The Conversion of cyclo*Hexanone into* 1 : 1-*Disubstituted* cyclo*Hexanes.*

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[Reprint Order No. 5988.]

*cyclo*Hexanone has been converted into 1 : 1-dimethyl-, 1-methyl-1-vinyl-, 1-formyl-1-methyl-, and 1-carboxy-1-methyl-*cyclo*hexane. The bearing of these results on synthetical problems in the diterpenoid field is discussed.

One of the characteristic properties of diterpenoid and triterpenoid structures is the frequent occurrence of disubstituted carbon atoms in one or more of the six-membered rings. This feature constitutes a considerable obstacle to the synthesis of these compounds, especially when the two groupings are dissimilar. This difficulty was recently clearly shown by the synthesis of a tricyclic ketone possessing the carbon skeleton of dehydroabietic acid, with the exception of the *gem*-methyl–carboxylic acid feature, these two radicals being replaced by an oxo-group (Stork and Burgstahler, *J. Amer. Chem. Soc.*, 1951, **73**, 3544). This communication describes a method for the introduction of *gem*-disubstitution in place of such an oxo-group and the use of the method to procure any of the *gem*-groupings typical of terpenoid structures.

*cyclo*Hexanone was used as the model ketone. This was converted into ethyl α-cyano-*cyclo*hexylideneacetate by the well-known ammonium acetate technique. Interaction of this ester and methylmagnesium iodide resulted in conjugate addition to the double bond with the production of ethyl α-cyano-1-methyl*cyclo*hexylacetate (Robinson and Birch, *J.*, 1943, 501; Alexander, McCollum, and Paul, *J. Amer. Chem. Soc.*, 1950, **72**, 4791). The nitrile group in this compound was very resistant to complete hydrolysis; aqueous or alcoholic alkali gave only 1-methyl*cyclo*hexylmalonamic acid while acid hydrolysis proceeded even less completely, the corresponding cyano-acid being the sole product. Ultimately complete hydrolysis to 1-methyl*cyclo*hexylmalonic acid was achieved by employing potassium hydroxide in ethylene glycol, and decarboxylation of this acid furnished 1-methyl*cyclo*hexylacetic acid. Treatment of silver 1-methyl*cyclo*hexylacetate with bromine in ethyl bromide gave 1-bromomethyl-1-methyl*cyclo*hexane, reductive debromination of which with zinc and acetic acid furnished 1 : 1-dimethyl*cyclo*hexane.

Methyl 1-methyl*cyclo*hexylacetate was reduced by lithium aluminium hydride to 1-2′-hydroxyethyl-1-methyl*cyclo*hexane. Dehydration of this alcohol by means of boric acid (Brandenberg and Galat, *J. Amer. Chem. Soc.*, 1950, **72**, 3275) gave 1-methyl-1-vinyl*cyclo*hexane.

Hofmann degradation of 1-methyl*cyclo*hexylmalonamic acid led to the corresponding α-amino-acid, 1-methyl*cyclo*hexylglycine, Strecker degradation of which with sodium hypochlorite gave 1-formyl-1-methyl*cyclo*hexane. As an alternative route to this aldehyde, 1-methyl*cyclo*hexylmalonic acid was converted into its dihydrazide which was then subjected to a double Curtius degradation. Acid hydrolysis of the resulting diurethane produced the aldehyde, identical with that prepared by the first route. In an attempted third route to the aldehyde, 1-methyl*cyclo*hexylmalononitrile was prepared by the addition of methylmagnesium iodide to *cyclo*hexylidenemalononitrile; mild hydrolysis furnished the corresponding diamide. Attempted double Hofmann degradation of the diamide was unsuccessful; only one of the amide groups was affected and the major product was the hydantoin of 1-methyl*cyclo*hexylglycine, proof of structure being obtained by hydrolysis to the amino-acid (cf. Rinkes, *Rec. Trav. chim.*, 1927, **46**, 271).

