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SOME NEWER ASPECTS OF CLEMMENSEN REDUCTION OF AROMATIC KETONES

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Abstract : 9,9'-Bifluorenyl (6), 1,1,2,2-tetraphenylethane (10) and 10,10'-bianthrone (18) have been obtained as a new type of products in Clemmensen reduction of 9H-fluoren-9-one (3), benzophenone (7) and 9,10-anthraquinone (13) respectively. Dibenzo*(g,p)*chrysene (5) is formed as the major product in the reduction of 3. Plausible mechanistic pathways for the formation of the unconventional products have been delineated.

Our recent work on some Orchidaceae plants resulted in the isolation of the only natural fluorenone derivatives[1-4]. In connection with their structural elucidation we attempted to convert them to the corresponding fluorenes. Clemmensen reduction[5], the well-known deoxygenation reaction for ketones, was applied to dengibsin (1) and dengibsinin (2), but the expected fluorene derivatives were not obtained[1]. The study of the Clemmensen reduction was then extended to 9H-fluoren-9-one (3) itself and three related ketones, *viz.* benzophenone (7), 9,10-anthraquinone (13) and anthrone (14). Although their Clemmensen reduction was studied four decades ago[6], we obtained somewhat different and interesting results which are presented in this paper.

Using toluene as a co-solvent (*cf.* reduction of β-benzoylpropionic acid[7]) Clemmensen reduction experiments were done under two conditions by varying the amount of conc. HCl. Thus, under condition-1 the total amount of the acid[7] was added in four instalments in the ratio 7:2:2:2, while under condition-2 only the first instalment of the acid was added, the reaction time being 24 hr in each case. The result of reduction of **3**, **7**, **13** and **14** under these two conditions are presented in Table-1.

So far, the formation of dimeric olefins like 9 in Clemmensen reduction has appeared in the literature only twice using α-tetralone[8] and some α, β-unsaturated ketones[9] as substrates. To our knowledge, there is still no report of the formation of bimolecular coupling products similar to 6, 10 and 18 in this reduction. As will be seen later, the formation of dibenzo*(g,p)*chrysene (5) is similar to that of tetraphenylethylene (9), followed by a skeletal rearrangement as an additional feature. Thus, Clemmensen reduction of 9H-fluoren-9-one (3) seems to be the easiest method for the preparation of 5 (yield 44%); the four-step conversion of 3 to 5 (overall yield 32%) was reported earlier[10].

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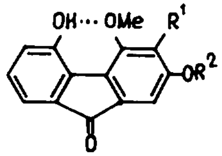
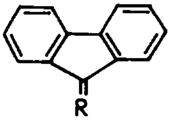
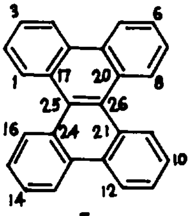


1 $R^1=R^2=H$
2 $R^1=OH, R^2=Me$



3 R=O
4 $R=H_2$



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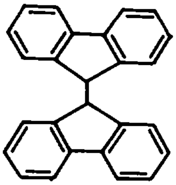

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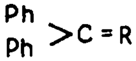


$\begin{matrix}Ph\\Ph\end{matrix}\!>C=R$

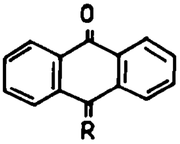
7 R =O
8 $R=H_2$

$Ph_2C=CPh_2$
9

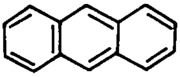
$Ph_2CH-CHPh_2$
10

$Ph_2C(OH).C(OH)Ph_2$
11

$Ph_2CH-C(OH)Ph_2$
12



13 R=O
14 $R=H_2$



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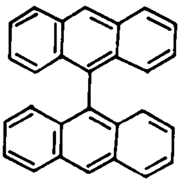

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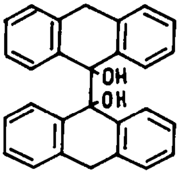

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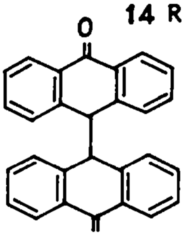

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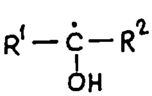
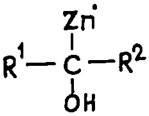


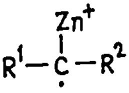
$R^1-\underset{OH}{\overset{\bullet}{C}}-R^2$

19



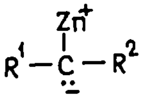
$R^1-\underset{OH}{\overset{Zn^{\bullet}}{C}}-R^2$

20



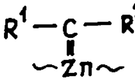
$R^1-\underset{\bullet}{\overset{Zn^+}{C}}-R^2$

