

Iodination of Tricyclo[4.1.0.0^{2,7}]heptane in the Presence of External Nucleophiles*

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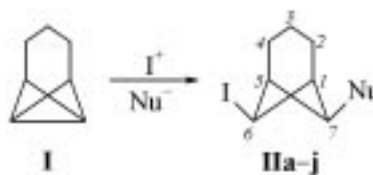
Abstract—Tricyclo[4.1.0.0^{2,7}]heptane reacted with iodine, N-iodosuccinimide, and iodine monochloride in the presence of external nucleophiles yielding products of conjugate *endo,syn* addition at the central C¹–C⁷ bond. The mechanism of these chemo- and stereoselective reactions is discussed.

Among the most interesting reactions of tricyclo[4.1.0.0^{2,7}]heptane (**I**) its reaction with iodine resulting in *endo,syn*-6,7-diiodobicyclo[3.3.1]heptane (**IIa**) [1] should be mentioned. Two reaction features call for attention: chemoselectivity (addition exclusively to the central C¹–C⁷ bond) and strict stereospecificity: *cis*-addition with reversal of configuration of both carbon atoms of the central bond. Yet the most addition reactions with hydrocarbon **I** occur nonselectively, either at the side bond C¹–C², or at the central C¹–C⁷ bond, as a rule nonselectively [2–5]. In studies carried out with application of the ESR spectroscopy [6, 7] with the use of 2,4,6-tribromonitrosobenzene as a spin trap in the reaction under discussion, and in the reaction of iodine with [1.1.1]propellane (**III**) a formation of paramagnetic intermediates was revealed that supported the previously assumed hypothesis [8] on the radical mechanism of addition to compound **III**. These results allowed extension of the hypothesis on the radical reaction mechanism to compound **I**. This assumption is well consistent with observed chemoselectivity of hydrocarbon **I** iodination since this feature is characteristic of all the known radical addition reactions to this hydrocarbon [3]. However in contrast to the reaction under discussion the other radical additions to compound **I** are not stereoselective: form *endo,syn* and *endo,anti* adducts with the latter prevailing [9]. An important evidence for alternative ionic mechanism of tricycloheptane **I** iodination were results of an experiment carried out in dissertation of J. Morf [10] performed under the guidance of Professor G. Szeimies: in the presence of external nucleophiles (bromide and chloride ions)

they entered into adducts, and alongside iodide **IIa** formed the products of conjugate addition **IIb** and **IIc**.**

Similar reasoning was used in [11, 12] to assume ionic mechanism with respect to iodination of propellane (**III**).

In this study we carried out a supplementary research on elemental iodine addition to hydrocarbon **I** in the presence of external nucleophiles with considerably wider range of these substances as compared with [10]. We also performed iodination reactions using as sources of electrophilic iodine N-iodosuccinimide (NIS) and iodine monochloride. In the most cases the reactions were carried out in DMF for it sufficiently well solved and activated by specific solvation the mineral salts used as a source of an external anionoid nucleophile. We should note at once, that virtually in all reactions performed in this solvent a formation of formate **IIc** as a side product was observed. Such involvement of DMF as a mild O-nucleophile into the conjugate addition in reactions of halofunctionalization of alkenes was reported



Nu = I (**a**), Br (**b**), Cl (**c**), O₂CH (**d**), SCN (**e**), N₃ (**f**), O₂CMe (**g**), O₂CPh (**h**), OMe (**i**), OH (**j**).

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Table 1. Reaction conditions and yield of products from reactions of hydrocarbon **I** with iodinating reagents in the presence of external nucleophiles

