COMMUNICATIONS

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A Selective Synthesis of (*E*)-2-Methyl-1-alkenyl Iodides via Zirconium-Catalyzed Carboalumination[1]

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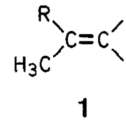
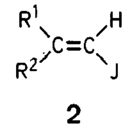
We have recently reported a highly stereo- and regio-selective zirconium-catalyzed carboalumination reaction of acetylenes[2]. The carbometallated products can be converted to carbon-carbon bonded derivatives[1,3] and alkenyl iodides **1**[2].



1

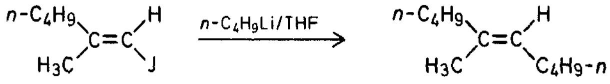


2

Since the latter products **1** can, in principle, be convertible to a variety of natural products of terpenoid origin, we have further explored the scope of the synthesis of **1** via zirconium-catalyzed carboalumination.

We now report that the procedure appears to be generally applicable and provides a highly stereo- and regio-selective route to **1**. The results are summarized in the Table. Although β,β-dialkyl-substituted alkenyl iodides represented by **2**, in which R^2 is ethyl or a higher alkyl group, have been prepared via carbocupration of acetylenes[4], the same procedure does not appear to provide a convenient route to **1**. To our knowledge, no convenient and selective procedure for the preparation of **1**, which is comparable to the presently reported method, appears to have been reported, although the carbocupration might eventually be developed into such a procedure.

As shown in the Table, various types of (*E*)-2-methyl-1-alkenyl iodides can be prepared in uniformly high yields. It is noteworthy that neither a conjugated nor an isolated alkenyl group interferes with the carbometallation-iodination sequence (Entries 4 and 5). Since the zirconium-catalyzed carboalumination of acetylenes has been found to be compatible with sulfide groups[5], sulfur-containing (*E*)-2-methyl-1-alkenyl iodides can now be readily obtained (Entry 6). The stereochemistry of 1-iodo-2-phenylpropene has been established by converting it to ≥96 % stereoisomerically pure (*E*)-1-deuterio-2-phenylpropene by treatment with *n*-butyllithium (ether, $-60°$) followed by deuterolysis (D_2O). The (*E*)-isomer exhibits a broad ^{1}H-N.M.R. singlet at $\delta = 5.27$ ppm, whereas the (*Z*)-isomer, readily obtainable by the carbometallation of 2-deuteriophenylacetylene followed by hydrolysis, shows the corresponding alkenyl proton signal as a finely split multiplet at $\delta = 4.9-5.0$ ppm. The stereochemistry of (*E*)-1-iodo-2-methyl-1-hexene has been established by converting it to ≥98 % pure (*E*)-5-methyl-5-decene via treatment with *n*-butyllithium in tetrahydrofuran.



The ^{1}H-N.M.R. spectra of the (*E*)- and (*Z*)-isomers show the allylic methyl proton singlets at 1.60 and 1.67 ppm, respectively. In the other cases, the ^{13}C-N.M.R. spectra of the alkenyl iodides do not show any indication of the presence of two stereoisomers. Thus, at least in cases where the two β substituents are of considerably different types, the alkenyl iodides appear to be essentially pure *E*.

The ratio of trimethylalane to an acetylene has been typically 2/1 or 3/1 to ensure completion of the carbometallation reaction. Thus, the stoichiometric ratio of iodine required for complete iodinolysis of all C—Al bonds to the acetylene is 6/1 or 9/1. In practice, however, the use of a 20–50 mol % excess of iodine, i.e., iodine/acetylene = 1.2–1.5, is sufficient to observe the yields reported in the Table, indicating that the alkenyl group is considerably more reactive toward iodine than the methyl group. The regioselectivity of the carbometallation in typical cases has been ~95 %[2]. However, all but one of the alkenyl iodides in the Table appear to be ≥97 % regioisomerically pure, as judged by their ^{13}C-N.M.R. spectra. Only the ^{13}C-N.M.R. spectrum of 2,6-dimethyl-1-iodo-1,5-heptadiene (Entry 5) indicates the presence of ~5 % of the regioisomer.

