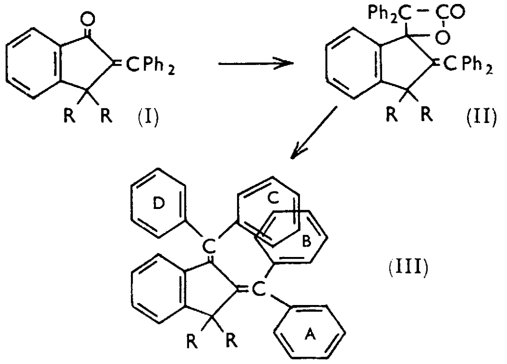
Overcrowded Molecules. Part I. 1,2-Bisdiphenylmethyleneindane and 1,2-Bisdiphenylmethylene-3,3-dimethylindane

By **H. G. Heller, D. Auld,** and **K. Salisbury,** Edward Davies Chemical Laboratory, University College of Wales, Aberystwyth

1,2-Bisdiphenylmethyleneindane and its 3,3-dimethyl derivative have been prepared by the interaction of diphenylketen and 2-diphenylmethylene-1-indanone and its 3,3-dimethyl derivative, respectively. These severely overcrowded hydrocarbons are stable but, when dissolved in organic solvents and exposed to sunlight, they cyclise to give dihydrotriphenyl-11-*H*-benzo[*b*]fluorenes and their derivatives.

DIPHENYLKETEN reacts with 2-diphenylmethylene-3,3-dimethyl-1-indanone (I; R = Me) at 160° to give 1,2-bisdiphenylmethylene-3,3-dimethylindane (III; R = Me) presumably through the β-lactone intermediate (II; R = Me).[1] The hydrocarbon, obtained as bright yellow crystals, m. p. 175—176°, is resistant to catalytic hydrogenation, and, unlike 2-benzylidene-1-diphenylmethyleneindane (IV; R = H), does not undergo Thiele reduction or form a Diels–Alder adduct with tetracyanoethylene.[2] Its structure follows from its ozonolysis to yield benzophenone, the similarity of its u.v. spectrum to that of the benzylidene compound (IV), its nuclear magnetic resonance (n.m.r.) spectrum, and its photo-rearrangement reactions.

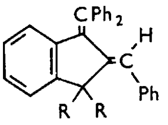
The stability of the hydrocarbon (III; R = Me) is surprising since the considerable steric strain produced by the extensive overlap of the phenyl group B and C cannot be relieved by their rotation nor to any appreciable extent by ring puckering. It is suggested that the overcrowding is relieved by the bending of the exocyclic double bonds away from each other in the plane of the indane nucleus and the twisting of these bonds out of the plane of the indane nucleus. This is supported by n.m.r. studies which show methyl proton absorptions at τ 8·3 and 9·0. The difference in chemical shift of the two methyl groups must be due to the anisotropic effects of the phenyl group A which is brought into close proximity to the methyl groups by the bond distortions. In contrast, 2-diphenylmethylene-3,3-dimethyl-1-indanone (I; R = Me) shows a single absorption at τ 8·7 due to both methyl groups. 2-Benzylidene-1-diphenylmethylene-3,3-dimethylindane (IV; R = Me) undergoes photocyclodehydrogenation to 11,11-dimethyl-5,10-diphenylbenzo[*b*]fluorene (VII).[2] 1,2-Bisdiphenylmethylene-3,3-dimethylindane (III; R = Me), when exposed to sunlight, in hexane undergoes rearrangement to 4b,5-dihydro-11,11-dimethyl-5,5,10-triphenylbenzo[*b*]fluorene (V; R = Me), m. p. 144—145° and 10,10a-dihydro-11,11-dimethyl-5,10,10-triphenylbenzo-[*b*]fluorene (VI; R = Me), m. p. 227—228°. The structure of the hydrocarbon (V; R = Me) follows from the similarity of its u.v. spectrum to that of 4b,5-dihydro-10-*p*-methoxyphenyl-5-phenyl-11-*H*-benzo[*b*]fluorene (VIII),[3] and from its n.m.r. spectrum. Dreiding models show that one of the methyl groups is sterically held below the plane of one of the 5-phenyl groups and should be abnormally shielded, as are the central methylene groups in [1,8]paracyclophane.[4] The n.m.r. spectrum shows the shielded methyl group absorption at τ 9·5, an absorption due to the other methyl group at τ 8·8, as well as the 4b proton absorption at τ 4·55.



