800. *Reduced Cyclic Compounds. Part VI.* The Preparation and Cyclisation of* trans-8-*Phenyloct-5-enoic and* trans-7-1′-*Naphthylhept-4-enoic Acid.*†

By M. F. Ansell and S. S. Brown.

The preparation, *via* the ring scission of 3-chlorotetrahydro-2-phenethyl- and -2-(2-1′-naphthylethyl)-pyran, of *trans*-8-phenyloct-5-enoic acid and *trans*-7-1′-naphthylhept-4-enoic acid is described. These acids with hot polyphosphoric acid yield respectively 1 : 2 : 3 : 7 : 8 : 9 : 10 : 10*a*-octahydro-7-oxo-*cyclo*hepta[*de*]naphthalene and 1 : 2 : 3 : 3*a* : 4 : 5-hexahydrobenz[*de*]anthr-6-one. On treatment with aluminium chloride in carbon disulphide, the phenyloctenoyl chloride yields 1 : 2 : 3 : 4 : 4*a* : 9 : 10 : 10*a*-octahydro-1-oxophenanthrene; the naphthylheptenoyl chloride resinifies.

Since reduced cyclic systems are formed by ring closure of ω-phenylalkenols [1] and by the intramolecular acylation [2] of alkenoic acids or acid chlorides, *trans*-8-phenyloct-5-enoic and *trans*-7-1′-naphthyl-hept-4-enoic acid (VII) were prepared and studied. The syntheses followed routes similar to those used [3] for alk-4- and -5-enoic acids. *trans*-7-Phenylhept-4-en-1-ol [1] gave *trans*-7-chloro-1-phenylhept-3-ene and thence, by carboxylation of the Grignard reagent, *trans*-8-phenyloct-5-enoic acid. Similar reactions from 3-chlorotetrahydro-2-(2-1′-naphthylethyl)furan yielded a difficultly separable mixture (cf. ref. 3) of *cis*- and *trans*-7-1′-naphthylhept-4-enoic acid. The pure *trans*-acid was however obtained by

* Part V, *J.*, 1958, 3388. † Cf. *Chem. and Ind.*, 1956, 980.

[1] Ansell and Selleck, *J.*, 1956, 1238.
[2] Ansell and Brown, *J.*, 1958, 2955.
[3] *Idem*, *J.*, 1957, 1788.

oxidation, with chromium trioxide–pyridine,[4] of *trans*-7-1′-naphthylhept-4-en-1-ol prepared by the ring scission of 3-chlorotetrahydro-2-(2-1′-naphthylethyl)pyran.

The ring closure of an arylalkenoic acid such as (I) to a tricyclic structure necessitates two intramolecular reactions—acylation and alkylation—and according to the order in which these occur, two different ring systems may be formed. Both cyclisation routes have been realised with *trans*-8-phenyloct-5-enoic acid. Treatment with hot polyphosphoric acid gave the tricyclic ketone (V) in good yield, evidently by way of the acid (IV) which is known [5] to afford the ketone (V) on treatment with hot polyphosphoric acid.

