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HYDROGENOLYSIS OF TERPENES IN THE INJECTION PORT OF A GAS CHROMATOGRAPH

I. MONOTERPENES

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SUMMARY

BEROZA's techniques for the hydrogenolysis of minute amounts of organic compounds have been applied to representative monoterpenes using a 2% palladium on Chromosorb W catalyst in the gas–liquid chromatographic injection port. The acyclic systems studied gave the parent saturated hydrocarbon with the exception of primary alcohols where the major product resulted from the loss of $-CH_2OH$. Under the experimental conditions used cyclopropane rings were cleaved, four- and five-membered rings remained intact, and six-membered rings predominantly gave the corresponding aromatic product together with small amounts of the isomeric menthanes. The hydrogenolysis products were identified by mass and infrared spectrometry. KOVATS indices of the products were determined on Carbowax 20M and SF-96 (50) capillary columns.

INTRODUCTION

The techniques of "carbon skeleton" analysis of micro amounts of organic compounds by hydrogenolysis and hydrogenation reactions have been developed and studied extensively by BEROZA *et al.*[1–6]. BEROZA did not include terpenes in his systematic study, but an example of the application of these techniques to terpenes has been reported[7]. Further knowledge of the reactions of the various terpene systems under these conditions could be of help in the identification of individual terpenes. The present paper discusses the investigation of the hydrogenolysis of selected monoterpenes using a neutral palladium catalyst in the injection port of the gas–liquid chromatograph.

EXPERIMENTAL

Materials

Sabinene was isolated by gas–liquid chromatography (GLC) from Origanum

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oil[8]. The other terpenes were obtained from a variety of sources and were purified gas chromatographically, as necessary, before use. The sample of *cis*-carane was obtained by courtesy of R. TER HEIDE, N.V. Chemische Fabriek Naarden, The Netherlands. The 1,2-dimethyl-3-isopropylcyclopentane isomers and the 1,3-dimethyl-1-isopropylcyclopentane and tricyclene were synthesized by A. C. TAS and R. J. C. KLEIPOOL in our laboratory.

Catalyst

A "neutral-type" palladium catalyst (2% as the metal) on acid-washed Chromosorb W, 60–80 mesh, was prepared as follows. A 330-mg sample of palladium chloride was dissolved in 100 ml of 5% aqueous acetic acid by heating on a hot plate for about 1 h with occasional swirling by hand. The solution was cooled, 200 mg of anhydrous sodium carbonate were added, and the solution was evaporated to dryness in contact with 10 g of Chromosorb W in a rotary film evaporator. The catalyst preparation was then heated in an oven at 110° for 1 h.

Considerable difficulty was experienced in obtaining an effective catalyst; only about one preparation in three gave a catalyst that was sufficiently active for our purpose. No simple explanation of the difficulty could be determined.

For hydrogenolysis reactions approximately 0.5 g of the catalyst was packed into an injection port tube (12 × 0.5 cm) to give a catalyst column 10 cm in length. The catalyst was activated in the injection port with a hydrogen flow of 25 ml/min for ½ h at 150° and for 1–3 h at 280°. The GLC column was not attached to the exit end of the injection port and the oven of the gas–liquid chromatograph was kept open during the activation period. The activated catalyst was used until it showed an appreciable loss of hydrogenolysis ability, normally about ten days.

Gas chromatography equipment

A Model 5750 Hewlett-Packard gas chromatograph equipped with dual flame ionization detectors and a Carle thermistor detector was used. The chromatographic columns used were 10 ft. × ⅛ in. O.D. stainless-steel tubes packed with 5% Apiezon L on 60–80 mesh Chromosorb W, A. W., and two 500 ft. × 0.03 in. I.D. stainless-steel capillary columns coated with Carbowax 20M and SF-96 (50), respectively. The exterior ends of the injection ports were fitted with water-cooled jackets to keep the septums cooled during the high temperatures of the hydrogenolysis experiments.

