502. *The Configurations of the Isomeric Forms of* 1 : 3-*Dimethyl*cyclo*pentane*.

By S. F. Birch and R. A. Dean.

The configurations of the two stereoisomers of 1 : 3-dimethyl*cyclo*pentane have been established by synthesis. The previous tentative assignments must be reversed.

The current assignment of configurations to the two geometrical isomers of 1 : 3-dimethyl*cyclo*pentane appears to have originated from the work of Glasgow (*J. Res. Nat. Bur. Stand.*, 1940, **24**, 509) who isolated one isomer from a Mid-Continent petroleum naphtha. The close similarity of the physical properties of the compound with an optically active, and therefore *trans*-, isomer prepared by Zelinsky and Rudsky (*Ber.*, 1896, **29**, 403; Zelinsky, *ibid.*, 1902, **35**, 2677) led Glasgow to conclude that his isomer was the *trans*-compound. When Rossini and his co-workers (Streiff, Zimmermann, Soule, Butt, Sedlak, Willingham, and Rossini, *J. Res. Nat. Bur. Stand.*, 1948, **41**, 323) prepared both isomers it became apparent that this assignment was suspect owing to the very similar properties of the *cis*- and the *trans*-form.

Our present work shows conclusively that the current assignment of the *cis*- and *trans*-configuration to the 1 : 3-dimethy*cyclo*pentanes should be reversed as was necessary with the 1 : 3-dimethyl*cyclo*hexanes (Mousseron and Granger, *Bull. Soc. chim.*, 1938, **5**, 1618; Pitzer and Beckett, *J. Amer. Chem. Soc.*, 1947, **69**, 977; Beckett, Pitzer, and Spitzer, *ibid.*, 1947, **69**, 2488; Haggis and Owen, *J.*, 1953, 408).

An optically active *trans*-form and an inactive *cis*-form of 1 : 3-dimethyl*cyclo*pentane were synthesised by Mousseron and Granger (*Compt. rend.*, 1942, **215**, 161; Mousseron, *Bull. Soc. chim.*, 1946, **13**, 218) but the physical properties of these compounds differ so considerably from those of the A.P.I. materials that their results only indicate the probability of the *trans*-isomer's being the higher boiling. Birch and Oldham (*Nature*, 1947, **160**, 368) prepared a small quantity of a 1 : 3-dimethyl*cyclo*pentane and tentatively suggested the revision of the assignment of the configurations. Their synthesis, from *cis-cyclo*pentane-1 : 3-dicarboxylic acid, has now been considerably improved, and in addition two optically active hydrocarbons have been prepared from the *trans*-acid.

The conversion of *cis-cyclo*pentane-1 : 3-dicarboxylic acid, readily obtained by oxidation of norbornylene (*bicyclo*[2 : 2 : 1]hept-2-ene) (Birch, Oldham, and Johnson, *J.*, 1947, 818), into the corresponding hydrocarbon involved four steps. The acid was first converted into the ethyl ester, which, after fractionation under reduced pressure, was reduced to the corresponding diol with lithium aluminium hydride. Previously this reduction had been carried out by the Bouveault–Blanc method and by catalytic hydrogenation in the presence of copper chromite. While the Bouveault–Blanc product and its toluene-*p*-sulphonate possessed physical properties closely agreeing with those of the material obtained by use of lithium aluminium hydride, the glycol obtained by catalytic hydrogenation was, from its physical properties, obviously impure. The conversion of the ester into the glycol by lithium aluminium hydride, however, proceeded smoothly and gave an excellent yield of a product, the toluene-*p*-sulphonate of which gave a material of constant melting point after only two crystallisations. Proof that no detectable rearrangement had taken place during the reduction was afforded by reconversion of the glycol into the original acid by

oxidation with permanganate. This is in agreement with the demonstration by Noyce and Denney (*J. Amer. Chem. Soc.*, 1950, **72**, 5743) that this method of reduction of an ester does not affect the stereochemistry of the α-carbon atom. Reduction of the toluene-*p*-sulphonate in ether with lithium aluminium hydride by Strating and Backer's method (*Rec. Trav. chim.*, 1950, **69**, 638), gave a good yield of the corresponding hydrocarbon which was purified by fractionation and percolation through silica-gel. It boiled at the same temperature as, and had physical properties similar to, those of the material tentatively designated by Rossini and his co-workers as the *trans*-isomer. The identity of the two was confirmed by spectroscopic analysis, a direct comparison between the two materials being made. This definitely established that the isomer hitherto regarded as *trans* is in fact *cis*.