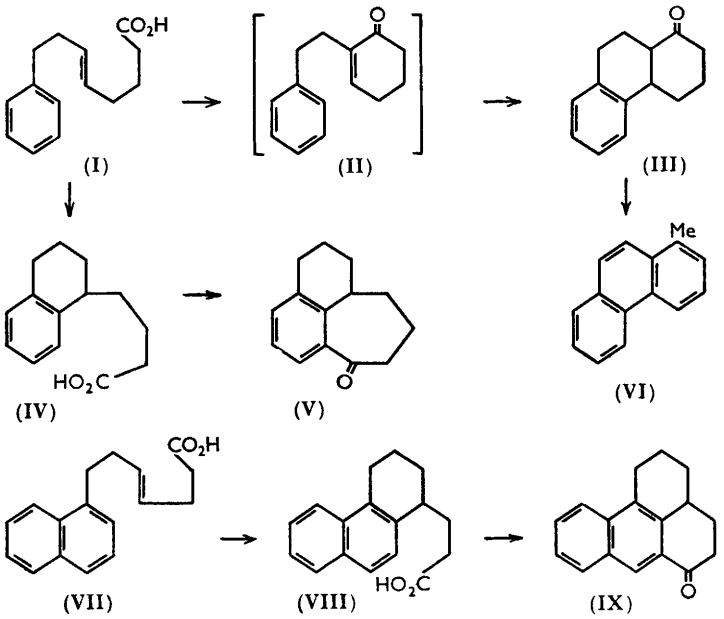
However, *trans*-8-phenyloct-5-enoyl chloride with aluminium chloride in boiling carbon disulphide (cf. ref. 6) gave mainly one ketone which on treatment with methylmagnesium iodide and then palladised charcoal afforded 1-methylphenanthrene (VI): the product was therefore the octahydro-1-oxophenanthrene (III), and in conformity had two closely spaced ultraviolet absorption maxima at *ca.* 270 mμ typical [1, 7] of *as*-octahydrophenanthrene derivatives, and infrared absorption maxima at 13·3 and 5·9 μ as in the spectra of *o*-disubstituted benzenes and six-membered *cyclo*alkanones respectively.[8] The mechanism of cyclisation of the chloride of (I) ⟶ (III) and the stereochemistry of the product have not been elucidated. If acylation of the double bond and alkylation of the aromatic ring form a concerted process a *trans*-octahydrophenanthrene would result: [9] if acylation precedes alkylation, then 2-phenethyl*cyclo*hex-2-enone (II) is the effective intermediate. Although the ring closure of this ketone has been reported [10] to fail, there is no doubt that the reaction is practicable in view of the successful cyclisation [6] of 1-acetyl-2′-phenyl*cyclo*hexene. If, therefore, cyclisation of the acid chloride proceeds *via* a carbonium ion derived from (II), a mixture of *cis*- and *trans*-hydrophenanthrenes would be expected (cf. refs. 9 and 11); but since a virtually homogeneous product was obtained, equilibration to the more stable epimer seems likely to have occurred. For *as*-octahydrophenanthrene the *trans*-isomer is known [12] to be the more stable.

The ring closure of *trans*-7-1′-naphthylhept-4-enoic acid (VII) with polyphosphoric acid proved analogous to that of the acid (I); a good yield of 1 : 2 : 3 : 3*a* : 4 : 5-hexahydrobenz[*de*]anthr-6-one (IX) was obtained. This ketone, whose melting point was at variance with the only recorded value,[13] was identified by comparison with a specimen prepared by the action of polyphosphoric acid on β-(1 : 2 : 3 : 4-tetrahydro-1-phenanthryl)-propionic acid (VIII) itself obtained by reduction of β-(3 : 4-dihydro-1-phenanthryl)-propionic acid.[14] It is of interest that the cyclisation of the acid (VII) occurs in only one sense. Successive intramolecular alkylation and acylation of positions 8 and 9, respectively, would have yielded the 3 : 4-benzo-derivative of (V).

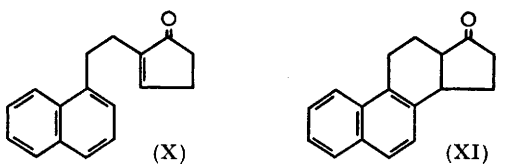
Attempted cyclisation of *trans*-7-1′-naphthylhept-4-enoyl chloride with aluminium chloride in carbon disulphide at temperatures from −10° to +46° gave tars, from which only traces of ketonic material were isolated. If, as expected (cf. ref. 2), 2-(2-1′-naphthylethyl)*cyclo*pent-2-enone (X) were the initial product, this should cyclise further [probably to (XI) [15]] or be recovered unchanged (cf. refs. 10 and 16). It must be assumed that intermolecular acylation of the reactive nucleus is faster than intramolecular acylation of the double bond, and so gives rise to polymers.