(*E*)-1-Iodo-2-phenylpropene:

To a slurry of dichlorobis[η^5-cyclopentadienyl]zirconium (2.92 g, 10 mmol) in 1,2-dichloroethane (25 ml) is added trimethylalane (1.44 g, 1.92 ml, 20 mmol) *(pyrophoric!)* under nitrogen at room temperature. All dichlorobis[η^5-cyclopentadienyl]zirconium dissolves within 10–15 min to produce a lemon-yellow solution. To this is added phenylacetylene (1.02 g, 1.11 ml, 10 mmol) at room temperature. After stirring of the reaction mixture for 24 h, iodine (3.04 g, 12 mmol) dissolved in tetrahydrofuran (15 ml) is added dropwise at 0°. After the iodine color has disappeared, the reaction mixture is quenched with water followed by the addition of ether. The organic layer is separated, dried over magnesium sulfate, and distilled to give (*E*)-1-iodo-2-phenylpropene; yield: 1.79 g (73 %); b.p. 72.5°/0.55 torr; n_D^{19} 1.6353.

^{1}H-N.M.R. ($CDCl_3$/TMS): $\delta = 2.27$ (d, $J = 1.5$ Hz, 3H); 6.45–6.6 (q, $J = 1.5$ Hz, 1H); 7.30 ppm (s, 5H).

I.R. (neat): $\nu_{max} = 3020$ (m), 1585 (m), 1485 (m), 1430 (s), 1365 (m), 1285 (m), 1195 (s), 1025 (m), 793 (m), 745 (s), 692 cm^{-1} (s).

(*E*)-1-Iodo-2-methyl-3-phenylthiopropene:

The title compound is prepared from phenyl propynyl sulfide (1.46 g, 1.38 ml, 10 mmol) in essentially the same manner as des-

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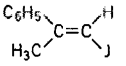
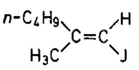
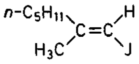
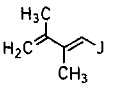
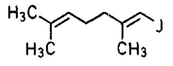
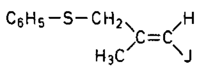
Table. (*E*)-2-Methyl-1-alkenyl Iodides

Entry	Product	Yield [%] (by G.L.C.)	b.p./torr	n_D (temp)	Molecular formula	^{1}H-N.M.R. (CCl_4/TMS) δ [ppm]	^{13}C-N.M.R. ($CDCl_3$/TMS) δ [ppm]
1		73 (83)	72.5°/0.55	1.6353 (19°)	C_9H_9J (244.1)	see experimental	see experimental
2		85[b]	42–43°/ 1.3[a]	1.5104 (19.6°)	$C_7H_{13}J$ (284.1)	0.90 (t, 3H, $J=6$ Hz); 1.1–1.6 (m, 4H); 1.85 (s, 3H); 2 21 (t, 2H, $J=$ 7 Hz); 5.84 (m, 1H)	—
3		83	—	1.5063 (25.5°)	$C_8H_{15}J$ (238.1)	0.87 (t, 3H, $J=6$ Hz); 1.1–1.6 (m, 6H); 1.80 (d, 3H); 2 20 (t, 2H, $J=$ 7 Hz); 5.84 (m, 1H)	14.01; 22.45; 23.79; 27.42; 31.24; 29.55; 74.51; 147.74
4		70	56°/ 25	1.5684 (25.5°)	C_6H_9J (208.0)	1.95 (s, 3H); 2.06 (s, 3H); 4.9–5.15 (m, 2H)[c]; 6.41 (s, 1H)[d]	20.84; 22.18; 81.46; 113.82; 142.29; 146.34
5		72 (79)	54–55°/ 0.55	—	$C_9H_{15}J$ (250.1)	1.60 (s, 3H); 1.67 (s, 3H); 1.80 (s, 3H); 2.0–2.4 (m, 4H)[e]; 4.8–5.2 (m, 1H); 5.80 (s, 1H)	17.68; 23.92; 25.68; 26.41; 39.50; 74.88; 123.09; 132.08; 147.46[f]
6		75 (83)	86–87°/ 0.02	1.6323 (23°)	$C_{10}H_{11}JS$ (258.1)	see experimental	see experimental