Hydrogenolysis experiments

The 10-ft. Apiezon L column, attached to the thermistor detector and the exit end of the injection port tube packed with catalyst, was used in the hydrogenolysis studies. The injection port temperature was 275° in most of the experiments; other temperatures were applied only when the effect of the conditions on the hydrogenolysis reaction was studied. The column temperature was 90° and the detector temperature 180°. The carrier gas was hydrogen at 25 ml/min in all experiments. The compounds being studied were dissolved in *n*-pentane to facilitate handling and the pentane solutions were injected directly onto the head of the catalyst column using a 10-μl Hamilton syringe.

Reaction products were trapped either completely or as individual components for analysis using 12-in. melting point capillaries cooled in liquid nitrogen.

Determination of KOVÁTS *indices*

A mixture of the reaction products in pentane and a heptane solution of the appropriate *n*-hydrocarbons were injected on to the Carbowax 20M and SF-96 (50) capillary columns with nitrogen as the carrier gas at 8 ml/min; hydrogen and air flows of 40 and 500 ml/min, respectively. An auxillary nitrogen flow of 40 ml/min was added at the flame head to optimize detection sensitivity. Column temperatures were isothermal at 65° on the Carbowax 20M column and 100° on the SF-96 (50) column.

Spectral analyses

The mass spectra of the hydrogenolysis products were determined by combining gas–liquid chromatography (GLC) and mass spectrometry (MS) using a Varian Mat CH_5 mass spectrometer and membrane separator in combination with either the Carbowax 20M or the SF-96 (50) capillary column, depending on which column gave the optimum separation of the products.

Infrared spectra were run on a Perkin-Elmer Model 257 spectrophotometer with the sample dissolved in carbon tetrachloride in an ultra-micro cavity cell and with carbon tetrachloride in a variable path length cell in the reference beam.

RESULTS AND DISCUSSION

The results of the hydrogenolysis of selected monoterpenes and related compounds using 2% Pd catalyst on Chromosorb W in the GLC injection port are summarized in Table I and in Figs. 1–4. The products obtained were identified primarily by MS from the molecular weights indicated and from comparison with literature mass spectra or the spectra of compounds synthesized in our laboratories. KOVÁTS indices were also determined on two capillary columns and were used for confirmation of the identities of the products from the different terpenes. The approximate composition of the product mixture, as calculated from peak heights, is given to indicate the relative amounts of the products obtained in each case. It must be emphasized that these product compositions are dependent on the experimental conditions used and may vary depending on the catalyst temperature, the activity of the catalyst, and the length of the catalyst column. In almost every case additional minor peaks, not included in the table, were observed which could be the result of trace impurities in the starting terpenes, thermal rearrangements, or further catalytic fragmentations[1]. Although no attempt was made to establish any quantitative relationship between the amounts of the products and the starting material, in most cases no starting material was left unreacted if the amount of material injected was kept quite small (0.3 μl or less). When somewhat larger amounts of material were injected in order to be able to trap the products for analysis, unreacted starting material was usually observed with runs on 1,8-cineole, α-thujone and α-terpineol in particular. *p*-Cymene and *cis*-carane gave unreacted starting material under all conditions.

Acyclic monoterpenes

The results of the hydrogenolysis of three acyclic monoterpenes are given in Table I and Fig. 1. These results are completely consistent with the observations of BEROZA[1–3] and BRODERICK[7]. Myrcene and the secondary alcohol, linalool, gave only