21



$R^1-\underset{:^{-}}{\overset{Zn^+}{C}}-R^2$

22



$R^1-\underset{\sim Zn\sim}{\overset{}{\underset{\|}{C}}}-R^2$

23

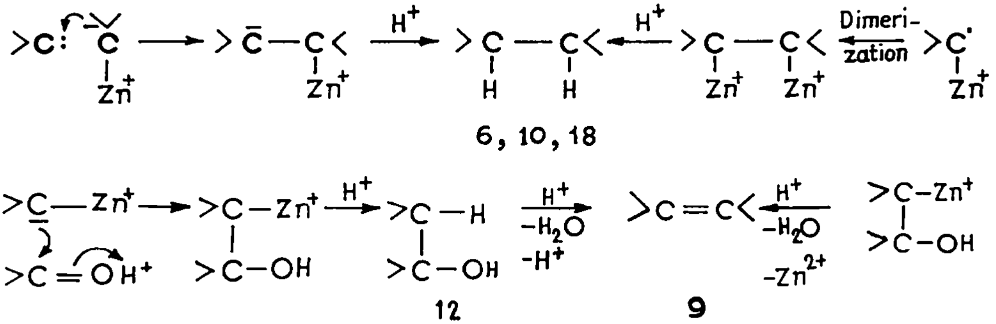
TABLE-1 : PRODUCTS OF CLEMMENSEN REDUCTION OF AROMATIC KETONES (3,7,13 & 14)

Ketone		Products	Yield (%)	
			Condition-1	Condition-2
9H-Fluoren-9-one (3)	i)	Fluorene (4)	14	22
	ii)	Dibenzo*(g,p)*chrysene (5)	44	44
	iii)	9,9'-Bifluorenyl (6)	27	22
Benzophenone (7)	i)	Diphenylmethane(8)	8	22
	ii)	Tetraphenylethylene (9)	43	9
	iii)	1,1,2,2-Tetraphenylethane (10)	15	11
	iv)	Benzopinacol (11)	-	11
	v)	1,1,2,2-Tetraphenylethanol (12)	-	17
9,10-Anthraquinone (13)	i)	Anthracene (15)	6	19
	ii)	9,9'-Bianthryl (16)	20	12
	iii)	Anthrapinacol (17)	22	-
	iv)	10,10'-Bianthrone (18)	6	44
Anthrone (14)	i)	9, 9'-Bianthryl (16)	6	32
	ii)	Anthrapinacol (17)	46	10

All products (Table 1) were characterised from their m.ps and spectral (IR, ^{1}H and ^{13}C NMR and Mass) data. The compounds 6, 10 and 18 exhibited ^{1}H NMR signals for their doubly benzylic proton at δ4.79, 4.69 and 4.76 respectively. The similar proton in 12 appeared at δ 5.25 while the chemical shift of its OH signal (δ 2.83) was comparable to that (δ 2.95) of 11. The C-10 protons of 17 were nonequivalent and had a relatively high geminal coupling constant (19.2 Hz).

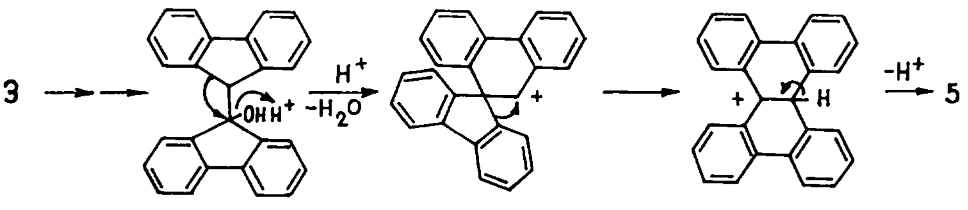
The earlier evidence about the mechanism of Clemmensen reduction[11] was in favour of the successive intermediacy of 19-22. On the other hand, the later evidence[11,12] indicated that 22, equivalent to the zinc-carbene (23), is formed at the metal surface directly from the carbonyl compound - acid complex and zinc. Although the actual nature of bonding in the zinc-carbene is not well-understood, its behaviour like a simple carbene is evident from the formation of cycloaddition product with olefins[11,12]. The unconventional products may thus be formed via any plausible path/s delineated in Schemes 1 and 2.

SCHEME - I



However, the mechanism proposed[8] by Vedejs may also be operative for the formation of the dimeric olefin 9. The formation of 9,9'-bianthryl (16) may occur through reduction of 13 to 14 followed by combination of two such units. The conversion of 13 to 16 may also take

SCHEME-2



place by one or more of the following plausible pathways which do not involve 14 as an intermediate :

[1] the reduction of a C=O of 18 to CH_2 (since under the reaction condition C=O is not reduced[11,12] to CHOH), followed by enolisation by loss of 9-H, loss of 9'-H with concomitant proton capture at 10 position and elimination of elements of H_2O from benzylic positions 10 and 10' ;

[2] the reduction of both C=O groups of 18 to CH_2, followed by aerial oxidation ;

[3] the reduction of both C=O groups of 9,9'-dehydro derivative of 18 (although not isolated, its intermediacy is likely in view of the formation of 9 from 7) followed by aerial oxidation.