Reaction no.	Reagents "I ⁺ " + "Nu ⁻ "	Solvent	"I ⁺ " / "Nu ⁻ " (mol)	Reaction products (composition, %)	Yield of the main reaction product, %
1	I ₂ +KI	DMF	1: 5	IIa (91), IIc (1), (8) ^a	IIa (65)
2	I ₂ +LiBr	DMF	1: 10	IIa (9), IIb (90), IIc (1)	IIb (74)
3		MeOH	1: 5	IIa (18), IIb (82)	IIb (31)
4	I ₂ +Et ₃ BnNCl	CCl ₄	1: 3	IIa (35), IIc (65)	IIc (11)
5	I ₂ +KSCN	DMF	1: 10	IIa (40), IIc (12), IIe (48)	IIe (42)
6	I ₂ +NaN ₃	DMF	1: 5	IIa (44), IIc (4), IIf (52)	IIf (20)
7	NIS+LiBr	DMF	1: 10	IIb (97), IIc (3)	IIb (40)
8	NIS+NaN ₃	DMF	1: 5	IIa (13), IIc (14), IIf (68), (5) ^a	IIf (22)
9	NIS+AcOH ^b	CH ₂ Cl ₂	1: 5	IIg (90), (10) ^a	IIg (56)
10	NIS+PhCO ₂ H ^b	CH ₂ Cl ₂	1: 5	IIh (>85)	IIh (30)
11	NIS+DMF	DMF	1: 39	IIa (12), IIc (84), (4) ^a	IIc (67)
12	NIS+HCO ₂ Na ^a	DMF	1: 10	IIa (49), IIc (50), (1) ^a	IIc (34)
13	NIS+MeOH	MeOH	1: 74	IIi (82), (18) ^a	IIi (48)
14	NIS+H ₂ O ^b	Acetone	1: 56	IIj (14), IV (65), V (21)	IIj (9), IV+V (40)
15	ICl+LiCl	DMF	1: 10	IIc (86), II (4), (10) ^a	IIc (46)
16	NIS+PhSO ₂ Na	DMF	1: 2	VIIa (28), VIIa (72)	VIIa+VIIa (47)
17	NIS+ <i>p</i> -MeC ₆ H ₄ SO ₂ H ^b	CH ₂ Cl ₂	1: 2	VIIb (46), VIIb (54)	VIIb+VIIb (32)

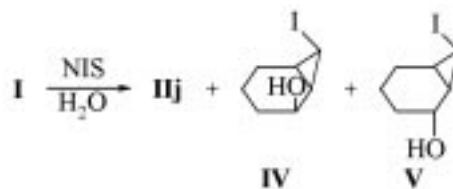
^a Unidentified impurities. ^b With addition of equimolar amount of triethylamine, see EXPERIMENTAL.

formerly in [13]. The data on composition of products obtained in reactions (1–15) of compound **I** initiated by electrophilic iodine in the presence of external nucleophile are presented in Table 1.

In reactions (2, 4–6) with elemental iodine in DMF in the presence of lithium bromide, potassium thiocyanate, or sodium azide, and also in CCl₄ in the presence of triethylbenzylammonium chloride (Et₃BzNCl) compounds **IIb**, **c**, **e**, **f** resulting from conjugate were obtained addition as main products. A similar result (formation of a mixed haloderivative **IIb**) was observed also in reaction (3) of compound **I** with I₂ in methanol in the presence of lithium bromide, but methanol did not participate in the conjugate addition.

The fraction of products of conjugate addition arising in reactions with NIS in the presence of sodium azide or lithium bromide in DMF (reactions 7, 8) was a little larger than in mixture treated with I₂. With NIS were also prepared acetate **IIg** and benzoate **IIh** by carrying out the reaction in dichloromethane in the presence of excess corresponding acids and triethylamine (reactions 9, 10). Formate **IIc** is the main product of reaction between hydrocarbon **I** and NIS in DMF (reaction 11). The yield of compound **IIc** did not grow on addition to the reaction mixture of sodium formate (reaction 12). Appearance

of diiodide **IIa** as an impurity in products of reactions with NIS (8, 11, 12) is apparently due to the partial reduction of the latter to I₂ either by solvent (DMF) or anionoid nucleophile. The reaction between hydrocarbon **I** and NIS in methanol (reaction 13) resulted in iodomethoxylation product **IIi** that failed to form in reaction with elemental iodine (reaction 3). In reaction (14) with NIS in aqueous acetone in the presence of triethylamine was revealed a formation of norpinane iodohydrin **IIj**, but the main products of this reaction were two stereoisomers **IV** and **V** resulting from iodohydroxylation of compound **I** at the side bond C¹–C².



The use as iodinating agent of iodine monochloride with lithium chloride as additive in DMF (reaction 15) both increased the fraction of the product of conjugate addition **IIc** in the reaction mixture and considerably increased its yield as compared to reaction (4).

