82. *Alicyclic Glycols. Part XI.** *A Chemical Proof of the Configurations of the* 1 : 2-, 1 : 3-, *and* 1 : 4-*Dimethyl*cyclo*hexanes, and of the* 2-, 3-, *and* 4-*Methyl*cyclo*hexylmethanols.*

By G. A. Haggis and L. N. Owen.

From the dimethanesulphonates or ditoluene-*p*-sulphonates of the *cis*- and the *trans*-forms of the 1 : 2-, 1 : 3-, and 1 : 4-bishydroxymethyl*cyclo*hexanes, the corresponding isomers of the 1 : 2-, 1 : 3-, and 1 : 4-dimethyl*cyclo*hexanes have been synthesised, thus providing rigid chemical proof of the configurations of these hydrocarbons. Similarly, from the monohalides or monotoluene-*p*-sulphonates the corresponding isomers of the 2-, 3-, and 4-methyl*cyclo*hexylmethanols have been synthesised. The Auwers–Skita rules are confirmed for the 1 : 2- and 1 : 4-disubstituted *cyclo*hexanes, but must be reversed for the 1 : 3-compounds.

The assignment of configurations to disubstituted *cyclo*hexanes is best founded on methods such as the resolution of the *trans*-isomer (only applicable to symmetrically substituted 1 : 2- and 1 : 3-compounds), or the preferential formation of a bicyclic compound, such as an intramolecular dehydration product, from the *cis*-isomer (only applicable when there is no possibility of change of configuration during the reaction). When these or similar methods are not available, the Auwers–Skita rules have been widely used (Auwers, *Annalen*, 1920, **420**, 89; Auwers and Ottens, *Ber.*, 1924, **57**, 437; Skita, *Ber.*, 1920, **53**, 1792; 1922, **55**, 144). According to these, of a pair of *cis–trans*-isomers, the *cis*-compound has the higher boiling point, refractive index, and density; it is also usual that the *trans*-compound has a higher melting point and a lower solubility, and is the more stable of the two.

In cases where configurations have been independently established by rigorous methods, the few exceptions encountered with 1 : 2- and 1 : 4-compounds have usually been confined to occasional anomalies in the melting points of derivatives (see, *e.g.* Owen and Robins, *J.*, 1949, 320). With 1 : 3-compounds, however, the position is much less satisfactory (cf. Auwers and Ottens, *loc. cit.*). Thus the melting points of all the known derivatives of *cis*-1 : 3-bishydroxymethyl*cyclo*hexane are higher than those of the corresponding *trans*-isomers (Part IX, *J.*, 1953, 399); many of the derivatives of *cyclo*hexane-1 : 3-diol show anomalous melting points (Clarke and Owen, *J.*, 1950, 2103); the resolvable *trans*-hexahydro*iso*phthalic acid has a lower melting point than the *cis*-form (Goodwin and Perkin, *J.*, 1905, **87**, 843); the resolvable *trans*-3 : 5-dimethyl*cyclo*hexanone has a higher refractive index than the *cis*-isomer (Braun and Haensel, *Ber.*, 1926, **59**, 1999; Braun and Anton, *Ber.*, 1927, **60**, 2438), and the same is true of the 3 : 5-dimethyl*cyclo*hexanols (Skita and Faust, *Ber.*, 1939, **72**, 1127). Another example of special interest is the preparation by Mousseron and Granger (*Bull. Soc. chim.*, 1938, **5**, 1618; 1946, 218) of an optically active 1 : 3-dimethyl*cyclo*hexane (which must therefore be *trans*) with a higher boiling point and refractive index than the inactive form, though the work can be criticised on the grounds that no yields or analytical data were recorded at any stage in their synthesis.

