Propyne Iminium Salts By *N*-Alkylation of Alkynyl Imines

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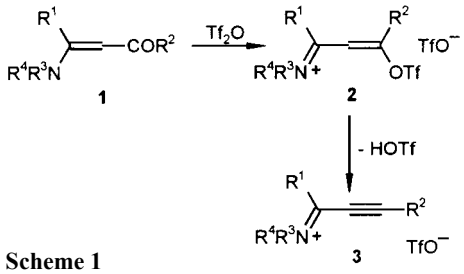
Abstract: *N*-Alkylation of alkynyl imines **5**, **6**, and **8** with methyl triflate or triethyloxonium tetrafluoroborate provides the open-chain propyne iminium salts **9** and **10**, the related salts **11a–e** and **12b** where the iminium function is a part of a heteroaromatic ring, and *p*-phenylene-bis(propyne iminium) salts **13a**,**c**. The method gives access to novel propyne iminium salts in which the C,C triple bond bears an alkyl, $SiMe_3$, or H substituent.

Key words: alkynyl imines, iminium salts, imine alkylation, imidoyl halides, C,C coupling with alkynes

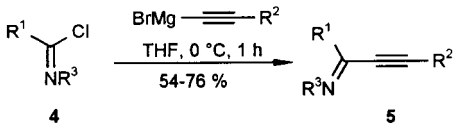
A convenient route to open-chain and semicyclic propyne iminium salts **3** is provided by *O*-sulfonylation of enamino ketones **1** with triflic anhydride followed by thermal or base-assisted 1,2-elimination of triflic acid from the resulting 3-trifloxypropene iminium salts **2**[1,2] (Scheme 1). However, this synthetic approach has several limitations. Thus, enamino aldehydes cannot be converted into propyne iminium salts due to subsequent rapid reaction of salts **2** (R^2 = H),[3] and treatment of 3-alkyl-3-trifloxypropene iminium salts (**2**, $R^2 = CHR_2$) with an amine base causes a deprotonation which initially leads to 1-amino-3-trifloxy-1,3-dienes rather than to propyne iminium salts.[4] So far, (1-methylbut-2-ynylidene)pyrrolidinium triflate (**3**, R^1 = R^2 = Me) represents the only propyne iminium salt with an alkyl-substituted C,C triple bond that could be prepared by the method under discussion; in this case, the conversion **2** → **3** was achieved by thermally induced HOTf elimination.[2]



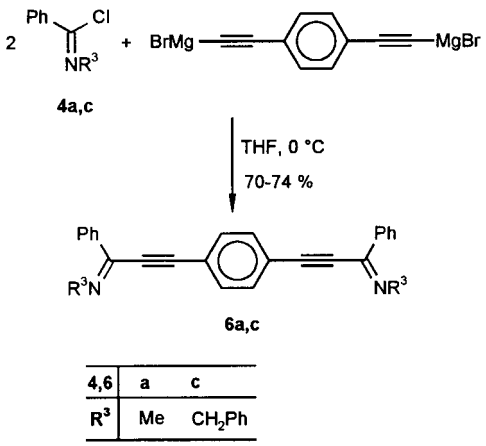
Scheme 1

Since propyne iminium salts have proven to be useful building blocks in organic synthesis (e.g. precursors to aminoallenes, 1- and 2-dienamines, and propargylamines[1c,5,6]), we were interested to circumvent some of the limitations of the synthetic approach mentioned above and to enlarge the collection of easily available propyne iminium salts, especially by addition of systems in which the C,C-triple bond is terminal or bears an alkyl or silyl substituent. We report here that *N*-alkylation of alkynyl imines is a useful and versatile alternative for the preparation of propyne iminium salts. Surprisingly enough, this obvious synthetic strategy has not been used before, except for the *N*-quaternization of rather special alkynyl imines such as 2-alkynylpyridines.[7,8]

Syntheses of a few acyclic alkynyl imines have been reported. They were prepared by palladium-catalyzed coupling of imidoyl chlorides with terminal alkynes[9,10] as well as (phenylethynyl)tributyltin,[11] by condensation of alkynyl ketones[12–14] and acetylenic aldehydes[15] with primary amines, or by reaction of alkyl alkynyl ketones with *N*-ethylidenecyclohexanamine.[12] We report here that *N*-alkyl-substituted alkynyl imines **5a–f** can be obtained conveniently from imidoyl chlorides **4a–f** and (alk-1-ynyl) Grignard reagents (Scheme 2). This method also gives access to the *p*-phenylene-bis(alkynyl imines) **6a**,**c** (Tables 1 and 2).



4,5	R^1	R^2	R^3
a	Ph	$SiMe_3$	Me
b	Ph	$SiMe_3$	Et
c	Ph	$SiMe_3$	CH_2Ph
d	Ph	*n*-Bu	Me
e	Ph	*n*-Bu	Et
f	Ph	*n*-Bu	CH_2Ph



4,6	a	c
R^3	Me	CH_2Ph

Scheme 2

Table 1 Alkynyl Imines **5**, **6** and **8** Prepared (Schemes 2 and 3) and their IR Data