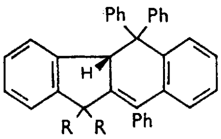
(I)

(II)

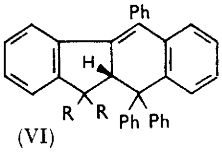
(III)



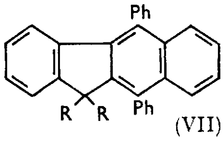
(IV)



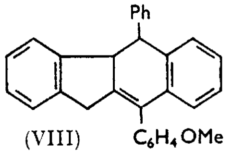
(V)



(VI)



(VII)



(VIII)

The n.m.r. spectrum of the isomer (VI; R = Me) shows a single six proton absorption at τ 9·0 due to both methyl groups, the 10a proton at τ 5·8, a high-field aromatic doublet at τ 3·8 due to the 4 proton shielded by the 5-phenyl group, and a complex absorption at τ 2·6—3·3, shown by the integral to be due to 22 aromatic protons, thus establishing the structure of this compound.

1,2-Bisdiphenylmethyleneindane (III; R = H), yellow crystals, m. p. 194—195°, was synthesised. Its n.m.r. spectrum shows the protons of the methylene group as an AB quartet centred at τ 6·8 and τ 8·2, J = 21 c./sec. The different environment of the hydrogens of the

---

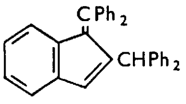
[1] H. Staudinger and N. Kon, *Annalen*, 1911, **384**, 38; H. Staudinger and R. Endle, *Annalen*, 1913, **401**, 263.

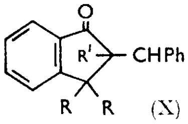
[2] N. Campbell, P. S. Davison, and H. G. Heller, *J. Chem. Soc.*, 1963, 993.

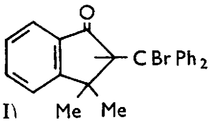
[3] N. Campbell and H. G. Heller, *J. Chem. Soc.*, 1965, 5473.

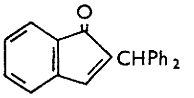
[4] D. J. Cram and L. A. Singer, *J. Amer. Chem. Soc.*, 1963, **85**, 1084.

methylene group must be due to the anisotropic effects of the phenyl group A. This hydrocarbon and its didimethyl derivative both show a high-field aromatic doublet at τ 3·6, which from Dreiding models is considered to be due to the shielding of the 7 proton by the phenyl group D. The u.v. spectrum of hydrocarbon (III; R = H) is similar to that of its 3,3-dimethyl derivative. It underwent cyclisation in ethanol, hexane, and chloroform on exposure to sunlight or 366 mμ radiation to give 4b,5-dihydro-5,5,10-triphenyl-11-*H*-benzo[*b*]fluorene (V; R = H), the corresponding fluorene-11-one (V; R, R = :O) and 10,10a-dihydro-5,10,10-triphenyl-11*H*-benzo[*b*]fluorene (VI; R = H). No isomerisation to 2-diphenylmethyl-1-diphenylmethyleneindene (IX) was observed. The structures of the hydrocarbons (V, VI; R = H) follow from the similarity of their u.v. spectra to the corresponding rearrangement products of the dimethyl series and from their n.m.r. spectra. The structure of the fluorenone follows from its synthesis by chromic acid oxidation of the hydrocarbon (V; R = H). Bromination of 2-diphenylmethyl-1-indanone (X; R = H, R′ = H) by the method of Leuchs[5] gave 2-bromo-2-diphenylmethyl-1-indanone (X; R = H, R′ = Br). Dehydrobromination by boiling with 2,4,6-trimethylpyridine yielded 2-diphenylmethylene-1-indanone (I; R = H), the structure of which follows from its ozonolysis to yield benzophenone and *o*-carboxyphenylacetic acid, and from its characteristic u.v. spectrum. 2-Diphenylmethylindenone (XII) was also formed.


