

1-methoxy-2-propanone, b.p. 120–121° (0.15 mm.); n_D^{25} 1.5652.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.16. Found: C, 80.54; H, 7.23.

Excess methylmagnesium bromide reacted with 2.26 g. of the α -methoxyketone to give 1.3 g. (54%) of V, identical with the product from the epoxyether reaction as shown by the physical properties, b.p. 110–112° (0.08 mm.), n_D^{25} 1.5623 and the infrared spectra.

Cleavage of 1-(α -methoxybenzhydryl)-cyclohexanol (VI) with base. A solution of 3.2 g. of methoxyalcohol VI in 10 ml. of 40% sodium hydroxide and 10 ml. of 95% glycerin was heated to the reflux temperature and 10 ml. of distillate removed and discarded. The remainder was heated at the reflux temperature for 1 hr., after which a distinct odor of cyclohexanone was present. Ten ml. of water was added and a 10-ml. portion of distillate collected. After this procedure was repeated once, the 20 ml. of distillate were combined, saturated with sodium chloride, and extracted with ether. The ether was evaporated and the cyclohexanone content of the residue determined by the method of Iddles and Jackson.⁹ The yield of 2,4-dinitrophenylhydrazone of cyclohexanone was 54% and the identity was established by comparison with an authentic sample.

Pinacol rearrangement of the methoxyalcohols III, IV, and VI. One-half gram of III was dissolved in 5 ml. of concentrated sulfuric acid, allowed to stand at room temperature for 2 hr., and then poured onto cracked ice. The resulting mixture was extracted with ether and the ether solution washed and dried. After the solvent was removed the residue crystallized. Recrystallization from petroleum ether gave 0.26 g. (60%) of the known 1,1-diphenyl-1-methyl-2-propanone,¹⁰ m.p. 40–42°. The semicarbazone¹¹ melted at 175–177°.

(9) H. A. Iddles and C. E. Jackson, *Ind. Eng. Chem., Anal. Ed.*, **6**, 454 (1934).

(10) K. Sisido and H. Nozaki, *J. Am. Chem. Soc.*, **70**, 777 (1948).

(11) W. Parry, *J. Chem. Soc.*, **99**, 1169 (1911).

For the pinacol rearrangement of IV, a solution of 0.4 g. of the methoxyalcohol in 5 ml. of dioxane and 5 ml. of concentrated hydrochloric acid was allowed to remain at room temperature overnight. The product was isolated as from the sulfuric acid procedure and recrystallized from petroleum, m.p. 98–100°. The yield was 0.21 g. (58%).

Anal. Calcd. for $C_{20}H_{18}O$: C, 87.55; H, 6.61. Found: C, 87.59; H, 6.87.

The methoxyalcohol VI gave 36% of 1-phenylcyclohexyl phenyl ketone,¹² m.p. 73–75° using the sulfuric acid procedure. Because the yield was low, an infrared spectrum was taken of an aliquot of the total crude product to determine whether a ketone was present with an unconjugated carbonyl group. Only the absorption band corresponding to the conjugated carbonyl (6.0 microns) appeared in the spectrum.

The hydrochloric acid-dioxane procedure gave 66% of the same ketone, m.p. 65–70°, but in this case an aliquot of the total crude ketone gave an infrared spectrum which contained a very small unconjugated carbonyl band at 5.85 microns.

The fused zinc chloride-acetic anhydride procedure of Lyle and Lyle¹² gave 100% of crude product, m.p. 58–66° with no evidence for the isomeric ketone.

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DETROIT 2, MICH.

(12) R. E. Lyle and G. G. Lyle, *J. Am. Chem. Soc.*, **74**, 4059 (1952).

[CONTRIBUTION FROM THE RESEARCH STATION, THE BRITISH PETROLEUM COMPANY LIMITED]

Preparation and Physical Properties of Sulfur Compounds Related to Petroleum. VIII. *trans*-2-Thiabicyclo[3.3.0]octane

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trans-2-Thiabicyclo[3.3.0]octane has been synthesized; its physical properties are recorded, and it has been characterized by the preparation of derivatives.

