Indian Journal of Chemistry
Vol. 36B, December 1997, pp.1103 - 1112

Chemoselective rhodium-carbenoid reaction with the aromatic nucleus: An efficient methodology for 2-indanones, 2- tetralones and 2-benzosuberones and its application in the synthesis of (±)-*ar*-Himachalene

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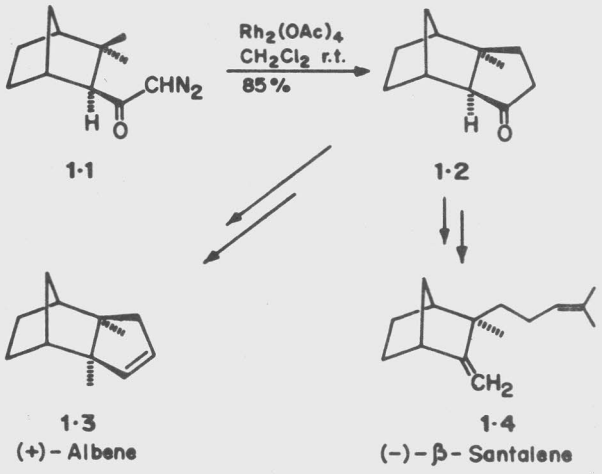
Received 30 May 1996; accepted 25 October 1996

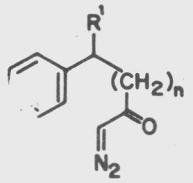
Rhodium-carbenoid species derived from rhodium acetate- catalyzed decomposition of aryl alkyl α- diazoketones have been shown to display a chemoselective addition into the aromatic nucleus, instead of insertion into an aliphatic C-H site. The synthetic utility of this chemoselective reaction is exemplified by the preparation of substituted fused aromatic systems such as 2-indanones, 2-tetralones and 2-benzosuberones. In addition, a short and efficient synthesis of (±)- *ar*- Himachalene, a naturally occurring sesquiterpene is realized.

With the advent of $Rh_2(OAc)_4$ as an efficient catalyst to generate transient electrophilic Rh-carbenoid species from α- diazocarbonyl compounds, intramolecular carbenoid insertion into unactivated C-H bonds has assumed strategic importance in C-C bond forming reactions in organic synthesis[1]. The initial investigations in this area were restricted to conformationally mobile aliphatic systems with the use of α-diazo- β-keto esters as carbenoid precursors[2-6]. On the other hand, we have successfully utilized the structural rigidity inherent in bicyclo[2,2,1]heptane systems in regioselective carbenoid insertion into primary and bridge-head C-H bonds using α-diazoketones as the carbenoid precursors[7], the salient feature being the cyclopentanone formation. Interestingly enough, this led to the first enantioselective synthesis of (+)- Albene **1.3**, a molecule unamenable to synthesis for a long time, and (-)-β-santalene **1.4**, a constituent of Indian sandalwood oil (Scheme I).



Scheme I

With a view to exploring further the selectivity obtainable by Rh-carbenoids derived from α-diazoketones in intramolecular insertion reactions, we have now chosen a different system such as **1** posessing competitive aromatic and aliphatic C-H sites.



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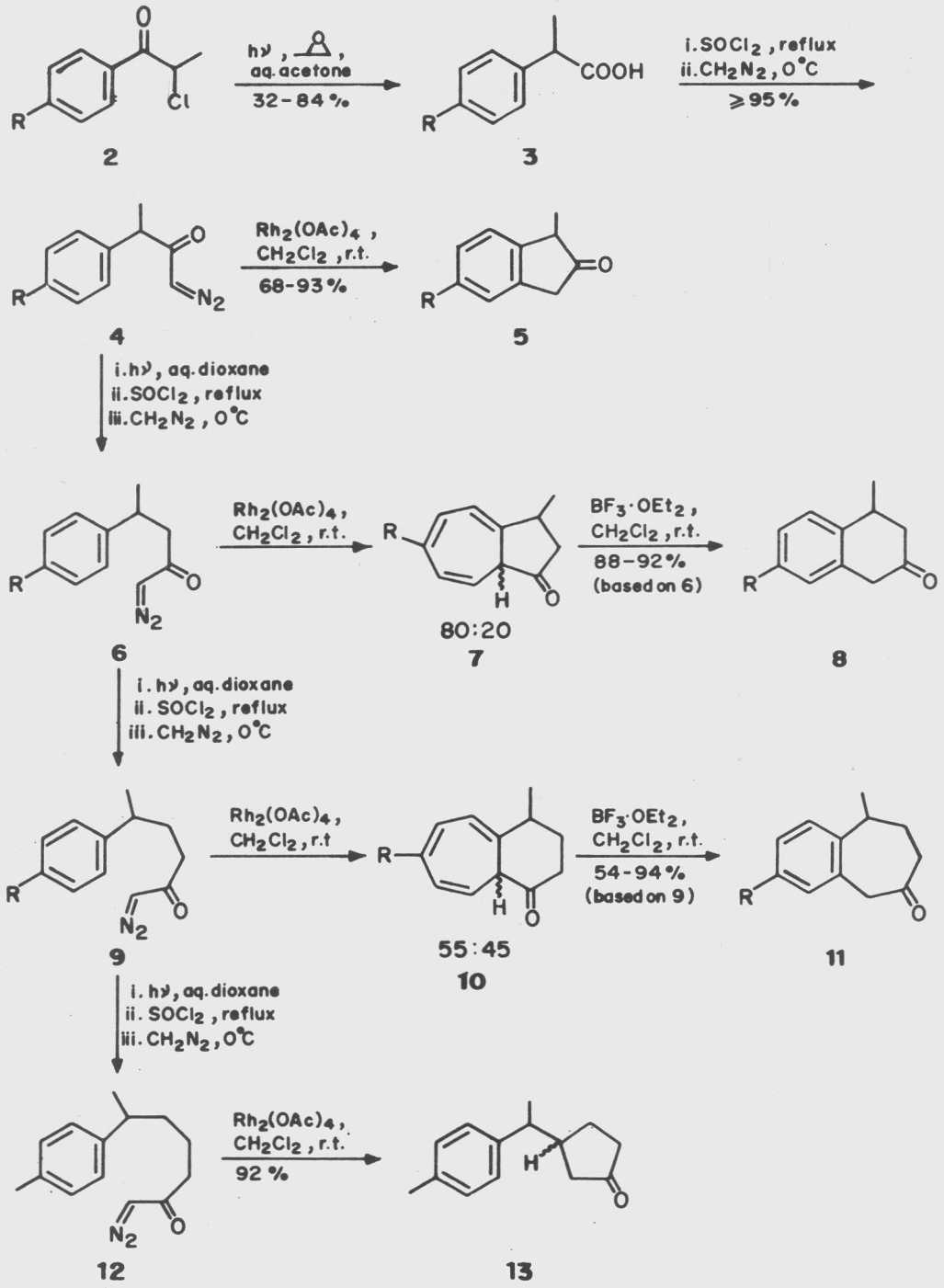
In this context, our work[8] on photochemical 1,2-aryl migration reaction in substituted α-chloropropiophenones **2** leading to α-arylpropionic acids **3** in practical yields gave us an added advantage in the realization of the desired substrates (Scheme II). This high yielding reaction not only provided a ready and convenient access to α- arylpropionic acids **3** but when coupled with the photo-wolff rearrangement reaction[9-10] provided higher homologated arylalkanoic acids. Another attractive incentive to undertake this study was the potential of this type of substrates in the synthesis of many important terpenoid molecules possessing an aromatic moiety such as Cadalenes[11], (+)-*ar*-Himachalene[11], Parvifoline[12], etc.