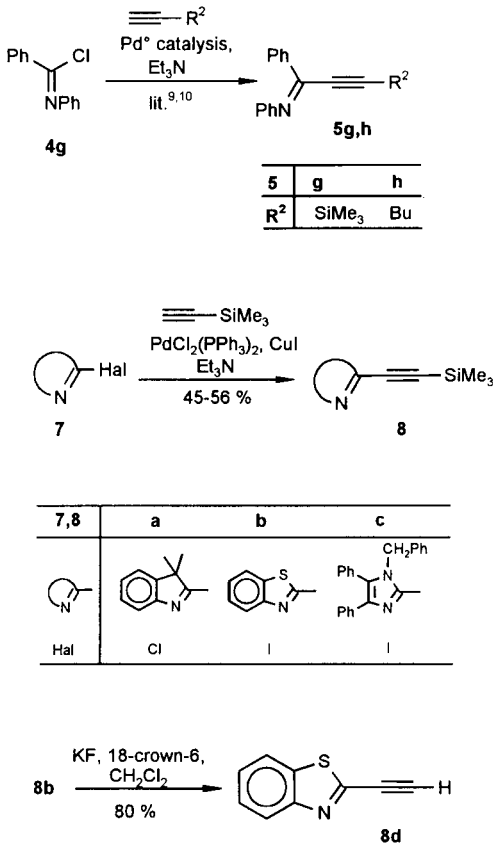
Product	Yield (%)	mp (°C) (solvent) or bp (°C)/mbar	IR (neat or KBr) (cm^{-1})	
			$\nu_{C\equiv C}$	Other Signals
5a	75	135/0.018	2151	2959, 2899, 1595, 1573, 1449, 1397, 1314, 1277, 1252, 1084, 1075, 1061, 1028
5b	76	155/0.01	2149	2967, 2933, 2899, 2868, 1591, 1570, 1449, 1314, 1275, 1252, 1100, 1057, 1015
5c	66	36–38 (Et_2O)	2152	2959, 1593, 1567, 1492, 1448, 1314, 1272, 1252, 1087, 1063, 1028
5d	69	145/0.003	2211	2957, 2931, 2871, 1596, 1574, 1466, 1447, 1327, 1314, 1284, 1028
5e	54	155/0.003	2207	2962, 2932, 2869, 1593, 1572, 1448, 1314, 1283
5f	74	oil[b]	2211	2956, 2930, 2870, 1594, 1571, 1491, 1453, 1314, 1282, 1028
6a	74	100–102 (Et_2O)	2205	1594, 1571, 1446, 1317, 1299, 1053, 1027
6c	70	119–120 (Et_2O)	2205	3025, 1586, 1561, 1491, 1446, 1315, 1297, 1054, 1027
8a	50	120/0.02	2066	2964, 2899, 1549, 1454, 1249, 1206, 1032
8b	56	112/0.028	2160	2959, 1476, 1428, 1324, 1251, 1161, 1140, 1124, 1064
8c	45	114–116[c]	2162	3046, 2955, 1600, 1496, 1482, 1448, 1392, 1354, 1247
8d	80	40–41[d]	2107	3195 (≡CH), 1472, 1429, 1313, 1121

[a] Satisfactory microanalyses obtained: C ± 0.40, H ± 0.23, N ± 0.31. EI-HRMS, *m/z*: **5c**: calcd. 291.1439, found 291.1441; **5f**: calcd. 275.1674, found 275.1673.
[b] Purified by column chromatography (silica gel, Et_2O).
[c] Purified by column chromatography (silica gel, $CHCl_3$).
[d] Lit.[15] mp 39–41°C.

Table 2 ^1H and ^{13}C NMR Data of Compounds **5**, **6**, **8**

Product	^1H NMR ($CDCl_3$/TMS), δ, *J* (Hz)	^{13}C NMR ($CDCl_3$) δ
5a	0.30 [s, 9 H, $Si(CH_3)_3$], 3.63 (s, 3 H, NCH_3), 7.34–7.39 (m, 3 H, CH_{arom}), 7.98–8.03 (m, 2 H, CH_{arom})	–0.39 [$Si(CH_3)_3$], 43.57 (NCH_3), 95.61, 105.86 (C≡C), 127.14, 128.06, 130.19, 137.03 (C_{arom}), 152.20 (C=N)
5b	0.30 [s, 9 H, $Si(CH_3)_3$], 1.35 (t, *J* = 7.3, 3 H, CH_3), 3.88 (q, *J* = 7.3, 2 H, NCH_2), 7.36–7.41 (m, 3 H, CH_{arom}), 8.01–8.06 (m, 2 H, CH_{arom})	–0.43 [$Si(CH_3)_3$], 15.34 (CH_3), 50.73 (NCH_2), 95.83, 104.78 (C≡C), 127.23, 128.02, 130.11, 137.16 (C_{arom}), 150.17 (C=N)
5c	0.30 [s, 9 H, $Si(CH_3)_3$], 5.06 (s, 2 H, NCH_2), 7.20–7.44 (m, 8 H, CH_{arom}), 8.09–8.14 (m, 2 H, CH_{arom})	–0.49 [$Si(CH_3)_3$], 59.97 (NCH_2), 96.08, 105.59 (C≡C), 126.56, 127.43, 127.86, 127.98, 128.16, 130.36, 136.82, 139.66 (C_{arom}), 151.00 (C=N)
5d	0.91 (t, *J* = 7.0, 3 H, CH_3), 1.39–1.61 (m, 4 H, CH_2CH_2), 2.44 (t, *J* = 6.8, 2 H, ≡CCH_2), 3.58 (s, 3 H, NCH_3), 7.32–7.35 (m, 3 H, CH_{arom}), 7.99–8.04 (m, 2 H, CH_{arom})	13.20 (CH_3), 18.67, 21.70 (CH_2CH_2), 30.13 (≡C*C*H_2), 42.96 (NCH_3), 73.33, 101.54 (C≡C), 126.97, 127.74, 129.74, 137.54 (C_{arom}), 152.32 (C=N)
5e	0.93 (t, *J* = 7.3, 3 H, CH_3), 1.32 (t, *J* = 7.3, 3 H, CH_3), 1.42–1.63 (m, 4 H, CH_2CH_2), 2.44 (t, *J* = 6.8, 2 H, ≡CCH_2), 3.83 (q, *J* = 7.3, 2 H, NCH_2), 7.31–7.39 (m, 4 H, CH_{arom}), 7.99–8.04 (m, 2 H, CH_{arom})	13.25 (CH_3), 15.31 (CH_3) 18.72, 21.74 (CH_2CH_2), 30.16 (≡C*C*H_2), 50.26 (NCH_2), 73.49, 100.58 (C≡C), 127.12, 127.79, 129.76, 137.73 (C_{arom}), 150.43 (C=N)
5f	0.92 (t, *J* = 7.0, 3 H, CH_3), 1.41–1.65 (m, 4 H, CH_2CH_2), 2.48 (t, *J* = 6.9, 2 H, ≡CCH_2), 5.01 (s, 2 H, NCH_2), 7.17–7.74 (m, 8 H, CH_{arom}), 8.06–8.11 (m, 2 H, CH_{arom})	13.33 (CH_3), 18.83, 21.81 (CH_2CH_2), 30.14 (≡C*C*H_2), 59.62 (NCH_2), 73.88, 101.39 (C≡C), 126.41, 127.41, 127.70, 127.87, 128.11, 130.09, 137.53, 139.92 (C_{arom}), 151.47 (C=N)
6a	3.71 (s, 6 H, NCH_3), 7.39–7.45 (m, 6 H, CH_{arom}), 7.58 (s, 4 H, CH_{arom}), 8.04–8.09 (m, 4 H, CH_{arom})	43.63 (NCH_3), 83.14, 98.03 (C≡C), 122.57, 127.13, 128.19, 130.36, 132.06, 137.12 (C_{arom}), 151.87 (C=N)
6c	5.13 (s, 4 H, NCH_2), 7.24–7.46 (m, 16 H, CH_{arom}), 7.59 (s, 4 H, CH_{arom}), 8.12–8.17 (m, 4 H, CH_{arom})	60.15 (NCH_2), 83.72, 97.63 (C≡C), 122.60, 126.79, 127.55, 127.91, 128.25, 128.39, 130.64, 132.21, 137.12, 139.66 (C_{arom}), 150.92 (C=N)
8a	0.30 [s, 9 H, $Si(CH_3)_3$], 1.50 [s, 6 H, $C(CH_3)_2$], 7.32–7.48 (m, 3 H, CH_{arom}), 7.62–7.70 (m, 1 H, CH_{arom})	–0.69 [$Si(CH_3)_3$], 22.67 (CCH_3), 55.04 (*C*CH_3), 85.55, 88.02 (C≡C), 120.25, 121.23, 125.98, 127.79, 144.26, 151.22 (C_{arom}), 176.79 (C=N)
8b	0.30 [s, 9 H, $Si(CH_3)_3$], 7.39–7.45 (m, 2 H, CH_{arom}), 7.74–7.78 (m, 1 H, CH_{arom}), 7.99–8.01 (m, 1 H, CH_{arom})	–0.84 [$Si(CH_3)_3$], 96.60, 102.72 (C≡C), 120.98, 123.36, 126.04, 126.35, 134.81, 147.81 (C_{arom}), 152.36 (C=N)
8c	0.21 [s, 9 H, $Si(CH_3)_3$], 5.09 (s, 2 H, NCH_2), 6.93–7.52 (m, 15 H, CH_{arom})	–0.52 [$Si(CH_3)_3$], 48.62 (NCH_2), 93.52, 101.55 (C≡C), 126.82, 126.99, 127.62, 127.99, 128.20, 128.42, 128.86, 128.98, 129.52, 130.73, 133.24, 133.87, 134.15, 136.17, 138.36 (C_{arom})
8d	3.60 (s, 1 H, ≡CH), 7.38–7.54 (m, 2 H, CH_{arom}), 7.80–7.85 (m, 1 H, CH_{arom}), 8.03–8.08 (m, 1 H, CH_{arom})	76.62, (*C*≡CH), 83.92 (≡CH), 121.21, 123.72, 126.45, 126.66, 135.00, 147.27 (C_{arom}), 152.45 (C-2)

