# Vinylogous Wolff Rearrangement of Cyclic β,γ-Unsaturated Diazomethyl Ketones: a New Synthetic Method for Angularly Functionalised Polycyclic Systems

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Decomposition of the rigid polycyclic β,γ-unsaturated diazomethyl ketones (1a) and (1b) and (2a) and (2b) promoted by 'activated CuO', Cu(acac)$_2$, Cu(OTf)$_2$, or Ni(acac)$_2$ in the presence of methanol are shown to give mainly the corresponding rearranged γ,δ-unsaturated angularly substituted esters (3a) and (3b) and (8a) and (8b) together with the α-methoxy ketones (4a) and (4b) and (9a) and (9b). While photo-Wolff rearrangement of the diazo ketones leads to the corresponding homologous esters (5a) and (5b) and (10a) and (10b) the silver benzoate–triethylamine induced reaction gives the rearranged esters in addition to the homologous esters.

The copper salt-catalysed decomposition of a number of monocyclic [1,2] and acyclic [2] β,γ-unsaturated-α'-diazomethyl ketones in the presence of a nucleophile, e.g. methanol, has been shown to lead to the respective γ,δ-unsaturated esters via skeletal rearrangement, [3] termed as the 'vinylogous Wolff rearrangement' [2] [equation (1)]. Surprisingly, the scope of this interesting

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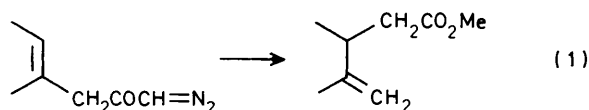
transformation, a synthetic alternative to Claisen rearrangement [4] and a potentially attractive method for a functionalised angular alkylation [5] in fused-ring systems remained unexplored. In conjunction with our interests in the intramolecular alkylation and rearrangements of polycyclic β,γ-unsaturated diazo ketones [6] we have investigated the decompositions of the easily accessible hexahydrophenanthrene and tetrahydrofluorene diazoacetyl derivatives (1a) and (1b) and (2a) and (2b) with a variety of copper and other metal catalysts in the presence of methanol, leading to a simple one-step method for the introduction of an angularly functionalised two carbon residue via vinylogous Wolff rearrangement. In addition, we have also investigated the reactions of these diazo ketone substrates under normal silver-catalysed and photo-Wolff rearrangement conditions in methanol. The present paper [7] constitutes a detailed account of these studies.

Results and Discussion

The comparative effectiveness of two established homogeneous catalysts, bis(pentane-2,4-dionato)copper(II) [Cu(acac)$_2$] and copper(II) bis(trifluoromethylsulphonate) [Cu(OTf)$_2$] for vinylogous Wolff rearrangement, [1,2] and 'activated CuO' [8] as well as bis(pentane-2,4-dionato)nickel(II) [9] [Ni(acac)$_2$] two highly efficient catalysts for the intramolecular oxocarbenoid insertion reactions in C–H and C=C bonds were first examined with methanol as the nucleophile with reference to the formation of various products from the diazo ketones (1a) [10] and (1b) [10] (Scheme 1) and (2a) [10] and (2b) [10] (Scheme 2). Quantitative evaluations of the products are outlined in Tables 1 and 2.

Treatment of the diazo ketone (1a) with anhydrous Cu(acac)$_2$ or Cu(OTf)$_2$ in boiling cyclohexane containing methanol for 3 h, in each case, gave mixtures of the rearranged ester (3a) and the methanol-insertion [11] product (4a) in a ratio of 1:1 (69%)
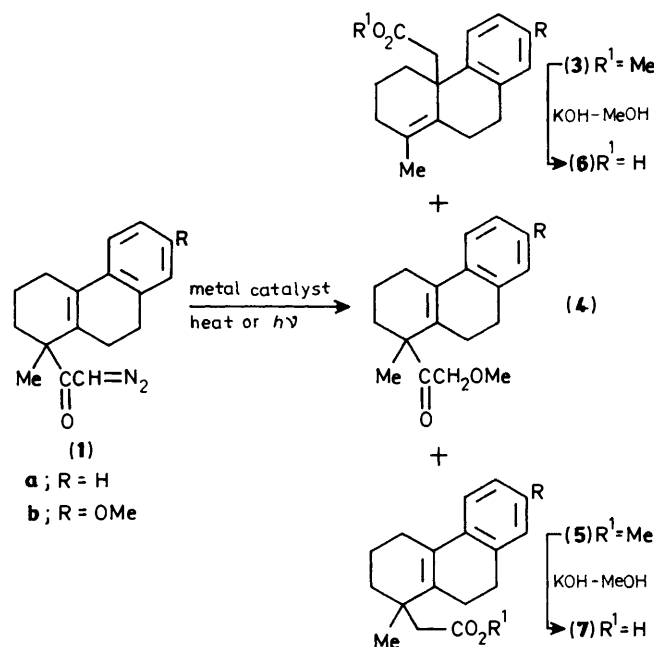
Scheme 1.

and 3:1 (93%), respectively as revealed from g.l.c. and ^{1}H n.m.r. analyses (Table 1). The decomposition of (1a) in the presence of 'activated CuO' or Ni(acac)$_2$ in cyclohexane and methanol under reflux and irradiation with tungsten lamps required 2 and 26 h, respectively for completion of the reaction and gave 2:1 (96%) and 9:1 (71%) mixtures of (3a) and (4a), respectively. In each case the mixtures were cleanly separated by chromatography and the structures of (3a) and (4a) were assigned from their elemental analyses and spectral data (see Experimental section). The ester (3a) was further characterized through saponification to the respective acid (6a). While an irradiated and 'activated CuO' catalysed reaction of the methoxy analogue (1b) with boiling cyclohexane containing methanol, gave practically pure rearranged ester (3b) (87%), the Cu(acac)$_2$ or Cu(OTf)$_2$ induced decomposition produced a mixture of (3b) along with the possible methanol insertion product (4b), as revealed from the ^{1}H n.m.r. spectral data. The Ni(acac)$_2$ catalysed decomposition of (1b) gave a complex mixture of products.