In fact 14 and 18 when subjected to the reaction condition, were converted to 16. The possibility of formation of 16 through dehydration of 17 was ruled out as the latter was found sufficiently stable in refluxing conc. HCl. It may be mentioned here that the formation of 16 by Zn/HCl reduction of 13 in HOAc is long known[13].

EXPERIMENTAL

Melting points are uncorrected. IR spectra were recorded on Perkin Elmer 782 spectrophotometer. All ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ solution using $SiMe_4$ as internal standard in a Brucker-300 (300 MHz), JEOL FX 100 (100 MHz) or Varian CFT-20 (80 MHz) spectrometer and the mass spectra at 70 eV. Petrol and petrol$^+$ refer to the 40-60° and 60-80° fractions respectively, the silica gel used for column chromatography was of 60-120 mesh; the TLC experiments were done on silica gel G.

Clemmensen Reduction of 9H-Fluoren-9-one (3), *Benzophenone* (7) , *9, 10-Anthraquinone* (13) *and Anthrone* (14) *(Condition - 1) :*

To amalgamated zinc [made from mossy Zn (4.8 g), $HgCl_2$ (.48 g), H_2O(8 ml) and conc. HCl (.2 ml)], water (3 ml), conc. HCl (7 ml), toluene (4 ml) and the aromatic ketone 3 (2g, .011 mole) or 7 (2g, 0.011 mole) or 13 (1g, 0.005 mole) or 14 (2g, 0.01 mole) were added. The mixture was refluxed for 24 hr with the addition of three 2 ml portion of conc. HCl at approximately 6 hr intervals. It was then diluted with water, extracted with ether and the extract was washed and dried (anhy. Na_2SO_4). The product mixtures obtained by removal of ether and toluene were chromatographed over silica gel using petrol and petrol - ethyl acetate mixtures as eluants (fractions of 15 ml each were collected in all cases). The results, separately for each starting ketone, are given below :

Products from 9H-Fluoren-9-one (3) :

Fluorene (4). Obtained from fractions 1 and 2 (eluant : petrol), colourless needles (petrol), m.p. 113° (lit.[14] 116°).

Dibenzo(g,p)chrysene (5). Obtained from fractions 3-6 (petrol), colourless needles ($CHCl_3$-MeOH), m.p. 214° (lit[10] 214°), ^{1}H NMR (100 MHz) : δ7.52-7.72 (8H, m, H-2, H-3, H-6, H-7, H-10, H-11, H-14 and H-15) and 8.60-8.72 (8H, m, H-1, H-4, H-5, H-8, H-9, H-12, H-13 and H-16), ^{13}C NMR (75 MHz) : 123.40 (C-1), 126.34 (C-2 and C-3), 127.30 (C-25), 128.71 (C-4), 129.04 (C-18) and 130.68 (C-17); MS : *m/z* 328 (M^+,100%).

9,9'-Bifluorenyl (6). Obtained from fractions 7-10 (petrol), colourless needles (petrol), m.p.243° (lit.[15] 246°); ^{1}H NMR (300 MHz) : δ4.79 (2H, s, H-9 and H-9'), 6.89-6.92 (4H, m, H-2, H-2',H-7 and H-7'), 7.01-7.06 (4H, m, H-3, H-3', H-6 and H-6'), 7.21-7.25 (4H, m, H-1, H-1', H-8 and H-8'), 7.58-7.61 (4H, m, H-4, H-4', H-5 and H-5'); MS : *m/z* 330 (M^+, 18.75%) and 165 (100).

Products from Benzophenone (7) :

Diphenylmethane (8). Obtained from fractions 1 and 2 (petrol) as an oil, identical with an authentic sample (IR).

Tetraphenylethylene (9). Obtained from fractions 3-5 (petrol), colourless needles (petrol), m.p. 223° (lit.^{14} 227°); ^{1}H NMR (300 MHz) : δ 7.01-7.12(m), MS : *m/z* 332 (M^+, 100%)

1,1,2,2-Tetraphenylethane (10). Obtained from fractions 6-8 (petrol) colourless needles (petrol); m.p. 210° (lit.^{14} 211°); ^{1}H NMR (300 MHz) : δ 4.69 (2H, s, H-1 and H-2) and 6.91-7.28 (20H, m); MS : *m/z* 334 (M^+, 5.3%) and 167 (100).

Products from 9,10-Anthraquinone (13) :

Anthracene (15). Obtained from fractions 1 and 2 (petrol$^+$), colourless needles ($CHCl_3$-MeOH), m.p. 210° (lit.^{14} 217°).