Scheme II

We wish to report herein our results from such a study which besides delineating various reactivity patterns of Rh-carbenoid insertion reactions led to a convenient methdology for the synthesis of 2-indanones **5**, 2-tetralones **8** and 2-benzosuberones **11**.

Synthesis of 2-indanones. A set of α- diazoketones **4a-e** (n=0, structure **1**) required in the first phase of this study were prepared from the corresponding α-arylpropionic acids **3a-e** following the standard sequence of reactions as outlined in Scheme II. The authenticity of these ketones was established by their typical spectral features — IR: 2110 ($COCH{=}N_2$, str.), 1640 (*CO* $CH{=}N_2$, str) and ^1H NMR: δ 5.0 (1H,s, $COCHN_2$).

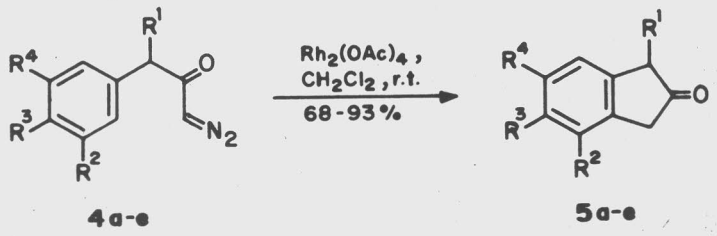
The $Rh_2(OAc)_4$ - catalysis of these α-diazoketones in CH_2Cl_2 at room temperature furnished the corresponding 1- methyl- 2-indanones **5a-e** as the sole products in nearly quantitative yields (Table I). The products have been well characterized by their spectral data.

Thus, the above sequence of reactions led to a simple and an effective methodology for the synthesis of phenyl substituted 2- indanones[13].

Synthesis of 2-tetralones. The success we realised in the one-step synthesis of 2-indanones prompted us to probe the generality of this intramolecular reaction leading to larger rings fused to the aromatic nucleus in the presence of competitive aliphatic C-H sites. Thus, the two substrates **6a,b** (n=1, structure **1**) were examined. It can be seen that these substrates offer a competitive aliphatic primary and secondary C- H sites for carbenoid insertion leading either to the generally preferred cyclopentane annulation or aromatic cycloaddition. α-Diazoketone **6a**, a higher homologue of **4a** was prepared by the previously indicated protocol involving the photo-Wolff rearrangement[7,9] and other standard transformations (Scheme II). Exposure of this α- diazoketone **6a** to catalytic amounts of $Rh_2(OAc)_4$, furnished a homogeneous product, which could be readily identified[14] from its spectral data (Experimental, Table II) as an 80:20 diastereomeric mixture of 3,5-dimethyl-3, 8a-dihydro-1(2*H*)- azulenones **7a**.

It is significant to note that there has been a selective Rh- carbenoid addition into the aromatic nucleus as against the insertion into aliphatic primary C-H bond. Prompted by this finding, we prepared the substrate **6b** containing a competitive secondary C-H site known for its higher reactivity[5]. However, on $Rh_2(OAc)_4$ - catalysis, this substrate gave a homogeneous product comparable in all respects to the one resulting from the α-diazoketone **6a**. The IR, NMR and mass spectral data collectively enabled the characterization of the product as an 80:20 diastereomeric mixture of 3-ethyl-6-methyl-3, 8a- dihydro-1(2*H*)-azulenones **7b**. An analysis of the structures of the Rh-carbenoid addition products namely **7a,b** reveals an interesting feature; the presence of three conjugated double bonds in a cyclic system which should trigger aromatization with the concomitant transformation of cyclopentanone into cyclohexanone affording 2-tetralones and this was found to be so. Thus, on BF_3- OEt_2-catalysis, azulenones **7a** and **7b** furnished exclusively 4,7- dimethyl-2-tetralone **8a** and 4-ethyl-7-methyl-2-tetralone **8b** respectively (Experimental). These results besides throwing some light on the reactivity pattern (*vide infra*) led to a convenient method for realizing 4-alkyl-2-tetralones. Recently, a similar type of carbenoid addition has