Table 1. Distribution of the rearranged products (**3a, b**), (**4a, b**), and (**5a, b**) in the metal-catalysed decompositions of the diazo ketones (**1a**) and (**1b**)

Diazo ketone Substrate	Entry	Catalysts	Yield (%)	Ratio of products[c]		
				(3a) or (3b)	(4a) or (4b)	(5a) or (5b)
(1a)	1	'Activated CuO', C_6H_{12}, MeOH (1%), heat, hv (W)	96[a]	2	1	d
(1a)	2	$Cu(acac)_2$, C_6H_{12}, MeOH (1%), heat	69[a]	1	1	d
(1a)	3	$Cu(OTf)_2$, C_6H_{12}, MeOH (1%), heat	93[a]	3	1	d
(1a)	4	$Ni(acac)_2$, C_6H_{12}, MeOH(1%), heat	71[a]	9	1	d
(1a)	5	$PhCO_2Ag$, NEt_3, MeOH	82[a]	1	d	1
(1a)	6	MeOH, hv	93[a]	d	d	100
(1b)	7	'Activated CuO', C_6H_{12}, MeOH (1%), heat, hv (W)	87[a]	100	d	d
(1b)	8	$Cu(acac)_2$, C_6H_{12}, MeOH (1%), heat	79[a]	7	3	d
(1b)	9	$Cu(OTf)_2$, C_6H_{12}, MeOH (1%), heat	75[a]	5	3	d
(1b)	10	$PhCO_2Ag$, NEt_3, MeOH	83[a]	1	d	1
(1b)	11	MeOH, hv	73[b]	d	d	100[e]

[a] Products isolated after filtration of the reaction mixture through a short column of alumina. [b] Pure acid (**7b**) isolated after saponification. [c] Determined by g.l.c. and ^1H n.m.r. [d] Could not be detected by g.l.c. and ^1H n.m.r. [e] Isolated as the corresponding acid (**7b**).

Table 2. Distribution of the rearranged products (**8a, b**), (**9a, b**), and (**10a, b**) in the metal-catalysed decompositions of the diazo ketones (**2a**) and (**2b**)

Diazo ketone Substrate	Entry	Catalysts	Yield (%)	Ratio of products[c]		
				(8a) or (8b)	(9a) or (9b)	(10a) or (10b)
(2a)	1	'Activated CuO', C_6H_{12}, MeOH (1%), heat, hv (W)	80[a]	4	1	e
(2a)	2	$Cu(acac)_2$, C_6H_{12}, MeOH (1%), heat	66[a]	3	5	2
(2a)	3	$Cu(OTf)_2$, C_6H_{12}, MeOH (1%), heat	67[a]	3	5	2
(2a)	4	$PhCO_2Ag$, NEt_3, MeOH	82[a]	2	e	3
(2a)	5	MeOH, hv	94[a]	e	e	100
(2b)	6	'Activated CuO', C_6H_{12}, MeOH (1%), heat, hv (W)	72[a]	100	e	e
(2b)	7	$Cu(acac)_2$, C_6H_{12}, MeOH (1%), heat	50[b]	100	e	e
(2b)	8	$Cu(OTf)_2$, C_6H_{12}, MeOH (1%), heat	93[a]	5	2	1
(2b)	9	$Ni(acac)_2$, C_6H_{12}, MeOH (1%), heat	66[b]	100	e	e
(2b)	10	$PhCO_2Ag$, NEt_3, MeOH	91[a]	5.5	e	4.5
(2b)	11	MeOH, hv	64[c]	e	e	100[f]

[a] Products isolated after filtration of the reaction mixture through a short column of alumina. [b] Pure ester (**8b**) isolated by chromatography. [c] Pure acid (**12b**) isolated after saponification. [d] Determined by g.l.c. and ^1H n.m.r. [e] Could not be detected by g.l.c. or ^1H n.m.r. [f] Isolated as the corresponding acid (**12b**).

The reactions of methanolic solutions of the diazo ketones (**1a**) and (**1b**) with silver benzoate and triethylamine under traditional Arndt–Eistert conditions[12] gave, in each case, over 80% yield of the mixtures of the respective homologated and rearranged[1,2a] esters (**5a**) and (**3a**), and (**5b**) and (**3b**) in ca 1:1 ratio. The photolysis[1,2a] of the diazo ketone (**1a**) in methanol smoothly produced (**5a**) (93%). In contrast, under identical conditions, the methoxy analogue (**1b**) afforded the homologated ester (**5b**) along with an unidentified material (Table 1). Saponifications of the esters (**5a**) and (**5b**) gave the acids (**7a**) and (**7b**) respectively (Scheme 1).

In parallel with the hydrophenanthrene analogues, the decomposition of the hydrofluorene diazo ketone (**2a**) when irradiated in the presence of 'activated CuO' gave the rearranged ester (**8a**) and the methanol-insertion product (**9a**) in a ratio of ca. 4:1 (80%), whilst the methoxy diazo ketone (**2b**) produced the rearranged[1,2a] esters (**5a**) and (**3a**) and (**5b**) and (**3b**) in ca 1:1 (Table 2). The irradiation with tungsten lamps of (**2b**) in the presence of $Cu(acac)_2$ (3 h) or $Ni(acac)_2$ (26 h), afforded, in each case, a mixture of the rearranged ester (**8b**) and an unidentified product in a ratio of 85:15 (ca. 67%). In contrast, the demethoxy analogue (**2a**) with $Cu(acac)_2$ or $Cu(OTf)_2$ produced a mixture of the rearranged ester (**8a**), the methanol-insertion product (**9a**), and the homologated ester (**10a**) in a ratio of 3:5:2 (66%). The $Ni(acac)_2$-promoted reaction of (**2a**), however, gave a complex mixture. The $Cu(OTf)_2$-catalysed reaction of (**2b**) again gave a mixture of (**8b**), (**9b**), and (**10b**) in a ratio of 5:2:1 (93%). Treatment of (**2a**) and (**2b**) in methanol with silver