Table 2. Constants and elemental analyses of bicycloheptanes **IIa–j**, **VIa, b**, **VIIa, b**

Compd no.	Compound name	mp, °C (solvent or crystallization), or bp, °C (mm Hg)	R_f	GLC analysis		Found, %		Formula	Calcd., %	
				Column temp., °C	R_t , min	C	H		C	H
IIa	<i>endo</i> -6- <i>syn</i> -7-Diiodobicyclo[3.1.1]heptane	120–121 (hexane) ^a	0.68	150	12.3	24.51	3.03	C ₇ H ₁₀ I ₂	24.16	2.90
IIb	<i>syn</i> -7-Bromo- <i>endo</i> -6-iodobicyclo[3.1.1]heptane	62–64 ^b (hexane)	0.77	150	7.1	28.03	3.52	C ₇ H ₁₀ BrI	27.94	3.35
IIc	<i>endo</i> -6-Iodo- <i>syn</i> -7-chlorobicyclo[3.1.1]heptane	24–25 ^c (hexane)	0.78	150	4.7	32.65	4.03	C ₇ H ₁₀ ClI	32.78	3.93
II d	<i>endo</i> -6-Iodo- <i>syn</i> -7-formoxybicyclo[3.1.1]heptane	48–49 (2)	0.70	150	7.4	35.89	4.13	C ₈ H ₁₁ IO ₂	36.11	4.17
II e	<i>endo</i> -6-Iodo- <i>syn</i> -7-thiocyanobicyclo[3.1.1]heptane	60–61 (ether)	0.38	150	4.2	34.33	3.56	C ₈ H ₁₀ INS	34.42	3.61
II f	<i>syn</i> -7-Azido- <i>endo</i> -6-iodobicyclo[3.1.1]heptane	66–68 (20)	0.68	150	6.0	32.10	3.91	C ₇ H ₁₀ IN ₃	31.96	3.83
II g	<i>syn</i> -7-Acetoxy- <i>endo</i> -6-iodobicyclo[3.1.1]heptane	Oily substance	0.58	150	8.0	38.66	4.82	C ₉ H ₁₃ IO ₂	38.59	4.68
II h	<i>syn</i> -7-Benzoyloxy- <i>endo</i> -6-iodobicyclo[3.1.1]heptane	83–84 (ether)	0.69	–	–	49.21	4.47	C ₁₄ H ₁₅ IO ₂	49.14	4.42
II i	<i>endo</i> -7-iodo- <i>syn</i> -7-methoxybicyclo[3.1.1]heptane	Oily substance	0.60	130	8.1	38.32	5.29	C ₈ H ₁₃ IO	38.12	5.20
II j	<i>syn</i> -7-Hydroxy- <i>endo</i> -6-iodobicyclo[3.1.1]heptane	81–82 (ether)	0.27	140	15.0	35.48	4.74	C ₇ H ₁₁ IO	35.32	4.66
VI a	<i>endo</i> -6-iodo- <i>syn</i> -7-phenylsulfonylbicyclo[3.1.1]heptane	127–128 (hexane–chloroform)	0.37	220 ^d	10.5	43.02	4.12	C ₁₃ H ₁₅ IO ₂ S	43.10	4.17
VI b	<i>endo</i> -6-iodo- <i>syn</i> -7- <i>n</i> -tolylsulfonylbicyclo[3.1.1]heptane	167–168 (hexane–chloroform) ^e	0.27	220 ^d	14.7	44.45	4.65	C ₁₄ H ₁₇ IO ₂ S	44.69	4.55
VII a	<i>exo</i> -6-iodo- <i>syn</i> -7-phenylsulfonylbicyclo[3.1.1]heptane	142–143 (hexane–chloroform)	0.48	220 ^d	6.0	43.09	4.24	C ₁₃ H ₁₅ IO ₂ S	43.10	4.17
VII b	<i>exo</i> -6-iodo- <i>syn</i> -7- <i>n</i> -tolylsulfonylbicyclo[3.1.1]heptane	147–148 (hexane–chloroform) ^e	0.33	220 ^d	9.6	44.55	4.36	C ₁₄ H ₁₇ IO ₂ S	44.69	4.55

^a mp 120–121°C (from methanol) [1]. ^b bp 72–80°C (0.1 mm Hg) [10]. ^c bp 40–50°C (0.1 mm Hg) [10]. ^d Column 1.5 m long. ^e In agreement with published data [9].