In previous papers in this series, the preparation and properties of eight of the nine possible thiabicyclo-octanes containing fused five- and six-membered rings, have been described.^{1–3} The preparation and properties of the remaining isomer, *trans*-2-thiabicyclo[3.3.0]octane (V), referred to in a

note⁴ on the *cis-trans* isomerization of cyclic sulfones, are detailed below.

In view of the attention recently paid to systems which contain two *trans*-1,2-fused five-membered rings, *trans*-2-thiabicyclo[3.3.0]octane is of special interest; little has been reported of these systems and only a few are known.⁵ Until recently, stereochemical considerations indicated that in such a system the *trans*-configuration would involve considerable strain within the molecule. The work of

(1) S. F. Birch, R. A. Dean, N. J. Hunter, and E. V. Whitehead, *J. Org. Chem.*, **20**, 1178 (1955).

(2) S. F. Birch, R. A. Dean, N. J. Hunter, and E. V. Whitehead, *J. Org. Chem.*, **22**, 1590 (1957).

(3) S. F. Birch and R. A. Dean, *Ann.*, **585**, 234 (1954).

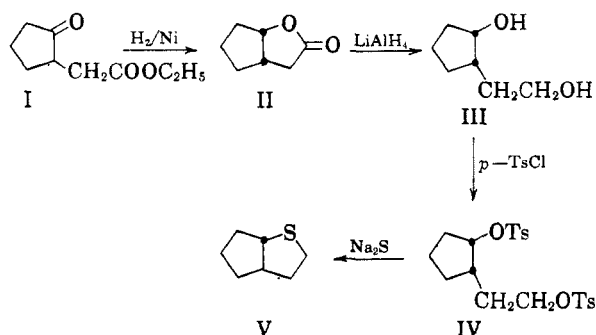
(4) S. F. Birch, R. A. Dean, and E. V. Whitehead, *Chem. & Ind. (London)*, 409 (1956).

(5) H. Booth, F. E. King, J. Parrick, and R. L. St. D. Whitehead, *Chem. & Ind. (London)*, 466 (1956).

Linstead and his co-workers,⁶⁻⁸ and that of Owen and his associates^{9,10} as well as our own work¹ has shown that, using comparatively mild conditions, the *trans*-isomer of a system containing two 1,2-fused five-membered rings is much more readily formed than might be expected. There is, however, little doubt that the *trans*-isomer involves a more strained configuration with the result that the *cis*-isomer is favored at equilibrium.⁴ *cis*- and *trans*-2-Thiabicyclo[3.3.0]octanes like the 3-thia analogs^{1,9} do not obey the Auwers-Skita rule, which again indicates that the *trans*-isomer has a greater degree of strain than the *cis*-isomer.

The assignment of a *trans*-configuration to this thiabicyclo[3.3.0]octane has been based primarily on the fact that its sulfone can readily be isomerized, under mild conditions, to the sulfone of the *cis*-isomer (the configuration of which has already been established¹). This assignment of *trans*-configuration confirms that the lactone (II) from which it is derived has a *cis*-configuration^{11,12} since it has been shown that a Walden inversion occurs in analogous cyclization reactions used in the preparation of 6-thiabicyclo[3.2.1]octane and 2-thiabicyclo[2.2.2]octane.² The previous assignment of configuration of this lactone was based on its ease of formation, a method which now appears to be less reliable than was originally thought.

The route used in the synthesis of *trans*-2-thiabicyclo[3.3.0]octane was as illustrated in the accompanying formulas.



The *cis*-lactone (II), accompanied by a small quantity of the corresponding *trans*-hydroxy ester, was obtained in good yield when ethyl cyclopentanone-2-acetate (I) was reduced with hydrogen over Raney nickel. Separation of the lactone from

the *trans*-hydroxy acid was effected, after hydrolysis, by removal of the acid as its ammonium salt, a method described by Hückel and Gelmroth.¹¹ These authors found that catalytic hydrogenation of cyclopentanone-2-acetic acid over a platinum catalyst gave a mixture of the *cis*-lactone (II) and *trans*-cyclopentanol-2-acetic acid, but using their conditions, hydrogenation was found to be very slow, the yield of the required lactone low, and isolation of cyclopentaneacetic acid from the product indicated that some hydrogenolysis had occurred.