Scheme 2.
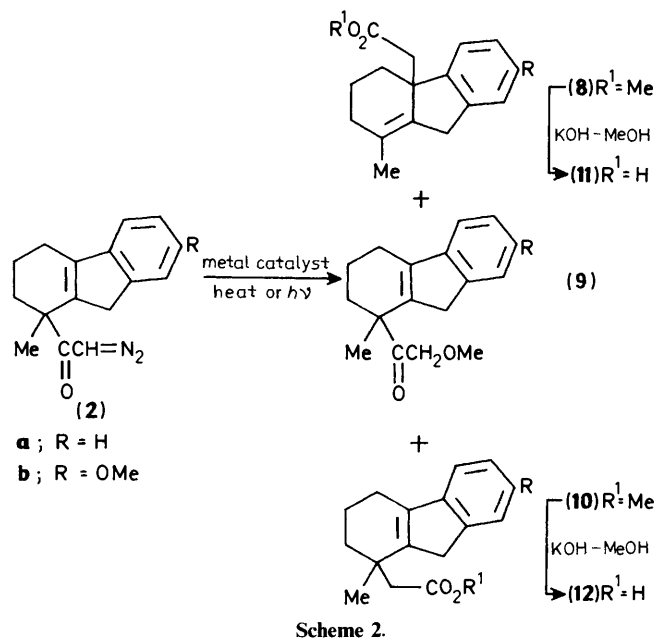
benzoate–triethylamine gave, in each case, a mixture of the homologated and the rearranged esters (**10a**) and (**8a**) (3:2), and (**10b**) and (**8b**) (4.5:5.5) respectively in excellent yields, along

with unidentified products. On photolysis in methanol, (2a) and (2b) gave the homologous ester (10a) (94%) and (10b) (61%) (Table 2) respectively. The esters (8a) and (10a), and (8b) and (10b) were saponified to the corresponding acids (11a) and (12a), and (11b) and (12b) (Scheme 2).

Best results for vinylogous Wolff rearrangement of the diazo ketones (1a) and (1b) and (2a) and (2b) with methanol were obtained with 'activated CuO' (Tables 1 and 2). However, reactions of these diazo ketones with $Cu(OTf)_2$ and benzyl alcohol under recently reported [2d] conditions gave complex mixtures of products in each case. The copper and nickel salt catalysed decompositions of the rigid β,γ-unsaturated diazo ketones (1a) and (1b) and (2a) and (2b), gave specific formation of the corresponding vinylogous rearranged esters together with methanol-insertion products in variable yields; silver benzoate–triethylamine catalysed reaction, however, gave both the homologous esters and rearranged esters as the main products. These results clearly indicate different mechanisms operate for the two sets of reactions.[13] Thus, a reasonable reaction pathway for the transformations of the diazo ketones (1a) and (1b) and (2a) and (2b) to the corresponding vinylogous Wolff rearrangement products (3a) and (3b) and (8a) and (8b) with copper and nickel catalysts involves formation of the bicyclo[2.1.0]pentane intermediate (A) via intramolecular addition of oxocarbenoids to the β,γ-unsaturation. The intermediacy of the metal carbenoid intermediates are also supported by the isolation of the methanol-insertion products in various proportions from these reactions. Fragmentation of the intermediate (A) would thus lead to a γ,δ-unsaturated ketene intermediate (B). The refinement of this scheme, as suggested by Smith et al.,[2e] allows for either carbenoid addition or fragmentation processes to proceed in a stepwise manner (see Scheme 3). On the other

hand, the silver-catalysed rearrangement of the diazo ketones (1a) and (1b), and (2a) and (2b) producing the homologous esters and the rearranged esters respectively, are possibly produced via an organosilver species in the rearrangements similar to that suggested by Wenkert et al,[14] along with the intramolecular addition path (Scheme 3).

In conclusion, the present results demonstrate clearly that depending upon the reaction conditions it is possible to control the nature of the rearrangement products in rigid β,γ-unsaturated diazo ketones. The most important outcome of the present work is the development of a simple one-step method for the introduction of an angular acetic acid residue from appropriately substituted polycyclic β,γ-unsaturated diazo ketones, via vinylogous Wolff rearrangement, thereby considerably increasing the flexibility of this reaction.