Table 1 — Synthesis of 2-indanones **5a-e**

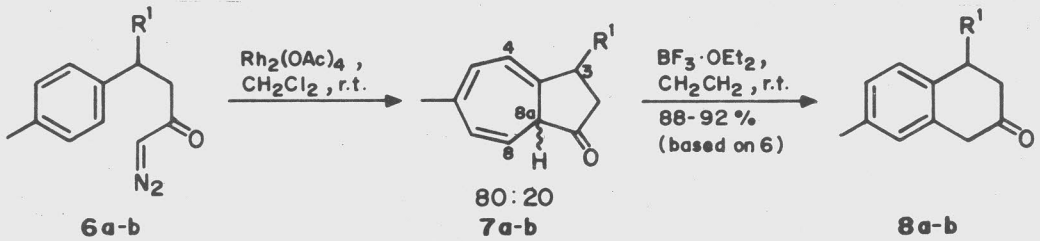


4a-e **5a-e**

	α-Diazoketones **4**				2-Indanones **5**			
	R^1	R^2	R^3	R^4	IR (cm^{-1}) C=O	^{13}CNMR(δ) C=O	^{1}H NMR(δ) CH_2CO	Yield (%)
a	CH_3	H	CH_3	H	1750	221.5	3.50(s)	93
b	CH_3	H	H	H	1750	-	3.52(s)	89
c	CH_3	H	*i*.Bu	H	1748	218.1	3.44(s)	91
d	CH_3	H	OCH_3	H	-1745		3.40(s)	88
e	H	CH_3	H	CH_3	1755	215.6	3.46(s)	68

*Yield of the analytically pure distilled product **5**.

Table II — Synthesis of 3,8a-dihydro-1(2*H*) - azulenones **7a, b** and 2-tetralones **8a,b**



6a-b **7a-b** **8a-b**

Substrate **6**		Azulenones **7**			2-Tetralones **8**			
	R^1	IR (cm^{-1}) C = O	^{13}C NMR δ C=O	^1H NMR (δ) C_8-H	IR (cm^{-1}) C=O	^{13}C NMR(δ) C=O	^1HNMR(δ) C_1-H	Yield (%)
a	CH_3	1750	217.40 (261.76)	5.00,dd (5.09, dd)	1720	210.40	3.43,s	88
b	CH_2CH_3	1748	217.18 (216.83)	4.96,dd (5.02, dd)	1718	210.41	3.5s	92

*Overall yield of the analytically pure distilled product **8** is based on starting α-diazoketone **6**.

been reported by Mckervey *et al*[15], and Taylor *et al*[16]; however, their substrates lacked competitive aliphatic C-H sites to observe any selectivity.

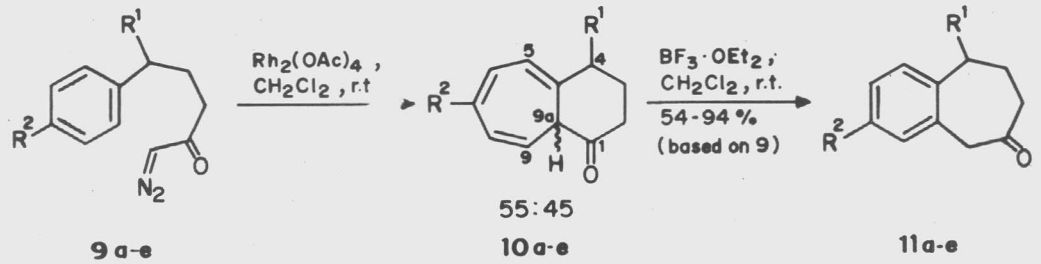
Synthesis of 2-benzosuberones The well-known high reactivity of a tertiary C-H bond[5] towards a carbenoid species prompted us to investigate this type of reaction in a substrate with a tertiary site. Such a proposition would also serve the purpose of finding the limit to which tether length could be increased without changing the reactivity pattern. Thus, the study of $Rh_2(OAc)_4$, catalysis of α-diazoketones **9a-e** (n = 2, structure **1**) was undertaken. Accordingly, the reaction of α- diazoketone **9a** with a catalytic amount of $Rh_2(OAc)_4$ was carried out. The homogeneous product obtained in nearly quantitative yield was readily characterized[14] from its spectral data (Experimental, Table III) as a 55:45 diastereomeric mixture of 4,7-dimethyl-2,3,4,9a-tetrahydro-1*H*- benzocyclohepten-1-one **10a**.

With a view to probing the generality of this intramolecular Buchner reaction[17], four more phenyl substituted α- diazoketones **9b-e** were subjected to $Rh_2(OAc)_4$ - catalysis. The results are summarized in Table III. It is apparent that Rh- carbenoid addition has occurred selectively into the aromatic nucleus despite the presence of the secondary (eg. **9e**) and tertiary (eg. **9a-d**) C-H sites. Besides this, carbenoid addition into the aromatic nucleus in the chloro-substituted substrate **9d** is significant in that the earlier workers used chlorobenzene as a solvent in Buchner reaction and found it inert[18,19]. These bicyclic homotrienones **10a-e** on BF_3- OEt_2-catalysis, readily rearranged to afford the corresponding 2-benzosuberones **11a-e** in practical yields except in the case of the methoxy substituted substrate **10c** which gave a complex mixture of products; however, the latter was not investigated (Experimental, Table III). Thus, these results amounts to the development of a convenient and efficient methodology for the synthesis of 2- benzosuberones, an important class of organic intermediates.

