy*-2-*tetralone* (**29**). When diazoketone (**11**) was treated with rhodium acetate, the tetralone (**29**) was obtained directly; TFA treatment was unnecessary. The product was identified on the basis of the published spectral data, and formation of a semicarbazone, m.p. 157–158 °C (from ethanol) (lit.,[10] 158–159 °C).

6-*Acetoxy*-2-*tetralone* (**33**). The diazoketone (**12**) furnished (**33**) in 80% yield, b.p. 130–140 °C at 0.01 mmHg; *m/z* 204 (M^+); ν_{max}(film) 1 755, 1 715, and 1 615 cm^{-1}; $\delta_H(CDCl_3)$ 2.26 (3 H, s, Me), 2.35–2.57 (2 H, t, *J* 6.5 Hz, 3-H_2), 2.88–3.08 (2 H, t, *J* 6.5 Hz, 4-H_2), 3.48 (2 H, s, 1-H_2), and 6.78–7.20 (3 H, m, ArH); $\delta_C(CDCl_3)$ 20.99 (q), 28.26 (t), 37.62 (t), 44.44 (t), 119.94 (d), 120.78 (d), 129.04 (d), 130.86 (s), 138.00 (s), 149.37 (s), 169.51 (s), and 209.74 (s).

8-*Methyl*-2-*tetralone* (**34**) *and* 6-*methyl*-2-*tetralone* (**35**). The diazoketone (**13**) furnished a mixture of (**34**) and (**35**) in 87% yield, b.p. 90–94 °C at 0.03 mmHg. NMR integration indicated that the mixture consisted of 70% of (**35**), and 30% of (**34**). On chilling the mixture white needles of the minor component (**34**) were deposited, m.p. 68–70 °C (lit.,[9] 72–73 °C); the spectral data of (**34**) were in close agreement with the published values.

6,7-*Dimethoxy*-2-*tetralone* (**39**) *and* 7,8-*Dimethoxy*-2-*tetralones* (**40**). When the diazoketone (**38**) was treated with rhodium acetate, a solid mixture of tetralones (**39**) and (**40**) was produced in 96% yield; TFA treatment was unnecessary. The mixture had m.p. 71–72 °C [*cf.* lit.,[11,12] 76 °C for (**40**); 85.5–86.5 °C for (**39**)]; ν_{max}(KBr) 1 710 cm^{-1}; $\delta_H(CDCl_3)$ 2.30–3.10 (4 H, m, 3- and 4-H_2), 3.43 (2 H, s, 1-H_2), 3.80 (6 H, s, 6,7/7,8-OMe), 6.59 (1 H, s, ArH), and 6.72 (1 H, s, ArH). GLC analysis on 2 m 2% Silicon Gum Rubber at 185 °C indicated that the isomer ratio was *ca.* 4:1. The major isomer was identified by reducing the mixture with lithium aluminium hydride, converting the resulting alcohols to tosylates, and finally, reductively removing the latter with lithium aluminium hydride whereupon a separable mixture of 6,7-dimethoxytetralin (80%) and 7,8-dimethoxytetralin (20%) was obtained whose structures were confirmed by ^{13}C NMR spectra.

6,7-*Methylenedioxy*-2-*tetralone* (**42**). This tetralone was obtained in 97% yield from the diazoketone (**41**) (TFA treatment was unnecessary), m.p. 77 °C (decomp.); *m/z* 190 (M^+); ν_{max}(KBr) 1 700 cm^{-1}; $\delta_H(CDCl_3)$ 2.30–3.00 (4 H, m, 3- and 4-H_2), 3.41 (2 H, s, 1-H_2), 5.91 (4 H, s, OCH_2O), 6.55 (1 H, s, ArH), and 6.65 (1 H, s, ArH). The compound decomposed rapidly on standing at room temperature. The NMR data suggested that it was largely or exclusively the 6,7 regioisomer.

6,7,8-*Trimethoxy*-2-*tetralone* (**44**). The *tetralone* (**44**) was obtained in 90% yield from the diazoketone (**43**) (TFA treatment was unnecessary), b.p. 150–160 °C at 0.2 mmHg, m.p. 67–69 °C (Found: C, 66.0; H, 6.8; $C_{13}H_{16}O_4$ requires: C, 66.1; H 6.8%); *m/z* 236 (M^+); ν_{max}(film) 1 590 and 1 715 cm^{-1}; $\delta_H(CDCl_3)$ 2.40–2.60 (2 H, t, *J* 6.5 Hz, 3-H_2), 2.87–3.07 (2 H, t, *J* 6.5 Hz, 4-H_2), 3.44 (2 H, s, 1-H_2), 3.80 (9 H, s, 6,7,8-OMe), and 6.55 (1 H, s, ArM); δ_C 28.98 (t), 38.07 (t), 38.72 (t), 56.14 (q), 60.75 (q), 60.88 (q), 107.14 (d), 119.10 (s), 132.03 (s), 140.86 (s), 151.00 (s), 152.30 (s), and 210.38 (s).