Reduction of the lactone (II) with lithium aluminum hydride gave the *cis*-glycol (III) in good yield. On tosylation, this yielded a thermally unstable ditosylate¹³ with the cyclic ether, 2-oxabicyclo[3.3.0]octane, as a by-product.¹⁴ (The stereochemical configuration of the latter is unknown but from its behavior on freezing it appears to be substantially a single stereoisomer.) Attempts to crystallize the ditosylate invariably resulted in partial conversion into an unsaturated monotosylate, apparently by elimination of a tosylate group. The crude ditosylate was accordingly used for the next stage without purification. Cyclization of the *cis*-ditosylate (IV) with sodium sulfide at 50° gave the *trans*-sulfide (V) in poor yield as expected, the by-products being polymeric sulfides boiling from 130–240°/0.8 mm. Analysis of the lower boiling portion of the latter indicated that it was probably the unsaturated sulfide $C_{14}H_{22}S$; the higher boiling material appeared to contain three atoms of sulfur per molecule.

The derivatives of *trans*-2-thiabicyclo[3.3.0]octane were prepared as described previously;¹⁵ their physical properties and those of the sulfide are given in Table I. The infrared absorption spectrum¹⁶ was obtained for this sulfide in the range 2–15 μ using a Grubb-Parsons double beam spectrometer. Both *cis*- and *trans*-2-thiabicyclo[3.3.0]octane appear to undergo an autoxidation reaction similar to that described by Bateman *et al.*¹⁷ for thiacyclohexane. Pure samples of each sulfide stored in stoppered glass containers for several months in diffuse light were re-examined spectroscopically and found to exhibit strong absorptions 5.74 μ and 9.56 μ at characteristic of carbonyl and sulfoxide groups, respectively. Distillation of the *trans*-sulfide after storage yielded almost pure sulfide and left a residue which contained, by titration¹⁸ 25% of sulfoxide. Reduction of the residue with

(6) R. P. Linstead and E. M. Meade, *J. Chem. Soc.*, 935 (1934).

(7) A. H. Cook and R. P. Linstead, *J. Chem. Soc.*, 946 (1934).

(8) J. W. Barrett and R. P. Linstead, *J. Chem. Soc.*, 436 (1935).

(9) L. N. Owen and A. G. Peto, *Chem. & Ind. (London)*, 65 (1955).

(10) L. N. Owen and A. G. Peto, *J. Chem. Soc.*, 2383 (1955).

(11) W. Hückel and W. Gelmroth, *Ann.*, 514, 233 (1934).

(12) W. E. Grigsby, J. Hind, J. Chanley, and F. H. Westheimer, *J. Am. Chem. Soc.*, 64, 2606 (1942).

(13) Di-*p*-toluenesulfonate.

(14) M. F. Clarke and L. N. Owen, *J. Chem. Soc.*, 2108 (1950).

(15) E. V. Whitehead, R. A. Dean, and F. A. Fidler, *J. Am. Chem. Soc.*, 73, 3632 (1951).

(16) To be submitted to A.P.I. Research Project 44 for inclusion in their Catalog of Spectral Data.

(17) L. Bateman, J. I. Cunneen, and J. Ford, *J. Chem. Soc.*, 1539 (1957).

(18) D. Barnard and K. R. Hargrave, *Anal. Chim. Acta*, 5, 536 (1951).

TABLE I
 PHYSICAL PROPERTIES OF *trans*-2-THIABICYCLO[3.3.0]OCTANE AND ITS DERIVATIVES

Temp., °C.	Sulfide							B.P., °C. at 20 mm.	M.P., °C.
	Refractive Index ^a								
	Wave Length Ångstrom Units								
	6678	6563	5893	5461	5016	4861	4358		
20	1.52475	1.52521	1.52845	1.53124	1.53497	1.53654	1.54302		
25	1.52249	1.52295	1.52619	1.52898	1.53272	1.53429	1.54077	86.5	-8
30	1.52018	1.52065	1.52388	1.52666	1.53039	1.53196	1.53843		
Derivatives									
Formula of Derivative	M.P., °C. (Corrected)	Analyses							
		Calcd.			Found				
		C	H	S	C	H	S		
C ₇ H ₁₂ Cl ₂ HgS	129.5-132.0	21.0	3.0	8.0	21.0	3.1	8.1		
C ₇ H ₁₂ O ₂ S	62.2-62.7	52.5	7.6	20.0	52.5	7.7	20.1		
C ₈ H ₁₆ IS	An oil								