Further enhancement of the tether length as in the α-diazoketone **12** (n = 3, structure **1**) led to an interesting result. Instead of furnishing the previously observed type of products arising from the reaction of Rh- carbenoid with the aromatic nucleus, this substrate selectively displayed a preference for insertion into secondary C-H bond leading to a diastereomeric mixture (60:40) of 3-[1-(4-methylphenyl)ethyl]-cyclopentanone **13** (Scheme II).

Reaction selectivity of metal-carbenoids derived from α-diazo-β-keto esters and α- diazo ketones. The results presented in this paper assume significance when they are compared with those reported by Taber *et al*[4-6] from the reactions of α-diazo-β-keto esters with $Rh_2(OAc)_4$ (Scheme III) directed towards asymmetric synthers of (+)- α-cuparenone.

Table III — Synthesis of 2,3,4,9a, - tetrahydro- 1*H* - benzocyclohepten - 1 - ones **10a-e** and 2-benzosuberones **11a-e**



9 a-e **10 a-e** **11 a-e**

	α-Diazoketone		Benzocycloheptenones**10**			Benzosuberones**11**			
	R^1	R^2	IR (cm^{-1}) C=O	^{1}H NMR (δ) C_9-H	^{1}H NMR(δ) C_4-R^1	IR (cm^{-1}) C=O	^{1}HNMRδ C_1-H	^{1}HNMR(δ) C_5-R-^{1}	Yield* (%)
a	CH_3	CH_3	1718	5.13, dd 5.34, dd	1.07, d 1.22, d	1718	3.61, q	1.37,d	94
b	H	CH_3	1718	5.20, dd 5.34, dd	1.05, d 1.22, d	1710	3.69, q	1.39, d	92
c	OCH_3	CH_3	1715	5.38, dd 5.58, dd	1.05, d 1.24, d	-	-	-	-
d	cl	CH_3	1716	5.32, dd 5.47, dd	1.05, d 1.23, d	1716	3.54, q	1.34, d	71
e	H	H	1715	5.22, dd	2.37-2.84 , m	1710	3.62, s	2.72- 3.04, m	54

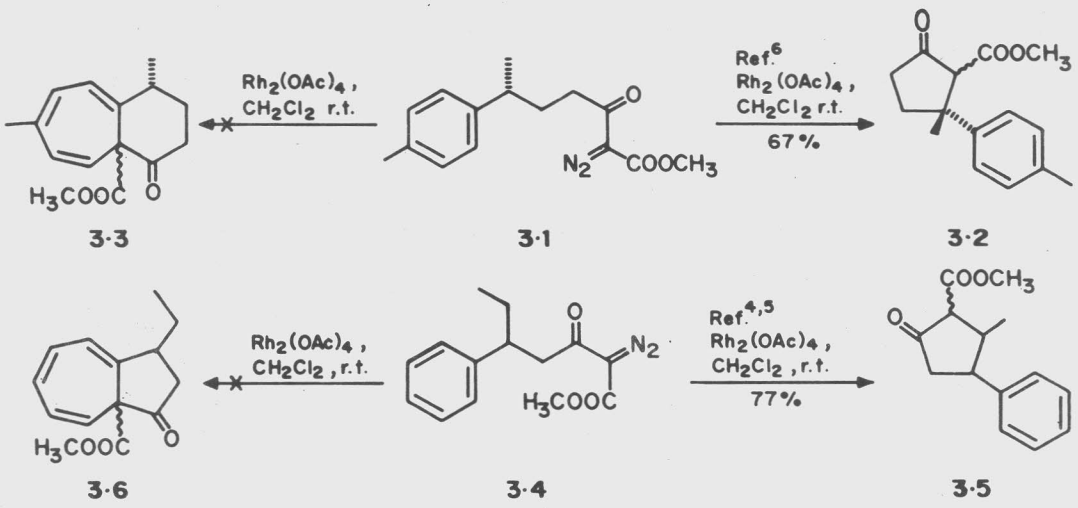
*Yield of the analytically pure distilled material **11** is based on the starting α-diazoketonone **9**.

The α-diazo-β-keto esters **3.1** and **3.4** on $Rh_2(OAc)_4$-catalysis afforded products arising from the Rh- carbenoid insertion into an aliphatic C-H site (3° and 2°) to the total exclusion of cycloaddition with the aromatic nucleus (Buchner reaction). On the other hand, our substrates, namely α-diazoketones **9a** and **6b** on similar catalysis furnished products arising from Buchner reaction, exclusively (Scheme II, Table II and Table III). Such a divergent behaviour may be attributed to the different electrophilicities of the Rh- carbenoid involved[20]. Another operating factor may be the different preferred conformations of the starting diazo substrates as well as the transient carbenoid intermediates[21, 22].

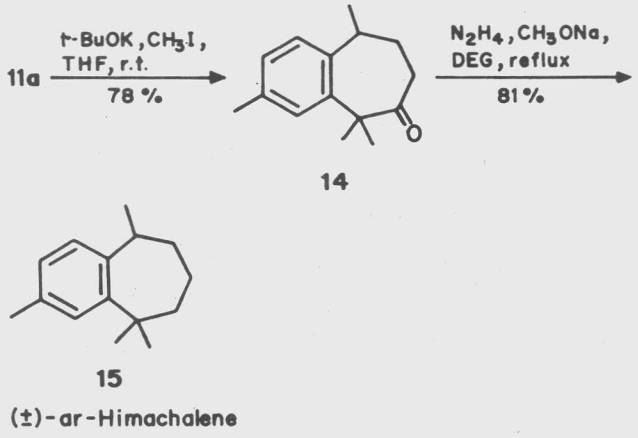
Synthesis of (±)-*ar*-Himachalene. The facile obtention of the 2-benzosuberone **11a**, the structural features of which resembled that of *ar*-Himachalene[23] **15**, prompted us to synthesize[24-32] the latter (Scheme IV).

