$[Et_2Al \leftarrow Py]^{\oplus}[Et_2AlCl_2]^{\ominus}$

CONCLUSIONS

1. The reaction of diethylchloroaluminum with pyridine in benzene leads to a stable complex.

2. ^{13}C NMR spectroscopy was used to establish the intermediate state as an ion pair of the dimer of diethylchloroaluminum and one pyridine molecule.

LITERATURE CITED

1. V. M. Denisov, Dissertation, Leningrad (1977).
2. S. I. Vinogradova, V. M. Denisov, and A. I. Kol'tsov, Zh. Obshch. Khim., 42, 1031 (1972).
3. G. Heublein, W. Kümpfel, and H. Schütz, Z. Chem., 18, 34 (1978).
4. H. Lehmkuhl and H. D. Kobs, Tetrahedron Lett., 2505 (1965).

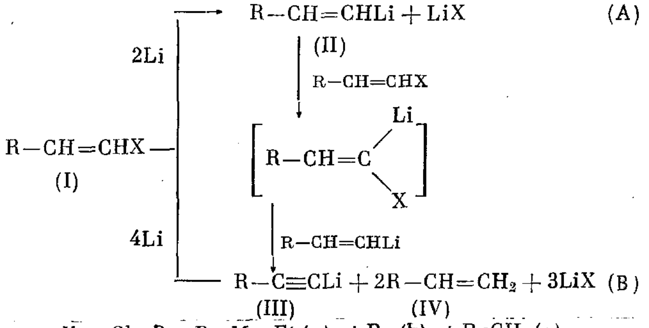
AN ANOMALOUS REACTION OF TERT-BUTYLVINYL AND NEOPENTYLVINYL HALIDES WITH LITHIUM

É. A. Mistryukov and I. K. Korshevets

UDC 542.91:547.413:546.34

Vinyllithium derivatives are usually obtained by the direct action of lithium on vinyl halides (I, R = Alk) (scheme, A) in TMF or ether [1-3]. Braude [1] and Curtin [2] noted the formation of up to 15% acetylenide (IIIa) in addition to (IIa). Formation of this acetylenide was not observed in the reaction of chlorides with lithium with a high sodium content (up to 2%) or bromides with ordinary lithium containing about 0.02% sodium using the hyperstirring method (6,000-10,000 rpm) [3].

In the present work, we showed that vinyl halides (Ib) and (Ic) with a bulky substituent in the β-position behave unusually in their reaction with lithium and are converted to acetylenides (IIIb) and (IIIc) instead of vinyllithium derivatives (IIb) and (IIc).



X = Cl, Br; R=Me, Et (a), *t*-Bu (b), *t*-BuCH$_2$ (c).

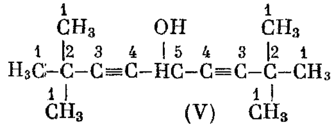
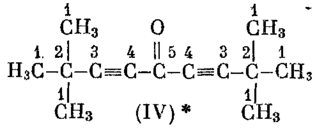
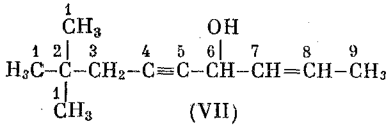
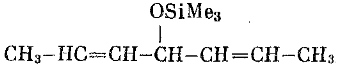
Despite the complete disappearance of the starting halide (Ib) or (Ic), significant amounts of lithium taken according to scheme A remain characteristically unreacted. Scheme B apparently is a more correct representation of this reaction, in which the lithium consumption occurs according to the (I):Li ratio of 1:1.3, and not (I):Li = 1:2 as in scheme A, due to the reduction of (I) to (IV). In contrast to the examples given above, the course of the reaction of haloolefins (Ib) and (Ic) is not altered depending on the sodium content. Acetylenides (IIIb) and (IIIc) are likely formed due to a subsequent reaction of the initial vinyllithium product (IIb) or (IIc) with a molecule of the starting haloolefin (Ib) or (Ic) (see scheme) by a mechanism analogous to that proposed by Nelson [4]. The formation of lithium acetylenides (IIIb) and (IIIc) was established by their further reaction with a carbonyl component (methyl formate or crotonaldehyde) leading to acetylenic alcohols (V) and (VII) (Table 1). The structures of the alcohols were supported by spectral data and the convergent synthesis of (V) from tert-butylacetylene according to our previous procedure [5]. It is also interesting that acetylenic alcohols are formed from substituted vinyl halides

---

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow.
Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 685-688, March, 1986. Original article submitted April 29, 1985.

0568-5230/86/3503-0626$12.50

TABLE 1. Spectral Indices of (V)-(VIII)