TABLE I

HYDROGENOLYSIS OF MONOTERPENES

Terpenes	*Hydrogenolysis products*				
	Identity of product	*Product (%)*[a]	*Type of evidence*		
			Kovats index[b]		*Spectra*
			SF 96 (50)	*Carbowax 20M*	
Acyclic					
Myrcene	2,6-dimethyloctane	99	938	922	MS, IR
Linalool	2,6-dimethyloctane	98	939	922	MS
Citronellol	2,6-dimethylheptane	89	834	825	MS
	2,6-dimethyloctane	10	938	923	MS
Monocyclic					
Terpinolene	*trans*-*p*-menthane	30	981	1022	MS
	cis-*p*-menthane	10	995	1045	MS
	p-cymene	55	1018	1260	MS
p-Cymene	*trans*-*p*-menthane	6	980	1022	MS
	cis-*p*-menthane	2	994	1046	MS
	p-cymene (unreacted)	92	1016	1260	MS
α-Terpineol	*trans*-*p*-menthane	21	981	1022	MS
	cis-*p*-menthane	7	995	1045	MS
	p-cymene	64	1018	1261	MS
1,8-Cineole	*trans*-*p*-menthane	6	981	1022	MS
	cis-*p*-menthane	2	995	1045	MS
	p-cymene	90	1018	1260	MS
Bicyclic					
α-Pinene	*trans*-pinane	40	973	1049	MS
	cis-pinane	55	983	1061	MS
β-Pinene	*trans*-pinane	35	973	1049	MS
	cis-pinane	57	983	1061	MS
Camphene	*trans*-isocamphane	35	975	1056	MS
	cis-isocamphane	62	980	1065	MS
3-Carene	1,1,4-trimethylcycloheptane	98	972	1020	MS, IR
cis-Carane	1,1,4-trimethylcycloheptane	25	972	1021	MS
	trans-*p*-menthane	3	981	1021	—
	cis-carane (unreacted)	26	986	1064	MS
	cis-*p*-menthane	2	994	1045	—
	m-cymene	19	1011	1261	MS
	p-cymene	20	1016	1261	MS
Sabinene	1-*trans*-3-dimethyl-1-isopropylcyclopentane	99	945	976	MS[d]
α-Thujone[c]	1-*trans*-2-dimethyl-*cis*-3-isopropylcyclopentane	66	933	953	MS[d]
	1-*trans*-3-dimethyl-1-isopropylcyclopentane	14	944	977	MS[d]
	1-*trans*-2-dimethyl-*trans*-3-isopropylcyclopentane	2	949	—	MS[d]
	1-*cis*-2-dimethyl-*trans*-3-isopropylcyclopentane	10	960	997	MS[d]
	1-*cis*-2-dimethyl-*cis*-3-isopropylcyclopentane	2	974	1015	—
Tricyclic					
Tricyclene	camphane	56	953	1021	MS
	trans-isocamphane	25	975	1056	MS
	cis-isocamphane	17	981	1066	MS

[a] Product percentages were approximated by measuring peak heights.

[b] Temperatures were 65° and 100° for Carbowax 20M and SF-96 (50) columns, respectively.

[c] The indicated configurations of the 1,2-dimethyl-3-isopropylcyclopentane isomers obtained by hydrogenolysis of α-thujone are based on the results of SISIDO *et al.*[17].

[d] These spectra were identical with those of the synthesized products.

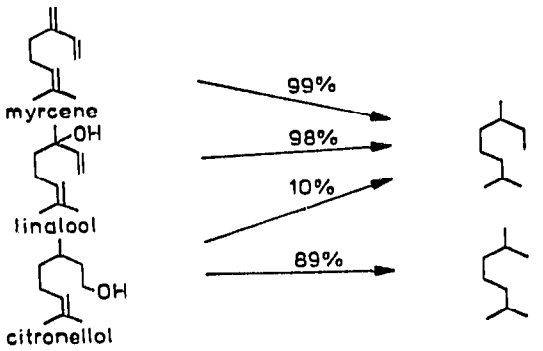

Fig. 1. Hydrogenolysis of acyclic monoterpenes.

the parent hydrocarbon. The primary alcohol, citronellol, gave a small amount of the parent hydrocarbon but the main product (89%) was the hydrocarbon resulting from the loss of the $-CH_2OH$ group. The large amount of cleavage observed in this case was expected at the relatively high temperature (275°) used for the hydrogenolysis reactor.