^a These values have been smoothed by the method of Forziati.¹⁹

lithium aluminum hydride gave an evil-smelling product containing both mercapto- and hydroxy-groups. This was possibly cyclopentanol-2- β -ethane-thiol derived from dicyclopentanone-2- β -ethyl disulfide, a probable end product of the autoxidation of the *trans*-sulfide. Unfortunately the quantity available was insufficient for further examination.

The physical properties of the sulfide being available, the appropriate fraction of the sulfur-containing oil, obtained in the process of refining kerosine, was examined but this sulfide was not found.

EXPERIMENTAL

All melting points are corrected. The purity was estimated by the freezing point method of Mair, Glasgow and Rossini.²⁰ The cryoscopic constant was estimated from the freezing time. Microanalyses are by Dr. Ing. A. Schoeller of Kronach/Oberfranken, Bambergerstrasse 20, Germany.

Cyclopentanone-2-acetic acid, m.p. 52.3-53.3°, was obtained in 79% yield from 2-carbethoxycyclopentanone using the method²¹ of Linstead and Meade.⁶ Continuous esterification²² of this acid gave the ethyl ester (I) in almost theoretical yield, b.p. 131°/18 mm., n_D^{20} 1.4528, and the methyl ester, b.p. 128-131°/25 mm., n_D^{20} 1.4579.

cis-Cyclopentanol-2-acetic acid lactone (II). (a) Cyclopentanone-2-acetic acid (40 g.) was hydrogenated over a platinum black catalyst in ether until hydrogen ceased to be absorbed (32 hr.). After removal of catalyst and extraction with sodium bicarbonate solution (500 ml., 6%) the *cis*-lactone (II) (6.4 g.) was obtained. Acidification and extraction of the aqueous portion yielded an oil (33 g.) which on distillation gave a fraction b.p. 130-140°/23 mm.;

(19) A. F. Forziati, *J. Research Natl. Bur. Standards*, **44**, 373 (1950).

(20) B. J. Mair, A. R. Glasgow, and F. D. Rossini, *J. Research Natl. Bur. Standards*, **26**, 591 (1941).

(21) To obtain the yield of carbethoxycyclopentanone reported by Linstead it is essential to add the total quantity of ester in one portion to the prescribed quantity of molecular sodium. Similarly the carbethoxycyclopentanone used in the preparation of cyclopentanone-2-acetic acid should be redistilled immediately prior to use [F. Ramirez and J. W. Sargent, *J. Am. Chem. Soc.*, **77**, 6297 (1955)].

(22) H. T. Clarke and A. W. Davis, *Org. Syntheses, Coll. Vol. I*, 261 (1944).

n_D^{20} 1.4582; (7.2 g.), which was dissolved in ether, saturated with dry ammonia, and filtered. Acidification of the ammonium salt gave an oil (3.7 g.); b.p. 134-140°/25 mm.; n_D^{20} 1.4542; m.p. 14-15°. Eykman²³ gives b.p. 139-140°/26 mm.; m.p. 13-14°; n_D^{19} 1.45234 for cyclopentaneacetic acid.

Anal. Calcd. for C₇H₁₂O₂: C, 65.6; H, 9.4. Found: C, 65.6; H, 9.6.

(b) Methyl cyclopentanone-2-acetate (69 g.) in methanol was hydrogenated over a Raney nickel catalyst at 140° and a pressure of 2000 p.s.i.g. The product (54 g.) distilled at 133-140°/25 mm.; n_D^{20} 1.4710 and was separated into *cis*-lactone (33 g.) and *trans*-acid (5.6 g.).

