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The Reactions of Selected Terpene Alcohols with Acetonitrile in the Presence of Boron Trifluoride Etherate

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A series of thirteen terpene alcohols **1–13** of bornane, fenchane and isotricyclene systems was subjected to the reaction with acetonitrile in the presence of $BF_3 \cdot Et_2O$ as a catalyst to give respective acetamides and/or alkenes. The use of boron trifluoride etherate instead of the usually applied protonic donors let us establish beyond any doubt the carbonium ion stage participation. The assumed reaction course was corroborated by cationic Wagner-Meerwein, Namietkin and homoallylic rearrangements observed during studies under investigation. Simultaneously no evidence for the imidate formation was found. Such a mode of the reaction mechanism was alternatively suggested earlier by Sjöberg [9] for the reaction of *sec*- and *tert*-butanol with acetonitrile in the presence of boron trifluoride etherate.

Key words: terpenes, Ritter reaction, rearrangements, boron trifluoride catalysis

Secondary and tertiary alcohols react with nitriles under acidic conditions (Ritter reaction) to give *N*-alkylamides [1], iminium salts [2,3] or heterocyclic compounds [4]. Concentrated sulphuric, perchloric, trifluoroacetic, hydrochloric, and methanesulfonic acids are catalysts commonly used for these purposes [5]. Use of other reagents such as hexachloroantimonates [6] or various cobalt(II) and cobalt(III) derivatives was also reported [7,8] much more rarely. However, the use of latter compounds is limited to amidation of allylic alcohols and their acetates. To our best knowledge there are only two papers concerning Ritter reaction catalyzed by boron trifluoride. Thus, according to Sjöberg [9] the reaction of *tert*- and *sec*-butanol with nitriles in the presence of boron trifluoride or its etherate, or nitrile–boron trifluoride complex can proceed *via* one of two postulated mechanisms. Those mechanisms involve either and initial attack of a carbonium ion on the nitrile nitrogen or formation of imidate and its further rearrangement to an amide. However, the results reported there did not let us choose a proper mode of such reaction. On the other hand, the reaction of the only investigated terpene alcohol, *cis*-carveol with acetonitrile in the presence of boron trifluoride etherate or perchloric acid reported by Kabore and coworkers [10] afforded different products. Continuing our studies on the Ritter reaction of terpene alcohols [11–14] we decided to investigate their reaction with acetonitrile catalyzed by boron trifluoride etherate. The choice of the non-protonic reaction conditions should prevent secondary rearrangements of alkenes formed in the initial stage of the reaction, which we observed earlier [11,12] using concentrated sulfuric acid.

RESULTS AND DISCUSSION

Secondary and tertiary bornyl, fenchyl and isotricyclenic alcohols **1**–**13** (see Table) were subjected to the reaction with acetonitrile in the presence of boron trifluoride etherate at room temperature for 24 h (in the case of 2-phenylfenchol (**8**) the reaction was quenched also after 1 h). The results obtained are presented in the Table. Thus, in the case of optically active isoborneol (**1**) and borneol (**2**) the same racemic isobornyl acetamide (**1a**) was formed. The reaction of the latter alcohol occurred only at the reflux temperature. The easier reaction of isoborneol (**1**) probably reflects an anchimeric assistance characteristic for *exo*-bicyclo[2.2.1]heptane derivatives [15].

