SYNTHESIS, STEREOCHEMISTRY AND ISOMERIC TRANSFORMATIONS OF 6,7-DIMETHYLBICYCLO[3.2.1]OCTANE*

I. A. MATVEYEVA, I. M. SOKOLOVA, T. I. PEKHK and AL. A. PETROV

Institute of Geology and Mining of Mineral Fuels

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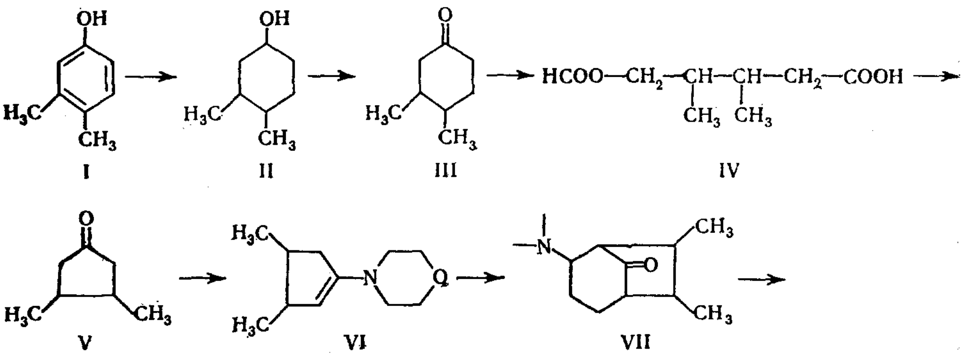
WE HAVE examined [1, 2] the synthesis, stereochemistry and mechanism of catalytic transformations in the presence of aluminium bromide of dimethylbicyclo[3.2.1]octanes of different types of substitution, namely: with two substituents in the six-membered ring, with substituents in the six-membered ring and in the top part of the bridge and with substituents in various rings.

Continuing the investigations of di-substituted bicyclo[3.2.1]octanes on the same level two further types of substitution were examined which had not been studied previously: with two methyl groups in the cyclopentane ring and with substitution in the top part of the bridge and in the cyclopentane ring.

This study is concerned with the synthesis and thermodynamic and kinetic parameters of the reactivity of bicyclo[3.2.1]octane with two methyl groups in the cyclopentane ring, i.e. 6,7-dimethylbicyclo[3.2.1]octane, which had not been described previously in the literature.

To explain general features and solve requisite problems of stereochemistry and the isomerization mechanism of dimethylbicyclo[3.2.1]octanes, it was interesting to synthesize repeatedly 6-methylbicyclo[3.2.1]octane previously described [1, 3, 4]; rates of isomerization of this preparation are not given in the literature.

6,7-Dimethylbicyclo[3.2.1]octane was synthesized by the following system:



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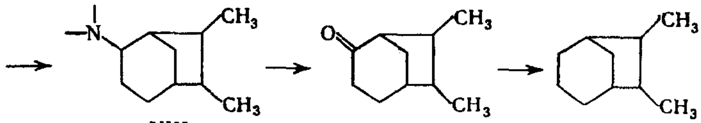


VIII IX X

3,4-Dimethylcyclopentanone (*V*) was obtained by hydrogenation of 3,4-xylenol (I) under hydrogen pressure in the presence of Raney Ni at a temperature of 150°, followed by oxidation of 3,4-dimethylcyclohexanol (II) (b.p. 182–189°, n_D^{20} 1·4588) with chromic anhydride [5]. Dimethylcyclohexanone (III) thus obtained (b.p. 187°, n_D^{20} 1·4496, yield 75%) was oxidized with nitric acid [6] and the dimethyladipic acid formed (m.p. 116–116·5°; yield 45%) was cyclized by a method previously described [7]. The yield of 3,4-dimethylcyclopentanone (V) was 40%; b.p. 65–70/13 mm, n_D^{24} 1·4345.

1-N-Morpholine-3,4-dimethylcyclopent-1-ene (*VI*). A mixture of 0·45 mole ketone (V), 0·6 mole morpholine and 0·5 g *p*-toluenesulphoacid in toluene (100 ml) was heated at the boiling point of the reaction mass to separate a theoretical amount of water in a Dyne–Stark trap. Toluene was distilled, the residue redistilled and a fraction taken of b.p. 105–110/3 mm, n_D^{30} 1·4935; yield 71%.