Hassel (for general references see Hassel and Ottar, *Acta Chem. Scand.*, 1947, **1**, 929; Hassel and Furberg, *ibid.*, 1950, **4**, 597; for diagrams see Birch, *Ann. Reports*, 1951, **48**, 192) has pointed out that in the more stable chair form of *cyclo*hexane the C–H bonds are of two types, and that a particular stereoisomer of a 1 : 3-disubstituted *cyclo*hexane is likely to correspond in spatial arrangement to that of the opposite stereoisomer of a 1 : 2- or a 1 : 4-compound. Beckett, Pitzer, and Spitzer (*J. Amer. Chem. Soc.*, 1947, **69**, 2488; Pitzer and Beckett, *ibid.*, p. 977; see also Prosen, Johnson, and Rossini, *J. Res. Nat. Bur. Stand.*, 1947, **39**, 173; Rossini and Spitzer, *Science*, 1947, **105**, 647), in emphasing these facts, have suggested that the Auwers–Skita rules, if applicable to 1 : 2- and 1 : 4-compounds, should be reversed for 1 : 3-disubstituted *cyclo*hexanes, and they have found thermodynamic evidence in favour of such a revision for the 1 : 3-dimethyl*cyclo*hexanes, thus supporting the observation of Mousseron and Granger (*loc. cit.*). In order to provide further chemical evidence, it was decided to study the synthesis of the stereoisomers of all

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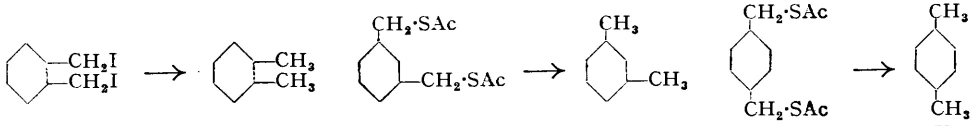
* Part X, preceding paper.

the dimethyl*cyclo*hexanes and methyl*cyclo*hexylmethanols by methods which would lead to a rigid proof of the configurations.

The dimethyl*cyclo*hexanes have usually been prepared by reduction of the corresponding xylenes under various conditions, but it is unlikely that any were obtained in a stereochemically pure form by the earlier workers. Miller and Piaux (*Bull. Soc. chim. Belg.*, 1932, **41**, 217; *Compt. rend.*, 1933, **197**, 412; 1935, **201**, 76), and also Forziati, Glasgow, Willingham, and Rossini (*J. Res. Nat. Bur. Stand.*, 1946, **36**, 129), carried out precision fractionations, and claimed to have obtained all six isomers in a pure state; their data for the 1 : 2- and the 1 : 3-compounds are in good agreement with those recorded by Bazhulin, Ukholin, Bulanova, Koperina, Plate, and Kazanskii (*Chem. Abs.*, 1950, **44**, 1332). The configurations were based only on the Auwers–Skita rules. The 2-, 3-, and 4-methyl*cyclo*hexylmethanols have been prepared by reduction of the 2-, 3-, and 4-methyl*cyclo*hexanecarboxylic esters with sodium and alcohol (Perkin and Pope, *J.*, 1908, **93**, 1078; Skita, *Annalen*, 1923, **431**, 1; Mousseron, Granger, Bourrel, and Cellier, *Bull. Soc. chim.*, 1946, 640), but owing to the occurrence of epimerisation under such conditions it is unlikely that stereochemically pure products were obtained even when stereochemically pure esters were used. When the reduction is effected by hydrogenation over a chromite catalyst, however, little or no epimerisation occurs, and by purification through crystalline derivatives both stereoisomers of the 2-methyl (Macbeth, Mills, and Simmonds, *J.*, 1949, 1011), both of the 4-methyl (Cooke and Macbeth, *J.*, 1939, 1245), and one of the 3-methyl (Darling, Macbeth, and Mills, personal communication) alcohols have been obtained, but again the accepted configurations are founded only on physical properties.

