α-Cyclopropylalkyl cations of a spiro[2.4]heptane system

S. A. Osadchii,[a] V. I. Mamatyuk,[a] V. G. Shubin,[a] A. C. Razus,[b] E. Bartha,[b] and Zs. Arvay[b]*

[a]*Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, 9 prosp. Akad. Lavrent'eva, 630090 Novosibirsk, Russian Federation. Fax: +7 (383 2) 35 4752*

[b]*C. D. Nenitzescu Institute of Organic Chemistry, Romanian Academy, 71141 Bucharest-15, Romania. Fax: (00401) 312 1601*

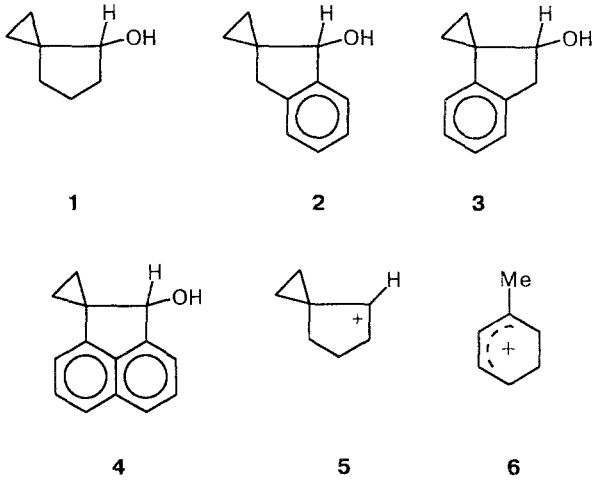
α-Cyclopropylalkyl cations of a spiro[2.4]heptane system, which are possible intermediates in solvolytic reactions of the corresponding cyclopropylalkanol derivatives, have been generated from compounds of the spiro(indan-2,1'-cyclopropane), spiro(indan-1,1'-cyclopropane), and spiro[acenaphthylene-1(2*H*),1'-cyclopropane] classes under "long life" conditions (HSO_3F—SO_2FCl—CD_2Cl_2, −100 °C).

Key words: α-cyclopropylalkyl cation; spiro[2.4]heptane; spiro(indan-1-ol-2,1'-cyclopropane); spiro(indan-2-ol-1,1'-cyclopropane); spiro[acenaphthylene-1(2*H*),1'-cyclopropane]; cyclobut[a]acenaphthylene.

It has been shown previously that the acid-catalyzed solvolysis of spiro[2.4]heptan-4-ols (**1**—**4**) ($HClO_4$—aqueous dioxane) affords predominantly cyclobutyl and allylalkanol derivatives.[1—3] The interconversion of cyclopropyl-, cyclobutyl-, and allylalkanols may result from an equilibrium between classical and nonclassical "short-lived" carbocationic intermediates.[4] In the present work, in order to confirm the schemes suggested for the solvolysis of compounds of the spiro[2.4]heptane system we studied the generation of these intermediates under the conditions of "long life".

To the best of our knowledge, the secondary spiro[2.4]hept-4-yl cation (**5**) has not yet been generated, apparently due to its instability. In fact, spiro[2.4]heptan-4-ol (**1**) is converted[5] into 1-methylcyclohexenyl cation (**6**) in SbF_5—SO_2FCl at −130 °C. We managed to generate "long-lived" cations of the spiro[2.4]heptane system from alcohols **2** and **4**. Their stability is obviously due to the participation of the aromatic rings in the delocalization of the positive charge.

When spiro(indan-1-ol-2,1'-cyclopropane) (**2**) is dissolved in the HSO_3F—SO_2FCl—CD_2Cl_2 system (−100 °C), the spiro(indan-1-yl-2,1'-cyclopropane) cation (**7**) is formed (Scheme 1). For comparison, we generated 1-methyl- and 1-hydroxyspiro(indan-1-yl-2,1'-cyclopropane) cations (**10** and **11**) by dissolution of 1-methylspiro(indan-1-ol-2,1'-cyclopropane) (**8**) and spiro(indan-1-one-2,1'-cyclopropane) (**9**) in the same acid system. The structures of cations **7**, **10**, and **11** were determined by ^1H and ^{13}C NMR spectroscopy (Tables 1 and 2). The assignment of the signals in the spectra was based on a comparison with the spectra of the 6-methyl-1,1a,6,6a-tetrahydrocycloprop[a]inden-6-yl cation (**12**).[6]



According to the ^1H NMR spectra, ions **7** and **10** are converted into complex mixtures of unidentified products as the temperature increases to −40 and −20 °C, respectively, whereas ion **11** is stable at −20 °C for 10 min.