The purity of this hydrocarbon, as determined by its melting point, indicated the presence of 5·5—7·5% of an impurity shown by spectroscopic analysis to be the *trans*-isomer. The presence of this in a product derived from carefully purified *cis*-toluene-*p*-sulphonate was unexpected. As discussed above, the glycol must have been the *cis*-isomer and the purity of the toluene-*p*-sulphonate, indicated by its constant melting point, was confirmed by the fact that the addition of 7% of (+)-*trans*-toluene-*p*-sulphonate lowered the melting point from 108·5—109° to 104·5—107°; one crystallisation raised it to 107·5—108·5°. Reduction of the (+)- and (−)-*trans*-toluene-*p*-sulphonates similarly gave small amounts of the *cis*-isomer, *i.e.*, some isomerisation took place at this stage. The extent of isomerisation appears to be limited, and it is probable that by varying the conditions of reduction it could be appreciably reduced although this could not be confirmed experimentally. As an alternative to the reduction of the toluene-*p*-sulphonate with lithium aluminium hydride the Raney nickel desulphurisation of the cyclic sulphide,* formed by heating the toluene-*p*-sulphonate with sodium sulphide and necessarily having a *cis*-structure, was considered. It was not, however, investigated because of the difficulty in preparing enough material for determination of purity from the freezing point which in our equipment requires a minimum of 35 ml. Furthermore, isomerisation seemed more likely by this method. It is difficult from the physical properties reported by Haggis and Owen (*loc. cit.*) for their isomeric dimethyl*cyclo*hexanes to judge whether, in fact, these contained isomeric hydrocarbons, but from the figures given it would certainly appear that this could be so.

While the presence of *trans*-isomer in the amount found in the *cis*-hydrocarbon does not seriously affect the conclusions with regard to the configuration of the 1 : 3-dimethyl*cyclo*pentanes, any possible doubt would be eliminated by the synthesis of the other (*trans*-) isomer in optically active forms. Both Zelinsky and Mousseron in their syntheses employed optically active compounds derived in the first place from a naturally occurring product. With a source of *cis-cyclo*pentane-1 : 3-dicarboxylic acid available it was more convenient to start with this which Pospischill (*Ber.*, 1898, **31**, 1950) had shown could be isomerised to the (±)-*trans*-acid by hydrochloric acid at 180°. Separation of the resultant mixed acids by treatment with acetyl chloride, followed by extraction with ether and resolution of the *trans-form* with the aid of brucine, was carried out as described by Perkin and Scarborough (*J.*, 1921, **119**, 1400). This *trans*-acid obtained from the mixture of *trans*-acid and *cis*-anhydride melted at 89—92°. This melting point is appreciably higher than that reported by other workers for the pure acid. Thus Pospischill (*loc. cit.*) gives 87—88·5°, Semmler and Bartelt (*Ber.*, 1908, **41**, 385) 86°, Perkin and Scarborough (*loc. cit.*) 85—86°, while Ingold and Mohrhenn (*J.*, 1935, 949) obtained an acid from carbon tetrachloride melting at 83—85°, raised however to 89° on desiccation over phosphoric oxide. Accordingly the acid was treated a few times with carbon tetrachloride as described by Pospischill (*loc. cit.*) but little change in melting point was observed. Crystallisation from a mixture of carbon tetrachloride and benzene raised the melting point to a constant value of 95·5—96·5°. Addition of 1% of the *cis*-acid produced a slight depression, and addition of 5% lowered the melting point to 93·4—95·5°. From this it would appear that 95·5—96·5° is the true melting point of the pure *trans*-acid.