1-Methyl*cyclo*hexanecarboxylic acid was obtained by a Barbier–Wieland degradation of methyl 1-methyl*cyclo*hexylacetate. Another method of obtaining the acid was as follows. Addition of potassium cyanide to the double bond of ethyl α-cyano*cyclo*hexylideneacetate, followed by hydrolysis and esterification produced methyl 1-methoxycarbonyl*cyclo*hexylacetate (Lapworth and McRae, *J.*, 1922, **121**, 2754). Selective alkaline hydrolysis of the primary ester grouping of this diester furnished 1-methoxycarbonyl*cyclo*hexylacetic acid. Hunsdiecker degradation of this acid (by the action of bromine on the silver salt) gave methyl 1-bromomethyl*cyclo*hexanecarboxylate which was then debrominated by zinc and acetic acid to methyl 1-methyl*cyclo*hexanecarboxylate. Hydrolysis then afforded 1-methyl*cyclo*hexanecarboxylic acid (cf. Saha, Bagchi, and Dutta, *Chem. and Ind.*, **1954**, 1143).

Applied to *cyclo*hexanone, both procedures yield the same acid. However, in the first process, the methyl group in the product is derived from the addendum to the double bond of the starting material whereas in the second procedure the addendum provides the carboxyl group. Hence, from an unsymmetrical starting ketone the two methods should afford different epimers as major product; the two procedures are therefore sterically complementary. That methylmagnesium iodide and hydrogen cyanide add in a sterically similar manner is indicated by the results of considerable studies in the steroid field (Fieser and Fieser, "Natural Products Related to Phenanthrene," Reinhold Publ. Corp., 1949, pp. 328, 376—379, 388, 410; Heusser, Herzig, Fürst, and Plattner, *Helv. Chim. Acta*, 1950, **33**, 1093) although the two processes are not stereospecific to the same degree.

From study of models it can be predicted that application of the second process to the tricyclic ketone obtained by Stork and Burgstahler (*loc. cit.*) should produce racemic dehydroabietic acid, and this supposition is now being tested. The first process should give rise to the epimeric structure in which the methyl and the carboxyl group have the steric relation occurring in podocarpic acid.

EXPERIMENTAL

*Ethyl α-Cyano*cyclo*hexylideneacetate.*—This was prepared by interaction of *cyclo*hexanone and ethyl cyanoacetate in the presence of ammonium acetate, with azeotropic removal of the water formed (Cope *et al.*, *J. Amer. Chem. Soc.*, 1941, **63**, 3452).

*Ethyl α-Cyano-1-methyl*cyclo*hexylacetate.*—To a solution of methylmagnesium iodide [from magnesium (29·2 g.) and methyl iodide (169 g.)] in dry ether (300 c.c.) was added one of ethyl α-cyano*cyclo*hexylideneacetate (193 g.) in ether (300 c.c.) at such a rate that the solvent refluxed gently; thereafter the mixture was heated by steam for 1 hr. It was then poured on crushed ice–ammonium chloride solution (15%), the organic layer separated, and the aqueous layer extracted with fresh ether. Removal of the solvent gave an oil which was treated with concentrated aqueous sodium cyanide (50 g.), followed by sufficient ethanol for dissolution. The solution was set aside overnight, water (1 l.) was then added, and the precipitated oil extracted with benzene. Washing with water, removal of solvent, and distillation gave ethyl α-cyano-1-methyl*cyclo*hexylacetate (139 g.; 67%), b. p. 92°/0·4 mm., n_D^{18} 1·4670.

*1-Methyl*cyclo*hexylmalonic Acid and 1-Methyl*cyclo*hexylacetic Acid.*—The above cyano-ester (50 g.) was refluxed with a solution of potassium hydroxide (80 g.) in a mixture of water (80 c.c.) and ethylene glycol (300 c.c.), until ammonia was no longer evolved (10—15 hr.). The mixture was poured into water (2 l.), and the cold solution acidified with ice-cold sulphuric acid (4N) and thoroughly extracted with ether. Washing with water, drying ($MgSO_4$), and evaporation gave an oily solid which was triturated with light petroleum (b. p. 40—60°). Filtration and crystallisation (ethyl acetate) gave 1-*methyl*cyclo*hexylmalonic acid* (23·7 g.; 50%), as stout needles, m. p. 194—195° (decomp.) (Found: C, 60·0; H, 8·05. $C_{10}H_{16}O_4$ requires C, 60·0; H, 8·05%). With ethereal diazomethane the acid gave the *dimethyl ester*, b. p. 78°/0·35 mm., n_D^{21} 1·4638 (Found: C, 63·35; H, 8·55. $C_{12}H_{20}O_4$ requires C, 63·1; H, 8·8%).