We did not manage to generate cation **13** from spiro(indan-2-ol-1,1'-cyclopropane) (**3**) in the same acid system (−100 °C). Instead, resinification of the reaction

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Table 1. ^{1}H NMR spectra (200.13 MHz) of cations **7**, **10**, and **11***

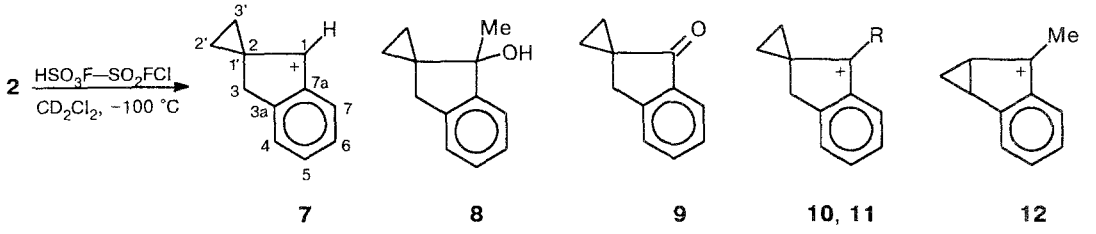
Cation	T/°C	δ								
		C(1)H$_3$	OH	H(1)	C(2')H$_2$, C(3')H$_2$	C(3)H$_2$	H(4)	H(6)	H(5)	H(7)
7	−100	—	—	10.11 (s)	3.3—3.7 (m)	3.77 (s)	8.05 (d)	7.84 (t)	8.28 (t)	8.34 (d)
10	−90	2.93 (s)	—	—	3.0—3.2 (m)	3.69 (s)	8.00 (d)	7.84 (t)	8.25 (t)	8.30 (d)
11	−60	—	13.3**	—	2.3—2.6 (m)	3.59 (s)	7.90 (d)	7.80 (t)	8.16 (t)	8.28 (d)

* For doublet and triplet signals of H(4)—H(7), J_{H-H} = 8 Hz.
** The broadened signals for acid protons are observed at δ 12.0.

Table 2. ^{13}C NMR spectra (50.32 MHz) of cations **7**, **10**, and **11**

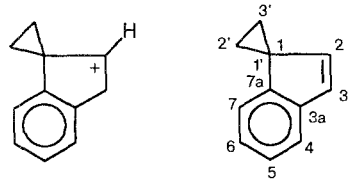
Cation	T/°C	δ, $^1J_{H-C}$/Hz										
		C(1)	C(2)	C(3)	C(3a)	C(4)	C(5)	C(6)	C(7)	C(7a)	C(2'), C(3')	CH$_3$
7	−100	225.1 (d, J = 175)	62.3 (s)	44.4 (t, J = 133)	172.7 (s)	126.9 (d, J = 165)	145.0 (d, J = 160)	130.2 (d, J = 165)	132.7 (d, J = 170)	143.7 (s)	42.0 (t, J = 172)	—
10	−90	243.4 (s)	57.3 (s)	44.1 (t, J = 136)	169.2 (s)	127.1 (d)	144.8 (d)	129.5 (d)	130.1 (d)	143.9 (s)	39.3 (t, J = 173)	17.7 (q)
11	−60	220.1 (s)	36.4 (s)	29.7 (t)	164.2 (s)	126.7 (d)	142.3 (d)	127.6 (d)	129.9 (d)	131.5 (s)	37.9 (t)	—

Scheme 1



7 **8** **9** **10, 11** **12**

R = Me (**10**), OH (**11**)