It can be seen that a sequence of two reactions resulting in *gem*- dimethylation[33] and decarbonylation[34] should lead to the target molecule **15**. These transformation infact, led to a facile and convenient synthesis of **15**[35], which was found to be identical in all respects with that of the naturally occurring sesquiterpene (+) - **15** except the optical activity. It may be mentioned that use of optically active α-diazoketone **9a** has the potential in the realization of the naturally occurring[23] (+)-*ar*- Himachalene.

The present methodology offers an efficient entry into fused bicyclic systems especially those of 2-indanones **5**, 3,8a-dihydro- 1(2*H*)-azulenones **7**, 2-tetralones **8**, 2,3,4,9a-tetrahydro-1*H*- benzocyclohepten - 1 - ones **10** and 2-benzosuberones **11**. It may be added that the starting materials are easily accessible and they offer single products. The homologation by one carbon unit, whenever needed can be done in an efficient and clean manner by photo-Wolff rearrangement. This rearrangement being stereospecific[10] can lead to the synthesis of optically active products, starting from the basic optically active α- diazoketones. Additionally, both the $Rh_2(OAc)_4$-catalysis and BF_3. OEt_2-catalyzed rear-



Scheme III



Scheme IV

rangements can be performed in one pot, that too in practical yields.

In summary, work presented in the paper highlights the preferential selectivity of carbenoids derived from α-diazoketones into aromatic nucleus versus an aliphatic C-H site. Further examination of the potential of these selective Rh-carbenoid reactions in the synthesis of natural products is in progress.

Experimental Section

General. Melting points (m.p.) are uncorrected IR spectra were recorded on a Perkin-Elmer infracord model 137-E and referenced to polystyrene. ^{1}HNMR and ^{13}C NMR spectra were obtained on a 200 MHz Bruker MSL-200, and a 75 MHz Bruker MSL-300 spectrometers, respectively using dilute solutions in $CDCl_3$ [chemical shifts are reported in ppm (δ-scale) relative to Me_4Si or $CHCl_3$ as internal standard]. NMR assignments were aided by INEPT, DEPT and COSY experiments. UV absorption spectra were recorded on a Carl Zeiss UV-Vis model 44069. Mass spectra (MS) were recorded on a CEC-mass spectrometer model 21- 110B, using an ionization potential of 70 eV and a direct inlet system. Elemental analyses were carried out on CHNSO-Carlo-Erba analyzer model 1108. Reactions were monitored either by TLC using neutral alumina plates (visualized with the help of I_2-vapours) or by capillary GC with flame ionisation detection (SE-30 column, 6 mX

0.25 mm i.d., 0.25 mm film thickness) programmed between 60–200°C. Flash chromatography[36] was performed on Eyela flash chromatograph EF-10 using silica gel (60-200 mesh). All solvents were purified and dried following standard procedures[37].

In the preparation of starting materials and intermediates a general procedure is given in detail and spectral data are provided for one typical compound in the series. Benzeneacetic acids **3a-d**[8], **3e**[38] and benzenebutanoic acid[39] were synthesized and characterized by following literature procedures. β-Ethyl-4-methylbenzenepropanoic acid, γ-methylbenzenebutanoic acid, 4-methoxy- γ-methylbenzenebutanoic acid were prepared by following a three step protocol[35] comprising a two-carbon homologation of appropriately substituted carbonyl compound[40] using triethylphosphonoacetate[41], palladium-catalyzed hydrogenation and alkaline hydrolysis in 76-84% overall yields. β,4-Dimethylbenzenepropanoic acid, γ,4-dimethylbenze- nebutanoic acid and δ,4-dimethylbenzenepentanoic acid were synthesized by photo-Wolff rearrangement[7] of α-diazoketones **4a**, **6a** and **9a** respectively, using Rayonet photochemical reactor[42] at λ=254 nm. These acids were characterized by their spectral and analytical data as exemplified below:

δ,4-Dimethylbenzenepentanoic acid: IR (neat) : 3500-2500, 1710 cm^{-1}; ^{1}HNMR ($CDCl_3$): δ 1.2 (d, 3H, *J*=6.68 Hz), 1.4-1.68 (m, 6H), 2.28 (m, 3H), 2.4-2.88 (m,1H), 7.04 (s, 4H); ^{13}CNMR ($CDCl_3$): δ20.66, 22.09, 22.63, 33.82, 37.41, 39.03, 126.53, 126.53, 128.84, 128.84, 135.04, 143.75, 179.82; MS: m/z 206(M^+20%), 175 (15), 132 (70), 131 (8), 120(10), 119(100), 118(8), 105(8), 91(45), 77(20) (Found: C, 75.61; H, 8.78. $C_{13}H_{18}O_2$ requires C,75.67; H, 8.80%).

Synthesis of 2-indanones 5a-e

Preparation of α-diazoketones 4a-e. These ketones were synthesized from the corresponding benzeneacetic acids **3a-e** following the general procedure outlined below, in nearly quantitative yields.

General Procedure: Thionyl chloride (70 mmoles) was added at 0°C to a solution of the acid (50 mmoles) in 25 mL hexane. The reaction mixture was allowed to warm to room temperature and then refluxed for 1-2 hr. After removal of excess thionyl chloride and solvent, the acid chloride was distilled under reduced pressure (100-120°C/10- 12 mm). The yields of the acid chlorides were 92-98%. The acid chloride (25 mmoles) was added at 0°C, under nitrogen atmosphere, to an ethereal solution of diazomethane (75 mmoles). After the solution was stirred for 2hr at 0°C, the cooling bath was removed and stirring continued for additional 4-6 hr. The reaction mixture was concentrated and the residue flash chromatographed (pet. ether - ether, 10:1) to yield the α-diazoketone as a pale- yellow oil in practically quantitative yield.