3,8a-*Dihydro*-8a-*methylazulen*-1(2H)-*one* (**54**).—2-Diazo-5-phenylpentan-3-one (**53**) (100 mg) in dichloromethane (10 ml) was added dropwise with stirring over 1 hour to a refluxing solution of rhodium(II) mandelate (2 × 0.5 mg portions; one initially and one half way through the addition) in dichloromethane (150 ml) under nitrogen. After a further 20 min the solution was cooled and then concentrated under reduced pressure to leave a yellow oil (98 mg) which was shown by ^1H NMR spectroscopy to consist of (**54**) and about 10% of an aromatic impurity. Purification by chromatography (dichloromethane) furnished the *ketone* (**54**) in a pure state (Found: C, 82.35; H, 7.9. $C_{11}H_{12}O$ requires C, 82.5; H, 7.55%); ν_{max}(film) 1 741 and 1 708 cm^{-1}; $\delta_H(CDCl_3)$ 0.89 (3 H, s, Me), 2.00–3.10 (4 H, m, CH_2CH_2), 4.33 (1 H, d, *J* 7.2 Hz, 8-H) and 5.90–6.30 (4 H, m, 4–7-H); $\delta_H(CDCl_3)$ 12.28 (q), 27.32 (t), 34.83 (t), 42.04 (s), 94.99 (d), 123.14 (d), 125.46 (d), 126.89 (d), 127.15 (d), 128.45 (s), and 219.80 (s).

Cyclisation of the Diazoketone (**55**).—The diazoketone (**55**) (0.334 g) in dichloromethane (15 ml) was added dropwise with stirring over 30 min to a solution of rhodium(II) trifluoroacetate (6 mg) in dichloromethane (70 ml) under reflux. The cooled reaction mixture was processed as just described for cyclisation of the diazoketone (**54**) to afford the trienone (**56**) (0.286 g, 100%) which was homogeneous by TLC analysis in two solvents; ν_{max}(film) 1 743 and 1 712 cm^{-1}; $\delta_H(CDCl_3)$ 0.70 (3 H, s, Me), 1.96 (3 H, s, Me), 2.20–2.60 (4 H, m, CH_2CH_2), 3.41 (1 H, d, 8-H), and 5.75–6.30 (3 H, m, 5–7-H).

cis- *and* trans-1,2,3,8a-*Tetrahydro*-8a-*methylazulen*-1-*ol* (**57**).—A sample of crude ketone (**54**) (98 mg) (containing about 10% of an aromatic impurity) in a mixture of ether (10 ml) and tetrahydrofuran (4 ml) was added dropwise with stirring under nitrogen to lithium tri-t-butoxyaluminium hydride (625 mg) in ether (5 ml) at 0 °C. The mixture was allowed to warm to room temperature and after 10 h was treated with water (4 ml) dropwise. The organic layer and ethereal extracts of the aqueous layer (3 × 10 ml) were combined, washed with water, and dried. Evaporation of the solvent, followed by purification of the residue by chromatography in dichloromethane furnished the alcohol mixture (**57**) as a colourless oil (57 mg, 67% based on diazoketone) (Found: C, 81.75; H, 8.9. Calc. for $C_{11}H_{14}O$ C, 81.4; H, 8.7%); ν_{max}(film) 3 360 and 1 631 cm^{-1}; $\delta_H(CDCl_3)$ 0.73 (3 H, s, Me), 1.70–2.80 (5 H, m, CH_2CH_2 and OH), 4.10 (1 H, t, 1-H), 5.20 and 5.74 (1 H, s, 2 × d, *J* 9.6 and 10.2 Hz, respectively, 8-H, *cis* and *trans*), and 6.00–6.40 (4 H, m, 4–7-H). When Eu(tfc)$_3$ was employed as the chiral shift reagent (2 × 10 mol % additions for the ^1H NMR analysis of (**57**) the absorption at δ 0.73 split into two singlets for the *cis* and *trans*-isomers (75–80% *cis* and 20–25% *trans* by integration). The signal for the methyl group in the *cis*-isomer further split into two singlets for the two

enantiomeric forms, revealing a 20% enantiomeric excess when the decomposition catalyst was rhodium(II) (*S*)-mandelate.