Evaporation of the light petroleum filtrate and distillation produced 1-*methyl*cyclo*hexylacetic acid* (11·3 g.), b. p. 145°/20 mm., n_D^{18} 1·4720 (Found: C, 69·0; H, 10·45. $C_9H_{16}O_2$ requires C, 69·2; H, 10·3%). More of the acid (26·9 g.; total yield 72%) was obtained by decarboxylation of the above malonic acid at 200°, followed by distillation. The *methyl ester* (prepared with diazomethane) had b. p. 40°/0·4 mm., n_D^{20} 1·4524 (Found: C, 70·6; H, 10·6. $C_{10}H_{18}O_2$ requires C, 70·55; H, 10·65%).

1-*Bromomethyl*-1-*methyl*cyclo*hexane*.—The Hunsdiecker degradation was carried out by using Rottenberg's procedure (*Acta Chem. Scand.*, 1953, **7**, 1001). 1-Methyl*cyclo*hexylacetic acid (7 g.) was dissolved in the equivalent quantity of aqueous 0·2N-potassium hydroxide, and a solution of silver nitrate (7·5 g.) in water (100 c.c.) was added; the precipitated silver salt was filtered off, washed successively with water, methanol, acetone, and ether and finally dried at 90°/18 mm. for 12 hr. (10·8 g.; 92%).

An intimate mixture of the silver salt (5 g.) and dry silver acetate (3·04 g.) was covered with dry ethyl bromide (250 c.c.), and the suspension gently heated under reflux. Dry bromine (5·95 g.) was then slowly introduced under the surface in a slow stream of nitrogen and the heating continued for a further hour. After filtration the filtrate was washed successively with potassium iodide solution, sodium thiosulphate solution, and water. Drying ($MgSO_4$), evaporation, and distillation furnished 1-*bromomethyl*-1-*methyl*cyclo*hexane* (3·44 g.; 94%), b. p. 79°/26 mm., $n_D^{17\cdot5}$ 1·4960 (Found: C, 50·05; H, 7·7; Br, 41·45. $C_8H_{15}Br$ requires C, 50·25; H, 7·9; Br, 41·8%).

1 : 1-*Dimethyl*cyclo*hexane*.—Zinc dust (2 g.) was added to a solution of 1-bromomethyl-1-methyl*cyclo*hexane (2 g.) in acetic acid (40 c.c.), and the mixture heated under reflux for 7 hr. The cooled solution was diluted with water (100 c.c.) and extracted with light petroleum (b. p. 40—60°). The extract was washed with sodium carbonate solution and water, and dried (Na_2SO_4). Removal of the solvent followed by fractional distillation at atmospheric pressure gave 1 : 1-dimethyl*cyclo*hexane (0·48 g.; 58%), b. p. 119—121°, $n_D^{21\cdot5}$ 1·4240, and starting material (0·6 g.). (Chavanne, Miller, and Cornet, *Bull. Soc. chim. Belg.*, 1931, **40**, 1673, give b. p. 119·5—120°, n_D^{15} 1·4314.)

1-2′-*Hydroxyethyl*-1-*methyl*cyclo*hexane*.—A solution of 1-methyl*cyclo*hexylacetic acid (11·7 g.) in dry ether (50 c.c.) was added slowly to a slurry of lithium aluminium hydride (5 g.) in ether (400 c.c.). The mixture was heated under reflux for 1 hr. and the excess of reagent then decomposed by ethyl acetate. Working up in the usual manner gave 1-2′-hydroxyethyl-1-methyl*cyclo*hexane (8·85 g.; 83%), b. p. 59°/0·3 mm., $n_D^{20\cdot5}$ 1·4692 (Found: C, 75·85; H, 12·5. Calc. for $C_9H_{18}O$: C, 75·95; H, 12·75%). The 3 : 5-dinitrobenzoate crystallised from ethanol in needles, m. p. 95°. (Schmerling, *J. Amer. Chem. Soc.*, 1949, **71**, 698, records b. p. 82°/3 mm., n_D^{20} 1·4686; 3 : 5-dinitrobenzoate, m. p. 95°.)