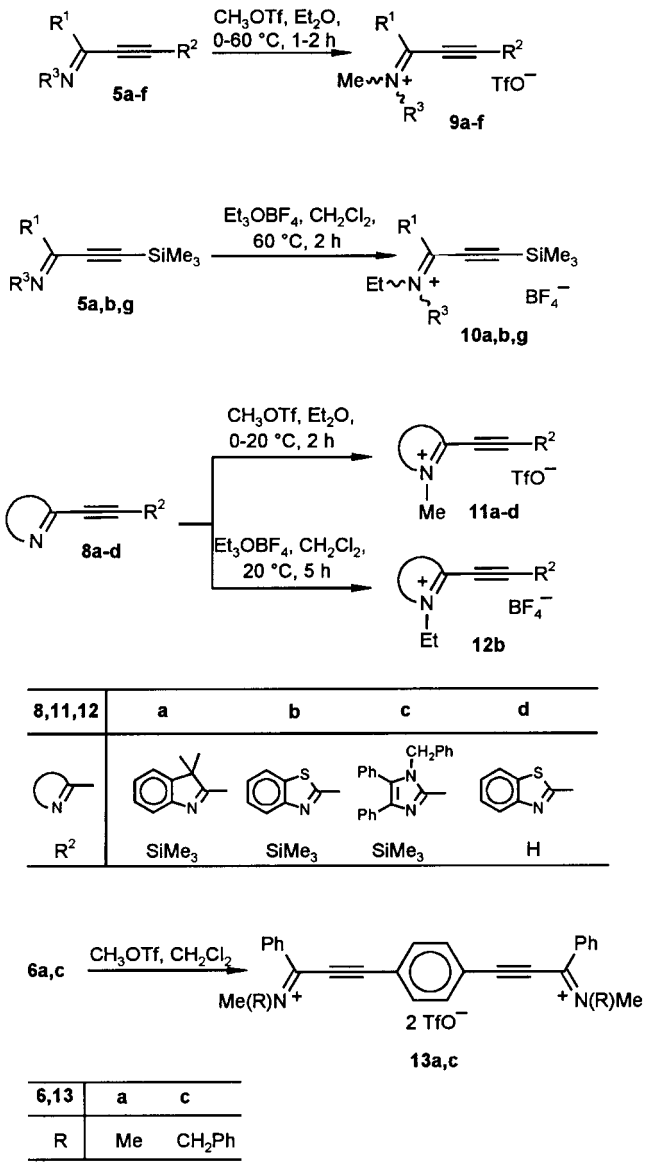
Efforts to synthesize *N*-phenyl alkynyl imines **5g**,**h** analogously were abandoned since the reactions were slow and preparatively useless product mixtures were obtained. However, these compounds have been obtained before by palladium-catalyzed coupling of imidoyl chloride **4g** with the corresponding alk-1-yne[9,10] (Scheme 3). Sonogashira-type coupling reactions also allowed the preparation of (trimethylsilyl)ethynyl imines **8a–c**, in which the imine function is part of a heteroaromatic system (Tables 1 and 2). Related systems, such as 2-[(trimethylsilyl)ethynyl]pyridine[16] and (2-alkynyl)imidazoles,[17] have been prepared before by this method.



Scheme 3

Desilylation of **8b** provided 2-ethynyl-1,3-benzothiazole (**8d**) in good yield. Certainly, this short route to **8d** is more convenient than the published procedure[18] which requires the synthesis and dehalogenation of 2-(2,2-dichloro-1-fluorovinyl)-1,3-benzothiazole.