Perhydro-8a-methyl-azulene-1-one (**58**).—A sample of ketone (**54**) (0.102 g) in ethanol (20 ml) containing 10% palladium on carbon (20 mg) was hydrogenated at room temperature and 40 psi pressure for 24 h. The mixture was then filtered and concentrated under reduced pressure to leave a residue which on distillation in a Kugelrohr apparatus at an oven temperature of 75–90 °C at 0.03 mmHg gave the *saturated ketone* (**58**) (0.088 g, 83%) as a colourless oil (Found: C, 79.6; H, 10.7. $C_{11}H_{18}O$ requires C, 79.5; H, 10.9%); ν_{max}(film) 1 736 cm^{-1}; $\delta_H(CDCl_3)$ 0.88 (3 H, s, Me) and 1.20–2.40 (15 H, m); no signal was visible for the methyl group of the *cis*-fused isomer,[15] indicating that exclusive hydrogenation to the *trans*-fused isomer had occurred.

Cyclisation of the Diazoketone (**59**).—A solution of the diazoketone (**59**) (1.0 g) in dichloromethane (25 ml) was added dropwise over 20 min to a solution of rhodium(II) acetate (2 mg) in dichloromethane under reflux. The crude product (**60**) (0.85 g, 100%) was isolated as a light yellow oil which was homogeneous on TLC analysis; ν_{max}(film) 1 715 cm^{-1}; $\delta_H(CDCl_3)$ 1.82–2.18 and 2.37–2.50 (7 H, m), 5.15 (1 H, dd, 6-H), 5.96–6.24 (2 H, m, vinylic), and 6.46–6.50 (2 H, m, vinylic).

Formation of Conjugated Trienone (**61**).—The diazoketone (**59**) (1.0 g) was cyclised as described above. The cooled dichloromethane solution was treated with triethylamine (0.2 ml). After 20 min the solution was washed with cold 1% hydrochloric acid and water, then dried. Removal of the solvent furnished an oil which was purified by PLC with chloroform as the eluant to afford the trienone (**61**) (0.76 g, 89%) as an oil; ν_{max}(film) 1 665 cm^{-1}; $\delta_H(CDCl_3)$ 1.78–2.19 (2 H, m), 2.30–2.75 (6 H, m), 5.48 (1 H, m, 3-H), 6.17 (1 H, dd, 4-H), 6.56 (1 H, dd, 5-H), and 6.78 (1 H, d, 6-H); $\delta_C(CDCl_3)$ 22.16 (t), 32.49 (t), 34.83 (t), 37.75 (t), 120.72 (d), 127.35 (d), 127.87 (d), 129.88 (d), 131.51 (s), 149.37 (s), and 197.65 (s); *m/z* 160 (M^+). The compound formed a *semicarbazone*, m.p. 204–206 °C (from ethanol) (Found: C, 66.15; H, 6.9; N, 19.5. $C_{12}H_{15}N_3O$ requires C, 66.3; H, 7.0; N, 19.3%).

7,7,8,8,9,9-*Hexahydrobenzocyclohepten-6(5H)-one* (*Benzosuberone*) (**62**).—The diazoketone (**59**) (0.5 g) was cyclised as described above to afford a dichloromethane solution of (**60**) to which was added at room temperature trifluoroacetic acid (0.2 ml). After 30 min the solution was washed with 2% aqueous sodium hydrogen carbonate and water, and then dried. Removal of the solvent followed by distillation at 70–75 °C at 0.05 mmHg afforded the ketone (**62**) in 81% yield; ν_{max}(film) 1 707 cm^{-1}; *m/z* 160 (M^+); the ^1H NMR data were in close agreement with those published.[16] The ketone formed a red 2,4-*dinitrophenylhydrazone*, m.p. 162–166 °C (Found: C, 60.0; H, 4.5; H, 16.7. $C_{17}H_{16}N_4O_4$ requires C, 60.0; H, 4.7; N, 16.5%).

trans-2-*Methyl-3-phenylcyclopentanone* (**64**).—The diazoketone (**63**) (0.1 g) and rhodium(II) mandelate (1 mg) in dichloromethane (50 ml) under reflux for 20 min furnished an oil (40 mg, 46%) after purification by chromatography. Comparison of the NMR data with those published[17] established that the product was the cyclopentanone (**64**).