1-*Methyl*-1-*vinyl*cyclo*hexane*.—1-2′-Hydroxyethyl-1-methyl*cyclo*hexane (5·55 g.) and boric acid (4·2 g.) were heated to 360°. Ether was added to the moist condensate and the resulting solution dried ($MgSO_4$). Evaporation and distillation gave 1-*methyl*-1-*vinyl*cyclo*hexane* (3·0 g.; 62%), b. p. 80°/95 mm., n_D^{21} 1·4570 (Found: C, 86·95; H, 12·6. C_9H_{16} requires C, 87·0; H, 13·0%). The infrared absorption spectrum showed the expected maxima characteristic of a vinyl group at 1630, 998, and 912 cm.$^{-1}$.

α-*Cyano*-1-*methyl*cyclo*hexylacetic Acid*.—A mixture of ethyl α-cyano-1-methyl*cyclo*hexylacetate (5 g.), concentrated hydrochloric acid (50 c.c.), and acetic acid (30 c.c.) was refluxed for 18 hr. Most of the solvent was removed under reduced pressure and the residue basified with sodium carbonate solution. A small amount of insoluble oil was removed with benzene, the aqueous solution acidified (4N-sulphuric acid), and the precipitated oil extracted with benzene. Drying (Na_2SO_4), removal of solvent, and distillation gave a highly viscous oil, b. p. 136—140°/0·15 mm., which slowly solidified. Crystallisation from light petroleum (b. p. 80—100°) gave α-*cyano*-1-*methyl*cyclo*hexylacetic acid* (3·2 g.; 74%) in needles, m. p. 75—77° (Found: C, 66·5; H, 8·2; N, 7·45. $C_{10}H_{15}O_2N$ requires C, 66·35; H, 8·35; N, 7·7%).

1-*Methyl*cyclo*hexylmalonamic Acid*.—Ethyl α-cyano-1-methyl*cyclo*hexylacetate (10 g.) was refluxed for 9 hr. with aqueous potassium hydroxide (16 g. in 32 c.c.). Water (50 c.c.) was then added and the solution acidified with concentrated hydrochloric acid. The precipitate was filtered off, washed with water, and crystallised from water; the amido-acid (4·75 g.; 50%) formed white plates, m. p. 151—153° (decomp.) (Robinson and Birch, *J.*, 1943, 501, give m. p. 151°).

1-*Methyl*cyclo*hexylglycine*.—A solution of 1-methyl*cyclo*hexylmalonamic acid (2·5 g.) in hot ethanol (25 c.c.) was added dropwise to a solution of hydrated barium hydroxide (23·8 g.) in water (1500 c.c.), and the solution stirred as the barium salt was precipitated. Bromine (0·75 c.c.) was carried into this suspension in a stream of nitrogen, and the mixture then heated by steam for 1 hr. The boiling solution was twice saturated with carbon dioxide and filtered, ammonium carbonate (7·25 g.) was then added, and the solution again heated to boiling and filtered. Concentration of the filtrate and cooling gave the amino-acid. 1-*Methyl*cyclo*hexylglycine* (1·85 g.; 85%) formed needles (from water), m. p. 205—207° (decomp.) (Found: C, 63·0; H, 9·85; N, 8·2. $C_9H_{17}O_2N$ requires C, 63·1; H, 10·0; N, 8·2%). The compound gave a strongly positive ninhydrin colour.

1-*Formyl*-1-*methyl*cyclo*hexane*.—(*a*) A solution of 1-methyl*cyclo*hexylglycine (1 g.) in 0·1N-sodium hydroxide (60 c.c.) was mixed with M-sodium hypochlorite solution (5·2 c.c.) and covered with ether (50 c.c.). The mixture was heated under reflux for 1 hr. Isolation by means of ether followed by distillation gave 1-*formyl*-1-*methyl*cyclo*hexane* (0·24 g.; 33%), b. p. 120°/546 mm., n_D^{21} 1·4490 (Found: C, 76·05; H, 10·9. $C_8H_{14}O$ requires C, 76·15; H, 11·2%). The 2 : 4-*dinitrophenylhydrazone* crystallised from ethanol as yellow needles, m. p. 154—155° (Found: C, 55·0; H, 5·9; N, 18·3. $C_{14}H_{18}O_4N_4$ requires C, 54·9; H, 5·9; N, 18·3%). Oxidation of the aldehyde with alkaline silver oxide furnished 1-methyl*cyclo*hexanecarboxylic acid, m. p. and mixed m. p. 37—38°.