Monocyclic monoterpenes

The monocyclic monoterpenes studied—terpinolene, *p*-cymene, *α*-terpineol, and 1,8-cineole—each gave a mixture of the *cis*- and *trans*-*p*-menthanes and *p*-cymene as reaction products (Table I and Fig. 2). The relative amounts of cycloaliphatic and aromatic products obtained were dependent on the starting material and also on the hydrogenolysis temperature. An increase in temperature favours the formation of the aromatic product, as was observed by BEROZA AND SARMIENTO[3] on similar systems. It is interesting to note that the ratio of *trans*- to *cis*-*p*-menthane in each case was approximately 3:1. The identification and assignment of configurations to the two *p*-menthanes was based on the mass spectra[9] and the order of appearance of the two peaks[10] on the various columns used. The KOVÁTS indices of each of the three main products obtained from the monocyclic terpenes were essentially identical on the two analytical columns used. *α*-Terpineol, in particular, gave a number of trace products from the hydrogenolysis reaction. Evidence from mass spectra indicated the presence of *p*-menthenes[9] and fragmentation products such as cumene among these trace products.

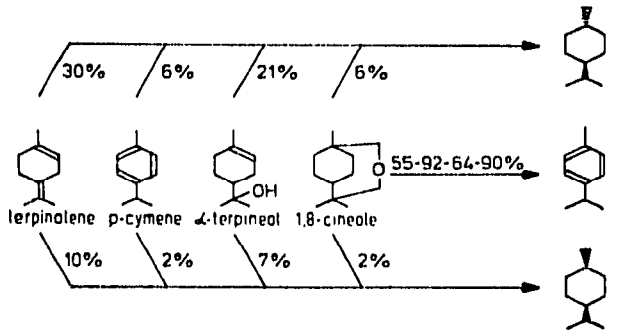

Fig. 2. Hydrogenolysis of monocyclic monoterpenes.

Bicyclic monoterpenes

The results of the hydrogenolysis of the bicyclic monoterpenes are presented in Table I and Fig. 3. Both α- and β-pinene predominantly gave a mixture of *cis*- and *trans*-pinanes as products, with the *cis* isomer in a slightly larger amount in each case under the conditions used. The assignment of the *trans* configuration to the peak emerging first from the GLC columns is consistent with previous observations[10,11] of the order of appearance of the two isomers on GLC columns. An increase in catalyst temperature increased the relative amount of the first peak, which is in agreement with the observation of COCKER *et al.*[11,12] that the proportion of *trans*-pinane increases with increasing temperature. Steric considerations[11,12] also indicated that the *cis* isomer should predominate. COCKER *et al.*[11] observed that under their conditions of catalytic hydrogenation β-pinene almost immediately isomerized to α-pinene with retention of configuration; no double bond isomerization took place when α-pinene was hydrogenated under the same conditions. The isomerization of β-pinene to α-pinene was also observed in our study. Under less than optimum conditions for hydrogenation (large injections, old catalyst) small amounts of α-pinene were detected in the products from hydrogenolysis of β-pinene but no unreacted β-pinene remained. The KOVATS indices and mass spectra were identical for the respective products from