Experimental

M.p.s and b.p.s are not corrected. I.r. spectra of solids (KBr) and liquids (film) were recorded on a Perkin-Elmer model PE 298 spectrometer. U.v. spectra were recorded on a Beckman DU or Hitachi 200 spectrometer for solutions in 95% ethanol. [1]H N.m.r. spectra were recorded at 60 or 200 MHz (if specified) on Varian Associates Models T-60A and XL-200 spectrometers, respectively, for solutions in CCl_4 or $CDCl_3$ (if specified), with $SiMe_4$ as internal standard. Analytical g.l.c. was performed on a Hewlett-Packard model 5730A chromatograph, 20 × 1/8 in 10% UCW-982 (Column A) and Shimadzu GC-9A model (6.5 ft × 0.25 in) 1.5% OV-17 (Column B) equipped with a flame-ionization detector using N_2 as the carrier gas. Elemental analyses were performed by P. P. Bhattacharyya of this laboratory. Column chromatography was performed on neutral
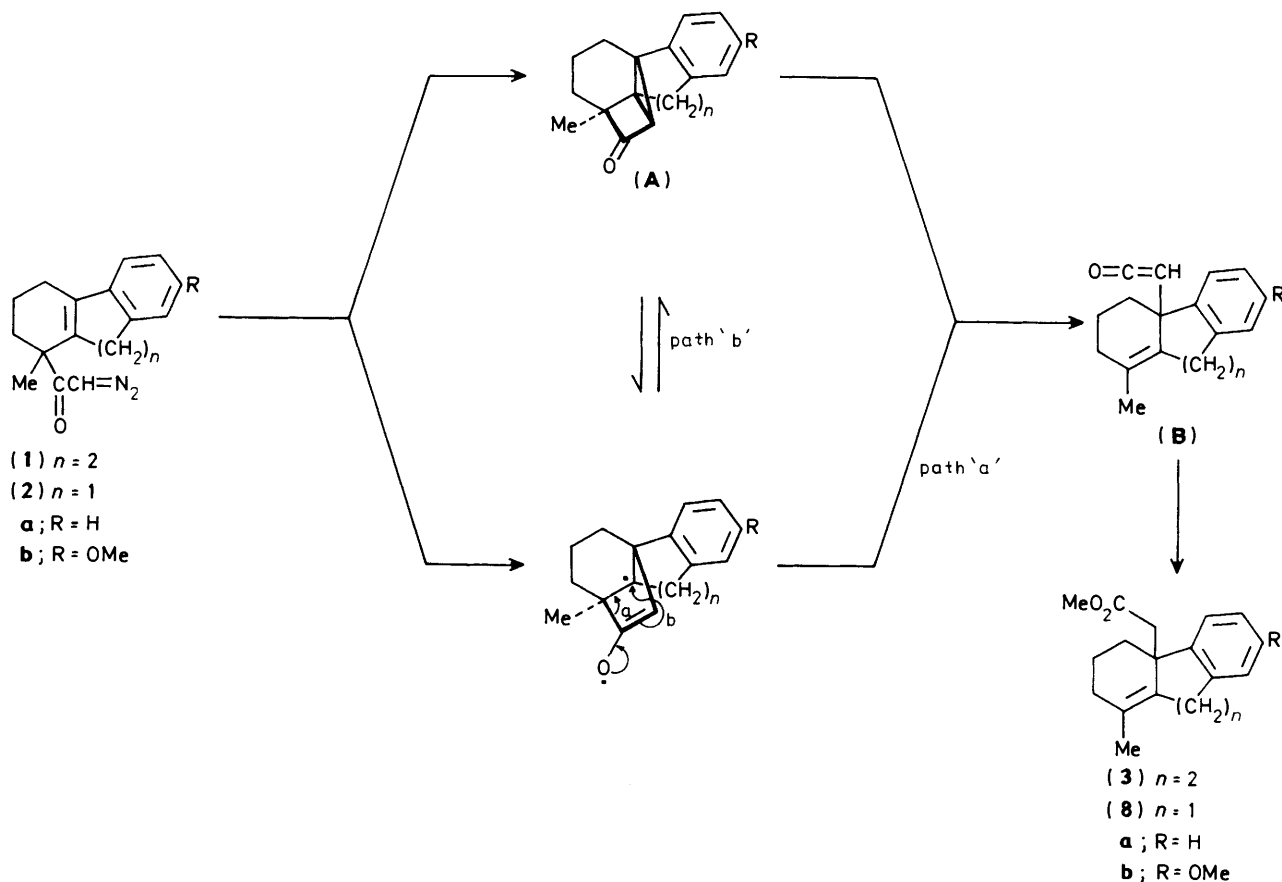
Scheme 3.

alumina (Brockman Grade I). Petroleum refers to fraction of b.p. 60—80 °C. Ether refers to diethyl ether.

Photo-Wolff Rearrangement of the Diazo Ketones (**1a**) *and* (**1b**) *and* (**2a**) *and* (**2b**): *Methyl* 1-*Methyl*-1,2,3,4,9,10-*hexa-hydrophenanthren*-1-*ylacetate* (**5a**).—A solution of the diazo ketone (**1a**)[10] (500 mg, 1.88 mmol) in dry methanol (120 ml) was irradiated with a 450-W Hanovia medium-pressure mercury vapour lamp using a Pyrex filter for 1.25 h. Evaporation of the solvent afforded a pale yellow liquid, which was filtered through a short column of alumina (15 g) using petroleum–ether (9:1) to afford (**5a**) (475 mg, 93%) as a colourless liquid, homogeneous by g.l.c. (Column A at 190 °C, R_t 3.7 min) (Found: C, 79.8; H, 8.25. $C_{18}H_{22}O_2$ requires C, 79.96; H, 8.20%); $v_{max.}$ 2 930, 2 870, 2 840, 1 735, 1 485, 1 460, 1 450, 1 435, and 1 320 cm^{-1}; δ 1.16 (s, 3 H, CMe), 1.38—2.8 (m, 10 H, CH$_2$s), 2.36 (s, 2 H, CH$_2$CO$_2$), 3.55 (s, 3 H, CO$_2$Me), and 6.8—7.16 (m, 4 H, ArH).

Saponification of (**5a**) (250 mg, 0.93 mmol) with 10% methanolic KOH (2.5 ml) afforded 1-*methyl*-1,2,3,4,9,10-*hexa-hydrophenanthren*-1-*ylacetic acid* (**7a**) (201 mg, 85%), m.p. 106—107 °C (ether–petroleum) (Found: C, 79.45; H, 8.0. $C_{17}H_{20}O_2$ requires C, 79.65; H, 7.86%); $\lambda_{max.}$ 270 nm (log ε 4.09); $v_{max.}$ 2 925, 2 870, 2 830, 2 600, 1 695, 1 600, 1 485, 1 450, 1 435, 1 400, 1 375, and 1 320 cm^{-1}.