[4] Poos, Arth, Beyler, and Sarrett, *J. Amer. Chem. Soc.*, 1953, **75**, 422; Poos, Johns, and Sarrett, *ibid.*, 1955, **77**, 1026.
[5] Gilmore and Horton, *ibid.*, 1951, **73**, 1411.
[6] Gutsche and Johnson, *ibid.*, 1946, **68**, 2239.
[7] Askew, *J.*, 1935, 512.
[8] Bellamy, " Infra-red Spectra of Complex Molecules," Methuen, London, Chapters 5 & 9.
[9] Stork and Burgstahler, *J. Amer. Chem. Soc.*, 1955, **77**, 5068.
[10] Cohen and Cook, *J.*, 1935, 1570.
[11] Barnes and Olin, *J. Amer. Chem. Soc.*, 1956, **78**, 3830.
[12] Cook, McGinnis, and Mitchell, *J.*, 1944, 286.
[13] Hoch, *Compt. rend.*, 1938, **207**, 921.
[14] Johnson, Peterson, and Schneider, *J. Amer. Chem. Soc.*, 1947, **69**, 74.
[15] Johnson and Posvic, *ibid.*, p. 1361.
[16] Harper, *J.*, 1937, 1859.

Acid-catalysed "double ring-closures," such as those described above, constitute a novel route to hydroaromatic ketones of the types (III), (V), and (IX). Cyclisation of these ω-arylalkenoic acids may be regarded as a logical extension of those reactions in



which an olefinic acid undergoes intermolecular condensation with an aromatic hydrocarbon to form a polycyclic system, as exemplified by the preparation of 1-methyl-3′-oxo-2 : 3-*cyclo*pentanoacenaphthene from acenaphthene and crotonic acid,[17] of 1-tetralone from benzene and γ-butyrolactone,[18] and of 3 : 4-benzopyrene-1 : 5-quinone from phthalidyleneacetic acid and naphthalene.[19]



Experimental

Ultraviolet absorption spectra were measured for 95% ethanol solutions.

trans-7-*Chloro*-1-*phenylhept*-3-*ene*.—Thionyl chloride (393 g., 3·3 moles) was added slowly to a stirred ice-cold mixture of *trans*-7-phenylhept-4-en-1-ol [1] (590 g., 3·1 moles), pyridine (1·5 ml.), and benzene (350 ml.). When about one half of the reagent had been added (*ca.* 40 min.), evolution of gas began, after which the remainder was run in quickly without cooling. The mixture was then boiled (caution) until vigorous evolution of gas ceased. It was then cooled and poured on excess of ice, and the organic layer was separated, washed with water, saturated sodium carbonate solution, and brine, dried ($MgSO_4$), and evaporated. Distillation gave trans-7-*chloro*-1-*phenylhept*-3-*ene* (588 g., 91%), b. p. 92—93°/0·3 mm., n_D^{20} 1·5202 (Found: C, 75·2; H, 8·3. $C_{13}H_{17}Cl$ requires C, 74·8; H, 8·2%). The α-*naphthalide* of *trans*-8-phenyloct-5-enoic acid (prepared *via* the Grignard reagent) formed prisms (from methanol), m. p. 113—114° (Found:

[17] Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1939, **61**, 1272.
[18] Olson and Bader, *Org. Synth.*, 1955, **35**, 95.
[19] Schroeder, Stilmar, and Palmer, *J. Amer. Chem. Soc.*, 1956, **78**, 446; cf. Norman and Waters, *J.*, 1956, 2379.

N, 4·1. $C_{24}H_{25}ON$ requires N, 4·1%). Hydrolysis of the Grignard reagent gave trans-1-*phenylhept-3-ene*, b. p. 108—109°/11 mm., n_D^{20} 1·500 (Found: C, 89·6; H, 10·4. $C_{13}H_{18}$ requires C, 89·6; H, 10·4%).

