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Synthesis and Reactions of Organic Compounds with a Nitrogen Atom. Part XVII. Reactions of Acyclic and Monocyclic Chlorides with Phenyltelluro- and Phenylselenosodium

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The reaction of neryl (**3**), geranyl (**4**), (+)-carvotanacetyl (**5**), (–)-carvyl (**6**) and perillyl (**7**) chlorides with phenylseleno- (**1**) or phenyltellurosodium (**2**), and then with chloramine-T afforded α,β-unsaturated toluenesulfonamides **8–11**, which were reduced with sodium in liquid ammonia to allylic amines **12–15**. Allylic phenyltellurides were oxidized by air to carbonyl compounds **29–31** or alcohol **28**.

Key words: phenyltellurides, phenylselenides, toluenesulfonamides, allylic amines

Previously [1–10], we demonstrated that optically active allylic mono- and ditoluenesulfonamides can be reduced with sodium in liquid ammonia to the corresponding optically active mono- and diamines, which are utilized in organic synthesis [11–15] and exhibit pharmacological activity [16]. The toluenesulfonamides are conveniently prepared by the reaction of alkenes or dienes with bis(*p*-toluenesulfonyl)selenediimide [1–8] and by the reaction of allylic chlorides with phenylseleno- (**1**) or phenyltellurosodium (**2**) and chloramine-T [9–10]. Toluenesulfonamidation reactions of α-pinene [9] and (+)-3-carene [10] chlorides were carried in one step to compare the reactivity of seleno- and telluroorganic compounds and in two steps with the isolation of phenylselenides. We demonstrated that in reactions of allylic chlorides with phenylselenosodium secondary allylic phenylselenides rearrange to more stable primary selenides. We also showed that allylic phenyltellurides are oxidized by air oxygen to the corresponding oxygen derivatives (carbonyls or alcohols).

In this paper, toluenesulfonamidation reactions of acyclic and monocyclic allylic chlorides with phenylseleno- (**1**) or phenyltellurosodium (**2**), and chloramine-T are described. We were interested in the influence of the structures of chlorides on the course of the toluenesulfonamidation reaction. We also compare the yields of toluenesulfonamidation reactions *via* telluroorganic and selenoorganic compounds. In addition, oxidation of acyclic and monocyclic allylic chlorides *via* the reaction with phenyltellurosodium followed by oxygen from air was studied. The reactions with phenylseleno- (**1**) or phenyltellurosodium (**2**) and chloramine-T were carried out with neryl (**3**), geranyl (**4**), (+)-carvotanacetyl (**5**), (–)-carvyl (**6**) and perillyl (**7**) chlorides. Monocyclic chlorides (**5**–**7**) used for the reaction were optically active. We were interested, whether in the toluenosulfonamidation reaction racemization of

phenylselenides, phenyltellurides and toluenosulfonamides takes place. Allylic toluenosulfonamides were reduced with sodium in liquid ammonia to the corresponding allylic amines.

