Petrol. Chem. U.S.S.R. Vol. 24, No. 4, pp. 223–228, 1984
Printed in Poland

0031-6458/84 $10.00+.00


# SYNTHESIS OF NORADAMANTANE BY ISOMERIZATION OF BREXANE OR BRENDANE IN THE PRESENCE OF ACIDIC CATALYSTS*

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(*Received* 25 *November* 1983)

ACHIEVEMENTS in petroleum chemistry during the past decades were marked by the discovery of bi- and tricyclic hydrocarbons containing five and six-membered rings [1]. Accordingly it is of interest to synthesize and study the properties of tricyclic hydrocarbons. Noradamantane, brendane, brexane and twist-brendane are known to be the most stable of the possible structures for $C_9H_{14}$, containing cyclopentane and cyclohexane rings under the least strain. Any study of the chemistry of these compounds until recently has been hindered as their synthesis is difficult and due to the scarcity of starting compounds [2–4].

The possibility of synthesizing compounds of brexane and brendane series using available 4,9,7,8-tetrahydroindene (I), (adduct of cyclopentadiene and butadiene, by-product of industrial production of vinylnorbornene), has been discussed [5, 6].

Considering synthetic routes to noradamantane by isomerization of brexane in the presence of $AlCl_3$ [7], and the possibility of mutual transitions of tricyclic hydrocarbons and differences in their stress energies, calculated by Schleyer and Ellinger [8] (Table 1), has inspired a study of their isomeric transformations in the presence of acidic catalysts.

This paper describes the behaviour of brexane (II) and brendane (III) in the presence of concentrated sulphuric acid and 5% aluminium bromide solution in n-hexane in liquid phase at room temperature.

Hydrocarbons (II) and (III) were synthesized on the basis of *exo*- and *endo*-brexanol-5 formates or acetates and *exo*-brendan-2-ol acetate [5, 6], proceeding

TABLE 1. STRESS ENERGIES OF TRICYCLIC HYDROCARBONS $C_9H_{14}$ (kJ/MOLE), ACCORDING TO CALCULATED DATA [8]

| Hydrocarbon | Schleyer's data | Ellinger's data |
|---|---|---|
| Twist-brendane (tricyclo[4,3,0,$0^{3,8}$]nonane) | 143·17 | 128·64 |
| Brexane (II) (tricyclo[4,3,0,$0^{3,7}$]nonane) | 106·73 | 106·72 |
| Brendane (III) (tricyclo[4,2,1,$0^{3,7}$]nonane] | 94·57 | 101·65 |
| Noradamantane (IV) tricyclo[3,3,1,$0^{3,7}$]nonane) | 84·09 | 79·95 |

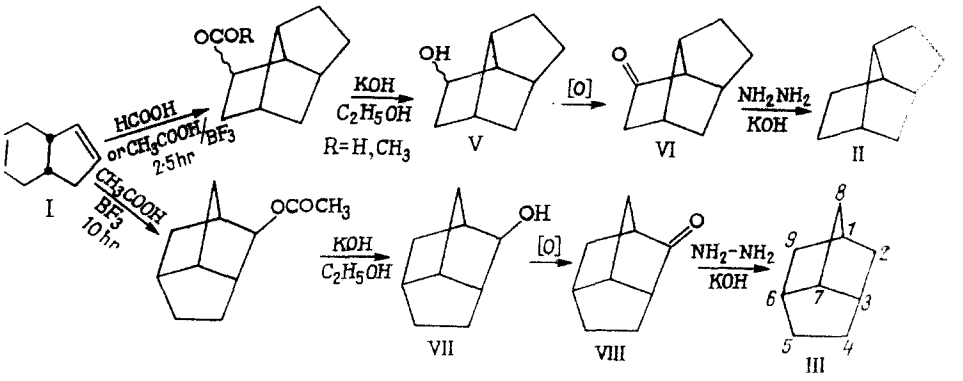
* Neftekhimiya **24**, No. 6, 773–778, 1984.