trans-8-*Phenyloct-5-enoic Acid.*—A solution of the Grignard reagent prepared from 7-chloro-1-phenylhept-3-ene (208 g., 1 mole) and magnesium (25·2 g., 1·05 g.-atom) in ether (900 ml.) was poured on a large excess of stirred, finely powdered carbon dioxide and left overnight. Water (750 ml.) and hexane (500 ml.) were then added, followed by sufficient 10N-hydrochloric acid (*ca.* 60 ml.) to give two clear phases. The organic layer was separated and the aqueous phase extracted with hexane (3 × 250 ml.). The combined hexane solutions were extracted with a saturated solution of sodium hydrogen carbonate, and the alkaline solution so obtained back-extracted with hexane and then acidified to Congo-red, at 0°, by stirring it with an equal volume of hexane and cautiously adding 5N-hydrochloric acid. After extraction, etc., as before, distillation gave trans-8-*phenyloct-5-enoic* acid (152 g., 70%), b. p. 134—136°/2 × 10^{-4} mm., n_D^{20} 1·5172 (Found: C, 77·2; H, 8·3. $C_{14}H_{18}O_2$ requires C, 77·0; H, 8·3%). The derived 4-*bromophenacyl ester* (laths from methanol) had m. p. 41—42° (Found: C, 63·4; H, 5·7; Br, 19·4. $C_{22}H_{23}O_3Br$ requires C, 63·6; H, 5·6; Br, 19·2%), and the *phenylhydrazide* (needles from ethanol), m. p. 98—99° (Found: C, 77·5; H, 9·6; N, 8·7. $C_{20}H_{24}ON_2$ requires C, 77·9; H, 7·8; N, 9·1%). Hydrogenation of the acid in the presence of Adams catalyst at room temperature and pressure gave 8-*phenyloctanoic acid* (plates from pentane), m. p. 24—25° (Found: C, 76·3; H, 9·2. $C_{14}H_{20}O_2$ requires C, 76·3; H, 9·2%). *trans*-8-Phenyloct-5-enoyl chloride was obtained by the addition of oxalyl chloride (25 g., 0·20 mole) during 15 min. to a warm (50°) stirred solution of the acid (39 g., 0·18 mole) in dry benzene (50 ml.). A stream of dry nitrogen was then passed through the hot solution for 1 hr., after which the solvent was evaporated off and the residue distilled to give *trans*-8-phenyloct-5-enoyl chloride (40 g.), b. p. 85—89°/5 × 10^{-4} mm., n_D^{20} 1·526—1·529. This material slowly resinified and was not obtained pure. Treatment with ammonia gave the *amide* (plates from aqueous ethanol), m. p. 94—95° (Found: C, 77·4; H, 8·7; N, 6·25. $C_{14}H_{19}ON$ requires C, 77·4; H, 8·8; N, 6·45%).

6-1′-*Naphthylhex-3-en-1-ol.*—From 1-bromonaphthalene,[20] 2-1′-naphthylethyl alcohol (88%) was prepared by the entrainment technique [21] and thence 2-1′-naphthylethyl chloride [22] (93%; b. p. 110—112°/0·4 mm., n_D^{20} 1·6182) by the method described above for *trans*-7-chloro-1-phenylhept-3-ene.

A decanted solution of the Grignard reagent prepared from 2-1′-naphthylethyl chloride (231 g., 1·22 moles) and magnesium (1·37 g.-atoms) in ether (700 ml.) was added during 1 hr. to a stirred solution of freshly distilled 2 : 3-dichlorotetrahydrofuran [23] (141 g., 1·0 mole) in ether (300 ml.) so that a steady reflux was maintained. The mixture was stirred until spontaneous refluxing ceased (*ca.* 15 min.), then poured on ice (700 g.) and ammonium chloride (30 g.). On vigorous stirring, two phases separated; the aqueous phase was extracted with ether (2 × 200 ml.). The combined ethereal solutions, which contained 3-chlorotetrahydro-2-(2-1′-naphthylethyl)furan (which decomposed on distillation and therefore was not isolated), were dried ($MgSO_4$; $CaSO_4$) and added to a stirred suspension of sodium sand [(51 g., 2·2 g.-atoms) in ether (150 ml.)] [the reaction having been initiated by the addition of tetrahydrofurfuryl chloride (1 ml.) so that controlled spontaneous reflux was maintained. When the addition was complete (*ca.* 1 hr.) the mixture was stirred for a further hour at room temperature. Sufficient water (*ca.* 500 ml.) (caution) was added to give two phases which were separated and the aqueous phase was extracted with ether. Distillation of the dried ($MgSO_4$) combined extracts gave, after elimination of low-boiling material, *cis* + *trans*-6-1′-naphthylhex-3-en-1-ol (83 g., 37% based on dichlorotetrahydrofuran), b. p. 145—55°/3 × 10^{-2} mm., n_D^{16} 1·591—1·593 (Found: C, 84·0; H, 8·5. Calc. for $C_{16}H_{18}O$: C, 84·9; H, 8·0%).