RESULTS AND DISCUSSION

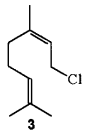
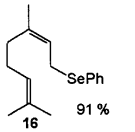
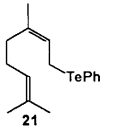
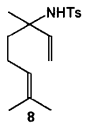
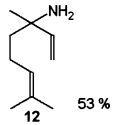
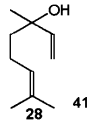
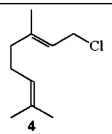
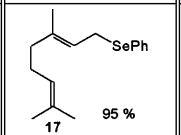
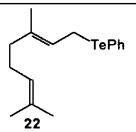
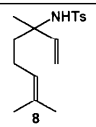
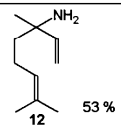
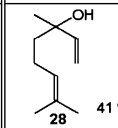
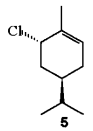
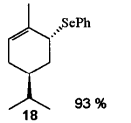
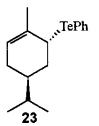
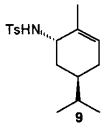
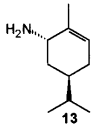
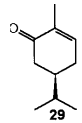
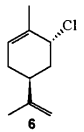
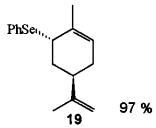
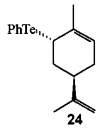
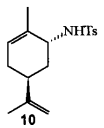
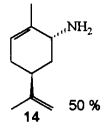
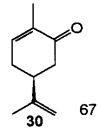
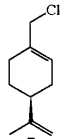
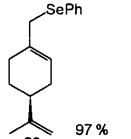
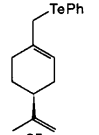
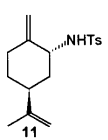
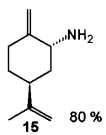
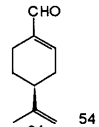
Comparison of the reactivity of allylic phenylselenides and allylic phenyltellurides in the reaction with chloramine-T was our first goal. The toluenosulfonamidation reaction was carried out in one pot version without isolation of intermediate phenylselenides and phenyltellurides. Allylic phenylselenides and phenyltellurides were obtained *in situ* from allylic chlorides **3**–**7** by the reaction with phenylselenosodium (**1**) ($NaBH_4$, PhSeSePh, MeOH) or phenyltellurosodium (**2**) ($NaBH_4$, PhTeTePh, MeOH), and were transformated into the corresponding toluenesulfonamides by the reaction with chloramine-T. Allylic chlorides **3**–**7** used for the toluenesulfonamidation reaction were synthesized from the corresponding alcohols by treatment with carbon tetrachloride and triphenylphosphine [17]. Allylic toluenosulfonamides **8–11** were obtained by toluenosulfonamidation of allylic chlorides **3–7** (Table 1). The structures of toluenosulfonamides were determined by the analysis of ^{1}H and ^{13}C NMR spectra. The yields of toluenosulfonamidation reactions *via* phenylselenides (Method A) or *via* phenyltellurides (Method B) are presented in Table 1. Allylic toluenosulfonamides **8–11** were reduced with sodium in liquid ammonia to allylic amines **12–15** (Table 1).

For the purpose of structure determination of phenylselenide intermediates, the toluenosulfonamidation reaction was carried out in the two-step version with the isolation of phenylselenides, which were subjected to the reaction with chloramine-T. Phenylselenides **16–20** were obtained by the reaction of chlorides **3–7** with phenylselenosodium (**1**). Structures of these phenylselenides were established by ^{1}H and ^{13}C NMR analyses. The yields of the reaction of allylic phenylselenides with chloramine-T are shown in Table 1 (Method C).

Phenyltellurides **21**–**25**, highly reactive forward oxygen from air, were not isolated. The structures of phenyltellurides **21**–**25** are based on the structures of the corresponding toluenosulfonamides **8**–**11** (Table1).

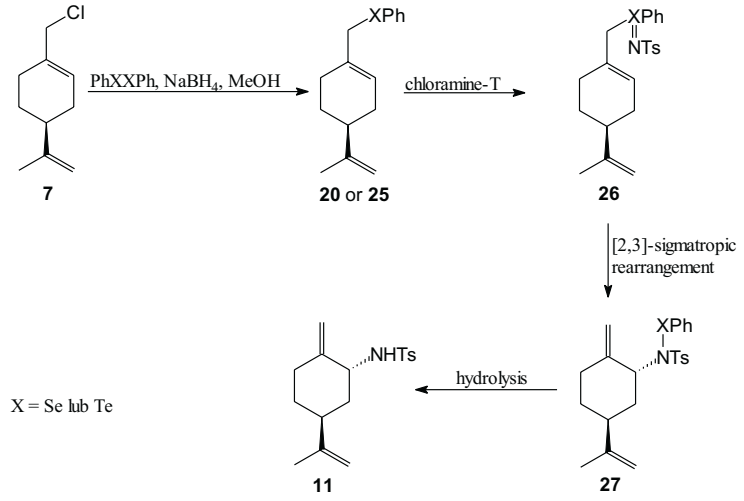
Our second goal was the study of the oxidation products of allylic phenyltellurides. The tellurides **21**–**25** prepared *in situ* by the reaction of allylic chlorides **3**–**7** with phenyltellurosodium (**2**) were oxidized with oxygen from air to give the alcohol **26**, ketones **27**–**28** and the aldehyde **29** (Table 1). Structures of this products were confirmed by ^{1}H and ^{13}C NMR analyses and by comparison with the literature data.