[a] Isolated by G.L.C.

[b] The stereochemistry was established by converting it to stereochemically pure (*E*)-5-methyl-5-decene by treatment with *n*-butyllithium in tetrahydrofuran at −60°. (*E*)-5-methyl-5-decene exhibits the following spectral properties:
^{1}H-N.M.R. ($CDCl_3$/TMS)/ $\delta=0.7$–1.1 (m, 6H); 1.1–1.5 (m, 8H); 1.60 (s, 3H); 1.8–2.3 (m, 4H); 5.10 ppm (t, 1H, $J=7$ Hz).
^{13}C-N.M.R. ($CDCl_3$/TMS): $\delta=14.11$; 15.88; 22.62; 27.89; 30.58; 32.46; 39.75; 124.81; 135.06 ppm.

[c] Including peaks at 4.95 and 5.10 ppm.

[d] In CCl_4 solution.

[e] Including peak at 2.20 ppm.

[f] Very minor peaks are observable at $\delta=28.26$; 45.31; 122.45; 129.21 ppm.

cribed in the preceeding experiment. The time required for the carbometallation is 3 h. After distillative work-up, (*E*)-1-iodo-2-methyl-3-phenylthiopropene is obtained; yield: 2.18 g (75 %); b.p. 86–87°/0.02 torr; n_D^{23} 1.6323.

^{1}H-N.M.R. (CCl_4/TMS): $\delta=1.93$ (d, $J=1.5$ Hz, 3H); 3.50 (s, 2H); 5.8–6.0 (q, $J=1.5$ Hz, 1H); 7.0–7.5 ppm (m, 5H).

^{13}C-N.M.R. ($CDCl_3$/TMS): $\delta=22.86$; 43.03; 78.71; 126.76; 128.66; 130.92; 135.02; 142.68 ppm.

I.R. (neat): $\nu_{max}=3050$ (w), 1580 (w), 1480 (w), 1440 (m), 1275 (s), 740 (s), 687 cm^{-1} (s).

Acknowledgments are made to the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society for support of this research. We thank Mr. M. J. Idacavage for his assistance in obtaining ^{13}C-N.M.R. spectra.

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[1] Controlled Carbometallation; 4. Part 3: N. Okukado, E. Negishi, *Tetrahedron Lett.* **1978**, 2357.

[2] D. E. Van Horn, E. Negishi, *J. Am. Chem. Soc.* **100**, 2252 (1978).

[3] E. Negishi, N. Okukado, A. O. King, D. E. Van Horn, B. I. Spiegel, *J. Am. Chem. Soc.* **100**, 2254 (1978).

[4] J. F. Normant, M. Bourgain, *Tetrahedron Lett.* **1971**, 2583. A. Alexakis, J. Normant, J. Villiéras, *J. Organometal. Chem.* **96**, 471 (1975).

[5] E. Negishi, D. E. Van Horn, C. L. Rand, M. W. Moore, N. Okukado, unpublished results.

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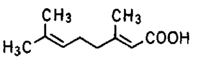
Errata and Addenda 1979

M. Contento, D. Savoia, C. Trombini, A. Umani-Ronchi, *Synthesis* **1979** (1), 30-32;
The structure for compound **3c** (p. 31, Table 1) should be:



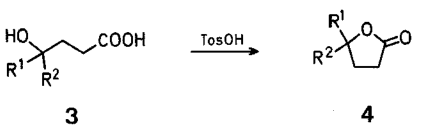
A. Mignot, H. Moskowitz, M. Miocque, *Synthesis* **1979** (1), 52-53;
The correct name for Tetramisole® should be 6-phenyl-2,3,5,6-tetrahydroimidazolo[2,1-*b*]thiazole.