Table 3. ^1H NMR spectra of bicycloheptanes **IIa–j**, **VIa**, **VIIa**, δ , ppm

Compd. no.	H ⁶	H ⁷	H ^{1,5}	H _{eq} ^{2,4}	H _{ax} ^{2,4}	H ³	Other signals
IIa	4.53 t		2.74 ^a	2.08–2.23		1.60–1.75	–
IIb	4.45 t	4.35 t ^b	2.80	2.12–2.36	1.85–2.12	1.52–1.80	–
IIc	4.35 t	4.30 t ^b	2.79	2.15–2.35	1.90–2.10	1.50–1.77	–
IId	4.26 t	4.96 t	2.86	2.00–2.15	1.85–2.00	1.49–1.73	8.12 s (CH=O)
IIe	4.51 t	4.07 t	2.85	1.95–2.23	1.70–1.95	1.42–1.90	–
IIf	4.32 t	4.05 t	2.74	2.05–2.25	1.76–2.00	1.51–1.75	–
IIg	4.25 t	4.83 t	2.82	1.95–2.15	1.82–1.95	1.47–1.61	2.10 s (Me)
IIh	4.35 t	5.12 t	2.96	2.08–2.25	1.90–2.05	1.56–1.80	7.5 t, 7.6 t, 8.1 d
IIi	4.20 t	3.71 t	2.75	1.98–2.15	1.76–1.95	1.54–1.72	3.37 s (OMe)
IIj	4.19 t	4.17 t	2.67	2.05–2.25	1.82–1.98	1.45–1.77	2.18 s (OH)
VIa	4.38 t	3.45 t	2.75	2.33–2.60	1.62–2.03		7.40–7.52 (3H), 7.74–7.86 (2H)
VIIa	4.01 s	4.14 t	2.73	2.44–2.64	1.65–2.13		7.43–7.62 (3H), 7.76–7.85 (2H)

^aAll signals of H^{1,5} are narrow multiplets. ^bAssignment of signals of H⁶ and H⁷ for compounds **IIb** and **IIc** may be interchanged.

Table 4. ^{13}C NMR spectra of bicycloheptanes **IIa–j**, **VIa**, **VIIa**, δ , ppm

Compd. no.	C ⁶	C ⁷	C ^{1,5}	C ^{2,4}	C ³	Other signals
IIa	18.9		47.0	28.8	9.9	–
IIb	22.4	42.2	47.0	26.8	10.7	–
IIc	24.0	51.0	46.9	25.4	11.0	–
IId	25.8	66.1	44.8	25.2	11.9	160.0 (C=O)
IIe	25.7	42.9	45.1	25.1	10.9	111.50 (SCN)
IIf	28.8	55.2	45.0	25.1	11.6	–
IIg	26.7	66.2	44.7	25.3	12.1	20.7 (Me), 170.1 (C=O)
IIh	26.6	66.6	45.0	25.5	12.2	128.4, 129.5, 129.7, 131.1 (C arom), 165.5 (C=O)
IIi	28.2	72.9	44.8	25.0	12.5	56.4 (OMe)
IIj	26.9	65.0	46.4	24.4	12.0	–
VIa	28.1	58.7	44.8	24.0	11.9	127.2, 129.2, 133.5, 139.9 (C arom)
VIIa	24.7	60.5	49.0	24.6	13.0	127.2, 129.2, 133.4, 140.0 (C arom)

It should be noted that the yield of diiodide **IIa** in reaction (1) of tricycloheptane **I** with elemental iodine significantly increased in the presence of external nucleophile as compared to the reaction carried out without this additive. This fact is in agreement with conclusion made in [10]. It was also established that in the absence of external nucleophiles reaction between hydrocarbon **I** and iodine monochloride or NIS in CH_2Cl_2 (cf. [14]) did not provide the corresponding addition products and yielded only unidentified polymeric substances.