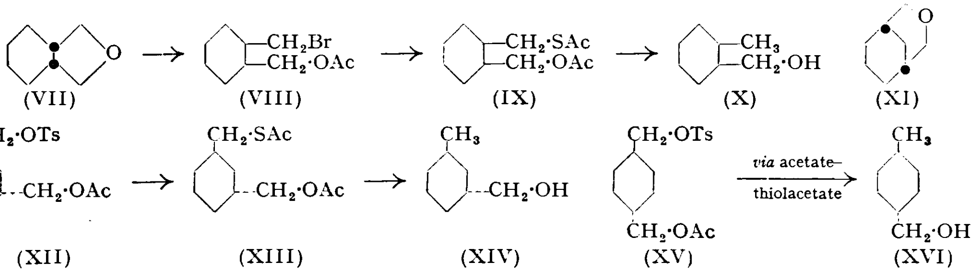
The syntheses now to be described are all based on derivatives of the various bishydroxymethyl*cyclo*hexanes, the configurations of which have been rigidly established (Parts VIII, IX, and X, preceding papers); the reactions involved are such that no change of configuration can occur, and that of the final hydrocarbon or alcohol is therefore known with certainty in each case.



(I) (II) (III) (IV) (V) (VI)

Hydrogenation of *cis*-1 : 2-bisiodomethyl*cyclo*hexane (I), the configuration of which is known from its preparation from the *cis*-1 : 2-dimethanesulphonate (Part VIII, *loc. cit.*), gave *cis*-1 : 2-dimethyl*cyclo*hexane (II); the *trans*-isomer of (I) similarly gave the *trans*-hydrocarbon. The physical properties of the products were in good agreement with those recorded by Forziati *et al.* (*loc. cit.*), and the earlier configurations are therefore confirmed. The method, however, suffered from the practical disadvantage that the large amount of methanol required as solvent in the hydrogenation caused difficulty in the isolation of the rather volatile hydrocarbon, and a different route was adopted for the 1 : 3- and 1 : 4-compounds. This was based on the conversion of a primary toluene-*p*-sulphonate into a thiolacetate (method of Chapman and Owen, *J.*, 1950, 579), followed by desulphurisation with Raney nickel, but although a smaller amount of solvent could then be used in the final stage, the separation of the pure hydrocarbon was still attended by considerable loss of material. Sufficient was obtained, however, from each experiment to render identification quite certain. The ditoluene-*p*-sulphonate of *cis*-1 : 3-bishydroxymethyl*cyclo*hexane gave the *cis*-bisthiolacetate (III) and thence *cis*-1 : 3-dimethyl*cyclo*hexane (IV); similarly, *cis*-1 : 4-dimethyl*cyclo*hexane (VI) was prepared from the *cis*-1 : 4-ditoluene-*p*-sulphonate, *via* the bisthiolacetate (V), and the two *trans*-hydrocarbons through the corresponding *trans*-intermediates. The properties of the 1 : 4-hydrocarbons agreed with those recorded by Forziati *et al.* (*loc. cit.*), but with the 1 : 3-dimethyl*cyclo*hexanes the properties of our *cis*-hydrocarbon agreed with those of their so-called *trans*-isomer and *vice versa.* It is therefore certain that the original assignments of configuration are correct for the 1 : 2- and 1 : 4-hydrocarbons, but that, in agreement with Mousseron and Granger (*loc. cit.*) and Pitzer *et al.* (*loc. cit.*), they must be reversed for the 1 : 3-isomers.

In order to apply the thiolacetate method to the unambiguous synthesis of the various methyl*cyclo*hexylmethanols a monohalide or monotoluene-*p*-sulphonate of the appropriate bishydroxymethyl*cyclo*hexane was required. In the 1 : 2-series (Part VIII, *loc. cit.*) it has been shown that fission of *cis*-octahydro*iso*benzofuran (VII) with acetyl bromide gives *cis*-2-bromomethyl*cyclo*hexylmethyl acetate (VIII). When the latter was treated with potassium thiolacetate it gave *cis*-2-(acetylthiomethyl)*cyclo*hexylmethyl acetate (IX), which on desulphurisation with Raney nickel, followed by deacetylation, then gave *cis*-2-methyl*cyclo*hexylmethanol (X). A similar series of reactions was used to synthesise the *trans*-alcohol from *trans*-octahydro*iso*benzofuran. The properties of the products, and of



their derivatives, agreed with those of the same configuration described by the earlier workers, and the validity of the Auwers–Skita rules in this instance is thereby proved.