cis + trans-7-1′-*Naphthylhept-4-enoic Acid.*—Conversion of the above alkenol (69 g.) into the chloride (70 g.; b. p. 135—145°/6 × 10^{-2} mm., n_D^{16} 1·587—1·592) and carboxylation of the Grignard reagent were carried out as for *trans*-8-phenyloct-5-enoic acid. The crude acid (30 g.) was a viscous oil, which slowly deposited crystals; after two years these were collected (8·7 g.) and crystallised from hexane, to give *trans*-7-1′-naphthylhept-4-enoic acid, whose m. p. (65—69°) was not depressed on admixture with the acid prepared from *trans*-7-1′-naphthylhept-4-en-1-ol.

[20] Merz and Weith, *Ber.*, 1882, **15**, 2708.
[21] Bachmann, Cole, and Wilds, *J. Amer. Chem. Soc.*, 1940, **62**, 824; Wilds and Close, *ibid.*, 1947, **69**, 3079.
[22] Cf. Cook and Hewett, *J.*, 1933, 1098.
[23] Crombie and Harper, *J.*, 1950, 1707, 1714.

trans-7-1′-*Naphthylhept*-4-*en*-1-*ol.*—This *alkenol*, b. p. 165—68°/0·8 mm., n_D^{20} 1·579—1·581 (Found: C, 84·3; H, 8·4. $C_{17}H_{20}O$ requires C, 84·9; H, 8·4%), was prepared (57% yield) by ring scission of the crude product of the coupling of 2-1′-naphthylethylmagnesium chloride (1·78 moles) and 2 : 3-dichlorotetrahydropyran [23] (1·42 moles) as described for the above naphthylhexenol.

Oxidation of trans-7-1′-*Naphthylhept*-4-*en*-1-*ol.*—Chromium trioxide (65 g., 0·62 mole) was added with stirring during 40 min. to pure pyridine (650 ml.), at 25°, the internal temperature being maintained at this value by intermittent cooling. The mixture was stirred at room temperature for 30 min. after which *trans*-7-1′-naphthylhept-4-en-1-ol (65 g., 0·27 mole) was added and stirring continued for 16 hr. After dilution with ice-water (1·5 l.) the solution was extracted with ether (3 × 1 l.), and these extracts were washed with water (2 × 500 ml.) and 0·5N-potassium hydroxide (2 × 250 ml.). Evaporation of the ethereal extracts and desiccation of the residual oil gave crude *trans*-7-1′-naphthylhept-4-enal (49 g., 76%). The derived 2 : 4-*dinitrophenylhydrazone* (yellow needles from ethanol) had m. p. 145—146° (Found: C, 66·4; H, 5·3; N, 13·0. $C_{23}H_{22}O_4N_4$ requires C, 66·0; H, 5·3; N, 13·4%).

The alkaline washings were extracted with ether and then acidified to Congo-red with 2N-hydrochloric acid. The red precipitate was extracted with benzene (2 × 100 ml.), the extract evaporated, and the residue neutralised with N-ammonia. The resulting solution was treated with a cold saturated aqueous solution of *S*-benzylthiuronium chloride (6·0 g.), and the precipitate was recrystallised from ethanol, to yield S-*benzylthiuronium* trans-7-1′-*naphthylhept*-5-*enoate* (10·5 g., 9·2%) as laths, m. p. 162—166°. A sample recrystallised twice more had m. p. 166—167° (Found: C, 71·1; H, 6·4; N, 6·9. $C_{25}H_{28}O_2N_2S$ requires C, 71·4; H, 6·7; N, 6·7%). The salt (10 g.) was shaken with ice-cold N-hydrochloric acid (25 ml.) and ether (25 ml.). Material from the ethereal layer yielded trans-7-1′-*naphthylhept*-4-*enoic acid* (5·9 g.), m. p. 67—69° (from hexane). Two further recrystallisations (in the presence of fuller's earth) gave the pure acid as prisms, m. p. 69—70° (Found: C, 80·3; H, 7·35. $C_{17}H_{18}O_2$ requires C, 80·3; H, 7·15%).