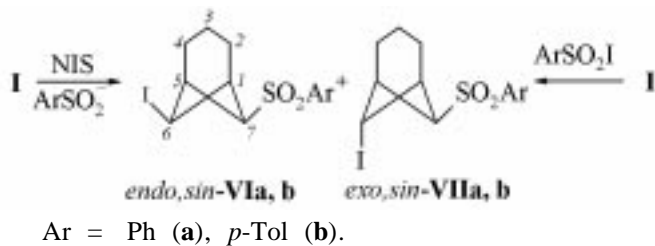
Norpinane adducts **IIa–j** were isolated as individual compounds by flash-chromatography followed by crystallization or distillation. The constants and

elemental analyses of the compounds are given in Table 2. Diiodide **IIa** and iodohalides **IIb** and **IIc** were identified by comparison of their constants and spectral characteristics with the published data [1, 10, 15]. The norpinane structure and configuration of compounds **IIa–j** is reliably established from the analysis of their ^1H and ^{13}C NMR spectra that are consistent with those of norpinanes **IIa–c** (see Table 3; also cf. [16]).

The structure of norcarane *endo,endo*-adduct **IV** was established from the expected similarity of its ^1H and ^{13}C NMR spectra with those of a known bromo analog [17]. The structure of compound **V** was ascribed to the third product of reaction (14) detected

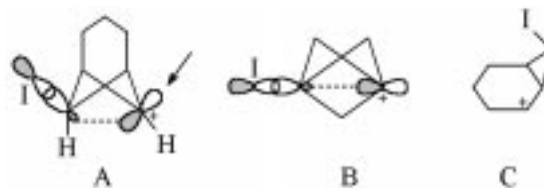
by GLC but not isolated individually by analogy to the results of reaction between hydrocarbon **I** and *N*-bromosuccinimide in water-acetone mixture [17], and proceeding from the ¹H NMR spectrum of a mixture of compounds **IV** and **V**. In the spectrum appeared a multiplet signal at 3.90 ppm characteristic of H² proton of *endo,endo*-adduct **V** (cf. with spectral data for its bromo analog [17]).

Thus the reaction of hydrocarbon **I** with sources of electrophilic iodine (I₂, NIS, ICl) in the presence of external nucleophiles proceeds as conjugate *endo,syn*-addition to the central C¹-C⁷ bond, i.e. it is characterized by the same chemo- and stereoselectivity as the standard reaction of compound **I** with elemental iodine. Our additional experimental data (compared to [10]) on the products of conjugate addition seem to support the conclusion of this study (also see [4]) on the ionic mechanism of the reaction in question. Yet the fact proper of formation of the conjugate addition products is not an unambiguous proof of this mechanism. Actually published data exist describing the possibility of NuI formation by preliminary reaction of the electrophilic iodine with the external nucleophile, and these compounds may further react with substrate by radical mechanism. For instance, this concept was applied to conjugate addition mechanism in reaction of elemental iodine with alkenes in the presence of NaN₃ and ArSO₂Na (with participation of IN₃ and ArSO₂I formed in situ) [18, 19]. Just this case occurred in our experiment when hydrocarbon **I** reacted with NIS in the presence as external nucleophiles of sodium benzenesulfinate or *p*-toluenesulfonic acid (with triethylamine added) (reactions 16 and 17). Here in contrast to previously considered reactions (1-15) alongside the corresponding *endo,syn*-adduct **VIa, b** formed its stereoisomer *exo,syn*-adduct **VIIa, b** in commensurable quantity. The formation of compound **VII** can be understood only from the viewpoint of radical mechanism as was confirmed with a direct experiment: a reaction of hydrocarbon **I** with ArSO₂I (see also [9]).



Thus for reactions (16, 17) we assume radical mechanism of conjugate addition, yet in the other cases we favor the ionic mechanism, and the key

reason thereto is the fact of strict *endo,syn*-selectivity of addition characteristic of reactions (1-15). To rationalize this stereochemistry of addition a non-classical carbocation A originating from an attack of electrophilic iodine on the nonbonding orbital of the nodal carbon atom in the central C¹-C⁷ bond should be assumed as an intermediate of the ionic reaction (cf. [4, 5]). The nucleophilic attack on the C⁷ atom of this cation should be strictly stereodirected and should proceed with reversal of the configuration.



The higher stability of cation A compared with analogous carbocation generated by electrophilic attack of a proton on the same substrate is due as we believe to the presence of a iodine atom in the *endo*-position 6. The cation arising from attack of a proton is known [20] to suffer a fast isomerization into more stable 2-norcaranyl cation. The stabilization of cation A by iodine atom is due to homohyperconjugation effect as has been previously presumed [21] for a related cation B, an intermediate in propellane **III** iodination (see also [22]).