N-Alkylation of imines **5**, **6**, and **8** could be achieved with hard alkylating reagents such as methyl triflate or triethyloxonium tetrafluoroborate (Meerwein's salt). All alkynyl imines **5** and **8** used in this study could be converted smoothly into the corresponding *N*-methyl propyne iminium triflates **9** and **11** (Scheme 4, Tables 3 and 4). The salts readily separated (as a solid or an oil) from the reaction mixture, when the alkynyl imine was added slowly to a solution of methyl triflate in diethyl ether. The twofold alkylation with methyl triflate of bis(imines) **6a**,**c**, however, was cleaner with CH_2Cl_2 as the solvent. Alkylation reactions with Et_3OBF_4 required a higher temperature to go to completion. Since they had to be performed in CH_2Cl_2 solution in order to dissolve the alkylating reagent, the formed propyne iminium salt remained in solution, and only the Me_3Si-substituted salts **10a**,**b**,**g** and **12b** could be prepared under these conditions, while the iminium salts derived from **5d–f** seemed not to be stable in the reaction medium and gave rise to further reactions such as oligomerization. Similarly, 2-ethynyl-1,3-benzothiazole (**8d**) underwent clean *N*-methylation with methyl triflate, while treatment with Meerwein's salt led to oligomerization.



Scheme 4

In this context, it is interesting to note that alkylation of 2-ethynylpyridine with alkyl halides in MeCN was used to prepare polyacetylene derivatives [poly-(*N*-alkyl-2-ethynylpyridinium salts)],[19] while methyl triflate gave the *N*-methylpyridinium salt monomer cleanly.[8] Mechanistic investigations[20] suggest that the neutral (ethynyl)pyridine acts as a nucleophilic initiator for the oligomerization of the *N*-methylpyridinium salts according to a zwitterionic/

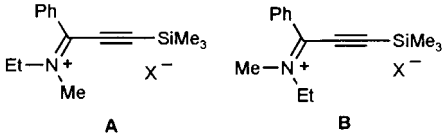
Table 3 Propyne Iminium Salts **9–13** Prepared[a] (Scheme 4)

Product	R^1	R^2	R^3	Conditions[b]	Yield (%)	mp (°C)[c]	IR (neat or KBr) (cm^{-1})	
							$\nu_{C\equiv C}$	Other Signals
9a	Ph	$SiMe_3$	Me	0°C, 2 h	73	83–85	2166	2954, 1633, 1458, 1377, 1344, 1275, 1223, 1153, 1034
9b	Ph	$SiMe_3$	Et	0°C, 2 h	61	62–64	2160	2966, 2853, 1614, 1450, 1376, 1344, 1275, 1222, 1151, 1030
9c	Ph	$SiMe_3$	CH_2-Ph	0°C, 1h; 20°C, 1 h	62	74–76	2159	2918, 2853, 1605, 1452, 1344, 1276, 1222, 1151, 1030
9d	Ph	Bu	Me	20°C, 2h,	34	oil	2219	2960, 2934, 2873, 1626, 1598, 1450, 1362, 1261, 1224, 1153, 1032
9e	Ph	Bu	Et	20°C, 2 h	40	oil	2214	2959, 1619, 1449, 1360, 1272, 1224, 1155, 1031
9f	Ph	Bu	CH_2-Ph	0°C, 2 h	60	oil	2213	2960, 2933, 1613, 1596, 1450, 1359, 1277, 1224, 1200, 1160, 1031
10a[d]	Ph	$SiMe_3$	Me	60°C, 2 h	70	74–76	2152	2962, 1598, 1451, 1375, 1339, 1283, 1250, 1166, 1048
10b	Ph	$SiMe_3$	Et	60°C, 2 h	72	107–109	2153	2924, 2854, 1591, 1450, 1377, 1341, 1274, 1252, 1051
10g[d]	Ph	$SiMe_3$	Ph	60°C, 2 h	59	112–114	2156	3065, 1596, 1581, 1563, 1490, 1449, 1339, 1318, 1269, 1255, 1056
11a[e]				0°C, 1 h; 20°C, 1 h	70	122–124	2073	2960, 1596, 1460, 1260, 1220, 1030
11b[e]				20°C, 2 h	95	147–149	2158	1285, 1251, 1221, 1032
11c[e]				20°C, 2 h	55	116–118	2121	1625, 1591, 1498, 1264, 1223, 1153, 1052, 1030
11d[e]				20°C, 2 h	80	120–122	2113	3184 (≡CH), 1466, 1446, 1257, 1224, 1163, 1030
12b[e]				20°C, 5 h	93	155–156	2159	3101, 1498, 1473, 1459, 1435, 1287, 1273, 1252, 1211, 1175, 1056
13a[e]				0°C, 2 h	60	130–132	2203	3055, 1620, 1596, 1361, 1277, 1224, 1155, 1030
13c[d,e]				0°C, 2 h	73	70–72	2199	3062, 1595, 1448, 1363, 1260, 1150, 1028

[a] Satisfactory microanalyses obtained: C ± 0.4, H ± 0.4, N ± 0.4.
[b] Reactions in CH_2Cl_2 solution at 60°C were carried out in a Schlenk pressure tube.
[c] Crystallization from CH_2Cl_2/Et_2O.
[d] Mixture of *E*- and *Z*-isomers with respect to the $C=N^+$ bond.
[e] For the structures of **11–13**, see Scheme 4.

anionic mechanism. Therefore, in order to suppress the oligomerization reaction of the formed propyne iminium salts, the *N*-alkylation of the alkynyl imines in general should be fast and quantitative, and the quick separation of the formed iminium salts from the reaction solution may also be helpful.

When alkynyl imines **5a**,**g** were alkylated with Et_3OBF_4 at 60°C, iminium salts **10a**,**g** were formed as a mixture of diastereomers with respect to the $C=N^+$ bond. In contrast, alkylation with MeOTf at 0°C gave only one diastereomer of **9**, while the reaction at 60°C furnished a diastereomeric mixture again, as was demonstrated for **5b** → **9b**. A ROESY NMR experiment carried out on **10a** suggested that **10aA** was the dominating isomer. By comparison with the chemical shifts observed for **10aA**/**B** [δ (Me-**A**) > δ (Me-**B**) and δ (CH_2-**A**) < δ (CH_2-**B**), see Table 4], isomeric pairs in other cases can be assigned either to series **A** or series **B**. We then conclude that *methylation* of *N-ethyl* imine **5b** forms isomer **9bB** exclusively at 0°C or predominantly at 60°C, while *ethylation* of *N-methyl* imine **5a** yields a mixture in which **10aA** predominates. Combined with the ^1H NMR spectroscopic test that pure **9bB** did not undergo *cis*/*trans* isomerization at 60°C, these findings suggest that the C=N configuration of alkynyl imines **5a**,**b** is exclusively (0°C) or largely (60°C) the one where the lone electron pair at N is *cis* to the phenyl group.