TABLE 2. PHYSICO-CHEMICAL CONSTANTS, RELATIVE RETENTION TIMES AND $^{13}C$ NMR SPECTRA OF HYDROCARBONS OBTAINED

| Hydrocarbon | B.p., °C: 133 × 10² Pa | $n_D^{20}$ or m.p., °C | Retention time in relation to n-hexane | | Chemical shifts of $^{13}C$ NMR (p.p.m. towards a weak field from TMS) |
|---|---|---|---|---|---|
| | | | 130°C squalane | 60°C PEG | |
| Brexane (II) | 89–90 | 1·4848<br>1·4845/2/* | 3·43 | 3·46 | Given in a former paper [6] |
| Brendane (III) | 93–94 | 92–93<br>(98–99/2/* | 3·65 | 3·73 | 32·5 ($C_4$, $C_5$), 36·1 ($C_1$), 39·4 ($C_3$, $C_6$), 40·3 ($C_8$), 41·3 ($C_2$, $C_9$), 48·4 ($C_7$) |
| Noradamantane (IV) | – | 201–202<br>203–204* | 3·94 | 4·12 | 35·8 ($C_9$), 36·9 ($C_1$, $C_5$), 37·7 ($C_3$, $C_7$), 44·3 ($C_2$, $C_4$, $C_6$, $C_8$) |

* Results of a former study [7].

from diene (I) by the following scheme:




Tricyclic esters separated from products of interaction of diene (I) with organic acids, were converted into corresponding alcohols (V, VII), which were then oxidized into ketones (VI, VIII) and reduced by the Kishner–Huang–Minlon method.

Physico-chemical constants of the hydrocarbons obtained agreed with data in the literature [2, 6, 7].

Isomeric conversions of brexane and brendane were examined in a static system with intensive mixing in n-hexane solution. In each experiment a control preparation (ethylcyclopentane) was added to the hydrocarbon examined, the rate of isomerization of which was 100. The hydrocarbon, catalyst and control preparation were taken in molar ratios of 1 : 2 : 0·2 and 1 : 5 : 0·2. The relative rate constant of isomerization of the hydrocarbon examined, which was represented as the ratio of rate constants of isomerization of hydrocarbons examined ($k_1$) and standard ($k_2$)

hydrocarbon, was calculated from the formula

$$k_{rel}=\frac{k_1}{k_2}\cdot 100$$

Rate constants of isomerization of hydrocarbons examined and standard hydrocarbons was calculated from a 1st order equation.

This method of determining relative rate constants of isomerization is widely applicable [1] since it enables us to avoid errors due to variation of the isomerization activity of catalysts in individual experiments.

Figure 1*a* shows a typical form of the dependence of reaction mixture composition on time for one of the experiments of isomerization of brexane and Fig. 1*b* shows that of isomerization of brendane. Figure 2 shows the diagrammatic determination of rate constants of isomerization.

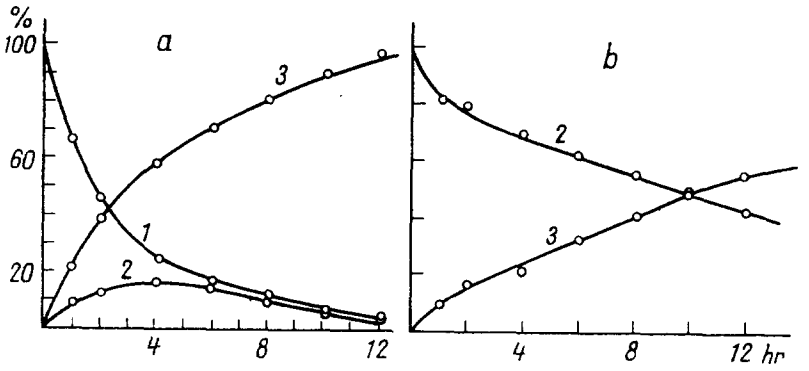



FIG. 1. Curves showing the use of brexane (*a*), brendane (*b*) and the formation of products of isomerization at room temperature in the presence of 99·5% $H_2SO_4$. Molar ratios of reagents 1 : 5 (*a*) and 1 : 2 (*b*): *1* – brexane; *2* – brendane; *3* – noradamantane.

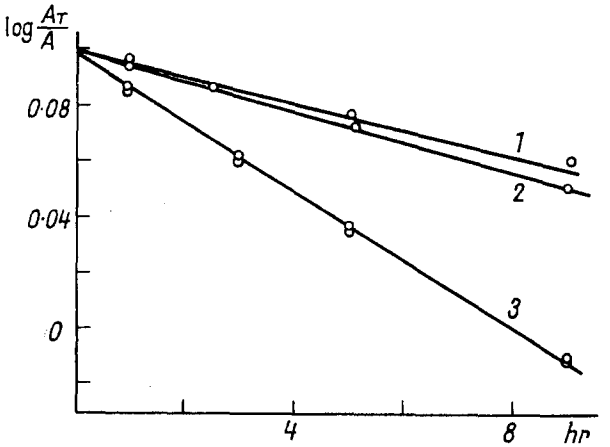



FIG. 2. Diagrammatic determination of rate constants of isomerization of the hydrocarbons examined: *1* – brexane; *2* – brendane; *3* – ethylcyclopentane.