The above crude *trans*-7-1′-naphthylhept-4-en-al (49 g., 0·20 mole) was added to a stirred suspension of dry freshly prepared silver oxide (58 g., 0·25 mole) in benzene (100 ml.). At 65°, an exothermic reaction set in and silver was deposited. After 30 minutes' stirring under reflux the mixture was cooled in ice, treated with 2N-nitric acid (200 ml.), and centrifuged to give a clear benzene layer, from which was obtained, *via* the *S*-benzylthiuronium salt as above, *trans*-7-1′-naphthylhept-5-enoic acid (8·3 g., 12%), m. p. 67—69°.

The derived *acid chloride*, prepared as for 8-phenyloct-5-enoyl chloride, had b. p. 165—168°/2 × 10^{-2} mm., n_D^{21} 1·5828 (Found: C, 75·7; H, 6·5; Cl, 12·1. $C_{17}H_{17}OCl$ requires C, 74·8; H, 6·3; Cl, 13·0%), and the *amide* (plates from aqueous ethanol) had m. p. 84—85° (Found: N, 5·9. $C_{17}H_{19}ON$ requires N, 5·5%).

Cyclisation of trans-8-*Phenyloct*-5-*enoic Acid.*—This acid (30 g.) was treated with polyphosphoric acid [24] (300 g.) at 110° for 2 hr., in an atmosphere of nitrogen as previously described.[2] Distillation of the oil obtained on evaporation of the ethereal extract gave 1 : 2 : 3 : 7 : 8 : 9 : 10 : 10*a*-octahydro-7-oxo*cyclo*hepta[*de*]naphthalene (20 g., 73%), b. p. 135—145°/0·5 mm., m. p. 60—63° (pale yellow). Recrystallisation from methanol yielded off-white plates, m. p. 63—64° (Found: C, 83·6; H, 8·6. Calc. for $C_{14}H_{16}O$: C, 83·95; H, 8·1%), $\lambda_{max.}$ 252 and 291, $\lambda_{min.}$ 230 and 278 mμ (log ε 3·88, 3·22, 3·33, and 3·10 respectively). The derived oxime (plates from aqueous ethanol) had m. p. 162—163°; the semicarbazone (from methanol) had m. p. 215—216° (decomp.) (Found: N, 16·3. Calc. for $C_{15}H_{19}ON_3$: N, 16·3%); and the 2 : 4-dinitrophenylhydrazone (orange laths from ethanol–chloroform) had m. p. 187—188° (Found: C, 63·2; H, 5·4; N, 14·7. Calc. for $C_{20}H_{20}O_4N_4$: C, 63·1; H, 5·3; N, 14·7%). The reported constants for this ketone are m. p. 63° (ref. 25) and 61·5—63° (ref. 5); semicarbazone, m. p. 221° (ref. 25); 2 : 4-dinitrophenylhydrazone (yellow), m. p. 162—165° (ref. 5). Reduction of the ketone with lithium aluminium hydride in ether gave the 7-hydroxy-compound (tablets from ethyl acetate–hexane), m. p. 87—89° (lit.,[26] m. p. 93—94°), dehydrogenation of which with palladised charcoal gave 7 : 8 : 9 : 10-tetrahydro*cyclo*hepta[*de*]naphthalene (plates from methanol), m. p. 57—58° (lit.,[27] m. p. 57—58°) [picrate (orange needles from

[24] Uhlig, *Angew. Chem.*, 1954, **66**, 325.
[25] von Braun and Rath, *Ber.*, 1927, **60**, 1182.
[26] Gardner and Horton, *J. Amer. Chem. Soc.*, 1952, **74**, 657.
[27] Boekelheide and Vick, *ibid.*, 1956, **78**, 653.

ethanol), m. p. 115—117°; styphnate (yellow needles from ethanol), m. p. 119—121° (lit.,[5] m. p. 114—115·5° and 118·5—121° respectively). The *trinitrobenzene complex* (golden needles from ethanol) had m. p. 138—139° (Found: N, 10·2. $C_{20}H_{21}O_6N_3$ requires N, 10·6%).