Diazo-3-(4-methylphenyl)-2-butanone 4a: IR (neat): 2110, 1640, 1605 cm^{-1}; ^{1}HNMR ($CDCl_3$): δ 1.42 (d, 3H *J*=7Hz), 2.28 (s, 3H), 3.59 (q, 1H, *J*=7 Hz), 5.00 (s, 1H), 7.12 (s, 4 H).

$Rh_2(OAc)_4$-catalysis of α-diazoketones 4a-e. These on $Rh_2(OAc)_4$-catalysis according to the general procedure furnished 1,3-dihydro-2*H*-inden-2-ones , i.e. 2- indanones **5a-e** in practical yields (Table I).

General procedure. A solution of α- diazoketone (5.0 mmoles) in 10 mL of anhydrous CH_2Cl_2 was added under nitrogen atmosphere over a period of 15 min. to a stirred suspension of $Rh_2(OAc)_4$ (2 mg) in 40 mL of CH_2Cl_2 at room temperature. Evolution of nitrogen was observed. After completion of the reaction (30-45 min), as indicated by TLC and confirmed by IR (disappearance of bands at 2100, 1640 cm^{-1}), the reaction mixture was filtered through Whatmann filter paper No.1 under nitrogen and the filtrate concentrated under reduced pressure. The product was purified either by flash chromatography (pet. ether-ether, gradient) or by distllation.

1,5-Dimethyl-1, 3-dihydro-2*H*-inden-2-one, i.e. 1,5- Dimethyl-2- indanone 5a: IR (neat): 1750, 1610 cm^{-1}; ^{1}HNMR ($CDCl_3$); δ 1.40 (d, 3H, *J*=7.0Hz), 2.31(s,3H), 3.15-3.75(m,1H),3.50(s,2H), 7.10(s,3H); ^{13}CNMR ($CDCl_3$) : δ 19.49, 25.28, 46.71, 51.35, 129.29, 131.98, 132.20, 140.33, 140.92, 144.39, 221.5 (Found: C, 82.04; H, 7.52. $C_{11}H_{12}O$ requires. C, 82.46; H, 7.54%).

Synthesis of 2-tetralones. The α- diazoketones **6a** and **.6b** were synthesized from the corresponding acids 3-(4- methylphenyl)butanoic acid and 3-(4-methylphenyl) pentanoic acid, respectively according to the general procedure (*vide supra*) in nearly quantitative yields.

Diazo-4-(4-methylphenyl)pentane-2-one 6a: IR (neat): 2110, 1645 cm^{-1}; ^1H NMR ($CDCl_3$): δ1.26 (d, 3H, *J*=7.0 Hz), 2.31(s,3H),2.53(d,2H,*J*=8.0 Hz), 3.0-3.22 (m, 1H), 5.04 (s, 1H), 7.06 (s, 4H); MS: m/z 202 (M^+, 5%), 174 (M^+-N_2,25), 161 (50), 159 (68), 149 (30), 146 (40), 132 (60), 131 (85), 119 (100), 117 (60), 104 (20), 81 (25), 77 (10); UV/Vis (ethanol): λ(logε) = 255 (13343).

$Rh_2(OAc)_4$ -catalysis of α-diazoketones 6a-b. These ketones were subjected to $Rh_2(OAc)_4$-catalysis according to the general procedure described (*vide supra*) to furnish the bicyclic homotrienones[32] **7a, b** in quantitative yields.

3,6-Dimethyl-3, 8a-dihydro-1 (2*H*) azulenone (diastereoisomers 80:20) 7a: IR (neat): 1750, 1640, 1620 cm^{-1}; ^1H NMR: δ 1.12 (d, 3H, *J*=6.9 Hz, C_3-CH_3, 80%), 1.32 (d, 3H, *J*=6.7 Hz, C_3-CH_3, 20%), 1.98 (s, 6H, C_6-CH_3 of both diastereoisomers), 2.51-3.26 (m, 8H, C_2-H, C_3-H and C_{8a}-H of both diasteroisomers), 5.01 (dd, 1H, $J_{8,8a}$ = 4.1 Hz and $J_{7,8}$ = 9.40 Hz, C_8-H, 80%), 5.09 (dd, IH, $J_{8.8a}$ = 4.02 Hz and $J_{7,8}$ = 9.65 Hz, C_8-H, 20%), 5.85-6.38 (m, 6H, C_4-H, C_5-H and C_7-H of both diastereoisomers); ^{13}C NMR (major diasteroisomer): δ 19.35, 24.05, 34.6, 46.52, 49.89, 114.93, 119.87, 127.35, 129.86, 138.01, 138.30, 217.4; (minor diasteroisomer): δ 20.89, 24.29, 33.99, 47.17, 50.95, 118.26, 118.53, 129.09, 130.22, 138.64, 140-46, 216.76.

$BF_3.OEt_2$-catalysis of 7a,b. These homotrienones $BF_3.OEt_2$-catalysis according to the general procedure described below furnished 2- tetralones **8a** and **8b** respectively in practical yields (Table II).

General procedure: To a stirred solution of homotrienone (5 mmoles) in CH_2Cl_2 (20 mL) was added catalytic amount of $BF_3.OEt_2$ (7.5 mg, 1 mole %) under nitrogen atmosphere at room temperature. After completion of the reaction (30-45 min), as indicated by TLC and confirmed by IR (disappearance of band at 1750 cm^{-1}), the reaction mixture was poured into cold saturated aq. $NaHCO_3$ solution and extracted with CH_2Cl_2 (3x50 mL). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The product was purified either by flash chromatography)pet. ether-ether, gradient) or by distillation under reduced pressure.