A. N. Pudovik, I. N. Konovalova, *Synthesis* **1979** (2), 81-96;
The first sentence of the experimental procedure on p. 96 should read as follows:

Dialkyl phosphite or phosphorothioate (0.01 mol) is added to the azo compound (0.01 ml) in ether (10 ml).

In Table 13 (p. 96) the entries R^2 for compounds **63b** and **63c** should be $4\text{-}H_3C\text{—}C_6H_4$ and $4\text{-}O_2N\text{—}C_6H_4$, respectively.

Abstract 5422, *Synthesis* **1979** (2), 160;
The formula scheme for the conversion **3**→**4** should be:



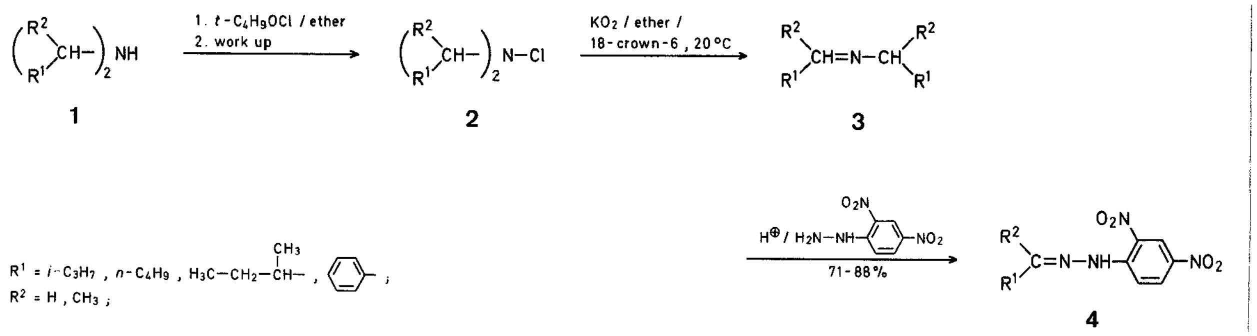
N. Blažević, D. Kolbah, B. Belin, V. Šunjić, F. Kajfež, *Synthesis* **1979** (3), 161-176;
Compounds **78a-e** (p. 173) should be named:
9-chloro-10b-phenyl-2,3,5,6-tetrahydro-10b*H*-[1,3]oxazolo[3,2-*c*]-quinazolines.

K. Herrmann, G. Simchen, *Synthesis* **1979** (3), 204-205
The lines 10 to 17 of the text (p. 204) should read as follows:

sche Acrylcyanide zugänglich[1,5,6]. Aliphatische Carbonsäure-halogenide hingegen setzen sich mit Tetraethylammoniumcyanid zu Acyloxymalodinitrilen („dimere Acrylcyanide") um, wofür auch die hohe Cyanidionen-Konzentration verantwortlich ist[1]. Die Reaktion aliphatischer Säurechloride (**2**) mit Cyanotrimethylsilan (**1**)[7-10] sollte deshalb eine geeignete Synthesenmethode für 2-Oxo-alkannitrile (aliphatische Acrylcyanide, **3**) darstellen. Bisher konnte allerdings nur

L. Caglioti, F. Gasparrini, D. Misiti, G. Palmieri, *Synthesis* **1979** (3), 207-208;
The italic sub-headings in the Table (p. 208) should be *From tosylhydrazones, From N-methyl-N-tosylhydrazones,* and *From 2,4-dinitrophenylhydrazones.*