3-*Benzylcyclopentanone* (**66**).—The diazoketone (**65**) (0.33 g) and rhodium(II) acetate (2 mg) in dichloromethane (70 ml) under reflux for 20 min furnished the *ketone* (**66**) as an oil in 79% yield, b.p. 95–100 °C at 0.03 mmHg (Found: C, 82.6; H, 8.2. $C_{12}H_{14}O$ requires C, 82.7; H, 8.0%); ν_{max}(film) 1 740 cm^{-1}; $\delta_H(CDCl_3)$ 1.55–2.75 (9 H, m) and 7.24 (5 H, m, ArH); $\delta_C(CDCl_3)$ 29.04 (t), 38.27 (t), 41.45 (t), 44.83 (t), 126.24 (d), 126.63 (s), 128.45 (d), 128.45 (d), 128.78 (d), 128.78 (d), and 219.02 (s). The compound gave a semicarbazone, m.p. 180–181 °C (from ethanol).

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References

1 For a comprehensive review of metal-catalysed reactions of diazocarbonyl compounds see G. Maas, *Top. Curr. Chem.*, 1987, **137**, 75.
2 L. T. Scott, *J. Chem. Soc., Chem. Commun.*, 1973, 882; L. T. Scott, M. A. Minton, and M. A. Kirms, *J. Am. Chem. Soc.*, 1980, **102**, 6311.
3 A. Constantino, G. Linstrumelle, and S. Julia, *Bull. Soc. Chim. Fr.*, 1970, 907, 912.
4 For a preliminary account of this work see M. A. McKervey, S. M. Tuladhar, and M. F. Twohig, *J. Chem. Soc. Chem. Commun.*, 1984, 129.
5 R. Paulissen, A. J. Hubert, and P. Teyssie, *Tetrahedron Lett.*, 1972, 1465; A. J. Hubert, A. F. Noels, A. J. Anciaux, and P. Teyssie, *Synthesis*, 1976, 600; A. J. Anciaux, A. J. Hubert, A. F. Noels, N. Petiniot, and P. Teyssie, *J. Org. Chem.*, 1980, **45**, 695; M. P. Doyle, W. H. Hamblyn, and V. Bagheri, *ibid.*, 1981, **46**, 5094; M. A. McKervey and P. Ratananukul, *Tetrahedron Lett.*, 1982, 2509; A. Demonceau, A. F. Noels, A. J. Hubert, and P. Teyssie, *J. Chem. Soc., Chem. Commun.*, 1981, 688.
6 A. J. Anceaux, A. Demonceau, A. F. Noels, A. J. Hubert, R. Warin, and P. Teyssie, *J. Org. Chem.*, 1981, **46**, 873.
7 P. K. Oommen, *Aust. J. Chem.*, 1976, **29**, 1393.
8 D. W. Johnson and L. N. Mander, *Aust, J. Chem.*, 1974, **27**, 1277.
9 J. J. Sims, M. Cadogan, and L. H. Selman, *Tetrahedron Lett.*, 1971, 951; A. Rosowsky, K. K. Chen, N. Papathanasopoulos, and E. J. Modest, *J. Heterocycl. Chem.*, 1972, **9**, 263.
10 J. Vebrel and R. Carrie, *Bull. Soc. Chim. Fr.*, 1982, 116; J. H. Burckhalter and J. R. Campbell, *J. Org. Chem.*, 1961, **26**, 4232.
11 A. S. Horn, C. J. Grol, and D. Dijstra, *J. Med. Chem.*, 1978, **21**, 825.
12 M. D. Soffer, J. C. Cavagnol, and H. E. Gellerson, *J. Am. Chem. Soc.*, 1949, **71**, 3857.
13 P. A. Agaskar, F. A. Cotton, C. R. Falvello, aand S. Hahn, *J. Am. Chem. Soc.*, 1986, **108**, 1214.
14 K. Hannemann, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 284.
15 B. B. Snider and C. P. Cartaya-Marin, *J. Org. Chem.*, 1984, **49**, 153.
16 G. Bodennee and M. St-Jacques, *Can. J. Chem.*, 1977, **55**, 1199.
17 R. C. Gadwood, I. M. Mallick, and A. J. de Winter, *J. Org. Chem.*, 1987, **52**, 774.
18 M. P. Doyle, M. S. Shanklin, and H. Q. Pho, *Tetrahedron Lett.*, 1988, **29**, 2639.
19 A. Pusino, A. Saba, and V. Rosnati, *Tetrahedron*, 1986, **42**, 4319; L. Chan and S. A. Matlin, *Tetrahedron Lett.*, 1981, **22**, 4025.
20 C. Iwata, M. Yamada, Y. Shinoo, K. Kobayashi, and H. Okada, *Chem. Pharm. Bull.*, 1980, **28**, 1932.

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