Methyl 7-*Methoxy*-1-*methyl*-1,2,3,4,9,10-*hexahydrophenan-thren*-1-*ylacetate* (**5b**).—Photo-Wolff rearrangement of the diazo ketone (**1b**)[10] (500 mg, 1.69 mmol) gave a dark brown liquid which on filtration through a short column of alumina (petroleum) afforded a mixture of two products (496 mg) in a ratio of ca. 3:1 (g.l.c. on Column A at 190 °C, R_t s 8.9 and 10.2 min). Saponification of the mixture and fractional crystallis-ation of the resulting solid afforded 7-*methoxy*-1-*methyl* 1,2,3,4,9,10-*hexahydrophenanthren*-1-*ylacetic acid* (**7b**) (351 mg, 73%), m.p. 170—172 °C (ethyl acetate–petroleum) (Found: C, 75.5; H, 7.75. $C_{18}H_{22}O_3$ requires C, 75.36; H, 8.02%); $\lambda_{max.}$ 273 nm (log ε 4.07); $v_{max.}$ 2 930, 2 830, 2 680, 1 690, 1 625, 1 600, 1 500, 1 460, 1 410, 1 375, 1 320, and 1 305 cm^{-1}. The minor acidic product could not be isolated in pure form.

The acid (**7b**) (351 mg, 1.23 mmol) was esterified (CH$_2$N$_2$ in ether) to afford (**5b**) (348 mg, 69%) (R_t 8.9 min, Column A at 190 °C) (Found: C, 75.6; H, 8.15. $C_{19}H_{24}O_3$ requires C, 75.97; H, 8.05%); $v_{max.}$ 2 925, 2 830, 1 725, 1 600, 1 570, 1 495, 1 430, and 1 305 cm^{-1}; δ 1.16 (s, 3 H, CMe), 1.33—3.33 (m, 10 H, CH$_2$s), 2.35 (s, 2 H, CH$_2$CO$_2$), 3.55 (s, 3 H, CO$_2$Me), 3.68 (s, 3 H, ArOMe), and 6.3—7.13 (m, 3 H, ArH).

Methyl 1-*Methyl*-1,2,3,4-*tetrahydrofluoren*-1-*ylacetate* (**10a**).—Photo-Wolff rearrangement of the diazo ketone (**2a**)[10] (500 mg, 1.98 mmol) gave (**10a**) (475 mg, 94%) (homogeneous by g.l.c. on Column B at 210 °C, R_t 3.2 min) (Found: C, 79.4; H, 7.9. $C_{17}H_{20}O_2$ requires C, 79.65; H, 7.86%); $v_{max.}$ 2 950, 2 930, 2 860, 1 735, 1 600, 1 455, 1 435, 1 345, 1 335, and 1 300 cm^{-1}; δ 1.26 (s, 3 H, CMe), 1.4—2.93 (m, 6 H, CH$_2$s), 2.43 (s, 2 H, CH$_2$), 3.21 (t, *J* 3 Hz, 2 H, ArCH$_2$), 3.56 (s, 3 H, CO$_2$Me), and 6.83—7.40 (m, 4 H, ArH).

Saponification of (**10a**) (250 mg, 0.98 mmol) afforded 1-*methyl*-1,2,3,4-*tetrahydrofluoren*-1-*ylacetic acid* (**12a**) (176 mg, 74%), m.p. 139—140 °C (ether–petroleum) (Found: C, 79.3; H, 7.6. $C_{16}H_{18}O_2$ requires C, 79.31; H, 7.49%); $\lambda_{max.}$ 260 nm (log ε 4.2); $v_{max.}$ 2 925, 2 900, 2 825, 2 660, 2 580, 1 690, 1 450, 1 410, 1 390, 1 330, and 1 310 cm^{-1}.

Methyl 7-*Methoxy*-1-*methyl*-1,2,3,4-*tetrahydrofluoren*-1-*yl-acetate* (**10b**).—Photo-Wolff rearrangement of the diazo ketone (**2b**)[10] (500 mg, 1.77 mmol) gave a dark-brown product which was filtered through a short column of alumina (petroleum) to afford a light yellow liquid (495 mg) containing two components

in the ratio of ca. 2:1 (g.l.c. on Column A at 190 °C with R_t s 8.0 and 5.5 min). Saponification of this mixture and fractional crystallisation of the resulting solid afforded 7-*methoxy*-1-*methyl*-1,2,3,4-*tetrahydrofluoren*-1-*ylacetic acid* (**12b**) (310 mg, 64%), m.p. 145—146 °C (ethyl acetate–petroleum) (Found: C, 74.8; H, 7.3. $C_{17}H_{20}O_3$ requires C, 74.97; H, 7.40%); $\lambda_{max.}$ 260 nm (log ε 4.12); $v_{max.}$ 2 960, 2 930, 2 850, 2 830, 1 690, 1 620, 1 580, 1 475, 1 455, 1 440, 1 405, 1 390, 1 370, 1 330, and 1 305 cm^{-1}.

The acid (**12b**) (310 mg, 1.14 mmol) was esterified (CH$_2$N$_2$ in ether) to afford (**10b**) (308 mg, 61%) (R_t 8.0 min, Column A at 190 °C) (Found: C, 75.2; H, 7.6. $C_{18}H_{22}O_3$ requires C, 75.49; H, 7.74%); $v_{max.}$ 2 950, 2 930, 2 850, 1 730, 1 615, 1 580, 1 475, 1 460, 1 435, 1 390, 1 370, 1 340, 1 330, and 1 300 cm^{-1}; δ(CDCl$_3$) 1.36 (s, 3 H, CMe), 1.42—2.95 (m, 6 H, CH$_2$s), 2.41 (s, 2 H, CH_2CO$_2$Me), 3.2 (br t, *J* 3 Hz, 2 H, CH_2Ar), 3.58 (s, 3 H, CO$_2$Me), 3.8 (s, 3 H, ArOCH_3), and 6.33—7.0 (m, 3 H, ArH).