Table

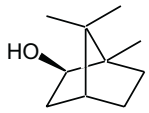
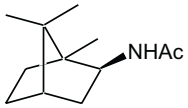
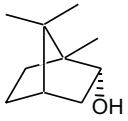
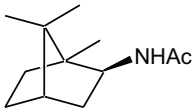
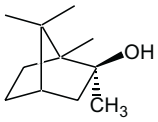
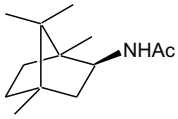
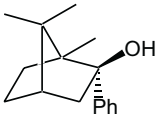
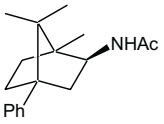
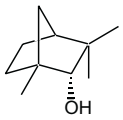
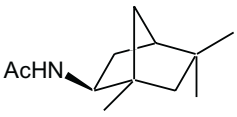
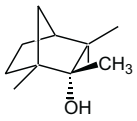
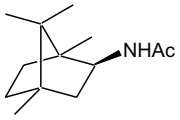
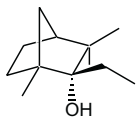
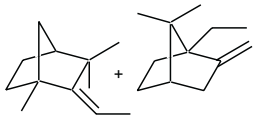
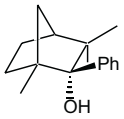
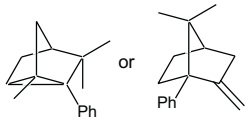
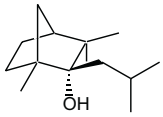
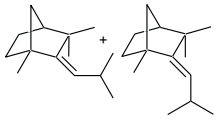
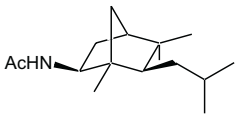
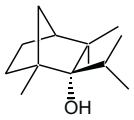
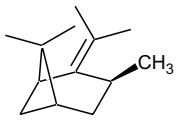
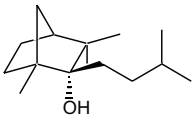
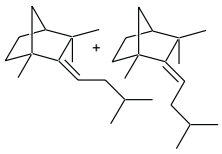
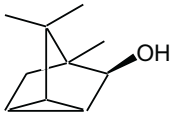
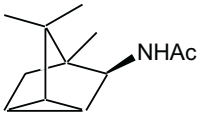
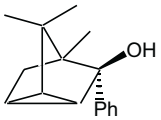
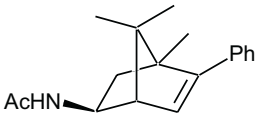
Alcohol	Products	Yield (%)
Bornane system		
 **1**	 (+/–)-**1a**	72
 **2**	 (+/–)-**1a**	69
 **3**	 **3a**	62
 **4**	 **4a**	48
Fenchane system		
 **5**	 **5a**	62
 **6**	 **3a**	58

Table (continuation)

 **7**	 **7a** **7b** 76:24 (GC ratio)	63 (**7a** + **7b**)
 **8**	 **8a** **8b** (after 1 h) (after 24 h)	73% (**8a**) 65% (**8b**)
 **9**	 **9a** **9b** 92:8 (GC ratio)	33% (**9a** + **9b**)
	 **9c**	22% (**9c**)
 **10**	 **10a**	38
 **11**	 **11a** **11b** 91:9 (GC ratio)	50
Isotricyclene system		
 **12**	 **12a**	47
 **13**	 **13a**	83

The loss of optical activity evidenced intermediary formation of a carbonium ion during the reaction. In the cases of tertiary alcohols **3** and **4** we obtained 4-substituted amides **3a** and **4a**, respectively. Their formation can be explained by consecutive Wagner-Meerwein, Namietkin, and again Wagner-Meerwein rearrangements, and 6,2-hydride shift [16,17]. Isofenchyl acetamide (**5a**) was the reaction product of fenchol (**5**). It has proven the 6,2-hydride shift to the initially formed carbonium ion, proceeding a nucleophilic attack of acetonitrile to form the resulted amide **5a** [12]. The character of the reaction product in the case of tertiary fenchyl alcohols **6**–**11** depended on a substituent at the C-2 position. Thus, for alcohol **6** we observed successive Namietkin and Wagner-Meerwein rearrangements to amide **3a** analogous to that obtained for 2-methylisoborneol (**3**). Formation of alkenes was a dominating process in the case of alcohols **7** and **9**–**11**. 2-Ethylfenchol (**7**) gave two alkenes **7a** and **7b** in ratio of 76:24. This result let as assume intermediary participation of a carbonium ion because such a cation can undergo the Wagner-Meerwein rearrangement to give alkene **7b**. On the other hand, unrearranged alkenes **9a** and **9b** or **11a** and **11b** were obtained from alcohols **9** and **11**, respectively. The amide **9c** was additionally obtained besides of a mixture of isomeric alkenes **9a** and **9b**. It evidenced 6,2-hydride shift occurring during a reaction course. For 2-isopropylfenchol (**10**) alkene **10a** was the only product. The same product has been obtained recently by us when concentrated sulfuric acid was used instead of boron trifluoride etherate [14]. An interesting result was observed in the case of 2-phenylfenchol (**8**). After one hour tricyclic compound **8a** was the only product. The same compound was obtained by Coxon and Steel [18] for alcohol **8** during its reaction with sulfuric acid/acetic acid. When the reaction was continued for 24 h compound **8a** underwent rearrangement to **8b**. Isotricyclenol (**12**) and 2-phenylisotricyclenol (**13**) were the representative alcohols for the isotricyclene system. The first of them gave the corresponding unrearranged amide **12a** to prove stabilization of the intermediate carbonium ion by the neighbouring cyclopropane ring. For 2-phenylisotricyclenol (**13**) a formation of *exo*-amide **13a** was observed as a result of a homoallylic rearrangement that is probably facilitated by a possibility of a conjugation between a phenyl ring and a double bond.