In the 1 : 3-series, fission of 3-oxa*bicyclo*[3 : 3 : 1]nonane (XI) with acetyl bromide has been shown (Part IX, *loc. cit.*) to give *cis*-3-bromomethyl*cyclo*hexylmethyl acetate, the analogue of (VIII). This was converted through the corresponding intermediates into *cis*-3-methyl*cyclo*hexylmethanol. Unlike the position in the 1 : 2-series, a similar synthesis of the *trans*-3-methyl alcohol was not possible because a *trans*-fused tetrahydropyran system stereoisomeric with (XI) cannot be formed (cf. Part IX, *loc. cit.*). *trans*-1 : 3-Bishydroxymethyl*cyclo*hexane, however, can be converted into a crude monotoluene-*p*-sulphonate; acetylation of this gave (XII), which with potassium thiolacetate gave the *trans*-acetate–thiolacetate (XIII), from which *trans*-3-methyl*cyclo*hexylmethanol (XIV) was obtained. The properties of the *cis*-alcohol and of its derivatives were in excellent agreement with those found by Darling, Macbeth, and Mills for their alcohol of undetermined configuration (we are grateful to Professor Macbeth and Dr. Mills for informing us of their experiments, and for providing specimens of their derivatives), but it had a lower refractive index than the *trans*-alcohol and thus provides a further example of the breakdown of the Auwers–Skita rules when applied to 1 : 3-compounds.

In the 1 : 4-series, no cyclic oxide had been obtained, and the route through the monotoluene-*p*-sulphonate of the diol was therefore followed. Acetylation of the *trans*-monoester gave the *trans*-acetate–toluene-*p*-sulphonate (XV), from which *trans*-4-methyl*cyclo*hexylmethanol (XVI) was prepared *via* the *trans*-acetate–thiolacetate. The properties of this alcohol and of its derivatives corresponded to those of the isomer previously designated *trans* on the basis of the Auwers–Skita rules.

As a result of these observations it is clear that the rules can be confidently applied to 1 : 2- and 1 : 4-disubstituted *cyclo*hexanes. Although the available evidence strongly suggests that they can be applied in the reverse sense to 1 : 3-compounds, the provision of further well-authenticated examples is desirable before the generality of such a procedure can be recognised.

EXPERIMENTAL

(Starting materials were prepared by the methods described in Parts VIII—X, *locc. cit.*)

1 : 3-*Di*(*acetylthiomethyl*)cyclo*hexane*.—(i) A solution of the ditoluene-*p*-sulphonate of *cis*-1 : 3-bishydroxymethyl*cyclo*hexane (5 g.) and potassium thiolacetate (4 g.) in ethanol (50 c.c.) was made slightly acid with thiolacetic acid (0·1 c.c.), and boiled under reflux for 2 hours. Most of the ethanol was then distilled off, and the residue diluted with water and extracted with chloroform. The extracts were washed with water, dried (Na_2SO_4), and distilled to give cis-1 : 3-*di*(*acetylthiomethyl*)cyclo*hexane* (2·05 g.), b. p. 120—124°/0·01 mm., n_D^{19} 1·5355 (Found :

C, 55·1; H, 7·75; S, 24·85. $C_{12}H_{20}O_2S_2$ requires C, 55·35; H, 7·7; S, 24·6%). (ii) The *trans*-1 : 3-ditoluene-*p*-sulphonate (2·8 g.) with potassium thiolacetate (2·5 g.) similarly gave trans-1 : 3-*di(acetylthiomethyl)*cyclo*hexane* (1·05 g.), b. p. 130—135°/0·03 mm., n_D^{23} 1·5285 (Found: C, 55·05; H, 7·7; S, 23·7%).