(c) The ethyl ester (I) (735 g.) hydrogenated without solvent gave a mixture of the *cis*-lactone and *trans*-ester, b.p. 124-140°/17 mm., which could not be separated by fractionation. This material was hydrolyzed with 10% aqueous potash, the ethanol removed by distillation, and the aqueous layer acidified and extracted with ether to give an oil (541 g.). This was dissolved in dry ether and separated into *cis*-lactone and the ammonium salt of the *trans*-acid by the technique described in (a). A portion of the *cis*-lactone (yield 83% on I) was crystallized twice from ether and redistilled, b.p. 124-126°/16 mm.; m.p. -14.28°; cryoscopic constant 3.0 mole % per deg.; purity 98 mole %; n_D^{20} 1.4755; d_4^{20} 1.1200.

Anal. Calcd. for C₇H₁₀O₂: C, 66.6; H, 8.0. Found: C, 66.7; H, 8.2.

The ammonium salt on acidification gave *trans*-cyclopentanol-2-acetic acid in 16% yield on I. Crystallized from benzene it melted at 52.3-54.3°. Hüchel and Gelmroth¹¹ gave m.p. 52.5-53.5° for this acid. The ethyl ester boiled at 107-108°/2.5 mm.; n_D^{20} 1.4595.

cis- β -(2-Hydroxycyclopentyl)ethanol (III). The *cis*-lactone (II), (430 g.), was reduced with lithium aluminum hydride (100 g.); the product worked up in the usual way gave 89% of the expected *cis*-diol (III) which boiled at 107-116°/0.4 mm.; n_D^{20} 1.4870; 396 g. It solidified on standing and crystallized from ether, had a constant melting point of 35.8-36.8° (Hüchel and Gelmroth,¹¹ m.p. 36°).

Ditosylate of cis- β -(2-hydroxycyclopentyl)ethanol (IV), was prepared by the usual method¹ which involved the slow addition (5 hr.) at 0° of the *cis*-diol (III), (350 g.) in redistilled pyridine (853 g.) to a solution of *p*-toluenesulfonyl chloride in the same solvent (853 g.). The product (808 g., 69%) melted at 113-114° dec. (plunging sample just below melting point otherwise decomposition occurs). A portion recrystallized below room temperature from ethanol melted at 113.5-114° (dec., plunge).

(23) J. F. Eykman, *Chem. Weekblad*, **6**, 699 (1909).

Anal. Calcd. for $C_{21}H_{26}S_2O_3$: C, 57.5; H, 6.0; S, 14.6. Found: C, 57.5; H, 6.0; S, 14.8.

Evaporation of the mother liquors from crystallization of the ditosylate from hot ethanol gave an oil, acid to litmus, which after washing well with alkali reacted with 50% of the quantity of bromine required to brominate the unsaturated monotosylate of III.

The aqueous mother liquors from the preparation of the ditosylate (IV) yielded an oil (54 g., 18% on the glycol) which boiled at 143–144°/760 mm.; n_D^{20} 1.4570. This was 2-oxabicyclo[3.3.0]octane for which Hückel and Gelmroth¹¹ give m.p. 144–145°/760 mm.

Anal. Calcd. for $C_7H_{12}O$: C, 75.0; H, 10.8. Found: C, 73.0; H, 10.3.

A freezing point determination indicated the presence of two crystalline modifications, m.p. -107° and -100° and although it appeared probable from the cooling curve that the sample was essentially one isomer no purity could be estimated.

trans-2-Thiabicyclo[3.3.0]octane (V). A solution of sodium sulfide nonahydrate (373 g.) in water (0.2 l.) and ethanol (5.6 l.) was stirred at 50° and the crude ditosylate (IV) (688 g.) was added portionwise to it concurrently with a solution of sodium sulfide nonahydrate (373 g. in water 0.2 l.) (4.6 hr.). Stirring at 50° was continued for a further 12 hr. after which the mixture was steam distilled. The steam-distillate was diluted with water (20 l.), treated with caustic soda (160 g.) and extracted with *n*-pentane; after removal of the solvent, distillation gave an oil (17 g., 8.5%) boiling below 44°/0.5 mm. which was mainly the required sulfide. The residue and that from steam distillation, on distillation gave the following fractions (1) b.p. 130–140°/0.8 mm.; 86 g.; (2) 140–230°/0.8 mm.; 16 g.; (3) 230–240°/0.8 mm.; 37 g., and a residue 12 g.