13 **14**

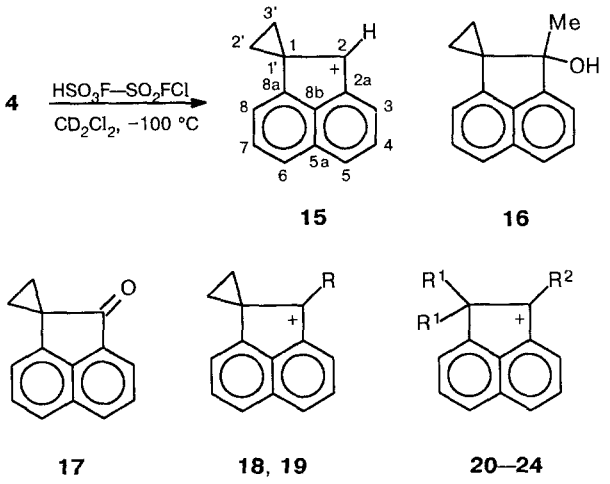
mixture occurred, which may be due to the easy formation of spiro(indene-2-1,1'-cyclopropane) (**14**), which is unstable in an acidic medium (see Ref. 7). Under similar conditions, the latter compound also affords products of resinification.

When spiro[acenaphthylene-1(2*H*),1'-cyclopropane]-2-ol (**4**) is dissolved in the same acid system (−100 °C), the spiro[acenaphthylene-1(2*H*),1'-cyclopropan]-2-yl cation (**15**) is formed (Scheme 2). This cation can also be generated from 8,8a-dihydrocyclobut[a]acenaphthylen-6b[7*H*]-ol (**25**) under similar conditions, obviously, due to rearrangement of the unstable cationic intermediate (**26**) (Scheme 3). Similar examples of the formation of stable α-cyclopropylalkyl cations from cyclobutane derivatives have been reported.[11]

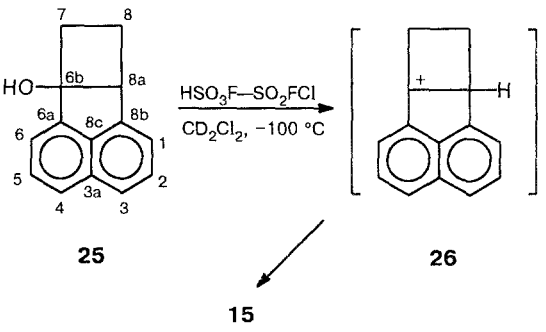
In the $HSO_3F—SO_2FCl—CD_2Cl_2$ acid system (−100 °C), 2-methylspiro[acenaphthylene-1(2*H*),1'-cyclopropan]-2-ol (**16**) and spiro[acenaphthylene-1(2*H*),1'-cyclopropan]-2-one (**17**) afforded 2-methyl- and 2-hydroxyspiro[acenaphthylene-1(2*H*),1'-cyclopropan]-2-yl cations (**18** and **19**). The structures of cations **15**, **18**, and **19** were confirmed by comparing their ^{1}H and ^{13}C NMR spectra (Tables 3, 4) with those recorded for the related neutral compounds **17** and **25** (see Table 5 and Experimental). The signals in the spectra were assigned by analogy with those of acenaphthylenonium ions (**20—24**).[8—10]

The assignment of signals in the ^{1}H NMR spectra of compounds **17** and **25** (see Experimental) was based on the multiplicities of the signals, double resonance, and took into account the effect of the oxygen atom, *viz.*, the downfield shift of signals for the nearest protons. In the case of compound **17**, allowance was made for the

Scheme 2



Scheme 3



anisotropic effect of the cyclopropane ring, *viz.*, an upfield shift of the signal for the H(8) proton that is the nearest to the ring. For compound **25**, the anisotropic effect of the aromatic rings, *viz.*, upfield shifts of the signals for H(7, *endo*) and H(8, *endo*) with respect to the corresponding signals for H(7, *exo*) and H(8, *exo*), and a downfield shift of the signal for H(8a) located at the "benzyl" position (*cf.* Ref. 2), were taken into account.

The ^{13}C NMR signals of compounds **17** and **25** were assigned on the basis of their multiplicities and the values of their residual splitting in the "off-resonance" spectrum, which are proportional to the differences between the radiation frequency and the frequencies of the signals for the corresponding protons in the ^1H NMR spectrum (*cf.* Ref. 6).