Table 1. The reaction of allylic phenylselenides and phenyltellurides with chloramine-T or with oxygen from air.

Chloride	Phenylselenide	Phenyltelluride	Amide	Method, yield %			Amine	Product
				A	B	C		
 **3**	 91 % **16**	 **21**	 **8**	38	45	83	 53 % **12**	 41 % **28**
 **4**	 95 % **17**	 **22**	 **8**	46	59	77	 53 % **12**	 41 % **28**
 **5**	 93 % **18**	 **23**	 **9**	38	57	54	 58 % **13**	 63 % **29**
 **6**	 97 % **19**	 **24**	 **10**	41	67	51	 50 % **14**	 67 % **30**
 **7**	 97 % **20**	 **25**	 **11**	29	56	62	 80 % **15**	 54 % **31**

As shown in Table 1, allylic chlorides **3**–**4** and monocyclic chlorides **5**–**7** react with phenylselenosodium (**1**) or phenyltellurosodium (**2**), and chloramine-T to give α,β-unsaturated toluenosulfonamides **8**–**11**. Reduction with sodium in liquid ammonia affords α,β-unsaturated amines **12–15**. In the first step of the toluenosulfonamidation reaction of allylic chlorides, phenylselenides **16–20** or phenyltellurides **21–25** are formed. We assumed, that the substitution reaction of chlorine with phenylselenide and phenyltelluride groups proceeds according to S_N2 mechanism for chlorides **3**, **4**, **7** and S_N2' mechanism for chlorides **5** and **6**. These assumptions were confirmed by comparison of the structure of produced amides and amines with the literature data [2,18,19]. Allylic phenylselenides can be easily isolated from the reaction mixture. On the contrary, allylic phenyltellurides even in the presence of traces of oxygen give oxidation products. For acyclic chlorides **3** and **4** during the formation of phenylselenides **16–17** and phenyltellurides **21–22**, the configuration was retained. The formation of only one toluenosulfonamide **8** from **3** and **4** follows from the mechanism of the toluenosulfonamidation reaction, which is shown for the synthesis of toluenosulfonamide **11** from perillyl chloride (**7**) (Scheme 1).

Scheme1



In first stage, chloride **7** reacts with phenylselenosodium (**1**) or phenyltellurosodium (**2**) to yield phenylselenide **20** or phenyltelluride **25**, reacting further with chloramine-T to give imide **26**. [2,3]-Sigmatropic rearrangament of the imide **26** and hydrolysis leads to toluenosulfonamide **11**. Toluenosulfonamides **9–11**, obtained from optically active chlorides **5–7**, showed optical activity. Amines **13–15**, prepared by the reduction of toluenosulfonamides, also exhibited optical activity. The results demonstrate higher reactivity of allylic phenyltellurides than allylic phenylselenides.

Oxidation of allylic tellurides **21** and **22** with air gave alcohol **28**. The tellurides **23**–**25** were oxidized to the carbonyl compounds **29–31**. When phenyltellurides **21–22** were used for the reaction, only the product formed by [2,3]-sigmatropic rearrangement of tellurooxides intermediates was isolated. In the case of monocyclic phenyltellurides **23–25**, oxidation products were formed *via* the 1,2-rearrangement. Our results do not confirm the reaction mechanism assumed by Uemura [20]. He postulated, that during the oxidation of allylic phenyltellurides with air, the mixture of products is formed *via* [2,3]-sigmatropic rearrangement as well as 1,2-rearrangement.

EXPERIMENTAL

Melting points were determined on a Boetius apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were obtained using a Varian Gemini 200 spectrometer for solutions in $CDCl_3$ (internal TMS). GLC analyses were carried out with a Hewlett-Packard 5890 gas chromatograph using a SPB-5 (30 m × 0.32 mm) column. Mass spectra were recorded on a Varian 3300 (E.I. 70 eV) mass spectrometer. Optical rotations were recorded with a Officine Galileo and C. Zeiss Jena, Polamat A, polarimeters. The organic solutions were dried over anhydrous $MgSO_4$. Column chromatography was performed on silica gel (Merck no 7734) using $CHCl_3$ as an eluent.