(IX)


(X)


(XI)


(XII)

2-Diphenylmethylene-3,3-dimethyl-1-indanone (I; R = Me) was prepared by this method or by bromination of 2-diphenylmethyl-3,3-dimethyl-1-indanone (X; R = Me, R′ = H) with *N*-bromosuccinimide which gave 2-diphenylbromomethyl-3,3-dimethyl-1-indanone (XI) which underwent spontaneous dehydrobromination to 2-diphenylmethylene-3,3-dimethyl-1-indanone (I; R = Me), and 2-bromo-2-diphenylmethyl-3,3-dimethyl-1-indanone (X; R = Me, R′ = Br) which can be converted into the desired ketone (I; R = Me).

The radical properties and the rearrangement reactions of the bisdiphenylmethylene compounds (III) and related systems are under current investigation.

EXPERIMENTAL

Ultraviolet spectra were measured for n-hexane solutions on a Unicam SP 500 spectrometer and the n.m.r. spectra in carbon tetrachloride on a Perkin-Elmer R10 (60 Mc.) spectrometer unless otherwise indicated.

1,2-*Bisdiphenylmethylene*-3,3-*dimethylindane* (III; R = Me).—Diphenylketen (0·7 g.) and 2-diphenylmethylene-3,3-dimethyl-1-indanone (1 g.) were heated under nitrogen at 160° for 5 hr. The product in benzene was chromatographed on alumina and developed with light petroleum, to give an orange band which yielded 1,2-bisdiphenylmethylene-3,3-dimethylindane (0·8 g.), yellow rhombohedra, m. p. 175—176°, after crystallisation from ethanol [Found: C, 93·5; H, 6·5%; *M* (Rast), 513, 509. $C_{37}H_{30}$ requires C, 93·7; H, 6·3% *M*, 474]. Its u.v. spectrum [$\lambda_{max.}$ 281, 340, and 353 mμ (log ε 4·58, 4·03, and 4·05), $\lambda_{min.}$ 258, 324, and 345 mμ (log ε 4·47, 3·94, and 4·02)] resembled that of 2-benzylidene-1-diphenylmethylene-3,3-dimethylindane, $\lambda_{max.}$ 245, 333, and 349 mμ (log ε 4·32, 4·40, and 4·30) $\lambda_{min.}$ 230, 280, and 342 mμ (log ε 4·27, 3·67, and 4·26). Ozone was passed through bisdiphenylmethylenedimethylindanone (0·4 g.) in carbon tetrachloride (70 ml.) at −20° until the ozonide separated (6 hr.). Steam distillation gave solvent first and then benzophenone (0·09 g.), identified by m. p., mixed m. p., i.r. spectrum, and dinitrophenylhydrazone. The hydrocarbon (III; R = Me) (0·8 g.) in light petroleum (200 ml.) gave a colourless solution after exposure to sunlight for 2 days. Evaporation of the solvent followed by chromatography on alumina with light petroleum gave, from elution of the first blue fluorescent band, 4*b*,5-*dihydro*-11,11-*dimethyl*-5,5,10-*triphenylbenzo*[b]*fluorene* (V; R = Me) needles, m. p. 144—145°, after crystallisation from light petroleum (Found: C, 92·5; H, 6·5. $C_{37}H_{30}$ requires C, 93·7; H, 6·3%); $\lambda_{max.}$ 290, 270, 263, 256, and 250 mμ (log ε 4·00, 4·24, 4·21, 4·17, and 4·22); $\lambda_{min.}$ 285, 267, 259, 254, and 249 mμ (log ε 3·97, 4·19, 4·12, 4·10, and 4·20). This spectrum was similar to that of 4b,5-dihydro-10-*p*-methoxyphenyl-5-phenyl[*b*]benzofluorene (VIII) [$\lambda_{max.}$ 285 and 269 mμ (log ε 4·06 and 4·18), $\lambda_{min.}$ 280 and 264 mμ (log ε 4·03 and 4·11)]; n.m.r. τ 2·7—2·75, 2·9—3·05, 3·3—3·7, complex multiplets, aromatic protons; τ 4·6 (1) singlet, 4b proton; τ 8·8 (3) singlet, methyl protons; τ 9·6 (3) singlet, methyl protons.