9,9'-Bianthryl (16) : Obtained from fraction 5-8 (petrol$^+$), greenish yellow needles $CHCl_3$-petrol$^+$), m.p. 306° (lit.^{15} 312°), ^{1}H NMR (80 MHz) : δ 7.0-7.12 (8H , m, H-2, H-2', H-3, H-3', H-6, H-6', H-7 and H-7'), 7.30-7.50 (4H, m, H-4, H-4', H-5 and H-5'), 8.11 (4H, dd, *J* = 8 and 1.5 Hz, H-1, H-1', H-8 and H-8'), MS : *m/z* 354 (M^+, 100%) and 178 (23.7).

Anthrapinacol (17). Obtained from fractions 31-39 (petrol$^+$ - EtOAc (19:1)), colourless needles ($CHCl_3$-petrol$^+$), m.p. 182° (lit.^{6} 185°), IR (KBr) : 3560 and 3330 cm^{-1} (OH), ^{1}H NMR (100 MHz) : δ 1.86 (2H, d, *J* = 19.2 Hz, H-10a and H-10'a), 3.24 (2H, d, J = 19.2 Hz, H-10b and H-10'b), 3.36 (2H, s, exchangeable with D_2O, 9-OH and 9'-OH, 6.86-7.24 (16H, m, Ar-H), MS : *m/z* 195 (83.8%, M^+/2), 194 (100), 178 (46.1) and 165 (74.4).

10,10'-Bianthrone (18). Obtained from fraction 44-48 (petrol$^+$ - EtOAc (19:1)), colourless needles ($CHCl_3$-petrol$^+$), m.p. 245° (lit^{15} 250°); IR (KBr) : 1665 cm^{-1} (C=O), ^{1}H NMR (300 MHz) : δ 4.76 (2H, s, H-9 and H-9'), 6.70-6.88 (4H, m, H-1, H-8, H-1' and H-8'), 7.41-7.44 (8H, m, H-2, H-3, H-6, H-7, H-2', H-3', H-6' and H-7') and 7.91-7.94 (4H, m, H-4, H-5, H-4' and H-5'), ^{13}C NMR (75 MHz) : 54.39 (C-9) 126.65 (C-2 and C-7), 127.85 (C-3 and C-6), 128.45 (C-4 and C-5), 123.11 (C-1 and C-8), 133.82 (C-12 and C-13), 139.90 (C-11 and C-14) and 182.87 (C-10); MS : *m/z* 386 (M^+, 0.14%) and 193 (100).

Products from Anthrone (14) :

9,9'-Bianthryl (16) and anthrapinacol (17) were obtained in this case.

Clemmensen Reduction of 9H-Fluoren-9-one (3) , *Benzophenone* (7), *9, 10-Anthraquinone* (13) *and Anthrone* (14) *(Condition-2) :*

Starting from same amount of reagent and ketone (3 or 7 or 13 or 14) reaction was set up in the same way as under condition-1. The addition of three instalments of conc. HCl done subsequently under condition-1 was omitted. The reaction mixtures were worked up and the product mixtures were chromatographed in the same way as under condition-1. The isolation of benzopinacol (11) and 1, 1, 2, 2-tetraphenylethanol (12), not occurring in the reduction of 7 under condition-1, are given below :

Benzopinacol (11). Obtained from fractions 9-11 (eluant : petrol - EtOAc (99:1)), colourless needles ($CHCl_3$-petrol), m.p.185° (lit.^{16} 188-90°), IR (KBr) : 3540 cm^{-1} (O-H), ^{1}H NMR (300 MHz) : δ 2.95 (2H, s, exchangeable with D_2O, C_1-OH) and 6.90-7.32 (20H, m, Ar-H), MS : *m/z* 348 (M^+-$H_2$0, 9.1%), 332 (31.9), 253 (7.1), 243 (5.3), 183 (100), 165 (40.5), 105 (100) and 77 (47.6).

1, 1, 2, 2-Tetraphenylethanol (12). Obtained from fractions 12-13 (eluant : Petrol- EtOAc (99:1)), colourless needles ($CHCl_3$-petrol$^+$), m.p. 235° (lit.^{16} 239-40°), IR (KBr) : 3540 cm^{-1} (O-H), ^{1}H NMR (300 MHz) : δ 2.83 (1H, s, exchangeable with D_2O, C_1-OH), 5.25 (1H, s, H-2), 7.06-7.41 (20H, m, Ar-H), MS : *m/z* 332 (M^+-H_2O, 1.05%), 243 (52.6), 183(58), 165(30), 105(100)and 77(54.7).

Clemmensen Reduction of 10, 10'-Bianthrone (18)

The compound 18 (0.1g) was reduced under condition-1 mentioned above. From the product mixture only 9,9'-bianthryl(16) (yield 10%) could be isolated by chromatography over silica gel.

ACKNOWLEDGEMENT

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