4,7-Dimethyl-3,4-dihydro-2 (1*H*) - naphthalenone, i.e. 4,7- dimethyl-2-tetralone 8a: IR (neat) : 1718, 1625, 1580 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.2 (d, 3H, *J = 7.0 Hz), 2.2 (s, 3H), 2.47 (d, 2H, J*=7.94 Hz), 2.83-3.33 (m, 1H), 3.43 (s, 2H), 6.84 (s, 1H), 7.0(s, 1H), 7.02 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 20.09, 20.8, 32.99, 44.36, 46.38, 125.73, 127.50, 128.90, 132.52, 136.3, 138.03, 210.4 (Found: C,82.38; H, 8.30. $C_{12}H_{14}O$ requires C, 82.7; H, 8.09%).

Synthesis of 2-benzosuberones 11a-e. The α- diazoketones **9a-e** were prepared according to the general procedure (*vide supra*) from the corresponding benzenebutanoic acids in nearly quantitative yields.

Diazo-5(4-methylphenyl)-2-hexanone 9a: IR (neat): 2120, 1640 cm^{-1}, ^{1} NMR ($CDCl_3$): δ 1.18 (d, 3H, *J*=6.25 Hz), 1.59- 2.30 (m, 4H,), 2.34 (s, 3H), 2.34-3.0 (m, 1H), 5.04 (s, 1H), 7.07 (s, 4H); MS: m/z 216 (M^+, 2%), 188 (M^+ -N_2-12), 173 (95), 145 (38), 132 (80), 119 (98), 118 (40), 117 (80), 116(20), 115(45), 105 (45), 103(23), 91 (100), 77 (40), 55 (65); UV/Vis (ethanol); λ (log ε) = 252 (14216).

$Rh_2(OAc)_4$-catalysis of α-diazoketones 9a-e. These ketones were subjected to $Rh_2(OAc)_4$-catalysis according to the general procedure (*vide supra*) furnished the bicyclic homotrienones[32] **10a-e** in nearly quantitative yields (Table III).

4,7-Dimethyl-2,3,4,9a-tetrahydro-1 *H*-benzocyclohepten-1-one (diastereoisomers 45:55) (10a): IR (neat) : 1718, 1615 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.07 (d, 3H, *J*=6.9 Hz, C_4-CH_3, 45%), 1.22 (d, 3H, *J = 6.6 Hz, C*$_4$-CH_3, 55%), 2.03 (s, 6H, C_7-CH_3, of both diasteroisomers), 1.68-2.75 (m, 12 H, C_2-H, C_3-H, C_4-H and C_{9a}-H, of both diastereoisomers), 5.13 (dd, 1H, $J_{9,9a}$ = 5.71 Hz and $J_{8,9}$ = 9.14 Hz, C_9-H, 45%), 5.34 (dd, 1H, $J_{9.9a}$ = 5.71 Hz and $J_{8,9}$ = 9.33 Hz, C_9-H, 55%), 5.92-6.4 (m, 6H, C_5-H, C_6-H and C_8-H, of both diastereoisomers), ^{13}CNMR (75 MHz, $CDCl_3$): λ 18.14,21.80,23.60,23.70, 29.31, 30.36, 33.63, 34.06, 36.12, 37.94, 50.83, 52.06, 114.2, 118.25, 126.6, 127.33, 127.53, 128.18, 128.73, 128.96, 134.77, 137.44, 138.19, 138.33, 211.29, 211.61; UV/Vis (*n*-hexane): λ (log ε) = 287 (2376).

$BF_3.OEt_2$-catalysis of 10a-e. These bicyclic homotrienones on $BF_3.OEt_2$-catalysis (*vide supra*) furnished 2- benzosuberones **11a-e** in very good yields (Table III).

3,9- Dimethyl - 5,7,8,9-tetrahydro - 6*H*- benzocycloheptene-6-one, i.e. 5,8-dimethyl-2-benzosuberone 11a: IR (neat) : 1718, 1617 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.37 (d, 3 H, *J* = 6.5 Hz), 1.52-2.64 (m, 4H), 2.28 (s, 3H), 2.84- 3.28 (m, 1H), 3.61 (*ABq*, 2H,

J=17.5 Hz), 6.93 (s, 1H), 7.06 (s,2H); ^{13}CNMR ($CDCl_3$): δ 19.41. 20.68, 34.02, 34.12,41.23, 49.44, 125.09, 128.09, 130.32, 133.65, 136.05, 139.9, 210.29; MS : m/z 188 (M^+ 46%), 173 (15), 159 (10), 145(35), 133 (100), 132 (40), 131(20), 117(30), 105(10), 91(10), 77 (4); UV/Vis (ethanol); λ (log ε) = 207 (8356), 243 (634), 254 (730) (Found : C,82.78; H, 8.61. $C_{13}H_{16}O$ requires C, 82.92; H, 8.57%).

BF_3. OEt_2-catalysis of 10c . The methoxy substituted bicyclic homotrienone **10c** was subjected to BF_3.OEt_2-catalysis in exactly the same manner as the other analgous homotrienones. However, the GLC of the reaction product revealed presence of a complex mixture. The ^{1}H NMR spectrum indicated the non-occurance of the expected rearrangement leading to **11c** (absence of aromatic resonances as well as *AB*-quartet for C_5-CH_2 flanked by aromatic ring and carbonyl group). This result was not further investigated.

Diazo-6-(4-methylphenyl)-2-heptanone 12. The α-diazoketone **12** was synthesized from the corresponding δ, 4-dimethylbenzenepentanoic acid in accordance with the general procedure (*vide supra*) in 89% yield.