Metal Salts-catalysed Decomposition of Diazo Ketone (**1a**): *Methyl* 1-*Methyl*-2,3,4,4a,9,10-*hexahydrophenanthren*-4a-*yl-acetate* (**3a**) *and* 1-*Methoxyacetyl*-1-*methyl*-1,2,3,4,9,10-*hexa-hydrophenthrene* (**4a**).—(A) *With 'activated* CuO'. A stirred solution of the diazo ketone (**1a**) (200 mg, 0.75 mmol) in anhydrous cyclohexane (80 ml) containing dry methanol (0.8 ml) and 'activated CuO'[8] (24 mg, 0.3 mmol) was irradiated with two 250-W tungsten lamps and heated to reflux for 2 h under N$_2$ (when the diazo ketone i.r. band had disappeared). Filtration and evaporation afforded a light yellow oil, g.l.c. analyses of which revealed the presence of (**3a**) and (**4a**) (195 mg, 96%) in the ratio of ca. 2:1 on Column B at 230 °C, R_t s 3.61 and 6.75 min ($v_{max.}$ 1 725 and 1 715 cm^{-1}). The mixture was cleanly separated by chromatography on neutral alumina (5 g). The fraction eluted with benzene–petroleum (1:1) gave the rearranged ester (**3a**) (102 mg, 50%) (R_t 3.61 on Column B at 230 °C) as a colourless oil (Found: C, 79.8; H, 8.3. $C_{18}H_{22}O_2$ requires C, 79.96; H, 8.20%); $v_{max.}$ 2 940, 2 920, 2 860, 2 840, 2 810, 1 725, 1 600, 1 480, 1 460, 1 450, 1 430, 1 370, 1 325, and 1 310 cm^{-1}; δ(CDCl$_3$; 200 MHz) 1.66 (s, 3 H, C=CMe), 1.56—3.6 (m, 10 H, CH$_2$s), 2.72 (br s, 2 H, CH_2CO$_2$Me), 3.42 (s, 3 H, CO$_2$Me), and 7.04—7.35 (m, 4 H, ArH).

The fraction eluted with benzene gave (**4a**) (45 mg, 22%) (g.l.c. on Column B at 230 °C, R_t 6.75 min as a colourless oil) (Found: C, 80.0; H, 8.0. $C_{18}H_{22}O_2$ requires C, 79.96; H, 8.2%); $v_{max.}$ 2 980, 2 930, 2 890, 2 830, 1 715, 1 620, 1 600, 1 485, 1 460, 1 450, 1 430, 1 410, 1 370, 1 200, 1 125, 1 040, and 1 030 cm^{-1}; δ(CDCl$_3$; 200 MHz) 1.34 (s, 3 H, CMe), 1.5—2.85 (m, 10 H, CH$_2$s), 3.39 (s, 3 H, ArOMe), 4.25 (δ$_A$) and 4.37 (δ$_B$) (AB$_q$, *J* 16 Hz, COCH$_2$), and 7.1—7.36 (m, 4 H, ArH).

Saponification of the ester (**3a**) (25 mg, 0.093 mmol) with 10% methanolic KOH (0.5 ml) under N$_2$ afforded 1-*methyl*-2,3,4,4a,9,10-*hexahydrophenanthren*-4a-*ylacetic acid* (**6a**) (20 mg, 84%), m.p. 99—100 °C (ether–petroleum) (Found: C, 79.6; H, 8.0. $C_{17}H_{20}O_2$ requires C, 79.65; H, 7.86%); $v_{max.}$ 2 925, 2 900, 2 825, 1 700, 1 490, 1 445, 1 430, and 1 395 cm^{-1}.

(B) *With* Cu(acac)$_2$. The diazo ketone (**1a**) (200 mg, 0.75 mmol) in cyclohexane (80 ml) was heated to reflux for 3 h with Cu(acac)$_2$[2d] (26 mg, 0.1 mmol) and methanol (0.8 ml). Work-up gave a mixture of (**3a**) and (**4a**) (140 mg, 69%) in the ratio of ca. 1:1 (g.l.c. and ^{1}H n.m.r.).

(C) *With* Cu(OTf)$_2$. The diazo ketone (**1a**) (200 mg, 0.75 mmol) in cyclohexane (80 ml) was heated to reflux for 3 h with Cu(OTf)$_2$[2d] (36 mg, 0.1 mmol) and methanol (0.8 ml). Work-up gave a mixture of (**3a**) and (**4a**) (190 mg, 93%) in a ratio of 3:1 (g.l.c. and ^{1}H n.m.r.).

(D) *With* Ni(acac)$_2$. A stirred solution of diazo ketone (**1a**) (200 mg, 0.75 mmol) in cyclohexane (80 ml) was irradiated with two 250-W tungsten lamps and heated to reflux for 26 h with Ni(acac)$_2$[9b] (26 mg, 0.1 mmol) and methanol (0.8 ml). Work-up

gave a mixture of (3a) and (4a) (144 mg, 71%) in the ratio of ca. 9:1 (g.l.c. and ^{1}H n.m.r.).

(E) *With* PhCO$_2$Ag–NEt$_3$. A solution PhCO$_2$Ag (20 mg, 0.087 mmol) in NEt$_3$ (0.16 ml) was added to a stirred solution of the diazo ketone (1a) (200 mg, 0.75 mmol) in dry methanol (4 ml) at room temperature during 2—3 min. The mixture was stirred at room temperature for a further 1 h and then worked to give the esters (3a) and (5a) (166 mg, 82%) in the ratio of ca. 1:1 (g.l.c. and ^{1}H n.m.r.).