The second blue fluorescent band gave 10,10*a-dihydro*-11,11-*dimethyl*-5,10,10-*triphenylbenzo*[b]*fluorene* (VI, R = Me) prisms, m. p. 227—228°, after crystallisation from benzene and light petroleum (Found: C, 93·6; H, 6·6. $C_{37}H_{30}$ requires C, 93·7; H, 6·3%) $\lambda_{max.}$ 294, 306, 323, 336, and 351 mμ (log ε 3·90, 4·01, 4·12, 4·23, and 4·11) $\lambda_{min.}$ 285, 299, 312, 326, and 346 mμ (log ε 3·79, 3·88, 3·97, 4·11, and 4·08); n.m.r. τ 2·4—3·3 (22) complex multiplet, aromatic protons, τ 3·8 (1) doublet, shielded aromatic proton; τ 5·8 (1) singlet, 10a proton; τ 9·0 (6) methyl group protons.

Attempted hydrogenation of bisdiphenylmethylenedimethylindane in ethanol with a platinum catalyst gave starting material. Attempted reduction with aluminium amalgam in moist ether gave on work up the hydrocarbon (VI; R = Me), identified by m. p. and mixed m. p.

1,2-*Bisdiphenylmethyleneindane* (III; R = H).—Equimolecular proportions of diphenylketen (2·3 g.) and 2-diphenylmethylene-1-indanone (3·2 g.) were heated under nitrogen at 160° for 6 hr. The product in benzene was chromatographed on alumina and developed with light petroleum to give an orange band which yielded 1,2-*bisdiphenylmethyleneindane* (3·6 g.) yellow crystals, m. p. 194—195°, after crystallisation from ethanol (Found:

---

[5] H. Leuchs, J. Wutke, and E. Gieseler, *Ber.*, 1913, **46**, 2200.

C, 93·8; H, 5·8. $C_{35}H_{26}$ requires C, 94·2; H, 5·8%). Its u.v. spectrum $\lambda_{max.}$ 282, 332, and 350 mμ (log ε 4·51, 3·97, and 4·00) $\lambda_{min.}$ 253, 325, and 340 mμ (log ε 4·44, 3·95, and 3·95) resembles that of the 3,3-dimethyl compound. N.m.r.* ($CDCl_3$) τ 2·6—3·4 (23) complex multiplet, aromatic protons; τ 3·6 (1) doublet, 7 proton; τ 6·2 (1) doublet J = 21 c./sec. methylene proton; τ 6·8 (1) doublet J = 21 c./sec. methylene proton. A second yellow band yielded a carbonyl compound of unknown structure (0·15 g.) m. p. 274—275° (from benzene and light petroleum) (Found: C, 90·5; H, 5·3%), ν 1750s (C:O) 1613m (C:C), and 1157s cm.$^{-1}$ (C–O). Benzophenone (0·2 g.) was isolated from a later fraction. The hydrocarbon (III; R = H) (0·5 g.) in light petroleum (500 ml.) was exposed (60 hr.) to 366 mμ radiation from a Hanovia Fluorescence lamp, until the yellow colour of the solution had disappeared. Removal of solvent, followed by chromatography in benzene on alumina with light petroleum as developer, gave, on elution of the blue fluorescent band followed by removal of the solvent, a solid (0·4 g.) which was crystallised from benzene and light petroleum to give a first crop of crystals (0·1 g.) of 10,10a-*dihydro*-5,10,10-*triphenyl*-11-H-*benzo*[b]*fluorene* (VI; R = H), m. p. 197—198° (Found: C, 93·7; H, 6·2. $C_{35}H_{26}$ requires C, 94·2; H, 5·8%). Its u.v. spectrum [$\lambda_{max.}$ 265, 305, 319, 333, and 350 mμ (log ε 4·39, 4·24, 4·23, 4·31, and 4·20) $\lambda_{min.}$ 285, 312, 326, and 344 mμ (log ε 4·10, 4·19, 4·18, and 4·15)] closely resembled that of the 11,11-dimethyl derivative. N.m.r. ($CDCl_3$) τ 2·4—3·3 (22) complex multiplet, aromatic protons, τ 3·7 (1) doublet, shielded aromatic proton; τ 5·9 (1) quadruplet $J_{cis\,H_{10a}H_{11}}$ = 6·5 c./sec., $J_{trans\,H_{10a}H_{11}}$ = 9·5 c./sec. 10a proton; τ 6·6 (1) quadruplet, $J_{cis\,H_{10a}H_{11}}$ = 6·5 c./sec., J_{gem} = 17 c./sec. methylene proton; τ 7·2 (2) quadruplet $J_{trans\,H_{10}H_{11}}$ = 9·5 c./sec., J_{gem} = 17 c./sec. methylene proton. Repeated crystallisation from benzene and light petroleum of the second crop of crystals gave 4*b*,5-*dihydro*-5,5-10-*triphenyl*-11-H-*benzo*[b]*fluorene* (V; R = H) (0·05 g.) needles m. p. 207—208° (Found: C, 93·7; H, 5·85. $C_{35}H_{26}$ requires C, 94·2; H, 5·8%). Its u.v. spectrum $\lambda_{max.}$ 273, 288, and 295 mμ (log ε 4·04, 3·74, and 3·78) $\lambda_{min.}$ 256, 283, and 290 mμ (log ε 3·90, 3·72, and 3·72) resembled that of the 11,11-dimethyl derivative. N.m.r. τ 2·4—3·7 (23) complex multiplet, aromatic protons; τ 4·6 (1) triplet $J_{H_{4b}H_{11}}$ 0·07 c./sec. 4b proton; τ 6·1 (1) quadruplet $J_{H_{4b}H_{11}}$ 0·07 c./sec. J_{gem} 22 c./sec. methylene proton; τ 6·8 (1) quadruplet $J_{H_{4b}H_{11}}$ 0·07 c./sec. J_{gem} 22 c./sec. methylene proton.