9a,b: X = TfO
10a: X = BF_4

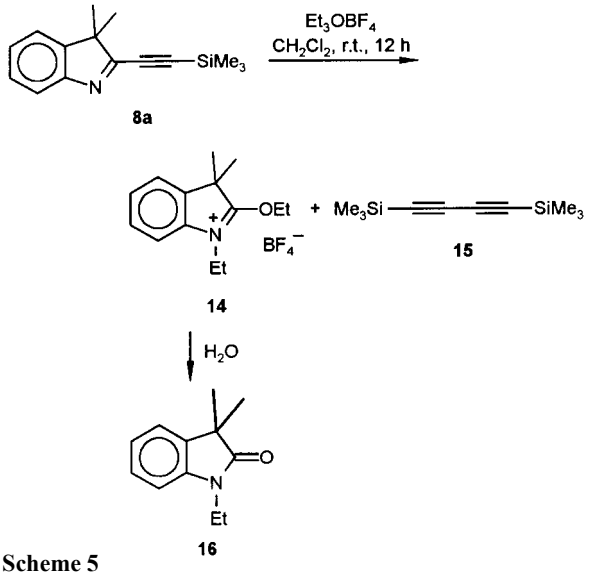
Different results were also obtained when **8a** was treated with the two alkylating reagents. Again, reaction with methyl triflate was fast and gave iminium salt **11a** cleanly (Scheme 4). On the other hand, reaction of **8a** with Et_3OBF_4 in CH_2Cl_2 at 20°C was much slower and instead