Synthesis of phenylselenides – general procedure: Sodium borohydride (1.8 g, 48.3 mmol) was added to a vigorously stirred solution of diphenyldiselenide (6.9 g, 21.9 mmol) in anhydrous methanol (40 ml) at 0°C under argon atmosphere. Then a chloride (45 mmol) was added, and the mixture was warmed to 50°C. After 1 h, the mixture was cooled to room temperature, water (100 ml) was added, the crude product was extracted with ether (3 × 100 ml) and was purified by column chromatography. The following compounds were obtained:

***Z*-1-(Phenylseleno)-3,7-dimethylocta-2,6-diene (16)**, (90%), n_D^{20} = 1.5651; ^{1}H NMR, δ: 7.52–7.48 (m, 2H, aromat.), 7.28–7.23 (m, 3H, aromat.), 5.40 (m, 1H, C-2), 5.08 (m, 2H, C-6), 3.56 (m, 2H, C-1), 1.98 (s, 4H, C-4, C-5), 1.71 (s, 3H, C-10), 1.68 (s, 3H, C-8), 1.60 (s, 3H, C-9); ^{13}C NMR, δ: 139.4 (C-3), 133.2 (CH×2 aromat.), 131.8 (C-7), 130.9 (C aromat.), 128.8 (CH×2 aromat.), 126.8 (CH aromat.), 124.0 (C-2), 120.7 (C-6), 31.7 (C-1), 26,5 (C-4), 25.7 (C-5), 25.6 (C-10), 23.3 (C-8), 17.7 (C-9).

***E*-1-(Phenylseleno)-3,7-dimethylocta-2,6-diene (17)**, (95%), n_D^{20} = 1.5644; ^{1}H NMR, δ: 7.54–7.50 (m, 2H, aromat.), 7.26–7.23 (m, 3H, aromat.), 5.39 (m, 1H, C-2), 5.07 (m, 2H, C-6), 3.56 (m, 2H, C-1), 2.00 (s, 4H, C-4, C-5), 1.69 (s, 3H, C-10), 1.60 (s, 3H, C-8), 1.50 (s, 3H, C-9); ^{13}C NMR, δ: 139.2 (C-3), 133.6 (CH×2 aromat.), 131.5 (C-7), 130.4 (C aromat.), 129.7 (CH×2 aromat.), 129.6 (CH aromat.), 123.9 (C-2), 120.0 (C-6), 39,6 (C-1), 26,5 (C-4), 25.9 (C-5), 25.6 (C-10), 17.7 (C-8), 15.6 (C-9).

***trans*-1-(Phenylseleno)-5-isopropyl-2-methylcyclohex-2-en (18)** (93%), n_D^{20} = 1.5713, $[\alpha]_D^{20}$ = +25.3 (neat); ^{1}H NMR, δ: 7.46–7.65 (m, 2H, aromat.), 7.25 (m, 3H, aromat.), 5.57 (m, 1H, C-3), 3.83 (m, 1H, C-1), 2.25(m, 1H), 1.86 (s, 3H, C-10), 1.48 (m, 5 H), 0.82 (m, 6H, C-8, C-9); ^{13}C NMR, δ: 134.4 (CH×2 aromat.), 134.3 (C aromat.), 131.5 (C-2), 128.8 (CH×2 aromat.), 127.1 (CH aromat.), 126.0 (C-3), 47.2 (C-1), 41.7 (C-5), 37.0 (C-4), 32.2 (C-7), 29.0 (C-6), 23.3 (C-10), 19.9 (C-8), 19.4 (C-9).