A specific behavior of hydrocarbon **I** in reaction with NIS in an aqueous acetone (reaction 14) as compared with the other reactions (1-13) may be also rationalized within the framework of the ionic mechanism: primarily formed carbocation A in the medium of high dielectric permittivity suffers stereodirectional isomerization into carbocation C (2-norcaranyl one), see [5], that is a precursor of norcaranes **IV** and **V**.

EXPERIMENTAL

¹H and ¹³C NMR spectra were registered on spectrometer Bruker AC-300 at operating frequencies 300.130 and 75.469 MHz respectively from solutions in CDCl₃. The spectra of norpinanes **IIa-j**, **VIa**, and **VIIa** are presented in Tables 3 and 4. GLC analyses were carried out on chromatograph Chrom-4 equipped with flame-ionization detector, glass column 3500 × 3 mm, stationary phase 3% OV-17 on Inerton N-Super (0.125-0.160 mm), carrier gas nitrogen, flow rate 40 ml min⁻¹. Analytical TLC was performed on Silufol UV-254 plates, eluent hexane-ether, 1:1, development in iodine vapor. Flash-chromato-

graphy was performed on silica gel L 40/100 μ , eluent light petroleum ether–ethyl ether, 3:1.

Tricycloheptane (**I**), bp 109–110°C was synthesized as described before [23]; its purity according to GLC (30°C) attained ~97%. Benzenesulfonyl iodide and *N*-iodosuccinimide were prepared by known procedures [24, 25].

Reaction of hydrocarbon I with iodinating reagents (I₂, NIS, ICl) in DMF in the presence of external nucleophiles. General procedure. To a mixture of 0.1 mol of an appropriate salt (KI, LiBr, LiCl, KSCN, NaN₃, HCOONa or PhSO₂Na [26], see Table 1), in 35 ml of DMF, and 0.01 mol of hydrocarbon **I** in 5 ml of the same solvent at cooling with ice bath was added dropwise under argon atmosphere within 30 min 0.01 mol of iodinating reagent in 20 ml of DMF. The reaction mixture was stirred at cooling for 1.5 h, and then for 1.5–2 h more at 20°C. Then it was diluted with water, reaction products were extracted with ether (3–30 ml), extract was treated with 5% water solution of Na₂SO₃ till disappearance of iodine color, washed with water, and dried with sodium sulfate. The solvent was removed in a vacuum, and the semicrystalline mixture obtained was analyzed by GLC and ¹H NMR. The compositions of the reaction mixtures are listed in Table 1. The main reaction products were isolated by flash-chromatography and/or fractional crystallization. The constants of bicycloheptanes **IIa–f**, **VIa, b**, **VIIa, b** are given in Table 2.

Reaction of hydrocarbon I with NIS in DMF. The reaction of 10 mmol of tricyclohexane **I** with 10 mmol NIS in DMF was performed as described above in the general procedure save with no anionoid nucleophile. The composition of the reaction mixture and yield of compound **IIc** isolated by vacuum distillation are reported in Table 1.

Reaction of hydrocarbon I with elemental iodine in CCl₄ in the presence of Et₃BzNCl. To a solution of 0.94 g of compound **I** in 40 ml of anhydrous CCl₄ was added 6.53 g of Et₃BzNCl, and at stirring under nitrogen atmosphere was added dropwise while cooling to 0°C a solution of 2.54 g of I₂ in 20 ml of CCl₄. The mixture was stirred for 0.5 h more at cooling and for 1 h at 20°C, then it was diluted with water. The organic layer was separated, and from the water layer the products were extracted into CCl₄ (3 × 10 ml). The combined organic solvents were washed with 5% water solution of Na₂SO₃, with water, and then dried with MgSO₄. On evaporating the extract in a vacuum we obtained 1.3 g of crystalline compound composed according to GLC data of a mixture of halides **IIa** and **IIc**, Table 1.

Reaction of hydrocarbon I with elemental iodine in methanol in the presence of LiBr. To a solution of 0.94 g of tricycloheptane **I** in 10 ml of anhydrous methanol containing 4.35 g of lithium bromide at stirring under nitrogen atmosphere was added dropwise while cooling to 0°C 2.54 g of iodine in 5 ml of anhydrous methanol. The reaction mixture was stirred for 1 h at room temperature, and then diluted with 20 ml of water. The reaction products were extracted into chloroform. We obtained 1.54 g of a mixture of halides **IIa** and **IIb** in 18:82 ratio (according to the data of GLC and ¹H NMR), Table 1.