Cyclisation of trans-8-*Phenyloct-5-enoyl Chloride*.—The acid chloride (41 g.) was cyclised as previously described,[2] but under nitrogen. The crude product from the carbon disulphide extract gave material (15 g.) of b. p. 155—158°/1 mm., n 1·559—1·567, containing only a trace of chlorine. This was fractionally distilled at 3·5 mm. (100 × 0·6 cm. spinning-band fractionating column from E. Haage, Mülheim) to yield fractions: (1) b. p. <130°, n_D^{20} 1·556 (0·3 g.); (2) b. p. 130—147°, n_D^{20} 1·550 (0·5 g.); (3) b. p. 147—150°, n_D^{20} 1·552 (0·5 g.); and (4) b. p. 150—150·5° (5·5 g.), m. p. 63—72°. From fraction (1) was prepared a 2 : 4-dinitrophenylhydrazone (red needles from benzene–ethanol), m. p. 266—267° (Found: N, 15·3. Calc. for $C_{20}H_{20}O_4N_4$: N, 14·7%) (not 2-phenethyl*cyclo*hex-2-enone 2 : 4-dinitrophenylhydrazone,[28] m. p. 155—157°). Fractions (2) and (3) yielded only complex mixtures of yellow and red 2 : 4-dinitrophenylhydrazones. The semicarbazones of fraction (3) were separated by fractional crystallisation into prisms, m. p. 203—204° (Found: C, 70·6; H, 7·5; N, 16·3. Calc for $C_{15}H_{19}ON_3$: C, 70·0; H, 7·45; N, 16·3%) (which could be converted into a yellow 2 : 4-dinitrophenylhydrazone), and tablets whose m. p. 216—218° was not depressed in admixture with the semicarbazone of fraction (4). Recrystallisation of fraction (4) from methanol yield 1 : 2 : 3 : 4 : 4*a* : 9 : 10 : 10*a*-*octahydro*-1-*oxophenanthrene* as prisms, m. p. 76—77° (Found: C, 83·7; H, 8·0. $C_{14}H_{16}O$ requires C, 83·95; H, 8·1%), $\lambda_{max.}$ 265 and 272, $\lambda_{min.}$ 241 mμ (log ε 1·79, 1·81, 1·38, 1·56 respectively). The *oxime* (needles from aqueous ethanol) had m. p. 184—186° (Found: C, 77·8; H, 7·8; N, 6·6. $C_{14}H_{17}ON$ requires C, 78·1; H, 8·0; N, 6·5%); the *semicarbazone* (phototropic tablets from ethanol) had m. p. 218—219° (Found: C, 70·1; H, 7·6; N, 16·0. $C_{15}H_{19}ON_3$ requires C, 70·0; H, 7·45; N, 16·3%); and the 2 : 4-*dinitrophenylhydrazone* (yellow plates from ethanol–chloroform) had m. p. 221—224° (Found: C, 62·7; H, 5·5; N, 15·3. $C_{20}H_{20}O_4N_4$ requires C, 63·1; H, 5·3; N, 14·7%).

The above ketone (1·2 g.) in ether (25 ml.) was added to the reagent from methyl iodide (3·5 g.) and magnesium (0·45 g.) in ether (50 ml.). The mixture was boiled under reflux for 4 hr., then cooled and treated with a cold saturated aqueous solution of ammonium chloride (2 g.). Evaporation of the dried (K_2CO_3) ethereal extract yielded an oil (giving no precipitate with Brady's reagent), which was heated with 5% palladised charcoal (1 g.) at 310° in nitrogen for 5 hr. The mixture was extracted with boiling ethanol, and the extract then evaporated to yield 1-methylphenanthrene (0·6 g.), m. p. 119—120° (lit.,[29] m. p. 118—119°). The picrate, styphnate, and 1 : 3 : 5-trinitrobenzene complex had m. p. 135—137°, 153—154°, and 158—159° respectively (lit.,[29] 135·5—137°, 150·5—152°, and 160—161° respectively).

