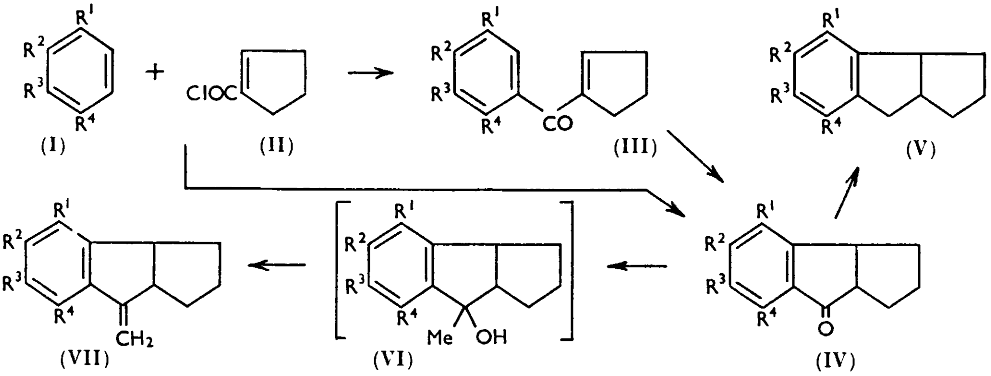
664. *Derivatives of* 1 : 2 : 3 : 3a : 8 : 8a-*Hexahydro*cyclo*pent*[a]*indene.*

By Alan Marchant.

Two methods for the synthesis of derivatives of 1 : 2 : 3 : 3*a* : 8 : 8*a*-hexahydro*cyclo*pent[*a*]indene are described.

Few derivatives of 1 : 2 : 3 : 3*a* : 8 : 8*a*-hexahydro*cyclo*pent[*a*]indene are known; the 3 : 3*a*-dihydroxy-1 : 2 : 3-triphenyl-derivative was reported by Ionescu and Popescu,[1] and the parent ketone (IV; $R^1 = R^2 = R^3 = R^4 = H$) has been prepared.[2]

The 5 : 6-dimethoxy-compound has now been prepared. 7-(3 : 4-Dimethoxyphenyl)-4 : 7-dioxoheptanoic acid with 2% potassium hydroxide solution underwent internal condensation to 2-(3 : 4-dimethoxyphenyl)-5-oxo*cyclo*pent-1-enylacetic acid, which, when heated with acetic anhydride, gave 5-acetoxy-7 : 8-dimethoxy-3-oxo*cyclo*penta[*a*]-naphthalene. Clemmensen reduction[3] in ethanol with granulated zinc gave 5-hydroxy-7 : 8-dimethoxy*cyclo*penta[*a*]naphthalene, which was oxidised by peracetic acid to 2-(2-carboxy*cyclo*pent-1-enyl)-4 : 5-dimethoxybenzoic acid. The acid obtained by hydrogenation of the double bond in the five-membered ring was cyclised by acetic anhydride to give the *cyclo*pentindene derivative (IV; $R^1 = R^4 = H$, $R^2 = R^3 = OMe$).



*cyclo*Pentene-1-carbonyl chloride (II) with benzene in the presence of 1 mol. of aluminium chloride at room temperature gives the *cyclo*pentenyl ketone (III; $R^1 = R^2 = R^3 = R^4 = H$), whilst at 80° with 3 mols. of aluminium chloride it undergoes further cyclisation to the *cyclo*pentindenone (IV; $R^1 = R^2 = R^3 = R^4 = H$). *cyclo*Pentene-1-carbonyl chloride (II) reacts similarly at 100° in the presence of 3 mols. of aluminium chloride with toluene, ethylbenzene, *o*-, *m*-, and *p*-xylene, veratrole, and *p*-dimethoxybenzene, to give ketones (IV). At 0° it reacts with anisole, to give ketone (III) but the methoxyl group is not stable to aluminium chloride at 100°.

Martin–Clemmensen reduction[4] of the carbonyl groups in these ketones gave the corresponding hexahydro-hydrocarbons (V). The ketones reacted with methylmagnesium iodide to give the corresponding 8-hydroxy-8-methyl compounds (VI), which were spontaneously dehydrated to the 8-methylene compounds (VII).