Metal Salt-catalysed Decomposition of the Diazo Ketone (1b): *Methyl 7-Methoxy-1-methyl-2,3,4,4a,9,10-hexahydrophenanthren-4a-ylacetate* (3b).—(A) *With 'activated* CuO'. The diazo ketone (1b) (250 mg, 0.84 mmol) in dry cyclohexane (100 ml) and methanol (1 ml) was treated with CuO (30 mg, 0.38 mmol) as described for (1a) to afford (3b) (220 mg, 87%) (homogeneous by g.l.c. on Column B at 230 °C, R_t 8.47 min) (Found: C, 76.1; H, 8.0. C$_{19}$H$_{24}$O$_3$ requires C, 75.97; H, 8.05%); $v_{max.}$ 2 990, 2 930, 2 860, 1 725, 1 605, 1 575, 1 495, 1 465, 1 430, 1 330, and 1 310 cm^{-1}; δ(CDCl$_3$) (200 MHz) 1.68 (s, 3 H, =CMe), 1.69—3.04 (m, 10 H, CH$_2$s), 2.9 (s, 2 H, CH$_2$CO$_2$Me), 3.46 (s, 3 H, CO$_2$Me), 3.78 (s, 3 H, ArOCH$_3$), and 6.6—7.32 (m, 3 H, ArH).

(B) *With* Cu(acac)$_2$. The diazo ketone (1b) (250 mg, 0.84 mmol) was treated with Cu(acac)$_2$ (30 mg, 0.11 mmol) in cyclohexane (100 ml) and methanol (1 ml) as described for (1a) to afford a mixture of (3b) and possibly (4b) (200 mg, 79%) in the ratio of ca. 7:3 as revealed from g.l.c. (Column A at 230 °C, R_ts 8.47 and 17.21, respectively). The ester (3b) (123 mg, 49%) was separated by chromatography of the mixture on alumina (5 g) in benzene–petroleum (1:1). The α-methoxy ketone (4b) [δ(CDCl$_3$) (200 MHz) 1.34 (s, CMe), 3.43 (s, CH$_2$O*Me*), 3.85 (s, ArO*Me*), and 4.25 (δ_A) and 4.37 (δ_B) (AB$_q$, J 16 Hz, COCH$_2$)] mixed with some (3b) was eluted with benzene–petroleum (3:1); which could not be obtained in the analytically pure form.

(C) *With* Cu(OTf)$_2$. The diazo ketone (1b) (250 mg, 0.84 mmol) was treated with Cu(OTf)$_2$ (45 mg, 0.12 mmol) in cyclohexane (100 ml) and methanol (1 ml) as described for (1a) to afford a mixture of (3b) and (4b) (191 mg, 75%) in the ratio of ca 5:3 (g.l.c. and ^{1}H n.m.r.) besides ca. 18% of an unidentified compound.

(D) *With* PhCO$_2$Ag–NEt$_3$. A stirred solution of the diazo ketone (1b) (250 mg, 0.84 mmol) in dry methanol (5 ml) was treated with PhCO$_2$Ag (30 mg, 0.13 mmol) in NEt$_3$ (0.25 ml), as described for (1a) to give (3b) and (5b) (210 mg, 83%) in the ratio of ca. 1:1 (g.l.c. and ^{1}H n.m.r.).

The results are given in Table 1.

Metal Salt-catalysed Decomposition of the Diazo Ketone (2a): *Methyl 1-Methyl-2,3,4,4a-tetrahydrofluoren-4a-ylacetate* (8a) *and 1-Methoxyacetyl-1-methyl-1,2,3,4-tetrahydrofluorene* (9a).—(A) *With 'activated* CuO'. The diazo ketone (2a) (250 mg, 0.99 mmol) in cyclohexane (100 ml) and methanol (1 ml) was treated with 'activated CuO' (30 mg, 0.38 mmol) as described for (1a) to afford (8a) and (9a) (202 mg, 80%) in the ratio of ca. 4:1, as revealed from g.l.c. (Column B at 210 °C, R_ts 5.1 and 4.39 min) ($v_{max.}$ 1 725 and 1 715 cm^{-1}). The ester (8a) (145 mg, 57%) was separated from this mixture by chromatography on alumina (6 g) in benzene–petroleum (1:1) (g.l.c. on Column B, R_t 5.1 min) (Found: C, 80.0; H, 8.1. C$_{17}$H$_{20}$O$_2$ requires C, 79.65; H, 7.86%); $v_{max.}$ 2 930, 2 830, 2 810, 1 730, 1 475, 1 430, 1 375, and 1 330 cm^{-1}; δ(CDCl$_3$) 1.66 (s, 3 H, =CMe), 1.71—3.3 (m with a doublet at 2.57, J 3 Hz, 8 H), 3.43—3.66 (m with a singlet at 3.50, 5 H, CO$_2$Me and ArCH$_2$), and 7.06—7.4 (m, 4 H, ArH). The ketone (9a) obtained in the benzene elutes was found to be identical (^{1}H n.m.r. and i.r.) with the pure sample described in experiment (B).

Saponification of the ester (8a) (125 mg, 0.49 mmol) afforded

1-*methyl*-2,3,4,4a-*tetrahydrofluoren*-4a-*ylacetic acid* (11a) (90 mg, 76%), m.p. 148 °C (ether–petroleum) (Found: C, 79.5; H, 7.5. C$_{16}$H$_{18}$O$_2$ requires C, 79.31; H, 7.49%); $v_{max.}$ 2 970, 2 910, 2 840, 2 820, 1 690, 1 470, 1 445, 1 430, 1 415, and 1 315 cm^{-1}.

(B) *With* Cu(acac)$_2$. The diazo ketone (2a) (250 mg, 0.99 mmol) was treated with Cu(acac)$_2$ (30 mg, 0.11 mmol) in cyclohexane (100 ml) and methanol (1 ml) as described for (1a) to afford a mixture of (8a), (9a), and (10a) (168 mg, 66%) in the ratio of ca. 3:5:2 as revealed from g.l.c. (Column B at 210 °C, R_ts 5.1, 4.39, and 3.2 min, respectively). The mixture was chromatographed on alumina (5 g). The fractions eluted with petroleum–benzene (2:1 to 1:1) gave mixtures of (8a) and (10a) which were identified by g.l.c. comparison.