Table 4 ^{1}H and ^{13}C NMR Data of Salts **9–13**

Product	^{1}H NMR (CD_3CN/TMS) δ, *J* (Hz); isomer **A**/isomer **B**	^{13}C NMR (CD_3CN) δ, *J* (Hz); isomer **A**/isomer **B**
9a	0.30 [s, 9 H, $Si(CH_3)_3$], 3.61 (s, 3 H, NCH_3), 3.92 (s, 3 H, NCH_3), 7.57–7.76 (m, 5 H, CH_{arom})	–1.27 [$Si(CH_3)_3$], 46.63 (NCH_3), 49.09 (NCH_3), 97.11 (NC*C*≡C), 122.04, (q, $J_{C,F}$ = 320.8, CF_3), 130.27, 130.37, 130.78 (NCC≡*C*), 134.84, 137.77 (C_{arom}), 163.19 (C=N)
9b[a]	**A**: 0.31 [s, 9 H, $Si(CH_3)_3$], 1.40 (t, *J* = 7.2, 3 H, CH_3), 3.87 (s, 3H, NCH_3), 3.90 (q, *J* = 7.2, 2H, NCH_2); **B**: 0.31 [s, 9 H, $Si(CH_3)_3$], 1.52 (t, *J* = 7.3, 3 H, CH_3), 3.60 (s, 3 H, NCH_3), 4.28 (q, *J* = 7.3, 2 H, NCH_2), 7.60–7.78 (m, CH_{arom})	**A:** –1.22 [$Si(CH_3)_3$], 13.04 (CH_3), 45.70 (NCH_3), 54.13 (NCH_2), 97.50 (NC*C*≡C), 129.39, 129.71, 130.53, 131.77, 134.49, 163.94 (C=N); **B**: –1.34 [$Si(CH_3)_3$], 12.21 (CH_3), 44.19 (NCH_3), 57.83 (NCH_2), 96.80 (NC*C*≡C), 122.07 (q, $J_{C,F}$ = 320.9, CF_3), 130.23, 130.65, 131.41 (NCC≡*C*), 135.03, 137.81 (C_{arom}), 162.86 (C=N)
9c	0.32 [s, 9 H, $Si(CH_3)_3$], 3.57 (s, 3 H, NCH_3), 5.54 (s, 2 H, NCH_2), 7.40–7.84 (m, 10 H, CH_{arom})	–1.38 [$Si(CH_3)_3$], 44.34 (NCH_3), 55.14 (NCH_2), 97.67 (NC*C*≡C), 122.02 (q, $J_{C,F}$ = 320.8, CF_3), 129.97, 130.16, 130.29, 130.62, 130.78, 130.93, 131.54, 135.36, 138.24, 164.02 (C=N)
9d	0.90 (t, *J* = 7.3, 3 H, CH_3), 1.33–1.67 (m, 4 H, CH_2CH_2), 2.72 (t, *J* = 7.0, 2 H, ≡CCH_2), 3.56 (s, 3 H, NCH_3), 3.86 (s, 3 H, NCH_3), 7.61–7.70 (m, 5 H, CH_{arom})	13.66 (CH_3), 20.84, 22.65 (CH_2CH_2), 29.87 (≡C*C*H_2), 46.36, 48.61 (NCH_3), 77.45 (NC*C*≡C), 122.55 (q, $J_{C,F}$ = 320.3, CF_3), 130.03, 130.20, 130.95, 132.25, 134.54 (C_{arom}), 164.30 (C=N)
9e	0.92 (t, *J* = 7.1, 3 H, CH_3), 1.36–1.74 (m, 7 H, CH_2CH_2, CH_3), 2.74 (t, *J* = 7.0, 2 H, ≡CCH_2), 3.60 (s, 3 H, NCH_3), 4.28 (q, *J* = 7.2, 2 H, NCH_2), 7.57–7.82 (m, 5 H, CH_{arom})	12.33 (CH_3), 13.72 (CH_3), 20.86, 22.68 (CH_2CH_2), 29.84 (≡C*C*H_2), 43.82 (NCH_3), 57.27 (NCH_2), 77.13 (NC*C*≡C), 130.11, 130.29, 130.59, 131.20, 134.59 (NCC≡*C* and C_{arom}), 164.10 (C=N)
9f	0.89 (t, *J* = 7.2, 3 H, CH_3), 1.35–1.78 (m, 4 H, CH_2CH_2), 2.85 (t, *J* = 6.9, 2 H, ≡CCH_2), 3.58 (s, 3 H, NCH_3), 5.56 (s, 2 H, NCH_2), 7.34–8.20 (m, 10 H, CH_{arom})	13.75 (CH_3), 21.07, 22.71 (CH_2CH_2), 29.82 (≡C*C*H_2), 44.00 (NCH_3), 54.80 (NCH_2), 64.65 (NC*C*≡C), 127.37, 129.78, 129.98, 130.21, 130.54, 130.67, 131.50, 135.00, 137.84 (NCC≡*C* and C_{arom}), 163.41 (C=N)
10a[b]	**A**: 0.31 [s, 9 H, $Si(CH_3)_3$], 1.40 (t, *J* = 7.3, 3 H, CH_3), 3.90 (s, 3 H, NCH_3), 3.92 (q, *J* = 7.3, 2 H, NCH_2); **B**: 0.33 [s, 9 H, $Si(CH_3)_3$], 1.54 (t, *J* = 7.3, 3 H, CH_3), 3.62 (s, 3 H, NCH_3), 4.31 (q, *J* = 7.3, 2 H, NCH_2), 7.59–7.79 (m, CH_{arom})	**A**: –1.22 [$Si(CH_3)_3$], 13.04 (CH_3), 45.70 (NCH_3), 54.13 (NCH_2), 97.50 (NC*C*≡C), 163.94 (C=N); **B**: –1.22 [$Si(CH_3)_3$], 12.24 (CH_3), 44.13 (NCH_3), 57.84 (NCH_2), 96.86 (NC*C*≡C), 162.9 (C=N); further signals: 129.39, 129.71, 130.28, 130.53, 130.63, 131.33, 131.77, 134.49, 135.04 (C_{arom})
10b	0.32 [s, 9 H, $Si(CH_3)_3$], 1.41 (t, *J* = 7.2, 3 H, CH_3), 1.57 (t, *J* = 7.2, 3 H, CH_3), 3.94 (q, *J* = 7.2, 2 H, NCH_2), 4.32 (q, *J* = 7.2, 2 H, NCH_2), 7.63–7.76 (m, 5 H, CH_{arom})	–1.25 [$Si(CH_3)_3$], 13.05 (CH_3), 13.64 (CH_3), 51.87 (NCH_2), 54.37 (NCH_2), 97.36 (NC*C*≡C), 129.44, 130.51, 131.28 (NCC≡*C*), 131.88, 134.54 (C_{arom}), 163.84 (C=N)
10g[c]	**A**: 0.40 [s, 9 H, $Si(CH_3)_3$], 1.41 (t, *J* = 7.3, 3 H, CH_3), 4.73 (q, *J* = 7.3, 2 H, NCH_2); **B**: 0.03 [s, 9 H, $Si(CH_3)_3$], 1.29 (t, *J* = 7.3, 3 H, CH_3), 4.36 (q, *J* = 7.3, 2 H, NCH_2), 7.30–7.98 (m, CH_{arom})	**A**: –1.29 [$Si(CH_3)_3$], 12.19 (CH_3), 60.38 (NCH_2), 97.77 (NC*C*≡C), 163.81 (C=N); **B**: –1.57 [$Si(CH_3)_3$], 13.35 (CH_3), 56.00 (NCH_2), 98.68 (NC*C*≡C), 166.20 (C=N); further signals: 126.03, 126.68, 128.10, 129.78, 130.49, 130.91, 131.24, 132.00, 132.26, 133.45, 133.96, 135.11, 135.70, 140.62, 142.37 (C_{arom})
11a	0.30 [s, 9 H, $Si(CH_3)_3$], 1.53 [s, 6 H, $C(CH_3)_2$], 4.00 (s, 3 H, NCH_3), 7.53–8.02 (m, 4 H, CH_{arom})	–0.70 [$Si(CH_3)_3$], 24.30 (C*C*H_3), 55.04 (*C*CH_3), 40.15 (NCH_3), 89.07 (NC*C*≡C), 121.20, 122.00, 124.63, 125.98, 126.80, 147.34, 155.22, 179.63 (C_{arom})
11b	0.40 [s, 9 H, $Si(CH_3)_3$], 4.32 (s, 3 H, NCH_3), 7.79–7.96 (m, 2 H, CH_{arom}), 8.11–8.15 (m, 1 H, CH_{arom}), 8.25–8.29 (m, 1 H, CH_{arom})	–1.20 [$Si(CH_3)_3$], 39.15 (NCH_3), 89.06 (NC*C*≡C), 118.31, 125.24, 127.37 (NCC≡*C*), 130.65, 130.80, 131.73, 141.48 (C_{arom}), 153.35 (C-2)
11c	0.30 [s, 9 H, $Si(CH_3)_3$], 3.73 (s, 3 H, NCH_3), 5.38 (s, 2 H, NCH_2), 7.10–7.45 (m, 15 H, CH_{arom})	–1.09 [$Si(CH_3)_3$], 35.37 (NCH_3), 51.60 (NCH_2), 85.06 (NC*C*≡C), 125.80, 128.49, 128.69, 129.42, 129.64, 129.89, 130.28, 130.98, 131.44, 131.50, 131.67, 131.85, 133.47, 134.34, 134.61, 134.88 (NCC≡*C* and C_{arom})
11d	4.32 (s, 3 H, NCH_3), 5.51 (s, 1 H, C≡CH), 7.72–7.99 (m, 2 H, CH_{arom}), 8.12–8.18 (m, 1 H, CH_{arom}), 8.26–8.33 (m, 1 H, CH_{arom})	39.40 (NCH_3), 69.80 (NC*C*≡C), 106.16 (NCC≡*C*), 118.38, 121.75 (q, $J_{C,F}$ =307, CF_3), 125.31, 130.87, 131.04, 131.92, 141.50 (C_{arom}), 153.60 (C=N)
12b	0.40 [s, 9 H, $Si(CH_3)_3$], 1.57 (t, *J* = 7.3, 3 H, CH_3), 4.86 (q, *J* = 7.3, 2 H, NCH_2), 7.81–7.99 (m, 2 H, CH_{arom}), 8.16–8.30 (m, 2 H, CH_{arom})	–1.23 [$Si(CH_3)_3$], 14.17 (CH_3), 48.67 (NCH_2), 88.83 (NC*C*≡C), 118.38, 125.49, 127.49 (NCC≡*C*), 130.90, 131.37, 131.92, 140.55 (C_{arom}), 152.60 (C-2)
13a	3.65 (s, 6 H, NCH_3), 3.98 (s, 6 H, NCH_3), 7.60–7.90 (m, 14 H, CH_{arom})	–
13c[d]	**A**: 3.59 (s, 6 H, NCH_3), 5.59 (s, 4 H, NCH_2); **B**: 3.87 (s, 6 H, NCH_3), 5.24 (s, 4 H, NCH_2), 7.35–8.06 (m, CH_{arom})	–