Structures have been assigned to the ketones (IV) by using the normal rules governing Friedel–Crafts reactions. Migration of the methyl groups, which might take place under

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[1] Ionescu and Popescu, *Bull. Soc. chim. France*, 1932, 1215, 1231.

[2] Chatterjee, *J. Indian Chem. Soc.*, 1938, 211; Baker and Leeds, *J.*, 1948, 974; Baker and Jones, *J.*, 1951, 785.

[3] Marker and Rohrmann, *J. Amer. Chem. Soc.*, 1939, **61**, 846.

[4] Martin, *ibid.*, 1936, **58**, 1438.

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the drastic conditions of the reaction, is believed not to occur, since all the ketones distilled as homogeneous oils, which gave derivatives of differing, sharp melting points. For each ketone the carbonyl group gives a sharp infrared absorption band at different characteristic frequencies, which show a bathochromic shift depending on the number, type, and position of the substituents in the aromatic ring (cf. Table 1).

EXPERIMENTAL

3 : 4-Dimethoxy-α-furfurylideneacetophenone was prepared by Robinson's method.[5] Its 2 : 4-*dinitrophenylhydrazone* crystallized from acetic acid in maroon needles, m. p. 170° (Found : C, 57·5; H, 4·0; N, 12·9. $C_{21}H_{18}O_7N_4$ requires C, 57·6; H, 4·1; N, 12·7%).

7-(3 : 4-*Dimethoxyphenyl*)-4 : 7-*dioxoheptanoic Acid*.—The foregoing ketone (90 g.), ethanol (900 g.), and concentrated hydrochloric acid (250 c.c.) were refluxed on the water-bath for 24 hr. The ethanol was evaporated and the residue refluxed for 3 hr. with concentrated hydrochloric acid (450 c.c.) and water (900 c.c.). The orange solution was decanted from the black oil. On cooling, the *heptanoic acid* (45 g.) crystallised. The mother liquors were used to re-extract the residual black oil by 2 hours' refluxing, and, when decanted and cooled, deposited more acid (22 g.). The acid crystallized from ethyl acetate in prismatic needles, m. p. 126° (Found : C, 61·0; H, 6·1. $C_{15}H_{18}O_6$ requires C, 61·2; H, 6·2%). Its *bis*-2 : 4-*dinitrophenylhydrazone* crystallized from ethyl acetate in vermilion needles, m. p. 244° (Found : C, 49·3 ; H, 4·1; N, 16·8. $C_{27}H_{26}O_{12}N_8$ requires C, 49·5; H, 4·0; N, 17·1%).

2-(3 : 4-*Dimethoxyphenyl*)-5-*oxo*cyclo*pent*-1-*enylacetic Acid*.—The heptanoic acid (30·7 g.) and potassium hydroxide (60 g.) in water (3 l.) were refluxed for 1 hr. Sodium chloride (150 g.) was added and the solution was cooled, filtered, and acidified with concentrated hydrochloric acid. The cyclo*pentenylacetic acid* (28 g.) which was precipitated crystallised from chloroform–light petroleum (b. p. 80—100°) in needles, m. p. 147° (Found : C, 64·85; H, 5·65. $C_{15}H_{16}O_5$ requires C, 65·1; H, 5·8%). Its 2 : 4-*dinitrophenylhydrazone* crystallized from ethanol–ethyl acetate in vermilion needles, m. p. 185° (Found : C, 55·0; H, 4·3; N, 12·1. $C_{21}H_{20}O_8N_4$ requires C, 55·3; H, 4·4; N, 12·3%).

5-*Acetoxy*-7 : 8-*dimethoxy*-3-*oxo*cyclo*penta*[a]*naphthalene*.—The preceding acid (20 g.) in acetic anhydride (200 c.c.) was refluxed for 45 min., cooled, and poured into water (250 c.c.). The 4-*acetoxy*cyclo*pentanaphthalene* (22 g.) was collected and crystallized from ethanol in colourless needles, m. p. 196° (Found : C, 67·97; H, 5·47. $C_{17}H_{16}O_5$ requires C, 68·0; H, 5·3%). Its 2 : 4-*dinitrophenylhydrazone* crystallized from acetic acid in bright red plates, m. p. 258° (Found : C, 59·6; H, 3·9; N, 12·0. $C_{23}H_{18}O_7N_4$ requires C, 59·7; H, 3·9; N, 12·1%).