Abstract 5440, *Synthesis* **1979** (3), 238;
The formula scheme for the conversion **1**→**4** should be as follows:

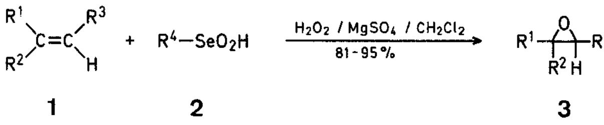


$R^1 = i\text{-}C_3H_7$, $n\text{-}C_4H_9$, $H_3C\text{—}CH_2\text{—}\overset{CH_3}{\overset{|}{C}H}\text{—}$, $C_6H_5\text{—}$;
$R^2 = H, CH_3$;

C. Venturello, R. D'Aloisio, *Synthesis* **1979** (4), 283-287;
Entries 3 and 4 of the Mass spectrum column of Table 1 (p. 284) should be 284 (^{35}Cl) and 318 (^{35}Cl), respectively.

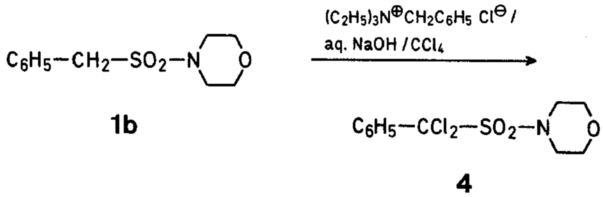
J. S. Davidson, *Synthesis* **1979** (5); 359-361;
Compounds **6** (p. 360) should be named:
3,4-diaryl-5-oxo-3,4-dihydro-1*H*-1,2,4-triazoles.

Abstracts 5494, *Synthesis* **1979** (5), 399;
The formula scheme for the conversion **1**→**3** should be as follows:

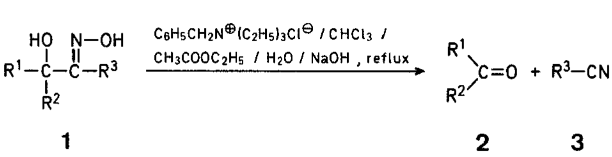


C. Skötsch, I. Kohlmeyer, E. Breitmaier, *Synthesis* **1979** (6), 449-452;
The name for compound **10a** should be:
3-Methyl-5,6,7,8-tetrahydroisoxazolo[5,4-*b*]chinolin.

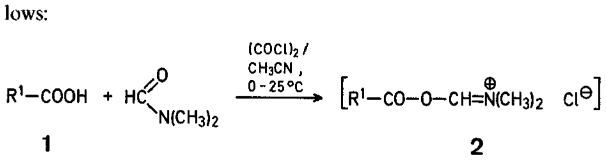
J. Goliński, A. Jończyk, M. Mąkosza, *Synthesis* **1979** (6), 461-463;
The formula scheme for the conversion **1b**→**4** (p. 462) should be as follows:



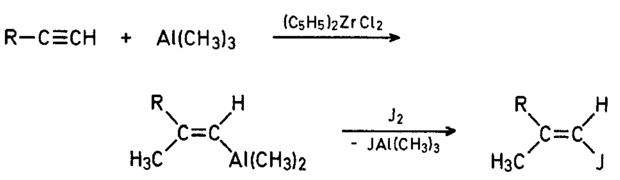
Abstract 5520, *Synthesis* **1979** (6), 479;
The formula scheme should be as follows:



Abstract 5521, *Synthesis* **1979** (6), 479;
The formula scheme for the conversion **1**→**2** should be as follows:



E. Negishi, D. E. Van Horn, A. O. King, N. Okukado, *Synthesis* **1979** (7), 501-502;
For clarity, the following formula scheme should be added:



A. McKillop, D. W. Young, *Synthesis* **1979** (7), 481-500;
The heading for Table 24 (p. 496) should be:

Table 24. Oxidation of Alcohols to Aldehydes and Ketones using Potassium Permanganate/Molecular Sieves[172].