Resolution of the (±)-*trans*-acid showed that the acids obtained by Perkin and Scar-

* To be described in a future communication.

borough after three crystallisations of the brucine salts were not optically pure and that the amount of optically pure material which could be obtained from the available *trans*-acid would be insufficient for the subsequent stages of the synthesis. Accordingly the synthesis was continued with incompletely resolved materials. The best samples of acids, obtained after many crystallisations of the brucine salts, had $[\alpha]_D^{15}$ +21·3°, and $[\alpha]_D^{15}$ −22·6°, compared with $[\alpha]_D^{15}$ +5·8° and $[\alpha]_D^{15}$ −5·3° quoted by Perkin and Scarborough (*loc. cit.*). The partly purified (+)- and (−)-acids ($[\alpha]_D^{15}$ +13·6°, −20·2°) were converted by the route already described into the corresponding hydrocarbons with the exception that, instead of the lithium aluminium hydride reduction being carried out on the esters, the free acids were reduced (Nystrom and Brown, *J. Amer. Chem. Soc.*, 1947, **69**, 2548).

The two glycols and the two hydrocarbons derived from them were optically active. Their physical properties, and in particular the infra-red absorption spectra of the hydrocarbons, corresponded with those of the A.P.I. *cis*-material. Both forms contained some of the *cis*-form, in an amount estimated by refractive index and spectroscopic analysis as *ca.* 17 and 8% for the (−)- and the (+)-forms respectively. The conversion of the *trans*-acid into optically active hydrocarbons leaves no doubt as to the *trans*-configuration of the latter.

Physical properties of 1 : 3-*dimethyl*cyclo*pentanes*.

	A.P.I.*		Present work		
	"*cis*"	"*trans*"	*cis*	(−)-*trans*	(+)-*trans*
F. p.	−133·90°	−133·690°	(M. p.) −135·30°	—	—
d^{20}	0·74880	0·74479	0·7450	0·7481	0·7485
d^{25}	0·74435	0·74025	—	0·7437	0·7442
n_D^{20}	1·41074	1·40894	1·40904	1·41043	1·41060
n_D^{25}	1·40813	1·40633	—	1·40778	1·40799
B. p.	91·725°	90·773°	90·92°	91·6°	91·6°

* American Petroleum Institute Research Project 44, Selected Values of the Properties of Hydrocarbons, Table 6A, 1949.

Experimental.

M. p.s are corrected.

Diethyl cis-cyclo*Pentane*-1 : 3-*dicarboxylate*.—*cis-cyclo*Pentane-1 : 3-dicarboxylic acid (2528 g.) was esterified with ethanol (4068 ml.) in a continuous esterification apparatus (*Org. Synth.*, Coll. Vol. I, 1944, p. 261), carbon tetrachloride (1774 ml.) being used as entrainer and sulphosalicyclic acid (40 g.) as catalyst; the diethyl ester (2750 g.), fractionated through a 25-plate column, boiled at 149°/23 mm. and had n_D^{20} 1·4481. It set to a glass on cooling (Found: C, 61·55; H, 8·7. Calc. for $C_{11}H_{18}O_4$: C, 61·7; H, 8·5%).

cis-1 : 3-*Bishydroxymethyl*cyclo*pentane*.—The above ester (414 g., 1·93 moles), diluted with ether (1 l.), was slowly added to a stirred solution of lithium aluminium hydride (90 g., 2·37 moles) in ether (2 l.) during 2 hr., the temperature being kept at 30—35°. Stirring was continued for a further 2 hr. and the product containing excess of the hydride was then decomposed with water and dilute sulphuric acid. The aqueous layer was extracted continuously overnight with fresh ether. The combined ethereal solutions were dried (K_2CO_3) and evaporated, leaving a colourless viscous liquid which on distillation gave the *glycol* (244 g., 96·8%), b. p. 118°/0·5 mm., n_D^{20} 1·4855 (Found: C, 64·7; H, 11·2. $C_7H_{14}O_2$ requires C, 64·6; H, 10·8%).

The *phenylurethane*, prepared in the usual way, after crystallisation from ethanol–ligroin melted at 139—139·5° (Found: C, 68·6; H, 6·4; N, 7·5. $C_{21}H_{24}O_4N_2$ requires C, 68·5; H, 6·6; N, 7·6%).