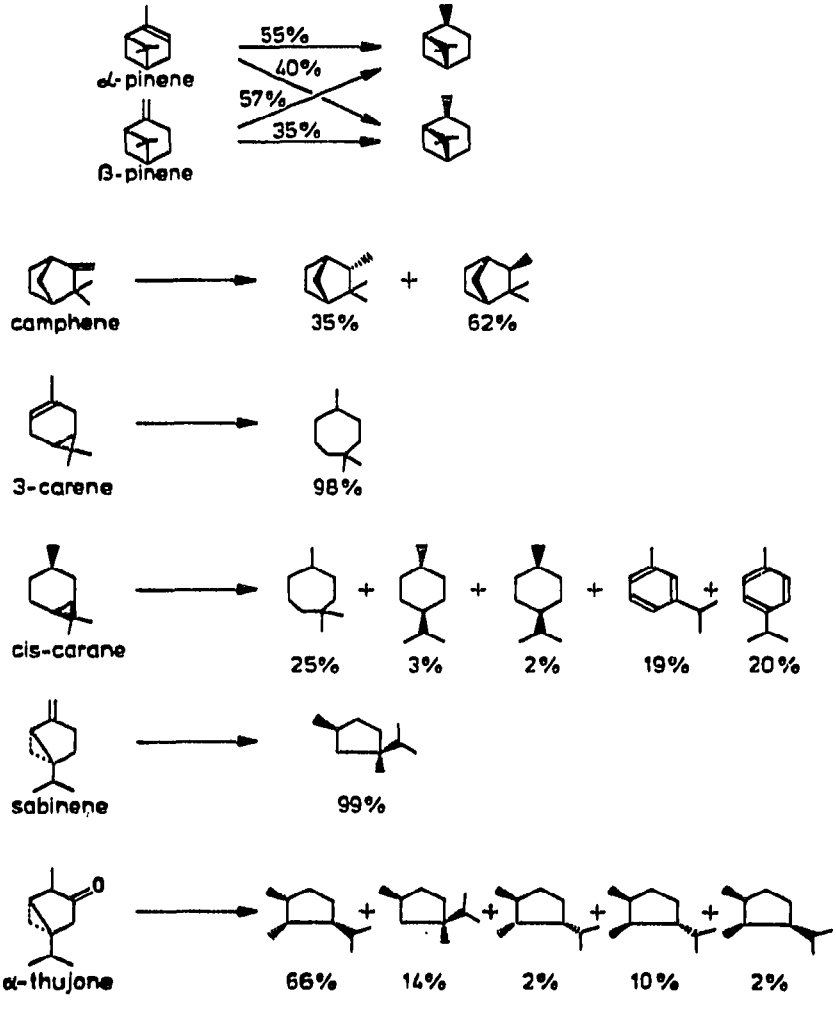

Fig. 3. Hydrogenolysis of bicyclic monoterpenes.

the hydrogenolysis of α- and β-pinene. The mass spectra of the *cis*- and *trans*-pinanes were very similar, with the main difference being in the relative ratios of the peaks at *m/e* 81, 82, and 83.

The reaction of camphene gives two products[13], which were shown by MS to result from simple hydrogenation of the double bond. The mass spectra are quite similar to, but not identical with, the mass spectra of THOMAS AND WILHALM[14] for the *cis*- and *trans*-isocamphanes. The relative retention times and steric considerations (which indicate a strong preferential formation of the *cis* isomer) are also consistent with the assignment of the *trans* and *cis* configurations of the two isocamphanes, as indicated in Table I.

The hydrogenolysis of 3-carene gives almost exclusively 1,1,4-trimethylcycloheptane, undoubtedly formed by isomerization to 2-carene, followed by 1,4 addition of hydrogen to the α,β-unsaturated cyclopropane system with cleavage of the internal cyclopropane ring bond, and further reduction to the cycloheptane derivative, as observed by COCKER *et al.*[11,12,15]. *cis*-Carane was shown not to be an intermediate by COCKER *et al.*[11,12] since it was unchanged under their hydrogenation conditions, which quantitatively converted 3-carene to 1,1,4-trimethylcycloheptane. When we injected *cis*-carane we observed that, under the more vigorous conditions (higher temperature) of our hydrogenolysis experiments, about 75% of the material was converted to other products, involving cleavage of each of the cyclopropane ring bonds in roughly equal amounts. Cleavage of the internal cyclopropane ring bond again gave 1,1,4-trimethylcycloheptane while cleavage of the external cyclopropane ring bonds predominantly gave the corresponding *p*- and *m*-cymenes. Small amounts of the *cis*- and *trans*-*p*-menthanes were identified by their KOVATS indices but the corresponding *m*-menthanes were not detected. Again, as was discussed above for the monocyclic terpenes investigated, under the experimental conditions used aromatic compounds rather than cyclohexane derivatives are formed whenever a six-membered carbon ring is involved. The results with *cis*-carane further support the 1,4 addition mechanism[11,12], after prior isomerization to 2-carene, as being the mode of reaction of 3-carene under our hydrogenolysis conditions.