Anal. Calcd. for $C_{14}H_{22}S$: C, 75.6; H, 10.0; S, 14.4. Found: C, 73.5; H, 9.9; S, 15.1 for Fraction 1.

Anal. Calcd. for $C_{23}H_{36}S_3$: C, 70.2; H, 9.7; S, 20.1. Found: C, 70.9; H, 9.5; S, 19.5 for Fraction 3.

The crude *trans*-2-thiabicyclo[3.3.0]octane (V) was purified by crystallization of its mercuric chloride complex from ethanol, and the sulfide regenerated by adding the complex suspended in Carbitol,²⁴ to a refluxing solution of aqueous sodium sulfide nonahydrate solution (50% w./w. in water) and collecting the sulfide in an oil water separator. After thorough water washing and drying the sulfide distilled at 86.5°/20 mm.; m.p. -8° ; n_D^{20} 1.52845.

Anal. Calcd. for $C_7H_{12}S$: C, 65.6; H, 9.4; S, 25.0. Found: C, 65.6; H, 9.4; S, 25.0.

The sulfide proved to be susceptible to oxidation by air. Distillation of a sample which had been stored for several months in a glass-stoppered container in diffuse light gave, in addition to a distillate of the almost pure *trans*-sulfide, a residue (0.31 g.) which by titration contained 25% of sulfoxide, estimated as $C_7H_{12}OS$. This residue in ether was reduced with lithium aluminum hydride (0.15 g.), the product was separated into a neutral portion (0.23 g.) (mainly *trans*-sulfide) and an evil-smelling acidic portion which gave a positive doctor test reaction and infrared examination confirmed the presence of a hydroxyl grouping. There was insufficient of this material left for characterization.

Acknowledgement. The authors wish to thank the Chairman and Directors of The British Petroleum Company Limited for permission to publish these results and Mr. J. C. Stalley for the determination of the physical constants.

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(24) Carbide and Carbon Chemical Corp. trade name; Carbitol is the monoethyl ether of diethylene glycol.

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

Dehydrogenation of 1-Isopropylindan and 1-Isopropylhydrindan

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The dehydrogenation of the hydrocarbons in the title has afforded 2,2-dimethyltetralin, β -methylnaphthalene, and a $C_{20}H_{16}$ hydrocarbon of unknown constitution. The significance of these results with regard to the structure of α -amyrin is discussed.

Spring and his co-workers³ have recently proposed for the triterpene, α -amyrin, a new structure (I) that differs from the generally accepted one (II)⁴ by having an isopropyl group attached to the five-membered ring E. Among the reasons for preferring structure I, Spring has suggested⁵ that it

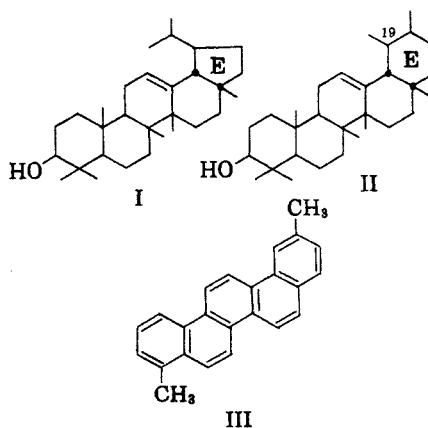
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(2) Alfred P. Sloan Predoctoral Fellow in Chemistry, 1956–1957.

(3) J. M. Beaton, F. S. Spring, R. Stevenson, and W. S. Strachan, *J. Chem. Soc.*, 2610 (1955).

(4) A. Meisels, O. Jeger, and L. Ruzicka, *Helv. Chim. Acta*, **32**, 1075 (1949); A. Meisels, R. Rügge, O. Jeger, and L. Ruzicka, *Helv. Chim. Acta*, **38**, 1298 (1955); A. Melera, D. Arigoni, A. Eschenmoser, O. Jeger, and L. Ruzicka, *Helv. Chim. Acta*, **39**, 441 (1956).

(5) F. S. Spring, private communication.



more satisfactorily explains the formation of 2,9-dimethylpicene (III) on selenium dehydrogenation