IR (neat): 2110, 1650 cm^{-1}, ^{1}H NMR ($CDCl_3$); δ 1.19 (d, 3H, *J*=6.5 Hz). 1.39-1.77 (m, 6H), 2.29 (s, 3H), 2.44- 2.88 (m,1H), 5.09 (s,1H), 7.04 (s, 4H); ^{13}CNMR ($CDCl_3$): δ 20.40, 21.83, 22.84.37.29, 38.86,40.1, 53.60, 126.28, 126.28, 128.54, 128.54, 134.73, 143.54, 194.37, MS : m/z 230 (M^+, 1%), 202 (M^+-N_2,5), 187(35), 159(20), 145(50), 132(20), 119 (100), 117(40), 115 (30), 105(50), 92(70), 77(25), 55(35).

3-[1-(4-Methylphenyl)ethyl]cyclopentanone (diastereoisomers 60:40) 13. The α-diazoketone **12** on $Rh_2(OAc)_4$- catalysis gave a diastereoisomeric mixture (60:40) of cyclopentanone **13** in 92% isolated yield.

IR (neat) : 1750 cm^{-1}, ^{1}H NMR ($CDCl_3$): δ 1.28 (d, 3H, *J*=6.9 Hz, 60%), 1.30 (d, 3H, *J*=6.8 Hz, 40%), 1.4-2.4 (m, 14H, of both diastereoisomers), 2.31 (s, 3H, 40%), 2.33 (s, 3H, 60%), 2.4-2.75 (m, 3H, of both diastereoisomers), 7.07 (s, 4H, 60%), 7.11 (s, 4H, 40%) (Found: C, 82.36; H, 8.81. $C_{14}H_{18}O$ requires C, 83.12; H, 8.96%).

Synthesis of (±)–*ar*-Himachalene 15

3,5,5,9- Tetramethyl-5, 7,8,9-tetrahydro-6*H*-benzocyclohepten-6- one 14. To a magnetically stirred solution of **11a** (500 mg, 2.65 mmoles) and CH_3I (1.87g, 13.3 mmoles) in anhydrous THF (5 mL) under nitrogen atmosphere was added *t*-BuOK (655 mg, 5.83 mmoles) in portions over a period of 30 min. The reaction mixture was stirred at room temperature (4 hr) and then poured over ice-water slurry and extracted with ether (3 x 50 mL). The combined organic layer was washed with aq. sat. $NaHCO_3$ solution (2 x 10 mL) followed by brine (2 x 10 mL) and dried over Na_2SO_4. The crude product obtained on flash chromatography (pet. ether - ether, 25:1) afforded the *gem*-dimethylated ketone **14** as colourless solid (442 mg, 78%), m.p. 69° (*n*-hexane); IR (nujol): 1716, 1615, 1580, 1390, 1370 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.31 (d, 3H, *J*=6.5 Hz), 1.47 (s, 3H), 1.56 (s, 3H), 2.0-2.45 (m, 4H), 2.35 (s, 3H), 2.5-3.0 (m, 1H), 7.06 (s, 2H), 7.12 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 18.74, 20.7, 25.31, 26.02, 32.09, 35.51, 36.41, 52.09. 124.31, 125.53, 127.46, 135.54, 137.34, 143.44, 216.78; MS: m/z 216 (M^+ 35%), 201 (12), 174 (100), 173(60), 161(40), 159 (90), 145 (60), 131 (30), 115(20), 105(10), 91(10), 77(2) (Found: C,83.50; H, 9.68. $C_{15}H_{20}O$ requires C, 83.28; H, 9.32%).

2,5,9,9-Tetramethyl-6,7,8,9-tetrahydro-5*H*- benzocyclohepten, i.e. (±)-*ar*-Himachalene 15. A mixture of **14** (109 mg. 0.5 mmoles), anhydrous hydrazine (65 mg, 62μL, 2 mmoles) and sodium methoxide (27 mg, 0.5 mmole) was heated with freshly distilled diethylene glycol (5 mL) at 150°C. After 1hr, excess hydrazine was removed and the bath temperature allowed to rise to 220°C. Refluxing was continued for an additional hour. The cooled reaction mixture was poured over ice, acidified with con. HCl and extracted with ether (3 x 50 mL). The combined organic layer was washed with aq. sat. $NaHCO_3$ solution (2 x 10 mL) followed by brine (2 x 10 mL) and dried over Na_2SO_4. The crude product obtained on flash chromatography (petroleum ether) and bulb to bulb distillation (120-125°C/4 mm) yielded (±)-**15** as a colourless oil (82 mg, 81%); IR (neat): 1615, 1580, 1400, 1390, 1380, 1370 cm^{-1}; ;^{1}H NMR ($CDCl_3$) : λ 1.33 (d, 3H, *J=6.5 Hz), 1.34 (s, 3H), 1.41 (s, 3H), 1.48-2.0 (m, 6H), 2.27 (s, 3H), 2.95-3.46 (m, 1H), 6.96 (s, 1H), 7.04 (s, 1H), 7.13 (s, 1H);* ^{13}CNMR ($CDCl_3$): δ 21.24, 21.39, 24.22, 30.27, 34.18.34.89 , 36.79, 39.81, 41.49, 125.85, 126.79, 127.89, 135.16, 141.49, 148.01. MS: m/z 202 (M^+, 40%), 187 (78), 159 (20), 145 (100), 143 (35), 141 (35), 131 (85), 129(50), 128(60), 119(40), 115(50), 105(40), 91(20),

77(8). (Found: C, 89.11; H, 10.78. $C_{15}H_{22}$ requires C, 89.04; H, 10.95%).

Acknowledgement

One of the authors (S.G.S) thanks CSIR, New Delhi for the award of a fellowship.

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43 It may be noted that bicyclic homotrienones **7a-b** and **10a-e** are sensitive to acid and alkali and are not amenable to purification procedures. Their preparation, handling and analysis are carried-out immediately using oven-dried apparatus washed with aqueous ammonia solution.