In conclusion, observations reported and, particularly, ionic rearrangements, allow to assume a carbonium ion participation for the investigated reactions of terpene alcohols with acetonitrile in the presence of boron trifluoride etherate. No evidence of the intermediary formation of imidates hypothetically suggested earlier by Sjöberg [9] was obtained.

EXPERIMENTAL

Melting points were measured on a Boetius apparatus and were uncorrected. ^{1}H- and ^{13}C- NMR spectra were recorded in $CDCl_3$ solutions with a Varian Gemini 200 spectrometer. Ratios and purity of the products obtained were determined by GC with a Hewlett Packard 5890 chromatograph (capillary column HP-1-phase). Optical rotations were measured with a POL S-2 polarimeter. (1*R*)-(+)-Camphor, [(1*S*)-*endo*]-(–)-borneol (**2**) and (1*R*)-*endo*-(+)-fenchol (**5**) were purchased from Aldrich. Other starting alcohols were prepared according to known procedures: **3** [16], **4** [17], **6** [19], **7** and **9** [20], **8** [18], **10** and **11** [14], **12** [21], **13** [22].

1. (1*R*)-(+)-Isoborneol (1). A solution of (1*R*)-(+)-camphor (20.0 g, 131 mmol) in 100 cc of dry Et_2O was slowly added to a suspension of 1.5 g (40 mmol) of $LiAlH_4$ in 100 cc of dry Et_2O. The reaction mixture was stirred at room temperature for 1 h and then 1.5 cc of water, 1.5 cc of 15 % aqueous of NaOH and once again 4.5 cc of water were added. The precipitate was filtered off and rinsed with ether. The combined ethereal solutions were washed with water and dried over anhydrous Na_2SO_4. Solvent was evaporated and the residue was sublimed under reduced pressure (15 Torr) to obtain 16.7 g (83% yield) of a product. M.p. 215°C (sealed capillary), (lit. [23] m.p. 214°C); $[\alpha_D^{20}] = 36.0$ (c = 2, $CHCl_3$), (lit. [24] $[\alpha_D^{20}] = 33.9$). ^{1}H-NMR, δ: 0.79 (s, 3H, CH_3), 0.88 (s, 3H, CH_3), 0.99 (3, 3H, CH_3), 1.45 (m, 1H), 1.69 (m, 6H), 1.80 (bs, 1H, OH), 3.50 (t, 1H, CH, J = 5.1 Hz) ; ^{13}C-NMR, δ: 11.25 (CH_3), 20.11 (CH_3), 20.41 (CH_3), 27.17 (CH_2), 33.85 (CH), 40.31 (CH), 45.02 (CH_2), 46.25 (C), 48.86 (C), 79.77 (CH_2).