A study of the composition of products of isomerization of brexane shows that in the presence of 99·5% sulphuric acid or a 5% solution of aluminium bromide in n-hexane they are brendane and noradamantane. Increasing the duration of experiments enables noradamantane to be obtained as product of isomerization, which contains a maximum of 2 to 3% brendane. Increasing the molar proportion of the catalyst only reduces the time of transformation.

The presence of a maximum on the curve showing the formation of brendane during isomerization of brexane proves that brexane is isomerized to noradamantane via the intermediate formation of brendane. The maximum concentration of brendane in products of isomerization of brexane is not higher than 12 to 15%.

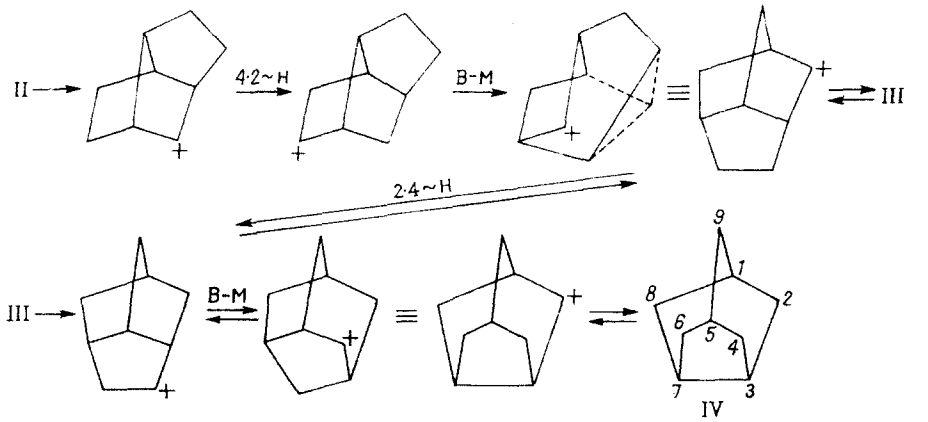
The direction of the reaction is practically independent of the catalyst used.

Study of isomerization of brendane shows that noradamantane is the only product of conversion. However, brendane cannot be converted completely, even with prolonged contact time since 2 to 3% brendane remains in the reaction mixture. Physico-chemical constants and spectra of hydrocarbons are given in Table 2.

Therefore, the only direction of brexane and brendane conversions in the presence of acidic catalysts, is the formation of noradamantane, which is most stable thermodynamically (according to calculation, Table 1).

The relative rate constant of isomerization of brexane was 28, and that of brendane – 32, i.e. transformations of both hydrocarbons take place at a commensurate rate. Products of isomerization, independent of the initial hydrocarbon, have the same final composition and consist basically of noradamantane.

Similar values of relative rate constants of isomerization of brexane and brendane enable some conclusions to be drawn about the mechanism of the structural regrouping taking place. It may be assumed that isomerization of brexane and brendane and then noradamantane in the presence of acid catalysts is effected by a carbonium-ion mechanism with hydride displacements and Wagner–Meerwein regrouping. The most likely primary point of attack of the catalyst upon these hydrocarbons is, apparently, the secondary carbon atom set between two tertiary carbon atoms, since this results in the formation of a more reactive secondary carbonium ion [1].



Hydride transfer [1], at a much lower rate than the Wagner–Meerwein regrouping, is the stage which, apparently, limits the rate of carbonium-ion regrouping.

## EXPERIMENTAL

The purity of the starting materials was controlled and reaction mixtures analysed by GLC using "Tsvet-1", "Khrom-5" and LCM-8-MD chromatographs with a flame-ionization detector and capillary columns of 50 m × 0·25 mm with PEG-6000, Apiezone-*L* and squalane as stationary phase.

$^{13}C$ NMR spectra were measured using a WH-90 device at a frequency of 22·6 MHz with storage and Fourier transform of the signal using a mini-computer (BNC-12). $CDCl_3$ was used as solvent. Symmetry of spectra, determining the classification of individual lines into CH- and CH-groups and chemical shift values measured show full agreement with the structure of tricyclic hydrocarbons obtained.