TABLE 1. EQUILIBRIUM CONCENTRATION AND RELATIVE RETENTION TIMES OF 6,7-DIMETHYLBICYCLO [3.2.1] OCTANE GEOMERS

Temperature 230°C; PT/brick

Stereoisomers	Equilibrium concentration, % wt.		Relative retention time
	theoretical	experimental	
endo, exo	88	85	178*
endo, endo	2	4	188
exo, exo	10	11	222

* The retention time of 1,5-dimehtylbicyclo[3.2.1]octane was assumed to be 100.

2-N-Morpholine-6,7-dimethylbicyclo[3.2.1]octan-8-one (*VII*). 0·32 mole acrolein was added to a solution of 0·32 mole (VI) in 250 ml benzene cooled to 0–5°C. The solution was agitated at the same temperature for an hour and then the mixture heated to boiling point in 3 hr. During vacuum distillation a fraction of b.p. 160–170/3 mm, n_D^{20} 1·5020 was taken; yield was 64%.

2-N-Morpholine-6,7-dimethylbicyclo[3.2.1]octane (*VIII*). A keto-group of compound VII was reduced by the Kizhner–Wolf method and a fraction taken of b.p. 114–126°/3 mm. Yield (VIII) was 46%; n_D^{20} 1·4985.

6,7-Dimethylbicyclo[3.2.1]octan-2-one (*IX*). A mixture of 0·09 mole (VIII), 173 g (0·86 mole) mercury acetate and 450 ml 10% acetic acid solution was heated for 3 hr at 120°. 76 ml concentrated HCl was then added to the reaction mixture and the ketone formed was distilled with steam. Ketone yield was 67%; b.p. 89°/3 mm, n_D^{20} 1·4800.

6,7-Dimethylbicyclo[3.2.1]octane (*X*). Hydrocarbon was obtained by the reduction of ketone IX according to Kizhner–Wolf. The yield of hydrocarbon purified with 93% H_2SO_4 and chromatographic separation on silica gel was 56% of theory; b.p. 173–173·5° (745 mm), n_D^{20} 1·4685.

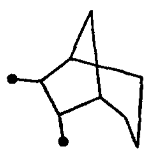
Analysis by GLC (stationary phase-squalane, copper column 60 m, 85°, carrier gas—hydrogen) shows that the hydrocarbon X obtained is represented by isomers in a 2 : 98 ratio in the order of elution.

6-Methylbicyclo[3.2.1] octane was obtained by a similar method from 3-methylcyclopentanone. A layout of synthesis and characteristics of intermediate products are given in a separate study [1]. The yield of hydrocarbon 40%, b.p. 158–160°, n_D^{20} 1·4690. Analysis by GLC on adding bicyclic C_9 hydrocarbons to a standard equilibrium mixture [8] shows that the hydrocarbon obtained is represented by exo, endo-isomers in a 96 : 4 ratio.

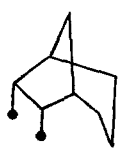
RESULTS

To determine the three-dimensional orientation of substituents in 6,7-dimethylbicyclo[3.2.1]octane isomers

exo exo



exo endo



endo endo

a method was used [1] involving the comparison of calculated and experimental equilibrium concentrations of 6,7-dimethylbicyclo[3.2.1]octane isomers. Results and relative retention times of 6,7-dimethylbicyclo[3.2.1]octanes are given in Table 1.

TABLE 2. EXPERIMENTAL AND CALCULATED CHEMICAL SHIFTS OF ^{13}C NUCLEI FOR 6,7-DIMETHYLBICYCLO [3.2.1] OCTANE GEOMERS
Internal standard—TMS

Hydrocarbon	Chemical shifts, p.p.m.									
	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(7)}$	$C_{(8)}$	6-CH_3	7-CH_3
6,7-exo, exo										
exper.	45·4	42·8	20·1	32·8	45·4	39·2	39·2	34·4	17·2	17·2
calculation	44·0	33·4	19·6	33·4	44·0	39·0	39·0	33·7	17·2	17·2
6·7-endo, exo										
exper.	46·6	27·2	13·4	19·9	38·5	41·0	43·4	32·7	17·1	22·4
calculation	43·0	31·0	15·6	22·0	40·0	43·0	46·0	35·0	16·0	22·7

* Calculation was made using results for hydrocarbons of the bicyclo[3.2.1]octane series given in a previous study [9].