2. Reaction of alcohols 1–13 with acetonitrile and boron trifluoride etherate (general procedure). 2.5 cc of $BF_3 \cdot Et_2O$ was added dropwise to a stirred at –15°C solution of 20 mmol of alcohols in 40 cc of acetonitrile. Then, a cooling bath was removed and the mixture was stirred for 24 h at room temperature (at 24 h reflux for alcohol **2**) The reaction mixture was poured out onto ice-water and extracted three times with Et_2O (3×10 cc). The combined extracts were washed with water and dried over anhyd. Na_2SO_4. After removal of ether, the residue was crystallized from EtOH (amides **1a**, **3**a-**5a** and **13a**) or distilled under reduced pressure to give respectively:

a) for alcohol **1** and **2**: 2.8 g (72%) of isobornyl acetamide (**1a**) (for alcohol **1**) and 2.7 g (69%) (for alcohol **2**); m.p. 144°C (lit. [25] m.p. 143.5–145°C (aq. MeOH)); ^{1}H-NMR, δ: 0.83 (s, 3H, CH_3), 0.84 (s, 3H, CH_3), 0.90 (s, 3 H, CH_3), 1.10–1.35 (m, 2H), 1.48–1.92 (m, 5H), 1.97 (s, 3H, CH_3), 3.89 (ddd, 1H, $CH_{2\text{-}endo}$), 5.38 (bs, 1H, NH); ^{13}C-NMR, δ: 11.54 (CH_3), 19.00 (CH_3), 20.15 (CH_3), 23.38 (CH_3), 26.85 (CH_2), 35.82 (CH_2), 38.85 (CH_2), 44.70 (CH), 46.90 (C), 48.30 (C), 56.63 (CH), 169.25 (C); b) for alcohol **3**: 2.6 g (62%) of *exo*-2-acetamido-4-methylbornane (**3a**), m.p. 161°C (lit. [16] m.p. 162°C (EtOH)); ^{1}H-NMR, δ: 0.68 (s, 3H, CH_3), 0.76 (s, 3H, CH_3), 0.85 (s, 3H, CH_3), 0.88 (s, 3H, CH_3), 1.15–1.90 (m, 6H), 1.95 (s, 3H, CH_3), 3.90 (ddd, 1H, $CH_{2\text{-}endo}$ J = 9.0 Hz, J = 9.0 Hz, J = 4.5 Hz), 5.32 (bd, 1H, NH, J = 8.0 Hz); ^{13}C-NMR, δ: 12.54 (CH_3), 15.90 (CH_3), 17.90 (CH_3), 18.25 (CH_3), 23.65 (CH_3), 34.33 (CH_2), 35.48 (CH_2), 46.05 (CH_2), 46.90 (C), 48.08 (C), 50.29 (C), 56.02 (CH), 169.26 (C); c) for alcohol **4**: 2.6 g (48%) of *exo*-2-acetamido-4-phenylbornane (**4a**), m.p. 147–148°C (lit. [17]; m.p. 144°C (EtOH); ^{1}H-NMR, δ: 0.76 (s, 3H, CH_3), 0.90 (s, 3H, CH_3), 0.94 (s, 3H, CH_3), 1.40–1.75 (m, 3H), 2.00 (s, 3H, CH_3), 2.05–2.30 (m, 3H), 4.05 (ddd, 1H, $CH_{2\text{-}endo}$, J = 9.0 Hz, J = 9.0 Hz, J = 4.5 Hz), 5.50 (bd, 1H, NH, J = 8 Hz), 7.30 (m, 5H, C_6H_5); ^{13}C-NMR, δ: 12.97 (CH_3), 18.92 (CH_3), 19.05 (CH_3), 23.78 (CH_3), 33.05 (CH_2), 35.42 (CH_2), 44.35 (CH_2), 50.75 (C), 51.82 (C), 54.35 (C), 55.85 (CH), 127.10 (CH), 128.15 (2 CH), 129.02 (2 CH), 141.15 (C), 169.82 (C); d) for alcohol **5**: 2.4 g (62%) of *exo*-isofenchyl acetamide (**5a**); m.p. 180°C (lit. [12] m.p. 181°C); ^{1}H-NMR, δ: 0.96 (s, 3H, CH_3), 0.98 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 1.03–1.80 (m, 5H), 1.68 (d, 1H, J = 4.5 Hz), 1.98 (s, 3H, CH_3), 2.35 (m, 1H), 3.76 (dt, 1H, J = 7.5 Hz, J = 4.3 Hz, CH), 5.26 (bs, 1H, NH); ^{13}C-NMR, δ: 17.04 (CH_3), 23.38 (CH_3), 26.37 (CH_3), 30.96 (CH_3), 36.91 (CH_2), 37.23 (C), 41.55 (CH_2), 47.18 (CH), 48.81 (C), 51.66 (CH_2), 53.68 (CH), 168.19 (C); e) for alcohol **6**: 2.4 g (58%) of *exo*-2-acetamido-4-methylbornane (**3a**) (the same data as from alcohol **3**); f) for alcohol **7**: 2.09 g (63%) of a mixture of 2-ethylidenefenchane (**7a**) and 1-ethyl-2-methylene-7,7-dimethylbicyclo[2.2.1]heptane (**7b**) (GC ratio: 76:24); b.p. 121–124 °C/3 Torr. Alkene **7a**: ^{1}H-NMR, δ: 1.12 (s, 3H, CH_3), 1.14 (s, 3H, CH_3), 1,21 (s, 3H, CH_3), 0.85–1.60 (m, 7H), 1.67 (d, 3H, CH_3, J = 6.0 Hz), 4.98 (q, 1H, =CH, J = 8.0 Hz); ^{13}C-NMR, δ: 13.76 (CH_3), 19.09 (CH_3), 24.93 (CH_3), 25.65 (CH_2), 26.65 (CH_3), 36.15 (CH_2), 42.42 (C), 44.04 (CH_2), 49.78 (CH), 50.38 (C), 109.52 (CH), 157.26 (C) (from a mixture). Alkene **7b**: ^{1}H-NMR, δ:

0.81 (s, 3H, CH_3), 0.91 (s, 3H, CH_3), 0.99 (t, 3H, J = 4.0, CH_3), 1.49–1.60 (m, 8H), 2.30–2.43 (m, 1H), 4.67 (m, 1H), 4.78 (m, 1H); ^{13}C-NMR, δ: 19.52 (CH_3), 20.24 (CH_3), 20.84 (CH_3), 27.74 (CH_2), 29.74 (CH_2), 31.70 (CH_2), 37.16 (CH_2), 45.40 (CH), 47.73 (C), 54.27 (C), 101.91 (CH_2), 158.19 (C) (from a mixture); g) for alcohol **8**: 1.43 g (65%) of 2-methylene-7,7-dimethyl-1-phenylbicyclo[2.2.1]heptane (**8b**), b.p. 132–134 °C/2 Torr, (lit. [18] b.p. 155-170/14 Torr). ^{1}H-NMR, δ: 0.76 (s, 3H, CH_3), 1.02 (s, 3H, CH_3), 1.30–1.65 (m, 2H), 1.80–2.18 (m, 3H), 2.52–2.78 (m, 2H), 4.55 (m, 1H), 4.84 (m, 1H), 7.20–7.45 (m, 5H); ^{13}C-NMR, δ: 19.17 (CH_3), 21.61 (CH_3), 27.38 (CH_2), 32.54 (CH_2), 38.13 (CH_2), 46.33 (CH), 50.13 (C), 60.63 (C), 105.24 (CH_2), 125.94 (CH), 127.43 (2 CH), 128.61 (2 CH), 139.64 (C), 158.62 (C). After 1 h: 1.61 g (73%) of 1,3,3-trimethyl-2-phenyltricyclo[2.2.1.$0^{2,6}$]heptane (**8a**): b.p. 88 °C/1 Torr, (lit. [18] b.p. 155–170 °C/14 Torr); ^{1}H-NMR, δ: 0.76 (s, 3H, CH_3), 0.90 (s, 3H, CH_3), 1.09 (s, 3H, CH_3), 1.00–1.20 (m, 2H), 1.60 (m, 2H), 1.85 (m, 2H), 7.20 (m, 5H); ^{13}C-NMR, δ: 15.13 (CH_3), 21.53 (2 CH_3), 25.16 (C), 25.46 (CH), 32.39 (CH_2), 38.08 (CH_2), 40.01 (CH), 40.92 (C), 46.95 (C), 125.9 (CH), 127.08 (2 CH), 131.66 (2 CH), 137.53 (C). h) for alcohol **9** (after separation by CC (SiO_2/EtOH)): 1.12 g (22%) of *exo*-6-acetamido-*exo*-2-isobutyl-1,3,3-trimethylbicyclo[2.2.1]heptane (**9c**) and 1.24 (33%) of a mixture of (*Z*)- and (*E*)-2-isobutylidenefenchane (**9a** and **9b**) (GC ratio: 92:8). Alkenes **9a** and **9b**: b.p. 86–88 °C/2 Torr. ^{1}H-NMR, δ: 0.90 (d, 3H, J = 2 Hz, CH_3), 0.91 (d, 3H, J = 2 Hz, CH_3), 1.02 (s, 3H, CH_3), 1.11 (s, 3H, CH_3), 1.19 (s, 3H, CH_3), 1.32–1.38 (m, 1H), 1.40–1.70 (m, 6H), 2.52–2.80 (m, 1H), 4.64 (, J = 10 Hz, –C=CH for *Z* isomer), and 4.76 (d, J = 10 Hz, –C=CH for *E* isomer); ^{13}C-NMR, δ: 19.30 (CH_3), 23.78 (CH_3), 23.88 (CH_2), 25.69 (CH_2), 25.93 (CH_3), 27.45 (CH), 27.99 (CH_3), 36.03 (CH_2), 42.61 (C), 44.19 (CH_2), 49.78 (CH), 49.98 (C), 123.52 (CH for *Z* isomer) and 124.23 (CH for *E* isomer), 153.70 (C for *Z* isomer) and 154.68 (C for *E* isomer). Amide **9c**: m.p. 217–218°C (EtOH), (lit. [14] m.p. 218°C (EtOH)); [α_D^{20}] = –26.8 (c = 2.5, EtOH), (lit. [14] [α_D^{20}] = –26.6 (c = 2.2, EtOH)). ^{1}H-NMR, δ: 0.82 (d, 3H, J = 6.0 Hz, CH_3), 0.87 (d, 3H, J = 6.0 Hz, CH_3), 0.88 (s, 3H, CH_3), 0.91 (s, 3H, CH_3), 0.98 (s, 3H, CH_3), 0.95–1.15 (m, 5H), 1.50–1.65 (m, 3H), 1.98 (s, 3H, $NHCOCH_3$), 2.38 (ddd, 1H, J = 13.5, J = 7.5 Hz, J = 2.0 Hz, CH), 3.75 (dt, 1H, J = 9.0 Hz, J = 9.0 Hz, CH), 5.20 (b.d, 1H, J = 6.0 Hz, NH); ^{13}C-NMR, δ: 14.51 (CH_3), 23.52 (CH_3), 23.56 (CH_3), 24.62 (CH_3), 27.00 (CH), 27.85 (CH_3), 36.38 (CH_2), 37.92 (CH_2), 39.76 (CH_2), 41.18 (C), 48.22 (CH), 51.54 (C), 51.61 (CH), 56.40 (CH), 169.11 (C); i) for alcohol **10**: 1.35 g (38%) of (+)-2-isopropylidene-3,6,6-trimethylbicyclo[3.1.1]heptane (**10a**). B.p. 138–140 °C/24 Torr, [α_D^{20}] = 62.2 (c = 9.4, CH_2Cl_2), (lit. [14] [α_D^{20}] = 62.2 (c = 9.8, CH_2Cl_2)); ^{1}H-NMR, δ: 0.85 (d, 3H, J = 6.0 Hz, CH_3), 1.15 (s, 3H, CH_3), 1.18 (s, 3H, CH_3), 1.60 (s, 3H, CH_3), 1.71 (s, 3H, CH_3), 0.79–1.85 (m, 5H), 1.90-2.08 (m, 1H), 2.74 (m, 1H); ^{13}C-NMR, δ: 17.38 (CH_3), 20.46 (CH_3), 22.61 (CH_3), 24.52 (CH_3), 27.44 (CH_3), 31.69 (CH_2), 35.05 (CH), 38.05 (CH_2), 42.27 (C), 49.03 (CH), 51.87 (CH), 121.91 (C), 144.82 (C); j) for alcohol **11**: 2.04 g (50%) of a mixture of (*Z*) and (*E*)-isopentylidenefenchane (**11a** and **11b**) (GC ratio: 91:9). B.p. 100–105 °C/10 Torr. ^{1}H-NMR, δ: 0.89 (d, 6 H, J = 6.0 Hz, 2 CH_3), 1.13 (s, 3H, CH_3), 1.14 (s, 3H, CH_3), 1.21 (s, 3H, CH_3), 1.10–1.65 (m, 6H), 1.70–1.85 (m, 3H), 1.98 (t, 1H, J = 6.6 Hz, CH_2), 4.90 (t, 1H, J = 7.5 Hz, –C=CH for (Z) isomer) and 5.18 (t, 1H, J = 7.5 Hz, –C=CH for (*E*) isomer); ^{13}C-NMR, δ: 19.17 (CH_3), 22.50 (CH_3), 22.65 (CH_3), 25.43 (CH_3), 25.54 (CH_2), 27.25 (CH_3), 29.23 (CH), 36.01 ((CH_2), 37.08 (CH_2), 42.11 (C), 43.92 (CH_2), 49.57 (CH), 50.18 (C), 114.40 (CH for *Z* isomer) and 115.88 (CH for *E* isomer), 155.92 (C for *Z* isomer) and 156.96 (C for *E* isomer); k) for alcohol **12**: 1.8 g (47%) of *exo*-2-acetamidoisotricyclene (**12a**). Viscous mass (after CC (SiO_2/EtOH)). ^{1}H-NMR, δ: 0.78 (s, 3H, (CH_3), 0.81 (s, 3H, CH_3), 0.91 (s, 3H (CH_3), 1.10–1.22 (m, 3H), 1.46–1.48 (m, 2H), 2.0 (s, 3H, (CH_3), 4.12 (d, 2H, J = 10.5 Hz, CH), 5.25 (b.s, 1H, NH); ^{13}C-NMR, δ: 8.33 (CH_3), 12.54 (CH), 17.70 (CH), 19.70 (CH_3), 19.72 (CH_3), 21.89 (CH_3), 25.85 (CH), 34.10 (CH_2), 43.51 (C), 45.64 (C), 56.82 (CH), 169.26 (C); l) for alcohol **13**: 4.5 g (83%) of *exo*-5-acetamido-2-phenyl-1,7,7-trimethylbicyclo[2.2.1]hept-2-ene (**13a**). M.p. 156–160°C (MeOH) (lit. [11] m.p. 158–160°C (MeOH)). ^{1}H-NMR, δ: 0.97 (s, 3H, (CH_3), 1.06 (s, 3H, (CH_3), 1.09 (s, 3H, (CH_3), 1.60 (dd, 1H, J = 12 Hz, J = 4Hz), 1.98 (s, 3H, (CH_3), 2.10 (dd, 1H, J = 10 Hz, J = 4 Hz), 2.48 (d, 1H, J = 4 Hz), 3.85 (m, 1H, CH_{5endo}), 5.88 (b.s., 1H, NH), 6.08 (d, 1H, –C=CH, J = 4 Hz), 7.25 (m, 5H, C_6H_5); ^{13}C-NMR, δ: 12.24 (CH_3), 20.82 (CH_3), 21.04 (CH_3), 23.41 (CH_3), 39.81 (CH_2), 52.20 (CH), 55.48 (C), 56.91 (CH), 57.61 (C), 126.45 (2 CH), 126.76 (CH), 128.04 (2 CH), 131.08 (CH), 137.64 (C), 157.10 (C), 169.56 (C).

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