1 : 4-*Di(acetylthiomethyl)*cyclo*hexane*.—(i) Reaction of the ditoluene-*p*-sulphonate of *cis*-1 : 4-bishydroxymethyl*cyclo*hexane (4 g.) with potassium thiolacetate (3 g.) in a similar way gave the cis-1 : 4-*bisthiolacetate* (1·7 g.), b. p. 123—125°/0·01 mm., n_D^{19} 1·5348 (Found: C, 54·3; H, 7·9; S, 23·4%). (ii) The *trans*-1 : 4-ditoluene-*p*-sulphonate (9·9 g.) with potassium thiolacetate (7·5 g.) under the same conditions gave the trans-1 : 4-*bisthiolacetate* (4 g.), needles, m. p. 51—52° (Found: C, 55·2; H, 7·8; S, 24·9%), from light petroleum (b. p. 40—60°).

1 : 2-*Dimethyl*cyclo*hexane*.—(i) A solution of *cis*-1 : 2-bisiodomethyl*cyclo*hexane (10·5 g.) and potassium acetate (5·8 g.) in methanol (200 c.c.) was hydrogenated at 1 atm. over a platinic oxide catalyst (0·3 g.). When no more gas was absorbed (10 hours) the solution was filtered and diluted with much water. The upper layer was collected, washed thoroughly with water to remove methanol (considerable losses occurred), and dried (K_2CO_3). Distillation then gave *cis*-1 : 2-dimethyl*cyclo*hexane (0·5 g.), b. p. 129—130°, n_D^{19} 1·4360. Forziati *et al.* (*loc. cit.*) gave b. p. 129·7°, n_D^{20} 1·4360. (ii) Similar hydrogenation of the *trans*-di-iodide (17 g.) in methanol (500 c.c.) containing potassium acetate (12 g.) gave the *trans*-hydrocarbon (2·1 g.), b. p. 123°, n_D^{18} 1·4280. Forziati *et al.* recorded b. p. 123·4°, n_D^{20} 1·4270.

1 : 3-*Dimethyl*cyclo*hexane*.—(i) A solution of *cis*-1 : 3-di(acetylthiomethyl)*cyclo*hexane (3 g.) in methanol (50 c.c.) was boiled under reflux for 2 hours with freshly prepared Raney nickel (*ca.* 20 g.). The filtered solution was then diluted with water, and the hydrocarbon washed and dried as described above. Distillation gave *cis*-1 : 3-dimethyl*cyclo*hexane (0·3 g.), b. p. 120—121°, n_D^{20} 1·4235. Forziati *et al.* gave b. p. 120·1°, n_D^{20} 1·4229, for their "*trans*"-compound. (ii) The *trans*-1 : 3-bisthiolacetate (1·05 g.) similarly gave the *trans*-hydrocarbon (0·05 g.), b. p. 124°, n_D^{24} 1·4287. Forziati *et al.* gave b. p. 124·4°, n_D^{25} 1·4284, for their "*cis*"-compound.

1 : 4-*Dimethyl*cyclo*hexane*.—(i) Under similar conditions the *cis*-1 : 4-bisthiolacetate (1·4 g.) gave *cis*-1 : 4-dimethyl*cyclo*hexane (0·1 g.), b. p. 123—124°, n_D^{18} 1·4291. Forziati *et al.* gave b. p. 124·3°, n_D^{20} 1·4297. (ii) The *trans*-1 : 4-bisthiolacetate (4 g.) gave the *trans*-hydrocarbon (0·35 g.), b. p. 119—119·5°, n_D^{22} 1·4210. Forziati *et al.* recorded b. p. 119·3°, n_D^{20} 1·4209.