Cyclisation of trans-7-1′-*Naphthylhept*-4-*enoic Acid*.—This acid (2·0 g.) was treated with polyphosphoric acid (20 g.) at 90°, in nitrogen, as previously described. The mixture rapidly became homogeneous and after 5 min. was poured into water. Evaporation of the neutral ethereal extract and recrystallisation of the residue (from ethanol) gave pale yellow 1 : 2 : 3 : 3*a* : 4 : 5-*hexahydrobenz*[de]*anthr*-6-*one* (1·3 g., 70%), m. p. 123—125°. The analytical sample (off-white needles) had m. p. 124—125° (Found: C, 86·2; H, 6·80. $C_{17}H_{16}O$ requires C, 86·4; H, 6·8%), $\lambda_{max.}$ 296, 307, 353, $\lambda_{min.}$ 270, 302, and 325 mμ (log ε 2·93, 2·92, 2·38, 2·45, 2·85, and 2·14 respectively). The oxime had m. p. 192—193° (decomp.), and the 2 : 4-dinitrophenylhydrazone m. p. 293—294° (decomp.). The m. p.s of the ketone and its derivatives were not depressed on admixture with authentic samples (see below).

β-(1 : 2 : 3 : 4-*Tetrahydro*-1-*phenanthryl*)*propionic Acid*.—β-(3 : 4-Dihydro-1-phenanthryl)-propionic acid [14] (1·5 g.) was hydrogenated in the presence of Adams catalyst (0·1 g.) in ethyl acetate (50 ml.) at atmospheric pressure and room temperature. After removal of the catalyst the solution was concentrated to *ca.* 5 ml. and cooled, depositing crystals which were filtered off and dried to yield β-(1 : 2 : 3 : 4-tetrahydro-1-phenanthryl)propionic acid (1·4 g., 93%), plates, m. p. 146—147° (from ethyl acetate) (Found: C, 79·7; H, 7·5. $C_{17}H_{18}O_2$ requires C, 80·3; H, 7·15%). Hoch [13] records m. p. 115°. The S-*benzylthiuronium* salt (tablets from ethanol) had m. p. 158—159° (Found: N, 6·9; S, 7·4. $C_{22}H_{28}O_2N_2S$ requires N, 6·7; S, 7·6%).

1 : 2 : 3 : 3*a* : 4 : 5-*Hexahydrobenz*[de]*anthr*-6-*one*.—The tetrahydrophenanthrylpropionic acid (1·0 g.) was treated with polyphosphoric acid (20 g.) at 95° in nitrogen as previously described and was poured into water after 50 min. Evaporation of the neutral ethereal extract left a

[28] Ansell and Ducker, unpublished work.
[29] Adkins and England, *J. Amer. Chem. Soc.*, 1949, **71**, 2958.

bright yellow solid (0·9 g.), m. p. 119—122°, which on repeated recrystallisation from methanol gave the ketone with the m. p. and spectrum recorded above (Found: C, 85·6; H, 7·3%). The *oxime* (tablets from ethanol) had m. p. 191—192° (decomp.) (Found: N, 5·5. $C_{17}H_{17}ON$ requires N, 5·6%), and the 2 : 4-*dinitrophenylhydrazone* (red rhombs from chloroform) had m. p. 291—292° (decomp.) (Found: C, 65·9; H, 4·7. $C_{23}H_{20}O_4N_4$ requires C, 66·3; H, 4·8%).

Attempted Cyclisation of trans-7-1′-*Naphthylhept*-4-*enoyl Chloride*.—Cyclisation of this acid chloride (2·0 g.) as previously described [2] gave tar. Heating for only 35 min. yielded material, from the methanolic extract of which was prepared a 2 : 4-dinitrophenylhydrazone [of 2-(2-1′-naphthylethyl)*cyclo*pent-2-enone(?) (red needles from chloroform), m. p. 228—229° (Found: N, 13·2. Calc. for $C_{22}H_{20}O_4N_4$: N, 13·5%)]. At lower reaction temperatures (−10° to +20°) no ketone was isolated; at −10°, some unchanged acid chloride was recovered.

The authors are indebted to the Senate of the University of London for the award of a Post-graduate Studentship (to S. S. B.) and to the Central Research Fund for financial assistance.

Chemistry Department, Queen Mary College,
University of London, Mile End Road, E.1. [*Received, May 22nd*, 1958.]