***trans*-1-(Phenylseleno)-5-isopropenyl-2-methylcyclohex-2-en (19)** (97%), n_D^{20} = 1.5894, $[\alpha]_D^{20}$ = –55.2 (neat); ^{1}H NMR, δ: 7.52–7.60 (m, 2H, aromat.), 7.24–7.29 (m, 3H, aromat.), 5.58 (m, 1H, C-3), 4.69 (m, 2H, C-8), 3.87 (m, 1H, C-1), 1.42–2.36 (m, 5H), 1.90 (s, 3H, C-9), 1.68 (s, 3H, C-10); ^{13}C NMR, δ: 148.7 (C aromat.), 134.5 (CH×2 aromat.), 132.9 (C-2), 129.9 (C-7), 128.8 (CH×2 aromat.), 127.2 (CH aromat.), 125.4 (C-3), 109.1 (C-8), 46.6 (C-1), 42.4 (C-5), 38.0 (C-4), 30.1 (C-6), 23.2 (C-9), 20.7 (C-10).

10-Phenylseleno-*p*-mentha-1,8-dien (20) (97%), n_D^{20} = 1.5881, $[\alpha]_D^{20}$ = –17.4 (neat); ^{1}H NMR, δ: 7.43–7.52 (m, 2H, aromat.), 7.19–7.29 (m, 3H, aromat.), 5.42 (m, 1H, C-2), 4.70 (m, 2H, C-8), 3.49 (s, 2H, C-10), 1.73–2.29 (m, 5H), 1.72 (s, 3H, C-9), 1.35–1.58 (m, 2H); ^{13}C NMR, δ: 149.6 (C aromat.), 133.8 (CH×2 aromat.), 133.7 (C-1), 130.7 (C-7), 128.7 (CH×2 aromat.), 127.0 (CH aromat.), 124.6 (C-2), 108.7 (C-8), 40.8 (C-4), 36.1 (C-10), 30.8 (C-3), 27.9 (C-6), 27.7 (C-5), 20.8 (C-9).

Synthesis of toluenesulfonamides – general procedure (Method C): Phenylselenide (20.8 mmol) was added to a vigorously stirred solution of anhydrous chloramine-T (9.6 g, 41.6 mmol) in anhydrous methanol (120 ml) at 25°C under argon atmosphere. After 24 h, 1.5 M NaOH (100 ml) was added, the crude product was extracted with ether (3 × 100 ml) and was purified by column chromatography to give toluenesulfonamide. The following compounds were obtained:

N-[3,7-dimethyl-1,6-octadienyl]toluenosulfonamide (8), (77%), ^{1}H NMR δ: 7.71–7.77 (m, 2H, aromat.), 7.20–7.26 (m, 2H, aromat.), 5.69 (m, 1H, C-2) 5.22 (m, 1H, NH), 5.01 (m, 3H, C-1, C-6), 2.40 (s, 3H, aromat.) 1.91 (m, 2H, C-5), 1.68 (m, 2H, C-4), 1.64 (s, 3H, C-10), 1.54 (s, 3H, C-8), 1.27 (s, 3H, C-9); ^{13}C NMR δ: 142.7 (C aromat.), 142.4 (C-2), 140.4 (C aromat.), 132.1 (C-7), 129.3 (CH×2 aromat.), 127.2 (CH×2 aromat.), 123.5 (C-6), 113.7 (C-1), 60.1 (C-3), 41.5 (C-5), 25.6 (CH_3 from Ts), 24.1 (C-8), 22.5 (C-7), 21.4 (C-9), 17.6 (C-10).

N-*trans*-[5-isopropyl-2-methylocyclohex-2-enyl]toluenosulfonamide (9), (54%), t.t. = 105–107°C, $[\alpha]_D^{20}$ = +0.4 (c = 22.2 , THF); ^{1}H NMR, δ: 7.72–7.81 (m, 2H, aromat.), 7.23–7.35 (m, 2H, aromat.), 5.49 (m, 1H, C-3,) 5.35 (m, 1H, NH), 3.80 (m, 1H, C-1) 2.41 (s, 3H, aromat.), 1.83 (m, 3H) 1.50 (s, 3H, C-10), 1.12 (m, 3H), 0.74 (m, 6H, C-9, C-8); ^{13}C NMR δ: 143.1 (C-2), 138.6 (C aromat.), 133.1 (C aromat.), 129.5 (CH×2 aromat.), 127.1 (CH×2 aromat.), 126.2 (C-1), 55.1 (C-3), 40.0 (C-5), 36.1 (C-6), 32.0 (C-7), 28.7 (C-4), 21.5 (CH_3 from Ts), 19.8 (C-10), 19.5 (C-8), 19.2 (C-9).