*Exo- and endo-brexanol-5 acetates* [6]. Diene I, 139 g and n-hexane, 150 ml were heated at 85°C with $CH_3COOH$, 150 g containing 3% $BF_3$ for 2·5 hr. After conventional treatment, extraction and drying, the ester was recovered and distillation gave the acetate mixture [70 g, 38%, b.p. 100°–130°C, $2 \times 10^3$ Pa, $n_D^{20}$ 1·4832] containing as impurities unreacted diene and indane. The last named were separated by distillation using a column (20 t.p.). The separating of a mixture of unsaturated bi- and saturated tricyclic acetates requires the difference in boiling points of these components to be increased. Accordingly acetate mixture 114·6 g in $CCl_4$ 345 ml, at 0°C, was treated with $Br_2$ 20·8 ml. Excess bromine was washed out and distillation gave *exo-* and *endo*-acetates of brexanol-5 (14·9 g, 13%, b.p. 108°–112°C/1·3 × × $10^3$ Pa, $n_D^{20}$ 1·4840, without bromination).

*Exo- and endo-brexanol-5 formates* [6] were obtained by heating diene I (69·7 g) with 98·5% HCOOH (225 g) at 96°C for 7 hr. After treatment and distillation the formate mixture [45·9 g, 48%, b.p. 109°–120°C/12 mm, $n_D^{20}$ 1·4890] was obtained. After the separation of bicyclo[4.3.0]nonenols by bromination *exo-* and *endo*-formates of brexanol-5 [9·1 g, b.p. 92°–94°C/1·3 × $10^3$ Pa, $n_D^{20}$ 1·4824] were obtained.

*exo- and endo-Brexanols-5* (*V*), were obtained by saponification of acetates or formates using an alcoholic solution of alkali. Yield 85%, b. p. 102°–108°C/1·3 × × $10^3$ Pa, $n_D^{20}$ 1·4974.

*Brexanone-5* (*VI*) was obtained by oxidation of alcohols V, 5·5 g, with $Na_2Cr_2O_7$, 6·8 g, in concentrated $H_2SO_4$, 0·7 ml and $H_2O$, 50 ml. Yield 4 g (74%), b.p. 97°–100°C/1·3 × $10^3$ Pa, $n_D^{20}$ 1·4985.

*Brexane* (*II*) was obtained by boiling ketone VI, 11 g with 85% hydrazine hydrate, 50 ml and KOH, 20 g in diethyleneglycol, 56 ml. After treatment brexane (II), (6·1 g, 62%) was separated. The hydrocarbon was purified chromatographically on silica gel.

*Exo-brendanol-2 acetate* [6]. Diene I, 139 g was heated at 110°C for 10 hr with $CH_3COOH$, 195 g containing 3% $BF_3$. Ester yield was 16·8 g (9%), b.p. 108°–113°C/ /1·6 × $10^3$ Pa, $n_D^{20}$ 1·4850. To remove impurities of bicyclic acetates, the ester mixture

was brominated. After treatment and distillation *exo*-brendanol-2 acetate, [11·0 g, b.p. 102°–103°C/1·3 × $10^3$ Pa, $n_D^{20}$ 1·4840] was obtained.

*exo-Brendanol-2* (*VII*), was obtained by saponification of acetate, 20·3 g, with an alcoholic solution of KOH. [Yield was 12·8 g (82%), b.p. 97°–99°C/1·3 × $10^3$ Pa, m.p. 130°C, after volatilization].

*Brendanone-2* (*VIII*). Alcohol VII, 12·8 g, was oxidized $Na_2Cr_2O_7$, 9·8 g, with $H_2SO_4$. After treatment ketone VIII, [10·8 g, 85% b.p. 81–83°C/8 × $10^2$ Pa] separated, it crystallized on standing and melted at 115°C (after volatilization).

*Brendane* (*III*) came from heating ketone VIII, 5·7 g, with hydrazine hydrate, 28·5 g, and KOH, 10·4 g, in diethylene glycol. The hydrocarbon, (4 g, yield 72%) was separated and purified chromatographically using $SiO_2$ and hexane.

*Hydrocarbons were isomerized* at room temperature, using the appropiate hydrocarbon (0·2 g) and 99·5% sulphuric acid [0·15 ml (1 : 2, mole) or 0·4 ml (1 : 5, mole)], n-hexane, 2 ml and ethylcyclopentane, 0·03 g. Alternatively reaction with $AlBr_3$ [17 ml (1 :2) or 30 ml (1 : 5) 5%], in n-hexane was used with hydrocarbon, 0·2 g and 0·03 control solution. Catalyst samples were taken after identical periods of time, washed with water, diluted with hexane, dried over anhydrous $CaCl_2$ and analysed by GLC.

## SUMMARY

Noradamantane was synthesized from tetrahydro-indene. Brexane and brendane and mixtures of these hydrocarbons were isomerized.

Isomerization of brexane to noradamantane proceeds via the intermediate formation of brendane.

Relative rate constants of isomerization of brexane and brendane are 28 and 32, respectively (ethylcyclopentane – 100).

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