The ^1J constants of the C(2') and C(3') atoms in ion **15** and ketone **17** (174 and 166 Hz, respectively), are typical for cyclopropanes[14] and quite different from ^1J for the C(7) and C(8) atoms (135 and 138 Hz, respec-

Table 3. ^1H NMR spectra (200.13 MHz) of cations **15**, **18**, and **19**

Cation	*T*/°C	δ, *J*/Hz					
		$C(2)H_3$	H(2)	$C(2')H_2$, $C(3')H_2$	H(4), H(6), H(7), H(8)	H(3)	H(5)
15	−85	—	9.91 (s)	3.6—3.8 (m)	8.0—8.4 (m)	8.9—9.1 (m)	
18	−60	3.14 (s)	—	3.1—3.7 (m)	7.8—8.1 (m, 2 H) 8.2—8.4 (m, 2 H)	8.93 (d, *J* = 8)	9.04 (d, *J* = 8)
19*	−60	—	—	2.6—3.0 (m)	7.61 (d, 1 H, *J* = 7); 7.90 (t, 1 H, *J* = 8); 8.1—8.3 (m, 2 H)	8.7—8.9 (m)	

* The signal for the proton of the OH group coincides with that for the acid proton (δ 11.9).

Table 4. ^{13}C NMR spectra (50.32 MHz) of cations **15**, **18**, and **19**

Cation	*T*/°C	δ						
		C(1)	C(2)	C(4), C(6), C(7) and C(8) (doublet signals)	C(3)	C(5)	C(2a), C(5a), C(8a) and C(8b) (singlet signals)	C(2'), C(3')	CH_3
15	−85	57.3 (s)	203.9 (d)	128.5; 131.2; 132.1; 132.7	141.7	151.7	129.7; 140.2; 142.6; 142.9	37.5 (t, $^1J_{H-C}$ = 174 Hz)	—
18	−60	54.9 (s)	225.3 (s)	125.8; 130.0; 131.0; 131.8	137.2	149.7	129.9; 140.2; 141.1; 142.0	36.3 (t)	16.8 (q)
19	−60	39.4 (s)	214.7 (s)	121.8; 127.2; 130.2; 130.4	131.8	143.2	126.7; 129.9; 136.2; 141.3	29.7 (t)	—

Table 5. ^{13}C NMR spectra of compounds **4**, **16**, and **17***

Compound	δ, $^1J_{H-C}$/Hz									
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(2a), C(5a), C(8a) and C(8b) (singlet signals)	C(2') and C(3')	CH_3
			(doublet signals)								
4 [2]	33.2 (s)	79.0 (d)	128.3	124.8	120.7	122.0	128.0	113.0	130.6; 136.6; 144.2; 147.6	12.9 (t); 18.2 (t)	—
16	37.5 (s)	79.8 (s)	128.2	124.4	118.6	121.8	128.0	113.0	130.4; 135.1; 147.4; 148.9	14.7 (t); 15.1 (t)	25.6 (q)
17	33.4 (s)	202.5 (s)	130.7 (J = 162)	127.4 (J = 160)	120.9 (J = 164)	122.9 (J = 166)	128.0 (J = 161)	114.4 (J = 159)	129.6; 133.3; 140.1; 140.3	19.2 (t, J = 166)	—

* The spectra were recorded on a spectrometer operating at 50.32 MHz (compounds **4** and **16**) or 100.61 MHz (compound **17**).

Table 6. ^{13}C NMR spectra (50.32 MHz) of compounds **2**, **3**, **8**, and **9**

Compound	δ						
	C(1)	C(2)	C(3)	C(4)—C(7) (doublet signals)	C(3a) and C(7a) (singlet signals)	C(2') and C(3') (triplet signals)	CH_3
2	80.0 (d)	27.6 (s)	39.7 (t)	124.1; 124.2; 126.2; 127.8	142.5; 144.4	7.7; 13.3	—
3	33.8 (s)	77.8 (d)	40.9 (t)	118.6; 124.4; 125.8; 126.6	140.4; 145.3	9.5; 16.6	—
8	79.2 (s)	31.8 (s)	40.1 (t)	122.3; 124.0; 126.3; 127.4	140.4; 148.8	9.0; 9.7	24.5 (q)
9	205.9 (s)	29.1 (s)	35.7 (t)	122.7; 125.7; 126.8; 133.5	137.1; 152.6	17.5	—

tively) of the cyclobutane moiety of alcohol **25**. The ^1H NMR spectral patterns of the multiplicities of the signals for the cyclopropane moieties of ions **15** and **18** and ketone **17** are similar, differing essentially from that for the cyclobutane moiety in the spectrum of alcohol **25**.