The benzene elutes gave (9a) (79 mg, 31%) (g.l.c. on Column B, R_t 4.39 min) (Found: C, 79.9; H, 7.7. C$_{17}$H$_{20}$O$_2$ requires C, 79.65; H, 7.86%); $v_{max.}$ 2 930, 2 880, 2 815, 1 715, 1 600, 1 465, 1 455, 1 395, 1 200, 1 052, and 1 030 cm^{-1}; δ(CDCl$_3$; 200 MHz) 1.38 (s, 3 H, CMe), 1.5—2.32 (m, 6 H, CH$_2$s), 3.35 (s, 3 H, ArOMe), 4.15 (δ_A) and 4.26 (δ_B) (AB$_q$, J 16 Hz, 2 H, COCH$_2$), and 7.2—7.56 (m, 4 H, ArH).

(C) *With* Cu(OTf)$_2$. The diazo ketone (2a) (250 mg, 0.99 mmol) was treated with Cu(OTf)$_2$ (45 mg, 0.12 mmol) in cyclohexane (100 ml) and methanol (1 ml) as described for (1a) to afford a mixture of (8a), (9a), and (10a) (169 mg, 67%) in the ratio of ca. 3:5:2 (g.l.c. and ^{1}H n.m.r.).

(D) *With* PhCO$_2$Ag–NEt$_3$. A stirred solution of the diazo ketone (2a) (250 mg, 0.99 mmol) in dry methanol (5 ml) was treated with PhCO$_2$Ag (30 mg, 0.13 mmol) in NEt$_3$ (0.25 ml), as described for (1a) to give (10a) and (8a) (209 mg, 82%) in the ratio of ca. 3:2 (g.l.c. and ^{1}H n.m.r.) along with some unidentified products.

The results are given in Table 2.

Metal Salts-catalysed Decomposition of the Diazo Ketone (2b): *Methyl 7-Methoxy-1-methyl-2,3,4,4a-tetrahydrofluoren-4a-ylacetate* (8b).—*With 'activated* CuO'. The diazo ketone (2b) (250 mg, 0.89 mmol) in cyclohexane (100 ml) and methanol (1 ml) was treated with CuO (30 mg, 0.38 mmol), as described for (1a) to afford (8b) (183 mg, 72%), (g.l.c. on Column A at 190 °C, R_t 5.2 min) (Found: C, 75.3; H, 7.6. C$_{18}$H$_{22}$O$_3$ requires C, 75.49; H, 7.74%); $v_{max.}$ 2 935, 2 915, 2 845, 2 815, 1 730, 1 605, 1 580, 1 485, 1 432, and 1 330 cm^{-1}; δ(CDCl$_3$; 200 MHz) 1.66 (br s, 3 H, C=CMe), 1.28—2.86 (m, 8 H, CH$_2$s), 2.44 (δ_A) and 2.62 (δ_B) (AB$_q$, J 14 Hz, 2 H, CH$_2$CO$_2$Me), 3.44—3.62 (m with a singlet at 3.50, 5 H, CO$_2$Me and ArCH$_2$), 3.74 (s, 3 H, ArOMe), and 6.66—7.22 (m, 3 H, ArH).

Saponification of the ester (8b) (125 mg, 0.44 mmol) afforded the acid (11b) as a thick oil (96 mg, 81%); $v_{max.}$ 2 920, 2 855, 2 835, 1 705, 1 605, 1 460, 1 420, 1 380, and 1 320 cm^{-1}. The compound could not be obtained in analytically pure state.

(B) *With* Cu(acac)$_2$. The diazo ketone (2b) (250 mg, 0.89 mmol) was treated with Cu(acac)$_2$ (30 mg, 0.11 mmol) in cyclohexane (100 ml) and methanol (1 ml) as described for (1a) to afford a mixture of (8b) and an unidentified product (158 mg) in the ratio of ca. 85:15 (g.l.c. on Column A at 190 °C, R_ts 5.2 and 3.7 min). The ester (8b) (128 mg, 50%) was separated by chromatography on alumina (5 g) in benzene–petroleum (1:1).

(C) *With* Cu(OTf)$_2$. The diazo ketone (2b) (250 mg, 0.89 mmol) was treated with Cu(OTf)$_2$ (45 mg, 0.12 mmol) in cyclohexane (100 ml) and methanol (1 ml) as described for (1a) to afford a mixture of (8b), (10b), and possibly (9b) (236 mg, 93%) in the ratio of ca. 5:1:2 as revealed from g.l.c. (Column A at 190 °C with R_ts 5.2, 8.0, and 6.8 min, respectively). The mixture was chromatographed on alumina (8 g). The fraction eluted with petroleum–benzene (2:1—1:1) gave mixtures of (8b) and (10b) (g.l.c. and ^{1}H n.m.r.). The α-methoxy ketone (9b) [δ(CDCl$_3$; 200 MHz) 1.40 (s, CMe), 3.35 (s, CH$_2$Me), 3.85 (s, ArOMe), 4.15 (δ_A) and 4.26 (δ_B) (AB$_q$, J 16 Hz, COCH$_2$)] mixed

with some (8b) was eluted with benzene–petroleum (3:1); which could not be obtained in the analytically pure form.

(D) *With* Ni(acac)₂. The diazo ketone (2b) (250 mg, 0.89 mmol) was treated with Ni(acac)₂ (32 mg, 0.12 mmol) in cyclohexane (100 ml) and methanol (1 ml) as described for (1a) to afford a mixture of (8b) (66%) along with an unknown component in a ratio of *ca.* 85:15 (g.l.c.).

(E) *With* PhCO₂Ag–NEt₃. A stirred solution of the diazo ketone (2b) (250 mg, 0.89 mmol) in methanol (5 ml) was treated with PhCO₂Ag (30 mg, 0.13 mmol) in NEt₃ (0.25 ml) as described for (1a) to afford a mixture of (10b) and (8b) (231 mg, 91%) in the ratio of *ca.* 4.5:5.5 (g.l.c. and ¹H n.m.r.) along with some unidentified products.

The results are given in Table 2.

Acknowledgements

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