N-*trans*-[5-isopropenyl-2-methylocyclohex-2-enyl]toluenosulfonamide (10), (51%), t.t. = 108–110°C, $[\alpha]_D^{20}$ = –3.7 (c = 25.2, THF); ^{1}H NMR, δ: 7.72–7.82 (m, 2H, aromat.), 7.23–7.32 (m, 2H, aromat.), 5.51 (m, 1H, C-3) 4.65 (m, 3H, C-8, NH), 3.86 (m, 1H), 2.40 (s, 3H, aromat.) 1.66–2.23 (m, 3H), 1.62 (s, 3H, C-9), 1.51 (s, 3H, C-10), 1.22–1.35 (m, 1H); ^{13}C NMR δ: 148.3 (C-2), 143.1 (C aromat.), 138.5 (C aromat.), 132.9 (C-7), 129.5 (CH×2 aromat.), 127.0 (CH×2 aromat.), 125.7 (C-3), 109.4 (C-8), 54.4 (C-1), 40.2 (C-5), 36.5 (C-4), 30.3 (C-6), 21.5 (C-9), 20.7 (C-10), 19.9 (CH_3 from Ts).

N-*trans*-(4′-isopropenyl-1′-methyl-cyclohexan-2′-yl)toluenosulfonamide (11), (62%), t.t. = 85–87°C, $[\alpha]_D^{20}$ = –11.6 (c = 20.0, THF); ^{1}H NMR, δ: 7.69–7.80 (m, 2H, aromat.), 7.23–7.33 (m, 2H, aromat.), 4.57–4.85 (m, 5H, NH, C-8, C-10) 3.94 (m, 1H, C-1), 2.41 (s, 3H, aromat.), 1.68–2.33 (m, 5H) 1.62 (s, 3H, C-9), 1.08–1.51 (m, 2H); ^{13}C NMR δ: 148.2 (C-2), 145.7 (C-7), 143.0 (C aromat.), 137.8 (C aromat.), 129.3 (CH×2 aromat.), 127.2 (CH×2 aromat.), 111.1 (C-10), 109.2 (C-8), 56.0 (C-1), 38.4 (C-5), 38.0 (C-3), 32.1 (C-6), 30.2 (C-4), 21.4 (CH_3 from Ts), 20.8 (C-9).

Synthesis of toluenesulfonamides in "one pot" reactions – general procedure:

– *Method A*: Sodium borohydride (0.5 g, 13.2 mmol) was added to a vigorously stirred solution of diphenyldiselenide (1.9 g, 6.1 mmol) in anhydrous ethanol (10 ml) at 0°C under argon atmosphere. Then, chloride (11.7 mmol) was added and the mixture was warmed to 50°C. After 1 h, the mixture was cooled to room temperature and anhydrous chloramine-T (2.7 g, 11.9 mmol) in anhydrous ethanol (16 ml) was added. After 24 h, 1.5 M NaOH (50 ml) was added and the crude product was extracted with ether (3 × 50 ml) and was purified by column chromatography. The yields of toluenesulfonamides are showed in Table 1 (Method A).

– *Method B:* Sodium borohydride (0.9 g, 24.2 mmol) was added to a vigorously stirred solution of diphenylditelluride (4.5 g, 11.0 mmol) in anhydrous ethanol (20 ml) at 0°C under argon atmosphere. Then, chloride (21.7 mmol) was added and the mixture was warmed to 50°C. After 1 h, the mixture was cooled to room temperature and anhydrous chloramine-T (5.0 g, 21.9 mmol) in anhydrous ethanol (30 ml) was added. After 24 h, 1.5 M NaOH (50 ml) was added and the crude product was extracted with ether (3 × 50 ml) and was purified by column chromatography. The yields of toluenesulfonamides are showed in Table 1 (Method B).