Sabinene gives a single product, 1-*trans*-3-dimethyl-1-isopropylcyclopentane, formed by a 1,4 addition of hydrogen to the α,β-unsaturated cyclopropane system with opening of an external cyclopropane ring bond and further reduction of the cyclopentene derivative formed[16]. The product from hydrogenolysis of sabinene had mass spectra and KOVATS indices identical to those of the synthetic product. α-Thujone, which has the same carbon skeleton as sabinene without the double bond conjugated with the cyclopropane ring, was also subjected to hydrogenolysis under the same conditions. BEROZA AND ACREE[4] have observed that simple ketones predominantly give the parent hydrocarbon with small amounts of products resulting from cleavage on either side of the carbonyl group. No products resulting from cleavage adjacent to the carbonyl group of α-thujone were identified in our study but they could have been present in trace amounts. The major products were all dimethylisopropylcyclopentane isomers formed by cleavage of the external cyclopropane ring bonds. In contrast to the results with sabinene, the major product from α-thujone was 1-*trans*-2-dimethyl-*cis*-3-isopropylcyclopentane (66%) while 1-*trans*-3-dimethyl-1-isopropylcyclopentane, the product obtained exclusively from sabinene, comprised only 14% of the product mixture. Synthesis of the 1,2-dimethyl-3-isopropylcyclopen-

tane isomers proceeded through a mixture of 1,2-dimethyl-3-isopropylcyclopentenes which, when hydrogenated under our experimental conditions, gave a mixture of the four isomeric 1,2-dimethyl-3-isopropylcyclopentanes essentially identical in composition to that obtained by SISIDO *et al.*[17] from hydrogenation of 1-methyl-2-methylene-3-isopropylcyclopentane over a palladium catalyst. The assignment of configurations to the isomers from α-thujone, as listed in Table I and Fig. 3, is based on the comparison of our results with those of SISIDO *et al*[17]. The mass spectra and KOVÁTS indices of the four isomeric 1,2-dimethyl-3-isopropylcyclopentanes obtained from the hydrogenolysis of α-thujone and from synthesis were identical for the corresponding compounds in each case. The mass spectra for all the *cis* isomers indicated contamination with a trace of olefin in each case. No evidence was observed for the presence of the *p*-menthanes or *p*-cymene which would result from cleavage of the internal cyclopropane ring bond of α-thujone.

Tricyclic monoterpenes

Hydrogenolysis of tricyclene (see Fig. 4) gave a mixture of products consisting principally of camphane (56%) along with relatively large amounts of the *cis*- and *trans*-isocamphanes (17% and 25%). Identification was based on the mass spectra[14]

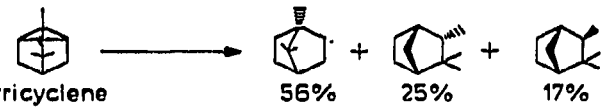

Fig. 4. Hydrogenolysis of tricyclene.

and comparison of the KOVÁTS indices of the isocamphanes with the values obtained for the products from the reduction of camphene. ZELINSKY AND LEVINA[18] have reported the formation of camphane from catalytic reduction of tricyclene. Reduction of camphene under our hydrogenolysis conditions gave a mixture of isocamphanes which favoured the *cis* (*exo*) isomer almost 2:1, consistent with steric considerations which suggest a preferential approach of the camphene to the catalyst surface with the bridge oriented away from the catalyst surface. In the hydrogenolysis of tricyclene, the *trans*-isocamphene is formed in slightly larger amounts than the *cis* isomer. If the hydrogenolysis of tricyclene proceeds by a simple *cis* addition of hydrogen across the carbon–carbon bonds of the cyclopropane ring, then the only products expected would be camphane and *trans*-isocamphane. The formation of the isocamphanes must therefore proceed by a mechanism which permits isomerization about the centre in question during the hydrogenolysis process, with formation of the less hindered *trans* (*endo*) isomer being somewhat favoured.

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