Reaction of hydrocarbon I with NIS in the presence of acetic, benzoic, and *p*-toluenesulfinic acids. General procedure. To a mixture of 50 mmol of anhydrous triethylamine and 50 mmol of acetic, benzoic, or *p*-toluenesulfinic acid [27] in 30 ml of anhydrous dichloromethane was added 0.94 g (10 mmol) of tricycloheptane **I**. Then at stirring under argon atmosphere and external cooling with an ice bath 2.25 g (10 mmol) of NIS was added by small portions. The stirring was continued for 1.5 h at 0°C and for 2 h at room temperature. The mixture was diluted with water, the organic layer was separated, from the water layer the products were extracted with CH₂Cl₂ (3 × 10 ml). The combined organic solutions were dried on MgSO₄. On removing the solvent in a vacuum the residue was purified by flash-chromatography. Yields of compounds **IIg, h** and their constants are given in Tables 1 and 2. The constants and spectral characteristics of compounds **IVb** and **VIIb** were consistent with the published data [9].

Reaction of hydrocarbon I with NIS in methanol. To a solution of 0.94 g of hydrocarbon **I** in 30 ml of anhydrous methanol at external cooling to 0°C was added while stirring by portions within 1 h 2.15 g of NIS. The reaction mixture was diluted with water, the reaction products were extracted with ether, the extracts were dried on MgSO₄, and evaporated. The colorless oily substance obtained was purified by flash-chromatography to obtain 1.2 g (48%) of compound **III**.

Reaction of hydrocarbon I with NIS in aqueous acetone. Into a mixture composed of 0.94 g of hydrocarbon **I**, 20 ml of acetone, 10 ml of water, and 2 ml of triethylamine cooled to 0°C was added within 0.5 h 2.15 g of NIS. The mixture was stirred at this temperature for 0.5 h more, and then for 1.5 h at 20°C. The workup was carried out as described above. The reaction products were divided by chromatography on silica gel in two fractions. The first one, *R_f* 0.27, contained norpinane **IIj**, yield 23%. The

second fraction, R_f 0.15, according to GLC data (140°C) contained two compounds in 3:1 ratio with R_t 10.5 and 9.6 min respectively. They were identified as *endo*-7-iodobicyclo[4.1.0]heptan-*endo*-6-ol (**IV**) and *endo*-7-iodobicyclo[4.1.0]heptan-*exo*-6-ol (**V**). The overall yield of compounds **IV** and **V** was 0.96 g (40%). The main component of the mixture, compound **IV**, was isolated in an individual state by crystallization, mp 71–72°C (from petroleum ether-ethyl ether, 3:1). ¹H NMR spectrum, δ , ppm: 1.10–1.50 m (3H); 1.55–1.70 m (3H); 1.80 m (1H); 1.95 d (OH, J 9 Hz); 2.20 m (1H); 3.05 t (H⁷, J 8 Hz); 4.35 m (H²). ¹³C NMR spectrum, δ , ppm: 3.5 (C⁷); 17.3, 18.0, 22.7 (2C); 30.3, 69.0 (C²). Found, %: C 35.49; H 4.64. C₇H₁₁IO. Calculated, %: C 35.32; H 4.66.

In the ¹H NMR spectrum of the residue obtained by removal of solvent from the mother liquor a multiplet signal was observed at 3.90 ppm characteristic of the H² proton in *endo,endo* adduct **V** (cf. with the spectral data of the bromo analog of compound **V** [17]).

Reaction of hydrocarbon I with benzenesulfonyl iodide. At external cooling with ice water solutions in 5 ml of anhydrous S₂Cl₂ of 0.94 g of tricycloheptane **I** and 2.68 g of PhSO₂I were mixed. The mixture was kept at 20°C under nitrogen for 20 h, and then the solvent was removed in a vacuum of water-jet pump. The solid residue containing according to GLC and ¹H NMR data a mixture of compounds **VIa** and **VIa** in 1:1 ratio was subjected to column chromatography on alumina. We obtained respectively 1.61 and 1.32 g (45 and 36.5%) of individual compounds with the constants listed in Table 2.

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