5-*Hydroxy*-7 : 8-*dimethoxy*cyclo*penta*[a]*naphthalene*.—(*a*) Huang-Minlon reduction of this ketone gave a poor yield of 5-hydroxy-7 : 8-dimethoxy*cyclo*penta[*a*]naphthalene which crystallized from acetic acid in needles, m. p. 188°.

(*b*) The acetoxy-ketone (15 g.) in ethanol (500 c.c.) was refluxed with granulated zinc (75 g.) and concentrated hydrochloric acid (250 c.c.) was added in portions every hour for 7 hr. 5-*Hydroxy*-7 : 8-*dimethoxy*cyclo*penta*[a]*naphthalene* (11 g., 88%) was precipitated. It crystallized from acetic acid in needles, m. p. 188° (Found : C, 73·97; H, 6·8. $C_{15}H_{16}O_3$ requires C, 73·8; H, 6·5%).

2-(2-*Carboxyl*cyclo*pent*-1-*enyl*)-4 : 5-*dimethoxybenzoic Acid*.—5-Hydroxy-7 : 8-dimethoxy-*cyclo*penta[*a*]naphthalene (5 g.) in acetic acid (100 c.c.) was added during 3 hr. to a stirred acetic acid solution (40 c.c.; 11·5%) of peracetic acid at room temperature. The mixture was kept for 4 days. The pale yellow precipitate was then collected and washed with water and dried (2·0 g., 33%). The *acid* crystallized from benzene in colourless needles, m. p. 117° (Found : C, 61·5; H, 5·3. $C_{15}H_{16}O_6$ requires C, 61·6; H, 5·5%).

This acid (1·8 g.) was then reduced with 4% sodium amalgam (20 g.). 2-2'-*Carboxy*cyclo*pentyl*-4 : 5-*dimethoxybenzoic acid* crystallized from benzene in needles, m. p. 160° (Found : C, 61·0; H, 6·1. $C_{15}H_{18}O_6$ requires C, 61·2; H, 6·1%).

1 : 2 : 3 : 3a : 8 : 8a-*Hexahydro*-5 : 6-*dimethoxy*cyclo*pent*[a]*inden*-8-*one*.—3 : 4-Dimethoxy-6-2'-carboxy*cyclo*pentylbenzoic acid (1·3 g.) in acetic anhydride (50 c.c.) was refluxed for 9 hr., cooled, and poured into water. Extraction with ether gave 1 : 2 : 3 : 3a : 8 : 8a-*hexahydro*-5 : 6-*dimethoxy*cyclo*pent*[a]*inden*-8-*one* which crystallised from light petroleum (b. p. 40—60°)

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[5] Robinson, *J.*, 1938, 1390.

in colourless prisms, m. p. 102° (0·5 g., 50%) (Found : C, 72·3; H, 7·0. $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·9%). Its 2 : 4-*dinitrophenylhydrazone* crystallized from acetic acid in deep red needles, m. p. 273° (Found : C, 58·0; H, 4·9; N, 13·9. $C_{20}H_{20}O_6N_4$ requires C, 58·2; H, 4·8; N, 13·6%), and its *oxime* from aqueous ethanol in colourless needles, m. p. 165° (Found : C, 67·8; H, 6·7; N, 5·7. $C_{14}H_{17}O_3N$ requires C, 68·0; H, 6·9; N, 5·7%).

1 : 2 : 3 : 3a : 8 : 8a-*Hexahydro*cyclo*pent*[a]*inden*-8-*ones*.—(a) *General method*. *cyclo*Pentene-1-carbonyl chloride (1 mol.) in a large excess of the other reactant was treated, at 0°, with stirring, with aluminium chloride (3 mols.) during ½ hr., heated on the water-bath for 1 hr., kept at room temperature overnight, and poured on concentrated hydrochloric acid and ice, and the organic layer was separated. The aqueous layer was extracted with ether and the combined organic material washed with sodium hydroxide solution and water and dried. After removal of the ether, the residue was distilled *in vacuo*. *Compounds* 1—6 (Table 1) were thus prepared.