(*b*) A mixture of freshly distilled dimethyl 1-methyl*cyclo*hexylmalonate (8 g.) and hydrazine hydrate (100%; 24 c.c.) was refluxed until a homogeneous solution resulted (3 hr.). The *dihydrazide*, which crystallised on cooling, was filtered off; it crystallised from ethanol in small needles (4 g.; 50%), m. p. 161—162° (Found: C, 52·5; H, 8·5; N, 24·35. $C_{10}H_{20}O_2N_4$ requires C, 52·6; H, 8·8; N, 24·55%).

Hydrogen chloride (0·68 g.) was passed into a mixture of the dihydrazide (2·1 g.), *n*-butyl nitrite (2·0 g.), and dry ethanol (5 c.c.), and the resulting solution set aside overnight. The mixture was refluxed for 9 hr., and the solvent then removed under reduced pressure. To the resulting crude diurethane 6N-sulphuric acid (10 c.c.) was added, and the mixture was steam-distilled. Ether extraction of the steam-distillate followed by distillation furnished 1-formyl-1-methyl*cyclo*hexane (0·44 g.; 45%), identical in all respects with the product obtained as in (*a*).

1-*Methyl*cyclo*hexylmalonamide*.—The preparation of *cyclo*hexylidenemalononitrile was carried out according to Cope and Hoyle's directions (*J. Amer. Chem. Soc.*, 1941, 63, 733).

Addition of methylmagnesium iodide [from magnesium (8·85 g.)] to *cyclo*hexylidenemalononitrile (43·8 g.) was carried out as in the above cognate preparation of ethyl α-cyano-1-methyl*cyclo*hexylacetate, yielding 1-*methyl*cyclo*hexylmalononitrile* (29 g.; 60%), b. p. 66°/0·1 mm., n_D^{16} 1·4715 (Found: C, 74·25; H, 8·25; N, 17·2. $C_{10}H_{14}N_2$ requires C, 74·05; H, 8·7; N, 17·3). The nitrile (14 g.) was heated under reflux with aqueous potassium hydroxide (11 g. in 60 c.c.) for 45 min. Cooling, filtration, washing with water, and crystallisation from ethanol yielded 1-*methyl*cyclo*hexylmalonamide* (8·5 g.; 50%) as plates, m. p. 264—265° (Found: C, 60·4; H, 8·45; N, 14·15. $C_{10}H_{18}O_2N_2$ requires C, 60·55; H, 9·15; N, 14·15%).

Hofmann Degradation of 1-*Methyl*cyclo*hexylmalonamide*.—Ice-cold bromine (18 g.) was added dropwise to a suspension of the amide (3·7 g.) in sodium methoxide solution (5·2 g. of sodium in 100 c.c. of methanol) at 0°. The resulting solution was heated by steam for 10 min., then acidified with acetic acid and evaporated to dryness under reduced pressure. Ethyl acetate extraction of the residue and removal of the solvent afforded an oily solid; crystallisation from ethanol gave the *hydantoin* of 1-methyl*cyclo*hexylglycine as needles, m. p. 228—230° (Found: C, 61·25; H, 7·95; N, 14·25. $C_{10}H_{16}O_2N_2$ requires C, 61·2; H, 8·2; N, 14·25%). Evaporation of the mother liquors from the above crystallisation gave an oil which was steam-distilled in the presence of sulphuric acid. Ether extraction of the steam-distillate gave a trace of an oil which furnished a yellow 2 : 4-dinitrophenylhydrazone, m. p. 154—155° after crystallisation from ethanol; the m. p. was unaffected by admixture with the corresponding derivative of 1-formyl-1-methyl*cyclo*hexane.

Hydrolysis of the hydantoin with aqueous barium hydroxide in an autoclave at 200° furnished 1-methyl*cyclo*hexylglycine, m. p. and mixed m. p. 205—207° (decomp.).

1-*Methoxycarbonyl*cyclo*hexylacetic acid*.—Treatment of 1-carboxy*cyclo*hexylacetic acid

(McRae and Lapworth, *loc. cit.*) with ethereal diazomethane afforded the *dimethyl ester*, b. p. 78°/0·5 mm., n_D^{19} 1·4621 (Found : C, 61·75; H, 8·2. $C_{11}H_{18}O_4$ requires C, 61·65; H, 8·45%).