Reduction of toluenesulfonamides with sodium in liquid ammonia – general procedure: Toluenesulfonamide (65.6 mmol) was dissolved in liquid, dry ammonia (200 ml). Sodium (3.0 g, 130 mmol) was added with stirring over 2 h at –45°C. After 2 h, crystalline ammonium acetate was added to decolorize the mixture, which was allowed to warm to room temperature and left overnight. Dry solid was treated with water (50 ml) and extracted with ether (3 × 100 ml). Organic layer was separated, washed with 2 M sodium hydroxide, water and brine, dried and concentrated. The product was distilled to give:

N-3,7-dimethyl-1,6-octadienylamine (12) [18], (53%), b.p. 27–29.5°C/0.1 mmHg, ^{1}H NMR, δ: 5.88 (m, 1H, C-2), 5.05 (m, 3H, C-1, C-6), 1.94 (m, 2H, C-5), 1.66 (s, 3H,C-8), 1.58 (s, 3H, C-9), 1.43 (m, 2H, C-4), 1.27 (s, 2H, NH_2), 1.14 (s, 3H, C-10); ^{13}C NMR δ: 147.3 (C-2), 131.2 (C-7), 124.4 (C-6), 110.4

(C-1), 53.6 (C-3), 43.1 (C-4), 28.4 (C-8), 25.6 (C-9), 23.0 (C-5), 17.5 (C-10); GC-MS (E.I.): 53 (6), 70 (13), 81 (6), 82 (6), 137 (23), 138 (8), 152 (9), 153 (17), 154 (100), 155 (9).

N-*trans*-5-isopropyl-2-methylcyclohex-2-enylamine (13) [2], (58%), b.p. 43–44°C/0.5 mmHg; $[\alpha]_D^{20} = +0.4$ (c = 33.0, $CHCl_3$); ^{1}H NMR, δ: 5.42 (m, 1H, C-3), 3.14 (m, 1H, C-1), 1.98 (m, 2H), 1.74 (s, 3H, C-10), 1.41 (m, 4H), 1.30 (s, 2H, NH_2), 0.89 (m, 6H, C-8, C-9); ^{13}C NMR δ: 136.3 (C-1), 123.1 (C-2), 49.9 (C-6), 36.1 (C-5), 33.9 (C-4), 31.9 (C-7), 29.0 (C-3), 21.1(C-10), 19.9 (C-8), 19.4 (C-9); GC-MS (E.I.): 71 (58), 82 (45), 83 (53), 96 (53), 110 (43), 137 (39), 138 (75), 152 (36), 153 (43), 154 (100).

N-*trans*-5-isopropenyl-2-methylcyclohex-2-enylamine (14) [19], (50%), b.p. 45.5–47.7°C/0.4 mmHg, $[\alpha]_D^{20} = -6{,}4$ (neat), $n_D^{20} = 1.4947$; ^{1}H NMR, δ: 5.44 (m, 1H, C-2), 4.70 (m, 2H, C-8), 3.34 (m, 1H, C-1), 1.79–2.31 (m, 5H), 1.67–1.76 (m, 6H, C-9, C-10), 1.19–1.41 (m, 2H, NH_2); ^{13}C NMR δ: 149.1(C-2), 122.8 (C-3), 108.7 (C-7), 108.6 (C-8), 51.9 (C-1), 41.2 (C-5), 39.4 (C-4), 31.2 (C-6), 20.5 (C-9), 19.6 (C-10); GC-MS (E.I.): 82 (50), 83 (100), 93 (39), 94 (40), 107 (35), 108 (93), 119 (39), 135 (36), 136 (80), 152 (42).