When the hydrocarbon (III; R = H) (0·8 g.) in light petroleum (250 ml.) was exposed to sunlight for 4 days, 10,10a-dihydro-5,10,10-triphenyl-11*H*-benzo[*b*]fluorene (VI; R = H) (0·4 g.) was obtained together with the oxidation product of hydrocarbon (V; R = H), 4b,5-dihydro-5,5,10-triphenylbenzo[*b*]fluoren-11-one (V; R = :O) which was separated by chromatography, m. p. 265—266°, after crystallisation from ethanol (Found: C, 90·4; H, 5·2. $C_{35}H_{24}O$ requires C, 91·3; H, 5·2%) $\nu_{max.}$ 1695s (CO) and 1626 cm.$^{-1}$ (C:C). N.m.r. τ 2·2—3·8 (23) complex multiplets, aromatic protons τ 4·8 (1) singlet, 4b proton.

Oxidation of the fluorene (V; R = H) (300 mg.) in acetic acid (30 ml.) with chromic acid (120 mg.) in water (1 ml.) and acetic acid (25 ml.) at 100° for 1 hr. gave the fluorenone (V; R, R = :O), m. p. 265°, after crystallisation from benzene, not depressed when admixed with the ketone obtained above.

2-*Diphenylmethyl*-1-*indanone* (X; R = R′ = H).—Aluminium chloride (4·6 g.) was added to 2-benzylidene-1-indanone (4 g.) dissolved on benzene (25 ml.), and saturated with hydrogen chloride. The reaction mixture was stirred (16 hr.) at room temperature, and then poured on to dilute hydrochloric acid. The benzene solution was evaporated to small volume and chromatographed. The first fraction gave diphenylmethylindanone (3 g.), m. p. 118—119°, after crystallisation from benzene and light petroleum, (lit.[6] m. p. 109—111°).

2-*Bromo*-2-*diphenylmethyl*-1-*indanone* (X; R = H, R′ = Br).—Bromination of 2-diphenylmethyl-1-indanone in chloroform with an equimolar quantity of bromine in chloroform gave the 2-*bromoketone* as needles in 95% yield, m. p. 194—195°, after crystallisation from benzene and light petroleum (Found: C, 69·7; H, 4·8; Br, 21·5. $C_{22}H_{18}BrO$ requires C, 69·8; H, 4·7; Br, 21·0%), $\nu_{max.}$ 1721s cm.$^{-1}$ (C:O).

Dehydrobromination of 2-*Bromo*-2-*diphenylmethyl*-1-*indanone*.—(cf. Dehydrobromination of 2-benzyl-2-bromo-1-indanone)[7]. The bromoketone (8 g.) was boiled (3 hr.) with 2,4,6-trimethylpyridine. Working up the mixture gave, from the first yellow fraction after chromatography, 2-*diphenylmethylindenone* (1·1 g.), m. p. 131—132° after crystallisation from ethanol (Found: C, 89·3; H, 5·6. $C_{22}H_{16}O$ requires C, 89·2; H, 5·4%), $\nu_{max.}$ 1712s (C:O) and 1608m cm.$^{-1}$ (C:C); $\lambda_{max.}$ 266, 244, and 240 mμ (log ε 3·35, 4·69, and 4·63), $\lambda_{min.}$ 263, 241, and 232 mμ (log ε 3·34, 4·58, and 4·23).