(b) 4 : 7-*Dimethoxy-compound*. *cyclo*Pentene-1-carbonyl chloride (2·0 g.) and *p*-dimethoxybenzene (2·1 g.) in nitrobenzene (100 c.c.) were treated at 0° with aluminium chloride (6·5 g.) during ½ hr., heated for 1 hr. on the water-bath, left to stand at room temperature overnight, and poured on concentrated hydrochloric acid (25 c.c.) and ice. The nitrobenzene was removed in steam. The residue was extracted with ether, which was washed with sodium hydroxide and water, dried, and distilled, giving *compound* 7.

2 : 4-*Dinitrophenylhydrazones* (see Table 2) crystallized from acetic acid, *oximes* from aqueous ethanol.

TABLE 1. 1 : 2 : 3 : 3a : 8 : 8a-*Hexahydro*cyclo*pent*[a]*inden*-8-*ones* (IV).

No.	R^1	R^2	R^3	R^4	Yield (%)	B. p./mm.	n_D^{20}	$\nu_{C=O}$ (μ)	Found (%) C	Found (%) H
1	H	Me	H	H	55	180—183°/12	1·5675	5·88	83·7	7·4 [d]
2	H	Me	Me	H	82	100—103°/0·1	1·5670	5·87	83·8	8·1 [e]
3	H	Me	H	Me	83	100—103°/0·1	1·5682	5·89	83·9	8·2 [e]
4	Me	H	H	Me	80	100—103°/0·1	1·5679	5·91	84·2	8·1 [e]
5	H	Et	H	H	80	130—133°/0·2	1·5558 [c]	5·88	84·3	8·2 [e]
6	H	OMe	OMe	H	60	205—207°/0·2 [a]	—	5·94	72·3	7·0 [f]
7	OMe	H	H	OMe	~18	204—206°/0·2 [b]	—	5·96	72·2	7·1 [f]

[a] M. p. 102°. [b] M. p. 132°. [c] At 24°. [d] $C_{13}H_{14}O$ requires C, 83·9; H, 7·5%. [e] $C_{14}H_{16}O$ requires C, 84·0; H, 8·0%. [f] $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·9%.

TABLE 2. *Derivatives of* 1 : 2 : 3 : 3a : 8 : 8a-*hexahydro*cyclo*pent*[a]*inden*-8-*ones*.

No.[a]	M. p.	Found (%) C	Found (%) H	Found (%) N	Formula	Required (%) C	Required (%) H	Required (%) N
				2 : 4-*Dinitrophenylhydrazones* [b]				
1	193° [c]	62·1	5·0	15·2	$C_{19}H_{18}O_4N_4$	62·3	4·7	15·3
2	215 [d]	63·3	5·5	14·5	$C_{20}H_{20}O_4N_4$	63·2	5·4	14·7
3	231 [e]	63·4	5·8	14·6				
4	226 [c]	63·1	5·3	14·4				
5	205 [c]	63·0	5·1	14·6				
6	273 [c]	58·0	4·9	13·5	$C_{20}H_{20}O_6N_4$	58·2	4·8	13·6
7	263 [c]	57·9	4·5	13·6				
				Oximes [c]				
1	136	77·5	7·4	6·7	$C_{13}H_{15}ON$	77·6	7·5	7·0
2	148	78·0	7·9	6·3	$C_{14}H_{17}ON$	78·1	7·9	6·5
3	145	77·9	7·8	6·4				
4	144	78·2	8·0	6·2				
5	144	78·0	7·8	6·4				
6	165	67·8	6·7	5·7	$C_{14}H_{17}O_3N$	68·0	6·9	5·7
7	168	67·9	7·0	5·5				

[a] Nos. as in Table 1. [b] Red. [c] Needles. [d] Prisms. [e] Plates.