N-*trans*-4-isopropenyl-1-methylenecyclohexan-2-ylamine (15), (80%), b.p. 40–42°C/0.5 mmHg, $[\alpha]_D^{20} = -6{,}8$ (c = 8.0, $CHCl_3$), $n_D^{20} = 1.4958$; ^{1}H NMR, δ: 4.63–4.76 (m, 4H, C-8, C-10), 3.64 (t, 1H, C-1, J = 4 Hz), 2.08–2.53 (m, 4H), 1.71 (s, 3H, C-9), 1.50–1.89 (m, 3H), 1.35 (s, 2H, NH_2); ^{13}C NMR δ: 151.9 (C-2), 149.2 (C-7), 108.8 (C-10), 107.5 (C-8), 53.4 (C-1), 39.5 (C-3), 38.1 (C-5), 32.7 (C-6), 29.8 (C-4), 20.9 (C-9); GC-MS (E.I.): 82 (25), 95 (17), 107 (23), 108 (42), 119 (20), 122 (18), 133 (22), 134 (26), 135 (30), 152 (100).

Air oxidation of the reaction mixture of chlorides and phenyltellurosodium – general procedure: Sodium borohydride (1.2 g, 31.8 mmol) was added to a vigorously stirred solution of diphenylditelluride (7.2 g, 17.6 mmol) in anhydrous ethanol (32 ml) at 0°C under argon atmosphere. Then, chloride (35.2 mmol) was added, and the mixture was warmed to 50°C. After 1 h, the mixture was cooled to room temperature and air was passed through for 1 h. A precipitate was formed and was separated, the solvent was removed and the product was distilled to give:

Linalool (28) [21], (41%), b.p. 42–42.5°C/0.5 mmHg, $n_D^{20} = 1.4619$; ^{1}H NMR δ: 5.91 (m, 1H, C-2), 5.12 (m, 3H, C-1, C-6), 2.01 (m, 2H, C-5), 1.68 (s, 3H, C-8), 1.60 (s, 3H, C-9), 1.58 (m, 1H, OH), 1.56 (m, 2H, C-4), 1.29 (s, 3H, C-10); ^{13}C NMR, δ: 145.1 (C-2), 131.6 (C-7), 124.4 (C-6), 111.5 (C-1), 73.3 (C-3), 42.1 (C-4), 27.8 (C-10), 25.6 (C-8), 22.5 (C-5), 17.6 (C-9).

Carvotanacetone (29), [22] (63%), b.p. 51–52°C/0.3 mmHg, $[\alpha]_D^{20} = -7.6$ (neat); $n_D^{20} = 1.4812$; ^{1}H NMR δ: 6.73 (m, 1H, C-3), 1.81–2.60 (m, 4H), 1.77 (m, 3H, C-10), 1.55 (m, 2H), 0.89 (m, 6H, C-8, C-9); ^{13}C NMR, δ: 200.3 (C-3), 145.0 (C-1), 135.2 (C-2), 42.0 (C-5), 41.9 (C-4), 31.9 (C-7), 29.8 (C-6), 15.5 (C-10), 13.5 (C-8), 13.4 (C-9).

Carvone (30) [21], (67%), b.p. 44–47°C/0.5 mmHg, $[\alpha]_D^{20} = +8.5$ (neat); $n_D^{20} = 1.5029$; ^{1}H NMR δ: 6.74 (m, 1H, C-3), 4.76 (m, 2H, C-8), 2.15–2.77 (m, 5H), 1.77 (s, 3H, C-9), 1.74 (s, 3H, C-10); ^{13}C NMR, δ: 199.4 (C-1), 146.5 (C-2), 144.4 (C-3), 135.3 (C-7), 110.3 (C-8), 43.1 (C-6), 42.4 (C-5), 31.2 (C-4), 20.4 (C-9), 15.6 (C-10).

Perillaldehyde (31) [21], (54%), b.p. 56–59°C/0.5 mmHg, $[\alpha]_D^{20} = -115.2$ (neat); $n_D^{20} = 1.5074$; ^{1}H NMR δ: 9.44 (s, 1H, C-10), 6.83 (m, 1H, C-2), 4.63–4.84 (m, 2H, C-8), 1.79–2.62 (m, 5H), 1.76 (s, 3H, C-9), 1.16–1.60 (m, 2H); ^{13}C NMR, δ: 193.5 (C-10), 150.2 (C-2), 148.1 (C-1), 141.1 (C-7), 109.3 (C-8), 40.6 (C-4), 31.6 (C-3), 26.2 (C-6), 21.4 (C-5), 20.5 (C-9).

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