[a] Reaction at 0°C: only **A**; at 60°C: isomer ratio **A**:**B** = 0.36.
[b] Isomer ratio **A**:**B** = 2.6.
[c] Isomer ratio **A**:**B** = 3.6.
[d] Isomer ratio **A**:**B** = 1.4.

of a propyne iminium salt, 2-ethoxy-3*H*-indolinium salt **14** and buta-1,3-diyne **15** were formed in an unidentified reaction sequence and were isolated in high yields (Scheme 5, Tables 3 and 4). The identity of **14** was established not only by its NMR and analytical data, but also by hydrolytic transformation into 3*H*-indolin-2-one **16**.[21]



Scheme 5

In summary, we have shown that *N*-quaternization of alkynyl imines with hard alkylating reagents constitutes a new, convenient method to prepare propyne iminium salts, especially those with an alkyl, silyl, or H substituent at the C,C triple bond, which were not easily accessible previously. Since a variety of alkynyl imines can be synthesized easily by coupling of imidoyl chlorides with terminal alkynes, the method is open to further substituent variations.

All reactions were carried out in rigorously dried glassware under an Ar atmosphere. THF was freshly distilled from Na/benzophenone ketyl. Et_2O was dried over Na/benzophenone ketyl and stored over 4 Å molecular sieves under Ar. CH_2Cl_2 was dried over P_2O_5 and stored over 4 Å molecular sieves under Ar. Column chromatography was performed using silica gel (Macherey & Nagel, 0.063–0.2 mm). NMR spectra were recorded on a Bruker AC 200 spectrometer operating at 200.13 MHz for ^1H and 50.32 MHz for ^{13}C. TMS served as internal standard for ^1H and $CDCl_3$ ($\delta = 77.0$) or CD_3CN ($\delta = 118.2$) for ^{13}C NMR spectroscopic measurements. IR spectra were obtained on a Perkin-Elmer IR-883 spectrometer. Elemental analyses were carried out using a Perkin-Elmer EA-240 instrument. Melting points were determined in a apparatus after Dr. Tottoli (Büchi) and are uncorrected.

The following starting materials were prepared according to literature procedures: **4a–c**,[22] **7a**,[23] 1,4-diethynylbenzene,[24] (trimethylsilyl)acetyl-ene,[25] methyl trifluoromethanesulfonate.[26]

_N_-Methyl-1-phenyl-3-(trimethylsilyl)prop-2-yn-1-imine (5a); Typical Procedure

To a solution of EtMgBr, prepared from magnesium turnings (0.80 g, 33.0 mmol) and bromoethane (2.9 mL, 39.6 mmol), in THF (30 mL) was slowly added at 0°C (trimethylsilyl)acetylene (5.4 mL, 39.6 mmol). The solution was stirred for 30 min and *N*-methylchloro(phenyl)methanimine[22] (**4a**) was added in one portion at 0°C. The mixture was stirred for 1 h at this temperature, and after addition of Et_2O (100 mL), it was washed with satd aq $NaHCO_3$ solution. The organic layer was dried (Na_2SO_4) and concentrated. The residue was distilled in vacuo to give **5a** as a colorless oil (5.30 g, 75%) (Tables 1 and 2).

EI-HRMS: $m/z = 215.1130$; calcd for $C_{13}H_{17}NSi$: 215.1130.

Compounds **5b–f**, **6a**, and **6c** were prepared analogously; see Tables 1 and 2 for yields, physical and spectroscopic data.

2-[(Trimethylsilyl)ethynyl]-1,3-benzothiazole (8b): Typical Procedure

A solution of 2-iodo-1,3-benzothiazole[27] (**7b**) (40.00 g, 0.153 mol), (trimethylsilyl)acetylene (40 mL, 0.280 mol), $PdCl_2(PPh_3)_2$ (0.56 g, 0.8 mmol) and CuI (0.50 g, 2.62 mmol) in Et_3N (300 mL) was stirred at 70°C for 2 days. The solvent was replaced by CH_2Cl_2 (200 mL), and after treatment with satd aq $NaHCO_3$ solution, the organic solution was dried (Na_2SO_4) and concentrated. The residue was distilled in vacuo to give **8b** as a yellow oil (20.0 g, 56%) (Tables 1 and 2).

Anal. calcd for $C_{12}H_{13}NSSi$ (231.41): C, 62.27; H, 5.65; N, 6.04. Found: C, 62.17; H, 5.61; N, 6.05.

Compounds **8a** (5 mmol scale) and **8c** were prepared analogously; see Tables 1 and 2 for yields, physical and spectroscopic data.

2-Ethynyl-1,3-benzothiazole (8d)

To a solution of **8b** (9.00 g, 37 mmol) in CH_2Cl_2 (50 mL) was added KF (5.00 g, 86 mmol) and 18-crown-6 (10.00 g, 37 mmol). After stirring at r.t. for 2 h, the mixture was washed twice with H_2O, and the organic layer was dried (Na_2SO_4) and concentrated in vacuo. Flash chromatography on silica gel (Et_2O as eluent) of the residual brown oil afforded **8d**; yield: 5.00 g (80%) (Tables 1 and 2).

Anal. calcd for C_9H_5NS (159.15): C, 67.91; H, 3.14; N, 8.79. Found: C, 67.93; H, 3.37; N, 8.74.

Dimethyl-[1-phenyl-3-(trimethylsilyl)-2-propyn-1-ylidene]ammonium Trifluoromethanesulfonate (9a); Typical Procedure for Alkylation with Methyl Triflate

To a solution of methyl triflate (0.87 mL, 8 mmol) in Et_2O (10 mL) was slowly added a mixture of **5a** (1.07 g, 5 mmol) in Et_2O (10 mL) at 0°C. The reaction mixture was stirred for 1 h at 0°C. The Et_2O layer was pipetted off, and the residual oil was triturated twice with Et_2O and crystallized from CH_2Cl_2/Et_2O at –30°C. Salt **9a** was obtained as white crystals (1.40 g, 73%).