Oxidation of cis-1 : 3-*Bishydroxymethyl*cyclo*pentane*.—The glycol (6·5 g.) was dissolved in water (100 ml.) and, while a stream of carbon dioxide was passed in, potassium permanganate (21 g.) in water (500 ml.) was added during 2 hr. Next morning the product was treated with sulphur dioxide, then concentrated, acidified, and extracted with ether. A solid product (3 g.) was obtained which after crystallisation from water melted at 118·5—119° alone or mixed with *cis-cyclo*pentane-1 : 3-dicarboxylic acid (Found: C, 52·8; H, 6·3. Calc. for $C_7H_{10}O_4$: C, 53·2; H, 6·4%). Extraction of the aqueous layer with ether in a continuous extractor gave 4 g. of an oil which was not further investigated.

Di-p-*toluenesulphonate of* cis-1 : 3-*Bishydroxymethyl*cyclo*pentane*.—The glycol was converted into the *di*-p-*toluenesulphonate* as described in *Org. Synth.* (1940, **20**, 50). After two crystallisations from benzene–ethanol, a product (92% yield) consisting of needles, m. p.

108·5—109°, was obtained (Found : C, 57·7; H, 5·9; S, 14·5. $C_{21}H_{20}O_6S_2$ requires C, 57·5; H, 6·0; S, 14·6%).

cis-1 : 3-*Dimethyl*cyclo*pentane*.—The di-*p*-toluenesulphonate (360 g., 0·82 mole) was added in small portions to a stirred and cooled solution of lithium aluminium hydride (80 g., 2·11 moles) in ether (2000 ml.) at such a rate that the solvent refluxed gently. Addition was complete in 2 hr. and stirring continued for a further 6 hr. Excess of hydride was destroyed by the cautious addition of water (100 ml.), followed by dilute sulphuric acid (250 ml. in 1125 ml. of water). After being washed with aqueous sodium hydroxide to remove traces of thiocresol, the ether was distilled through a 50-plate column. The residual hydrocarbon after passing through silica-gel, with propanol as eluant, was fractionated through a low-hold-up column containing packing of the Bower and Cooke type (*Ind. Eng. Chem., Anal.*, 1943, **15**, 290) equivalent to 30 theoretical plates. For the properties of the hydrocarbon (70·3 g., 87·4%) see the Table.

trans-cyclo*Pentane*-1 : 3-*dicarboxylic Acid*.—*cis-cyclo*Pentane-1 : 3-dicarboxylic acid (12 g.) was heated with concentrated hydrochloric acid (15 ml.) at 180° for 6 hr. The product was washed out with water and evaporated to dryness on the steam-bath under reduced pressure. Treatment of the residue with acetyl chloride at room temperature for 24 hr., followed by removal of the volatile material in a desiccator over solid potassium hydroxide as recommended by Perkin and Scarborough (*loc. cit.*), yielded an approx. 1 : 1 mixture of *trans*-acid and *cis*-anhydride. Extraction four times with dry ether (20 ml.) dissolved the *trans*-acid, m. p. 81—85°. Repetition of this treatment of the acid with acetyl chloride, etc., gave crude *trans*-acid, m. p. 88—92°. It was dissolved in water (charcoal), then filtered, and the water evaporated off. A total of 130 g. of the *trans*-acid was prepared in this way. It was crystallised from benzene–carbon tetrachloride until a constant m. p. of 95·5—96·5° was reached.

(+)- *and* (−)-trans-cyclo*Pentane*-1 : 3-*dicarboxylic Acids*.—The (±)-*trans*-acid was converted into the brucine salt and resolved by fractional crystallisation from water as described by Perkin and Scarborough (*loc. cit.*). Approx. 3 l. of boiling water were required to dissolve the acid (123 g.) and the brucine (738 g.). The brucine salt of the (+)-acid was concentrated in the less soluble portion which crystallised out. Although a considerable number of crystallisations were carried out and both (+)- and (−)-acids were obtained possessing considerably higher optical activity than those previously described, complete optical purity was not achieved with either. The air-dried salt which gave a (+)-acid of highest activity had $[\alpha]_D^{15}$ +20·09° (*c*, 2 in 1 : 1 H_2O–EtOH, by vol.).