Satisfactory confirmation of the accuracy of assigning isomers was obtained by a study of 6,7-dimethylbicyclo[3.2.1]octanes by ^{13}C NMR.

This method was used to describe the exo, exo-isomer and the exo endo-isomer obtained by liquid-phase isomerization of the latter (Pt/C, 300°, 25 atm). Results (Table 2), as well as information concerning the three-dimensional orientation of substituents suggest that the cyclohexane ring in 6,7-exo, endo and 6,7-endo, endo-isomers is in the 'bath' conformation. This conclusion, although confirms our previous assumption about the bath-shaped conformation of the cyclohexane ring in dimethylsubstituted bicyclo[3.2.1] octanes with an endo-substituent in the cyclopentane ring [2] cannot, however, be regarded final since chemical shifts for endo-6-methylbicyclo[3.2.1]octane have not been determined up to the present time.

TABLE 3. COMPOSITION OF PRODUCTS AND RELATIVE RATE CONSTANTS OF ISOMERIC TRANSFORMATIONS OF 6,7-DIMETHYLBICYCLO [3.2.1] OCTANES
Temperature 20°C; $AlBr_3$

Initial hydrocarbon	Degree of transformation, %		Composition of products of isomerization, % wt.			k_{rel}
	standard ethylcyclopentane	hydrocarbon	1,4-dimethylbicyclo-[3.2.1]octane: endo-1,4	1,4-dimethylbicyclo-[3.2.1]octane: exo-1,4	1,3-dimethylbicyclo[2.2.1] octane	
6,7-exo, exo	27	2	30	20	25	5±1
6,7-endo, exo	20	4	45	20	36	16±3

A study was made by selective isomerization [1, 2] of 6-methyl- and 6,7-dimethylbicyclo[3.2.1]octanes to observe the mechanism of isomeric transformations and evaluate the reactivity of hydrocarbons with substitution in the cyclopentane ring.

Products of isomerization were identified either by adding individual hydrocarbons to the isomerizates, or by the addition of standard mixture of C_9 and C_{10} hydrocarbons.

Exo, exo- and endo, exo-isomers of 6,7-dimethylbicyclo[3.2.1]octane were used for isomerization, the first being the product of synthesis (98%) and the second (89% exo, endo; 11% exo, exo) being obtained by liquid-phase isomerization in an autoclave of exo, exo-6,7-dimethylbicyclo[3.2.1]octane.

Tables 3 and 4 show compositions of products of isomerization of hydrocarbons in the initial stage of transformation.

When examining results of isomerization of 6,7-dimethylbicyclo[3.2.1 octane] first of all the general composition of isomerizates and secondly, the relatively low rates of transformation should be noted. The composition of isomerizates is similar to hydrocarbon isomerizates of this series of another type of substitution [1, 2]. This once more confirms the unique mechanism of regrouping for all dimethylbicyclo[3.2.1]octanes taking place via an intermediate state—a carbonium ion—which is mutual for the structure of bicyclo[3.2.1]-octane and bicyclo[2.2.2]octane with subsequent redistribution of methyl groups dictated by most favourable steric and thermodynamic factors.

TABLE 4. COMPOSITION OF PRODUCTS AND RELATIVE RATE CONSTANTS OF ISOMERIC TRANSFORMATIONS OF 6-METHYLBICYCLO [3.2.1] OCTANE
Temperature 20°C; $AlBr_3$

Initial hydrocarbon	Degree of transformation, %		Composition of product of isomerization, % wt.				k_{rel}
	standard	hydrocarbon	methylbicyclo [3.3.1] octane	methylbicyclo [3.3.0]octane		2-methylbicyclo [2.2.2] octane	
			exo-3	exo-2	exo-3		
6-exo	86	4	17	11	36	36	10±3
6-endo	34	70	—	—	—	100	300±15

As far as rates of isomerization are concerned, this low rate of transformation is only typical of a given type of substitution. Judging by the existence of unfavourable interactions in this structure (*cis*-vicinal interaction of methyl groups in an exo,exo-isomer and methyl groups with bonds of the cyclohexane ring in an endo, exo-isomer), this structure is very unstable. However, the thermodynamic factor is not, apparently, here of decisive significance. A comparison of results with those of isomerization of endo- and exo-6-methylbicyclo[3.2.1]octane (Table 4) indicates that the addition of even one substituent into the cyclopentane ring hinders ionization of hydrocarbon and probably slows down the stage of 1,3-hydride transfer and thus re-grouping. This fact is especially interesting as in the endo, exo-isomer the cyclohexane ring is in the 'bath' conformation.