A solution of this diester (9·52 g.) in 0·867N-methanolic potassium hydroxide (51·3 c.c.; 1 mol.) was refluxed for 3 hr. The solvent was removed under reduced pressure, water (50 c.c.) was added, and neutral component extracted with ether. Acidification with 6N-sulphuric acid, followed by isolation by means of ether, gave 1-*methoxycarbonyl*cyclo*hexylacetic acid* (6·64 g.; 75%) which crystallised from methanol in needles, m. p. 64—65° (Found : C, 60·05; H, 7·9. $C_{10}H_{16}O_4$ requires C, 60·0; H, 8·05%).

*Methyl 1-Bromomethyl*cyclo*hexanecarboxylate.*—Dry silver 1-methoxycarbonyl*cyclo*hexylacetate was prepared and converted into methyl 1-bromomethyl*cyclo*hexanecarboxylate by the process described for 1-bromomethyl-1-methyl*cyclo*hexane. The *ester* (60%) had b. p. 130°/35 mm., $n_D^{23·5}$ 1·4845 (Found : C, 45·8; H, 6·6; Br, 33·8. $C_9H_{15}O_2Br$ requires C, 45·95; H, 6·45; Br, 34·0%).

1-*Methyl*cyclo*hexanecarboxylic Acid.*—(*a*) A solution of methyl 1-bromo*cyclo*hexanecarboxylate (1·5 g.) in acetic acid (40 c.c.) was treated with zinc dust (2 g.) and refluxed for 5 hr. After the acetic acid had been removed under reduced pressure, ether (50 c.c.) was added, and the ethereal extract was washed with sodium carbonate solution and water. Drying ($MgSO_4$) and distillation gave *methyl 1-methyl*cyclo*hexanecarboxylate* (0·5 g.; 51%), b. p. 70°/35 mm., $n_D^{18·5}$ 1·4450 (Found: C, 69·0; H, 10·3. $C_9H_{16}O_2$ requires C, 69·2; H, 10·3%). The ester (0·5 g.) was heated with methanolic potassium hydroxide (0·9 g. in 10 c.c.) for 3 hr. Removal of solvent, acidification, isolation with ether, and distillation of the crude product gave 1-methyl*cyclo*hexanecarboxylic acid (0·31 g.; 68%), b. p. 234°, m. p. 38° undepressed on admixture with an authentic specimen. The corresponding amide crystallised in tiny needles, m. p. 68°, from ethyl acetate (Gutt, *Ber.*, 1907, **40**, 2069, gives m. p. 38—39° for the acid and m. p. 68—69° for the amide).

(*b*) To an ethereal solution of phenylmagnesium bromide [from magnesium (4·4 g.) and bromobenzene (38·2 g.)] was added methyl 1-methyl*cyclo*hexylacetate (14 g.) in an equal volume of ether, and the mixture was refluxed for 2·5 hr. The cooled mixture was poured into 6N-sulphuric acid and worked up as usual. The solvent was removed and the product heated to 200° for 30 min., cooled, and dissolved in ether. Drying, evaporation, and distillation gave 1-(2 : 2-*diphenylvinyl*)-1-*methyl*cyclo*hexane* (16·1 g.; 70%), b. p. 148°/0·5 mm., n_D^{17} 1·5861 (Found : C, 91·25; H, 8·5. $C_{21}H_{24}$ requires C, 91·25; H, 8·75%).

A solution of chromium trioxide (5·7 g.) in water (10 c.c.) was added during 10 min. to a vigorously stirred solution of this hydrocarbon (7·7 g.) in acetic acid (80 c.c.) at 60°. During the next hour more acetic acid (40 c.c.) and chromium trioxide (1 g.) were added and the mixture was stirred for a further 5 hr. at 60—70°. The acetic acid was removed under reduced pressure, 6N-sulphuric acid added, and the product extracted with benzene. Extraction with sodium carbonate solution, re-acidification, and isolation with ether and distillation gave a solid, m. p. 38° (1·87 g.; 47%) undepressed on admixture with an authentic sample of 1-methyl*cyclo*hexanecarboxylic acid.

One of us (W. P.) thanks the Department of Scientific and Industrial Research for a maintenance award. We are indebted to Dr. G. D. Meakins for the infrared data.

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[*Received, December 20th,* 1954.]