Anal. calcd for $C_{15}H_{20}F_3NO_3SSi$ (379.47): C, 47.47; H, 5.31; N, 3.69. Found: C, 47.45; H, 5.35; N, 3.65.

Compounds **9b–f** and **11a–d** were prepared in the same manner. Reactions to prepare **13a**,**c** were run in CH_2Cl_2 at 0°C, and the products were precipitated as brown solids with Et_2O. For yields, physical and spectroscopic data see Tables 3 and 4.

Diethyl-[1-phenyl-3-(trimethylsilyl)-2-propyn-1-ylidene]ammonium Tetrafluoroborate (10b); Typical Procedure for Alkylation with Meerwein's Salt

A mixture of **5b** (2.29 g, 10 mmol) and Et_3OBF_4 (1.89 g, 10 mmol) in CH_2Cl_2 (20 mL) was heated for 2 h at 60°C in a Schlenk pressure tube. The crude product was precipitated with Et_2O. Crystallization from CH_2Cl_2/Et_2O gave brown crystals (2.50 g, 72%) (Tables 3 and 4).

Anal. calcd for $C_{16}H_{24}BF_4NSi$ (345.03): C, 55.69; H, 7.01; N, 4.05. Found: C, 55.68; H, 6.98; N, 4.03.

Compounds **10a**,**g** and **12b** were prepared analogously; for yields, physical and spectroscopic data see Tables 3 and 4.

1-Benzyl-2-iodo-4,5-diphenylimidazole (7c)
To a solution of 1-benzyl-4,5-diphenylimidazole[28] (0.85 g, 2.7 mmol) in THF (20 mL) at 0 °C was added BuLi (1.6 M in hexane, 2 mL, 3.2 mmol). The solution was stirred for 1 h and then cooled to –78 °C. A solution of I_2 (0.80 g, 3.1 mmol) in THF (5 mL) was added and stirred for 30 min. The reaction mixture was allowed to reach r.t. The solution was evaporated, triturated with CH_2Cl_2 (50 mL) and washed with aq $Na_2S_2O_3$ solution, then with H_2O, and dried (Na_2SO_4). Evaporation of the solvent and column chromatography on silica gel ($CHCl_3$ as eluent) gave a yellow powder; yield: 0.58 g (50%); mp 103–104 °C.

IR (KBr): ν = 3056, 3028, 1598, 1493, 1447, 1411, 1349, 1325, 1177, 1118, 1070, 1024 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 4.98 (s, 2 H, NCH_2), 6.83–7.48 (m, 15 H, CH_{arom}).

^{13}C NMR ($CDCl_3$): δ = 50.4 (NCH_2), 91.8 (C-2), 126.2, 126.4, 126.6, 127.4, 127.9, 128.5, 128.8, 129.0, 130.2, 130.6, 132.6, 133.6, 136.1, 141.8 (C_{arom}).

Anal. calcd for $C_{22}H_{16}N_2$ (433.90): C, 60.56; N, 3.92; N, 6.42. Found: C, 60.33; H, 4.11; N, 6.16.

Alkylation of 8a with Meerwein's Salt
A solution of **8a** (5.00 g, 20.7 mmol) and Et_3OBF_4 (3.92 g, 20.7 mmol) in CH_2Cl_2 (30 mL) was stirred for 12 h at r.t. 2-Ethoxy-1-ethyl-3,3-dimethyl-3H-indolinium tetrafluoroborate (**14**) was precipitated with Et_2O and recrystallized from CH_2Cl_2/Et_2O; yield: 4.50 g (74%); mp 104–106 °C. Evaporation of the mother liquor left crude 1,4-bis(trimethylsilyl)buta-1,3-diyne (**15**). Purification by column chromatography on silica gel (petroleum ether as eluent) furnished colorless crystals, (1.74 g, 90%), mp 109–111 °C (Lit[29] mp 106–107 °C).

Treatment of salt **14** in a mixture of CH_2Cl_2/H_2O (30/10 mL) overnight, evaporation and distillation of the residue at 80–82 °C/ 0.02 mbar gave N-ethyl-3,3-dimethyl-3H-indolin-2-one (**16**).

14:
IR (KBr): ν = 2984, 2944, 2878, 1598, 1575, 1447, 1392, 1246, 1045 (very broad, BF_4) cm^{-1}.

^1H NMR (CD_3CN): δ = 1.46–1.67 (m, 12 H, 2 × CH_2CH_3, $C(CH_3)_2$), 4.58 and 4.66 (2 q, each 2 H, OCH_2, NCH_2), 7.62–7.91 (m, 4 H, CH_{arom}).

^{13}C NMR (CD_3CN): δ = 12.7, 12.8 (CH_2CH_3), 23.3 [$C(CH_3)_2$], 45.7 (NCH_2), 57.0 [$C(CH_3)_2$], 84.8 (OCH_2), 116.7, 124.8, 130.7, 131.8, 141.0, 142.0 (C_{arom}), 185.1 (C-2).

Anal. calcd for $C_{14}H_{20}BF_4NO$ (305.12): C, 55.11; H, 6.60; N, 4.59. Found: C, 54.83; H, 6.72; N, 4.38.

16:
IR (neat): ν = 2968, 2930, 2869, 1713, 1614, 1487, 1469, 1462, 1382, 1361, 1212, 1131 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.06 (t, *J* = 7.2, 3 H, CH_3), 1.17 [s, $C(CH_3)_2$], 3.57 (q, *J* = 7.2, 2 H, NCH_2), 6.67 (d, *J* = 7.8, 1 H, CH_{arom}), 6.83 (t, *J* = 7.4, 1H, CH_{arom}), 6.99–7.08 (m, 2 H, CH_{arom}).

^{13}C NMR ($CDCl_3$): δ = 12.3 (CH_3), 24.0 [$C(CH_3)_2$], 34.1 (NCH_2), 43.6 [$C(CH_3)_2$], 107.8, 121.9, 122.0, 127.2, 135.6, 141.2 (C_{arom}), 180.4 (C=O).

Anal. calcd for $C_{12}H_{15}NO$ (189.24): C, 76.15; H, 7.98; N, 7.40. Found: C, 76.06; H, 7.97; N, 7.02.

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