1 : 2 : 3 : 3a : 8 : 8a-*Hexahydro*cyclo*pent*[a]*indenes*.—The *cyclo*pentindenone (1 g.) in toluene (10 c.c.) was added to amalgamated zinc (10 g.), concentrated hydrochloric acid (20 c.c.),

and water (15 c.c.), stirred under reflux for 9 hr., concentrated hydrochloric acid (10 c.c.) being added every hour. After cooling, the toluene layer was separated, washed with aqueous sodium carbonate and water, dried, and evaporated. The residue was distilled *in vacuo*. The products are shown in Table 3.

p-*Anisoyl*cyclo*pentene.*—*cyclo*Pentene-1-carbonyl chloride (2·4 g.) in anisole (150 c.c.) was treated at 0°, with stirring, with aluminium chloride (7·5 g.) during ½ hr., left at room temperature for 24 hr., and poured on concentrated hydrochloric acid (50 c.c.) and ice. The anisole layer was separated and the aqueous layer extracted with ether. The combined extracts were washed with sodium hydroxide solution and water, dried, and evaporated. *Anisoyl*cyclo*pentene* (0·7 g., 19%) distilled at 145—148°/10·2 mm. and had n_D^{20} 1·5941 (Found : C, 77·5; H, 6·3. $C_{13}H_{12}O_2$ requires C, 78·0; H, 6·0%), having an infrared peak at 6·14 μ. This compound could not be cyclized under the conditions described above owing to demethylation by the aluminium chloride.

TABLE 3. 1 : 2 : 3 : 3a : 8 : 8a-*Hexahydro*cyclo*pent*[a]*indenes* (V).

No.	R¹	R²	R³	R⁴	Yield (%)	B. p./mm.	n_D^{20}	d_{24}^{24}	Found (%) C	Found (%) H
1	H	Me	H	H	82	126—128°/12	1·5363 [c]	0·9971	91·1	8·9 [e]
2	H	Me	Me	H	88	155—158°/12	1·5452	0·9980	90·5	10·0 [f]
3	H	Me	H	Me	83	154—157°/12	1·5471	0·9982	90·0	9·8 [f]
4	Me	H	H	Me	86	160—162°/12	1·5450	0·9979	90·0	8·6 [f]
5	H	Et	H	H	85	163—165°/12	1·5258 [d]	0·9987	90·1	10·0 [f]
6	H	OMe	OMe	H	80	150—151°/0·1 [a]	—	—	77·0	8·4 [g]
7	OMe	H	H	OMe	85	151—153°/0·15 [b]	—	—	77·1	8·1 [g]

[a] M. p. 37°. [b] M. p. 55°. [c] At 24°. [d] At 21°. [e] $C_{13}H_{16}$ requires C, 91·3; H, 8·7%. [f] $C_{14}H_{18}$ requires C, 90·3; H, 9·7%. [g] $C_{14}H_{18}O_2$ requires C, 77·0; H, 8·3%.

1 : 2 : 3 : 3a : 8 : 8a-*Hexahydro*-8-*methylene*cyclo*pent*[a]*indenes.*—The hexahydro*cyclo*pent[*a*]-inden-8-ones in ether were added, dropwise with shaking at 0°, to methylmagnesium iodide (1 mol.) in ether, then kept at room temperature overnight. The mixture was poured on dilute hydrochloric acid, the ether layer was separated, washed with aqueous sodium carbonate and water, and evaporated, and the residue distilled. *Products* are shown in Table 4.

TABLE 4. 1 : 2 : 3 : 3a : 8 : 8a-*Hexahydro*-8-*methylene*cyclo*pent*[a]*indenes* (VII).

No.[a]	Yield (%)	B. p./mm.	n_D^{20}	d_{24}^{24}	Found (%) C	Found (%) H	Formula	Required (%) C	Required (%) H
1	82	155—158°/12	1·5520	0·9989	91·5	8·6	$C_{14}H_{16}$	91·3	8·7
2	83	170—172°/12	1·5542	0·9995	91·1	9·3	$C_{15}H_{18}$	90·9	9·1
3	83	172—174°/12	1·5580	0·9991	90·6	8·9			
4	92	168—171°/12	1·5570 [b]	0·9993	90·7	9·4			
5	75	173—175°/12	1·5481 [b]	0·9998	90·6	8·9			

[a] Nos. as in Table 1. [b] n_D^{24}.

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