According to the ^1H NMR spectra, ions **15** and **18** are converted into complex mixtures of unidentified products when the temperature increases to −60 and −20 °C, respectively. Ion **19**, like anion **11**, is stable at −20 °C for 10 min.

Thus, α-cyclopropylalkyl cations of the spiro[2.4]-heptane series, possible intermediates in the solvolytic reactions of cyclopropylalkanols, were generated for the first time under "long-life" conditions.

Experimental

^1H and ^{13}C NMR spectra were recorded on Bruker AM-400, AC-200, and WP-200 SY spectrometers (for ^1H, 400.13 and 200.13 MHz, for ^{13}C, 100.61 and 50.32 MHz). Chemical shifts are given in ppm with respect to TMS for solutions in $CDCl_3$. The signal of the solvent at δ_H 7.24 ($CHCl_3$) and δ_C 76.90 ($CDCl_3$) was used as the internal standard. In the case of carbocations, CD_2Cl_2 (δ_C 53.30) containing an admixture of $CDHCl_2$ (δ_H 5.33) was used as the internal standard.

For the generation of carbocations, bidistilled HSO_3F (b.p. 158—160 °C) and SO_2FCl purified by the known procedure[6] were used. The samples of carbocations for NMR studies were withdrawn from the reaction mixtures as has been described previously.[12]

Molecular weights and elemental compositions were determined on a Finnigan MAT-8200 high-resolution mass spectrometer. IR spectra were recorded on a UR-20 spectrometer and UV spectra were obtained on a Specord UV-VIS instrument.

The starting alcohols **2**—**4** and **25**, indene **14** (see Refs. 2 and 7), and ketones **9** and **17** (see Refs. 7 and 13) were prepared by the previously reported procedures.

The parameters of the ^1H NMR spectra of compounds **2**—**4**, **9** and **14** agree with the literature data.[2,7,13] The ^{13}C NMR spectra of compounds **2**—**4**, **8**, **9**, **16**, and **17** are given in Tables 5 and 6.

Compound **14**: ^{13}C NMR (50.32 MHz), δ: 14.5 (t, C(2') and C(3')); 33.0 (s, C(1)); 117.2 (d); 121.2 (d); 124.0 (d); 125.2 (d); 128.1 (d, C(3)—C(7)); 140.6 (d, C(2)); 143.4 and 147.7 (both s, C(3a), C(7a)).

Ketone **17**: ^1H NMR (400.13 MHz), δ: 1.47 (m, 2 H); 1.74 (m, 2 H, C(2')H_2 and C(3')H_2); 6.86 (d, 1 H, H(8), J = 6.8 Hz); 7.42 (dd, 1 H, H(7), J = 6.8 and 6.4 Hz); 7.58 (dd, 1 H, H(4), J = 8.0 and 7.0 Hz); 7.82 (d, 1 H, H(6), J = 6.4 Hz); 7.87 (d, 1 H, H(5), J = 7.0 Hz); 7.91 (d, 1 H, H(3), J = 8.0 Hz), *cf.* Ref. 13.

Alcohol **25**: ^1H NMR (400.13 MHz), δ: 1.26 (m, 1 H, H(8, *endo*), $J_{8,\ endo-8,\ exo}$ = 12.1, $J_{8,\ endo-7,\ endo}$ = 9.2, $J_{8,\ endo-7,\ exo}$ = 8.5, and $J_{8,\ endo-8a}$ = 5.9 Hz); 2.21 (s, 1 H, OH); 2.32 (m, 1 H, H(7, *endo*), $J_{7,\ endo-7,\ exo}$ = 12.4, $J_{7,\ endo-8,\ exo}$ = 4.6, and $J_{7,\ endo-8a}$ = 1.3 Hz); 2.45 (m, 1 H, H(8, *exo*), $J_{8,\ exo-7,\ exo}$ = 11.2 and $J_{8,\ exo-8a}$ = 9.9 Hz); 2.62 (m, 1 H, H(7, *exo*), $J_{7,\ exo-8a}$ = 0.6 Hz); 3.84 (m, 1 H,

H(8a)); 7.13 (d, 1 H, H(1), J = 6.8 Hz); 7.38 (m, 2 H, H(2), H(4)); 7.46 (dd, 1 H, H(5), J = 8.1 and 7.0 Hz); 7.55 (d, 1 H, H(3), J = 8.3 Hz); 7.65 (d, 1 H, H(6), J = 8.1 Hz), *cf.* Ref. 2.