2-*(Acetylthiomethyl)*cyclo*hexylmethyl Acetate*.—(i) A solution of *cis*-2-bromomethyl*cyclo*hexylmethyl acetate (1·5 g.), potassium thiolacetate (1·3 g.), and thiolacetic acid (0·1 g.) in ethanol (50 c.c.) was boiled under reflux for 3 hours. The product was isolated as described for the bisthiolacetates above, and on distillation gave the cis-*acetate–thiolacetate* (0·8 g.), b. p. 105—110°/0·1 mm., n_D^{20} 1·5016 (Found: C, 58·45; H, 8·2; S, 13·0. $C_{12}H_{20}O_3S$ requires C, 59·0; H, 8·25; S, 13·1%). (ii) Similar treatment of *trans*-2-bromomethyl*cyclo*hexylmethyl acetate (2·8 g.) with potassium thiolacetate (1·8 g.) gave the trans-*acetate–thiolacetate* (2·35 g.), b. p. 105—108°/0·1 mm., n_D^{20} 1·4992 (Found: C, 57·9; H, 8·2; S, 12·9%).

3-*(Acetylthiomethyl)*cyclo*hexylmethyl Acetate*.—(i) Reaction of *cis*-3-bromomethyl*cyclo*hexylmethyl acetate (3·1 g.) with potassium thiolacetate (1·8 g.) similarly gave the cis-*acetate–thiolacetate* (1·8 g.), b. p. 115—117°/0·3 mm., n_D^{22} 1·4978 (Found: C, 58·45; H, 8·2; S, 13·5%). (ii) Monotoluene-*p*-sulphonation of *trans*-1 : 3-bishydroxymethyl*cyclo*hexane (3 g.) under the conditions described for the *cis*-isomer (Part IX, *loc. cit.*) gave a crude monotoluene-*p*-sulphonate (2 g.), which was characterised as the p-*nitrobenzoate–toluene*-p-*sulphonate* of the diol; this formed a microcrystalline powder, m. p. 97—98°, from light petroleum (b. p. 60—80°) (Found: C, 58·7; H, 5·8. $C_{22}H_{25}O_7NS$ requires C, 59·0; H, 5·6%). The monotoluene-*p*-sulphonate (1·9 g.) was acetylated with acetic anhydride (0·8 g.) in pyridine (10 c.c.), and the resulting product (2·2 g.) was boiled under reflux with potassium thiolacetate (0·8 g.) in ethanol (10 c.c.) for 2 hours to give the crude *trans*-acetate–thiolacetate (0·92 g.), b. p. 110—130°/0·1 mm., n_D^{22} 1·4951 (Found: S, 10·9%).

4-*(Acetylthiomethyl)*cyclo*hexylmethyl Acetate*.—The monotoluene-*p*-sulphonate of *trans*-1 : 4-bishydroxymethyl*cyclo*hexane (1·7 g.) was acetylated with acetic anhydride (0·7 g.) in pyridine (10 c.c.) to give the trans-*acetate–toluene*-p-*sulphonate* as a yellow oil (Found: S, 9·9. $C_{17}H_{24}O_5S$ requires S, 9·4%). This (1·6 g.) was boiled under reflux with potassium thiolacetate (0·7 g.) in methanol (10 c.c.) for 2 hours, and gave the crude *trans*-acetate–thiolacetate (0·8 g.), b. p. 130—150°/0·5 mm., n_D^{22} 1·4921 (Found: S, 11·3%).

2-*Methyl*cyclo*hexylmethanol*.—(i) A solution of *cis*-2-(acetylthiomethyl)*cyclo*hexylmethyl acetate (0·75 g.) in ethanol (50 c.c.) was boiled under reflux for 2 hours with Raney nickel (*ca.* 5 g.) and then filtered. Sodium hydroxide (2 g.) was then added, and after being boiled under reflux for a further 2 hours the solution was evaporated to small bulk under reduced pressure.