The second yellow fraction from the column yielded 2-*diphenylmethylene*-1-*indanone* (3·2 g.) yellow crystals, m. p. 152—135°, after crystallisation from ethanol (Found: C, 89·3; H, 5·45. $C_{22}H_{16}O$ requires C, 89·2; H, 5·4%) $\nu_{max.}$ 1675s (C:O) and 1608s cm.$^{-1}$ (C:O); $\lambda_{max.}$ 306, 262, and 223infl. mμ (log ε 4·36, 4·27, and 4·29); $\lambda_{min.}$ 282 and 245 mμ (log ε 4·11 and 4·16). On ozonolysis in carbon tetrachloride, this ketone yields benzophenone and *o*-carboxyphenylacetic acid.

2-*Diphenylmethyl*-3,3-*dimethyl*-1-*indanone* (X; R = Me, R′ = H).—2-Benzylidene-2,3-dimethyl-1-indanone (12 g.) was heated (2 hr.) with aluminium chloride (30 g.) and benzene (150 ml.). Working up the mixture gave the *ketone* (3·8 g.), m. p. 165—166°, after crystallisation from ethanol (Found: C, 88·0; H, 6·9. $C_{24}H_{22}O$ requires C, 88·4; H, 6·8%) $\nu_{max.}$ 1715s cm.$^{-1}$ (C:O). 3,3-Dimethyl-1-indanone (3·7 g.) and anthracene (0·6 g.) were byproducts of the reaction.

Bromination of 2-*Diphenylmethyl*-3,3-*dimethyl*-1-*indanone*.—(*a*) Bromine (0·9 g.) in chloroform (10 ml.) was added during ½ hr. to the ketone (1·8 g.) in chloroform (30 ml.) at 50° and stirred for 8 hr. Work up of the colourless solution gave 2-*bromo*-2-*diphenylmethyl*-3,3-*dimethyl*-1-*indanone* (X; R = Me, R′ = Br) (2·1 g.), m. p. 170—171° (Found: C, 71·3; H, 5·1; Br, 20·1. $C_{24}H_{21}BrO$ requires C, 71·1; H, 5·2; Br, 19·7%) $\nu_{max.}$ 1727s cm.$^{-1}$ (C:O).

(*b*) The ketone (7 g.) with *N*-bromosuccinimide (3·8 g.) in carbon tetrachloride (160 ml.) containing a small quantity of benzoyl peroxide catalyst, underwent reaction with evolution of hydrogen bromide. Chromatography of the oil remaining after filtration and evaporation, gave the *bromoindanone* (X; R = Me, R′ = Br) (3 g.) and 2-*di*-

---

* Measured on a Varian HA 100 Mc.

[6] C. F. Koelsch, *J. Amer. Chem. Soc.*, 1943, **65**, 1639.

[7] N. H. Cromwell, B. D. Pearson, and R. P. Ayer, *J. Org. Chem.*, 1962, **27**, 3038; N. H. Cromwell and R. P. Ayer, *J. Amer. Chem. Soc.*, 1960, **82**, 133.

*phenylmethylene-*3,3-*dimethyl-*1-*indanone* (I; R = Me) (3·2 g.) yellow needles, m. p. 172—173°, after crystallisation from ethanol (Found: C, 88·4; H, 6·2. $C_{24}H_{22}$ requires C, 88·9; H, 6·2%) $\nu_{max.}$ 1689s (C:O) and 1613m cm.$^{-1}$ (C:C) $\lambda_{max.}$ 311, 267, and 229 mμ (log ε 4·15, 4·29, and 4·32); $\lambda_{min.}$ 294, 246, and 225 mμ (log ε 4·09, 4·14, and 4·31). The unsaturated ketone (I; R = Me) was also obtained in 76% yield by boiling the bromoketone (X; R = Me, R′ = Br) with 2,4,6-trimethylpyridine.

Thanks are expressed to Miss M. Methven for measuring the n.m.r. spectra and to the S.R.C. for a maintenance grant to one of us (K. S.).

[6/1218 *Received, September* 28*th*, 1966]