Alcohol **25**: ^{13}C NMR (100.61 MHz), δ: 22.4 (t, C(8), $^1J_{H-C}$ = 138 Hz); 34.5 (t, C(7), $^1J_{H-C}$ = 135 Hz); 52.3 (d, C(8a), $^1J_{H-C}$ = 143 Hz); 84.0 (s, C(6b)); 118.7 (C(1), $^1J_{H-C}$ = 161 Hz); 122.6 (d, C(3), $^1J_{H-C}$ = 162 Hz); 125.0 (d, C(6), $^1J_{H-C}$ = 163 Hz); 118.8, 128.15, and 128.2 (all d, C(2), C(4), C(5), $^1J_{H-C}$ = 160, 165, and 157 Hz); 131.4, 138.0, 146.2, and 147.6 (all s, C(3a), C(6a), C(8b), C(8c)), *cf.* Ref. 2.

1-Methylspiro(indan-1-ol-2,1'-cyclopropane) (8) was prepared by the reaction of ketone **9** (4 mmol) with MeMgI (from 6 mmol of methyl iodide and 6.5 mg-at. of Mg in 6.5 mL of ether). Yield 75 %, m.p. 44—45 °C (from pentane). Mol. weight found by mass spectrometry: 174.1034, $C_{12}H_{14}O$. ^1H NMR (10 % solution in $CDCl_3$), δ: 0.45—1.05 (m, 4 H, C(2')H_2, C(3')H_2); 1.35 (s, 3 H, CH_3); 2.34 (s, 1 H, OH); 2.93 and 2.97 (both d, 1 H, AB system, C(3)H_2, J = 16 Hz); 7.1—7.5 (m, 4 H, H(4)—H(7)). ^{13}C NMR spectrum is given in Table 6. IR (1 % solution in CCl_4), ν/cm^{-1}: 950, 1025, 1050, 1090, 1110, 1130, 1160, 1330, 1370, 1440, 1460, 1480, 2850, 2940, 2980, 3005, 3080, 3600 (OH). UV [10^{-4} N solution in EtOH), λ_{max}/nm (log ε): 212 (3.93), 260 (2.78), 265 (3.00), and 272 (3.05).

2-Methylspiro[acenaphthylene-1(2*H*),1'-cyclopropan]-2-ol (16) was prepared from ketone **17** in a similar way. Yield 76 %, m.p. 110—111 °C (from hexane). Mol. weight found by mass spectrometry: 210.1047, $C_{15}H_{14}O$. ^1H NMR (10 % solution in $CDCl_3$), δ: 0.9—1.6 [m, 7 H, C(2')H_2, C(3')H_2, and CH_3 (the singlet for the CH_3 group is recorded at δ 1.38)]; 2.18 (s, 1 H, OH); 6.76 (d, 1 H, H(8), J = 7 Hz); 7.3—7.8 (m, 5 H, H(3)—H(7)). The ^{13}C NMR spectrum is given in Table 5. IR (1 % solution in CCl_4), ν/cm^{-1}: 940, 1060, 1080, 1125, 1180, 1325, 1375, 1610, 2980, 3005, 3045, 3600 (OH). UV [a 10^{-4} N solution in EtOH), λ_{max}/nm (log ε)]: 227 (4.80) and 297 (3.94).

Generation of carbocations: general procedure. A suspension of 0.03 mmol of a carbocation precursor (indene **14**, alcohol **2—4**, **8**, or **25**, or ketone **19** or **17**) in 0.2 mL of CD_2Cl_2 and 0.5 mL of SO_2FCl cooled to −120 °C was added dropwise with a pipette cooled with liquid nitrogen to a solution of 1.8 mmol of HSO_3F in 0.4 mL of SO_2FCl cooled to −120 °C. The mixture was stirred for 15 min at −120 °C until a transparent solution formed. Alcohol **3** and indene **14** yielded products of resinification under these conditions.

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