The acids, recovered from the brucine salts as described (*loc. cit.*), were recrystallised from benzene–carbon tetrachloride. The best samples had the following properties : (+)-acid, m. p. 79·5—80·5°, $[\alpha]_D^{15}$ +21·3°; (−)-acid, m. p. 85·0—85·7°, $[\alpha]_D^{15}$ −22·6° (*c*, 8 in H_2O). For conversion into the glycol, acids having rotations of $[\alpha]_D^{15}$ +13·6° (46·1 g.) and $[\alpha]_D^{15}$ −20·2° (34·5 g.) were used.

(−)- *and* (+)-trans-1 : 3-*Bishydroxymethyl*cyclo*pentane*.—Reduction of the acids with lithium hydride as described by Halford and Wassmann (*J. Org. Chem.*, 1952, **17**, 1276) gave a low yield of glycol and a considerable amount of unchanged acid. The molar ratio of acid to hydride was therefore increased to 1 : 4, 1800 ml. of ether being used per mole of the latter. The reaction mixture was decomposed with water and acidified with dilute sulphuric acid, and the aqueous portion continuously extracted with ether. Washing the combined ethereal layers with a little concentrated sodium hydroxide solution removed unchanged acid which was recovered from the alkaline extract by acidification and ether-extraction. This was similarly reduced and the glycol combined with the main product. After drying with potassium carbonate and removal of the ether, the glycol which remained was distilled under reduced pressure. It boiled at 117—118°/0·5 mm. and had n_D^{20} 1·4868. The glycol (76% yield) from the (+)-acid ($[\alpha]_D^{15}$ +13·6°) was a colourless viscous liquid, $[\alpha]_D^{15}$ −1·7°; the glycol (77% yield) from the (−)-acid ($[\alpha]_D^{15}$ −20·2°) had $[\alpha]_D^{15}$ +4·2° (*c*, 3·4 in EtOH).

The *di*-p-*toluenesulphonate* was prepared from the (−)-glycol, as for the *cis*-compound, in 84·4% yield. Crystallised once from ethanol it melted at 78—81° (Found : C, 57·3; H, 6·1; S, 14·5%). The corresponding *derivative* from the (+)-glycol, obtained similarly in 78·7% yield, melted after one crystallisation from ethanol at 69—75° (Found : C, 58·0; H, 6·1; S, 14·3%).

(−)- *and* (+)-trans-1 : 3-*Dimethyl*cyclo*pentane*.—The di-*p*-toluenesulphonate of (−)-*trans*-1 : 3-bishydroxymethyl*cyclo*pentane (80 g.) was slowly added to lithium aluminium hydride (34 g.) in ether (1000 ml.) at such a rate that the ether refluxed gently. When addition was complete, stirring was continued for a further 3 hr. after which the mixture was surrounded by a cooling-bath and decomposed first with water and then with dilute sulphuric acid. Washing,

drying ($CaCl_2$), and fractionation as for the *cis*-isomer gave a fraction (16·56 g., 92·5%) which was purified by percolation over silica gel to remove traces of ether and toluene (propanol as eluant). The properties of the final product are given in the Table; it had $[\alpha]_D^{15}$ −1·5°.

Similarly treated, the di-*p*-toluenesulphonate (57 g.) of (+)-*trans*-1 : 3-bishydroxymethyl-*cyclo*pentane yielded a hydrocarbon (11·8 g., 92·6%) which, purified as above, had the properties given in the Table, also $[\alpha]_D^{15}$ +2·3°.

We thank the Chairman of the Anglo-Iranian Oil Company Limited for permission to publish these results. We also acknowledge the help of Dr. H. Powell for the determination of the infra-red spectra of our hydrocarbons and of Messrs. J. F. Osborne and D. Ellis in the preparative work.

THE ANGLO-IRANIAN OIL CO., LIMITED, RESEARCH STATION,
SUNBURY, MIDDX.

[*Received, March* 16*th*, 1953.]