The residue was extracted with ether, and furnished *cis*-2-methyl*cyclo*hexylmethanol (0·2 g.), b. p. 110—115°/30 mm., n_D^{20} 1·4689, characterised as the 3 : 5-dinitrobenzoate, m. p. 91·5—92·5°. Macbeth, Mills, and Simmonds (*loc. cit.*) give b. p. 83°/10 mm., n_D^{20} 1·4690, and m. p. 92—93°, respectively.

(ii) Similar treatment of the *trans*-acetate–thiolacetate (2·2 g.) gave *trans*-2-methyl*cyclo*hexylmethanol (0·5 g.), b. p. 95—98°/14 mm., n_D^{16} 1·4652, characterised as the *p*-nitrobenzoate, m. p. 58—59°, and the 3 : 5-dinitrobenzoate, m. p. 68—69°. Macbeth, Mills, and Simmonds (*loc. cit.*) give b. p. 80°/10 mm., n_D^{20} 1·4633, and m. p.s 59—60° and 68·5—69·5° respectively.

3-*Methyl*cyclo*hexylmethanol.*—(i) A solution of *cis*-3-(acetylthiomethyl)*cyclo*hexylmethyl acetate (1·6 g.) in methanol (25 c.c.) was boiled with Raney nickel (*ca.* 15 g.) for 2 hours under reflux. The solution was filtered, sodium hydroxide (1 g.) was added, and after a further 2 hours' boiling the bulk of the methanol was distilled off, and the residue was diluted with water. Extraction with light petroleum (b. p. 40—60°) gave cis-3-*methyl*cyclo*hexylmethanol* (0·63 g.), b. p. 92—94°/16 mm., n_D^{18} 1·4598 (Found: C, 74·45; H, 12·55. $C_8H_{16}O$ requires C, 74·95; H, 12·5%). The 3 : 5-*dinitrobenzoate* formed plates, m. p. 81—82°, from methanol (Found: C, 55·9; H, 5·6; N, 9·1. $C_{15}H_{18}O_6N_2$ requires C, 55·9; H, 5·6; N, 8·7%), and the *phenylurethane*, needles, m. p. 71—72°, from light petroleum (b. p. 60—80°) (Found: C, 72·9; H, 8·6; N, 5·6. $C_{15}H_{21}O_2N$ requires C, 72·8; H, 8·6; N, 5·7%). The m. p.s of these derivatives were not depressed on admixture with those of the m. p.s 81·5—82° and 73·5—74·5°, respectively, kindly provided by Professor Macbeth.

(ii) From the crude *trans*-acetate–thiolacetate (0·85 g.) there was similarly obtained trans-3-*methyl*cyclo*hexylmethanol* (0·21 g.), b. p. 112—114°/35 mm., n_D^{22} 1·4628 (Found: C, 74·6; H, 12·7%). The 3 : 5-*dinitrobenzoate* formed needles, m. p. 77—78°, from methanol (Found: C, 55·8; H, 5·7; N, 9·0%), and the α-*naphthylurethane*, nodules, m. p. 84—85°, from light petroleum (b. p. 60—80°) (Found: C, 76·4; H, 7·9; N, 4·8. $C_{19}H_{23}O_2N$ requires C, 76·7; H, 7·8; N, 4·7%). The m. p. of the 3 : 5-dinitrobenzoate was depressed to 60—63° on admixture with the *cis*-isomer.

4-*Methyl*cyclo*hexylmethanol.*—Crude *trans*-4-(acetylthiomethyl)*cyclo*hexylmethyl acetate (0·7 g.) on similar treatment gave *trans*-4-methyl*cyclo*hexylmethanol (0·2 g.), b. p. 99—101°/23 mm., n_D^{29} 1·4538, characterised as the 3 : 5-dinitrobenzoate, m. p. 111°, and the α-naphthylurethane, m. p. 110°. Cooke and Macbeth (*loc. cit.*) give b. p. 74°/3 mm., n_D^{20} 1·4578, and m. p.s 112° and 110·5°, respectively.

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