SUMMARY

1. 6,7-Dimethylbicyclo[3.2.1]octane was synthesized, which had not been described previously in the literature.

2. Ratios of geomers and their steric structure were determined by configuratioin isomerization.

3. K netics and mechanism of isomerization of 6,7-dimethylbicyclo[3.2.1]-octane were investigated in the presence of aluminium bromide. Low rates of conversion due to steric hindrances of ionization are a distinctive feature of isomerization of dimethylbicyclo[3.2.1]octanes.

REFERENCES

1. I. A. MATVEYEVA, I. M. SOKOLOVA and Al. A. PETROV, Neftekhimiya 15, 9, 1975
2. I. A. MATVEYEVA, I. M. SOKOLOVA, T. I. PEKHK and Al. A. PETROV, Neftekhimiya 15, 17, 1975

3. V. N. **IPATIEFF**, J. E. **GERMAIN**, W. W. **THOMPSON** and H. **PINES**, J. Organ. Chem. 17, 272, 1962
4. Ye. M. **MIL'VITSKAYA**, A. F. **PLATE** and A. V. **TARAKANOVA**, Zh. organ. khimii 3, 515, 1967
5. N. S. **BROWN** and C. P. **GARG**, J. Amer. Chem. Soc. 83, 2953, 1961
6. N. D. **ZELINSKII** and N. V. **YELAGINA**, Dokl. AN SSSR 49, 591, 1945
7. Sintezy orhanicheskikh preparatov (Syntheses of Organic Preparations), Edited by B. A. **KAZANSKII**, 1. Izd. inostr. lit., 518, 1949
8. N. A. **BELIKOVA**, A. A. **BOBYLEVA** and A. F. **PLATE**, Zh. organ. khimii 4, 424, 1968
9. T. I. **PEKHK**, E. **LIIPMAA**, A. F. **PLATE**, N. A. **BELIKOVA** and A. A. **BOBYLEVA**, XI Evrop. kongr. po molekulyarnoi spektroskopii (XI European Congress on Molecular Spectroscopy). Tallin, 1973
10. Al. A. **PETROV**, Khimiya naftenov (Chemistry of Naphthenes). Nauka, Moscow, 1971

SYNTHESIS OF *p*-XYLENE BY HYDRO-CRACKING OF DITOLYLMETHANE*

N. K. Moshchinskaya, L. Ye. Tertychko, L. N. Artem'eva and M. D. Shapiro

Dnepropetrovsk Chemico-Technological Institute

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The high heat stability of many hydrocarbons of the diarylmethane series is well known and this enables some of them to be recommended as high temperature heat-transfer agents [1–3].

Destructive hydrogenation (hydro-cracking) resulting in the separation at the bond of C_{arom}–C_{aliph} to form aromatic hydrocarbons and dehydrocyclization to form polycyclic aromatic hydrocarbons are typical of these hydrocarbons.

By destructive hydrogenation of diphenylmethane and its nearest polymer-homologues under hydrogen pressure in the presence of catalysts [4, 5] benzene and toluene were obtained with high yields, while on carrying out the reaction without pressure, *p*-benzyltoluene and anthracene [6] were also obtained

$$C_6H_5CH_2C_6H_5 + H_2 \rightarrow C_6H_6 + C_6H_5CH_3 \quad (1)$$

$$C_6H_5CH_2C_6H_4CH_2C_6H_5 \ (o, n) \xrightarrow{H_2} \begin{cases} C_6H_5CH_2C_6H_5 + C_6H_5CH_3 & (2) \\ C_6H_5CH_2C_6H_4CH_3 + C_6H_6 & (3) \end{cases}$$

* Neftekhimiya 15, No. 5, 682–686, 1975.