Compound	PMR spectrum (δ, ppm)	^{13}C NMR spectrum (δ, $CDCl_3$)	IR spectrum (ν, cm^{-1})	Mol. mass (mass spectrum), Found/Calculated
 $H_3C-C(CH_3)_2-C\equiv C-HC(OH)-C\equiv C-C(CH_3)_2-CH_3$ (V)	(CCl_4), 1,18 s (18H, *t*-Bu). 1,81 br.s (1H, OH), 4,84 br.s (1H, CHOH)	27,24(2), 30,68(1), 52,41(5), 77,19(4), 92,56(3)	(KBr), 2240(C≡C), 3360 (CHOH), 1270, 1365 (*t*-Bu)	$\frac{192}{192{,}29}$
 $H_3C-C(CH_3)_2-C\equiv C-C(=O)-C\equiv C-C(CH_3)_2-CH_3$ (IV)*	(CCl_4), 1,17 s (*t*-Bu)	27,69(2), 29,82(1), 80,97(4), 100,95(3), 161,4(5)	(KBr), 2210 (C≡C), 1620 (>C=O), 1270, 1365 (*t*-Bu)	$\frac{190}{190{,}28}$
 $H_3C-C(CH_3)_2-CH_2-C\equiv C-CH(OH)-CH=CH-CH_3$ (VII)	($CDCl_3$), 0,94 s (9H, *t*-Bu), 1,76 d.d.d (3H, *J*=6,5, 1,5, 1,15 Hz, CH_3), 2,05 d (2H, *J*==2 Hz, CH_2), 2,77 br.s (1H, OH), 4,78 d.d.q (1H, *J*=6, 1,25, 1,15Hz, CHOH) 5,5–5,62 d.d.q (1H, *J*=15,6, 1,5 Hz Me–CH=), 5,73–5,9 d.q.d (1H, *J*=15, 6,5; 1,25 Hz =CH–CHOH)	16,81 q (C^9, ^1J=126,7 Hz), 28,53 q (C^1, ^1J=124,9 Hz,, 30,47 s (C^2), 33,37 t (C^3, ^1J==130 Hz), 62,18 d (C^6, ^1J==147 Hz), 81,32 s (C^5), 83,82 t (C^4, ^1J=10,2, Hz), 126,73 d (C^8, ^1J=152,6 Hz), 131,05 d (C^7, ^1J=156,0 Hz)†	(neat), 967, 1675 (trans-C=C), 2220 (C≡C), 1365 (*t*-Bu) 3360–3370 (OH), 2875, 2960 (CH_3), 2835–2875, 2910, 1440–1480 (CH_2)	$\frac{166}{166{,}26}$
 $CH_3-HC=CH-CH(OSiMe_3)-CH=CH-CH_3$ (VIII) ≈50:50 mixture of cis-trans and trans-trans isomers	(CCl_4), 1,5–1,67 three doublets from two isomers(*J*≈5 Hz, 6H, CH_3), 4,26–4,88 two multiplets from two isomers (1H, CH–$COSiMe_3$) 5,20–5,67 complex multiplet from two isomers (4H, –CH=CH–)		(neat), 690 w., 970 s, 1305 w, 1405 w., 1675 w, 3030 s (RCH=CHR′), 1440–1450 m, 2965 v.s (CH_3), 1060 v.s. (Si–O–C), 755 v.s, 840 v.s, 1250 v.s. ($SiMe_3$)	$\frac{184}{184{,}35}$

---

*UV spectrum (EtOH), nm (ε): 240 (13700), 252 (13700).

†The assignment of C^7 and C^8 may be reversed.

(Ib) and (Ic) independently of the reaction procedure. This reaction may be carried out by initial reaction with Li and subsequent addition of the carbonyl compound or by the Barbier method [6], in which a mixture of the haloolefin and carbonyl component is added to lithium. On the other hand, the order of the addition of the reagents in the case of haloolefins with a small substituent (Ia) affects the reaction direction. Thus, carrying out the reaction according to the Barbier method gives only olefinic product (VIII) in 65% yield, while the stepwise procedure gives a mixture of acetylenic and olefinic alcohols.

Diacetylenic carbinol (V) was described by Miller et al. [7], who noted an anomalous absorption at 239.5 and 251 nm (ε 250). We have established that these results are incorrect. The UV data given by Miller et al. [7] are not, in fact, related to alcohol (V) but rather to ketone (VI), which is readily formed from (V) by oxidation by atmospheric oxygen upon storage. The structure of (VI) was supported by spectral comparison with an authentic sample obtained by the standard method (see Experimental).

EXPERIMENTAL

The gas–liquid chromatography was carried out on a Biokhrom-1 chromatograph with a flame ionization detector, nitrogen gas carrier and a 0.25 mm × 50 mm glass column packed with 0.25% XE-60. The PMR and ^{13}C NMR spectra were taken on a Bruker WM-250 spectrometer at 250 MHz and Tesla BS-497 spectrometer at 100 MHz. The IR spectra were taken on a UR-20 spectrometer and the UV spectra were taken on a Specord spectrometer. The mass spectra were taken on Finnegan MAT-112 and Kratos MS-30 mass spectrometers. All the reaction components were subjected to prior distillation and storage over CaH_2. The spectral indices of products (V)-(VIII) are given in Table 1.

2,2,8,8-Tetramethyl-3,6-nonadiyn-5-ol (V). A sample of 40 ml (0.31 mole) t-Bu–CH=CHCl was added over 5 h to 4.35 g (0.62 g-atom) Li (with ~2% Na) as fine pieces, which had been washed twice with absolute THF, in 300 ml abs. THF under argon. Di-tert-butyldiphenyl (DTD) was used as the phase-transfer agent; the radical-anion of DTD with Li is green but becomes red in the presence of the halide. The temperature was maintained at 4-5°C during the addition of the chloride. At the end of the exothermal reaction the reaction mixture was stirred for 1 h and then 10 ml (0.155 mole) methyl formate was cooled with water cooling to ~20°C. The lithium present did not react fully. The reaction mixture was treated with an acid solution obtained by the addition of 50 ml conc. hydrochloric acid to 50 ml distilled water. The organic layer was separated and the aqueous layer was washed with two 30-ml portions of ether. The solvents were distilled off. Sublimation at 60°C at 10 mm gave 5.5 g (56%) alcohol (V). Carrying out this reaction with t-BuCH=CHBr also gave (V), mp 78°C (from pentane).

2,2,8,8-Tetramethyl-3,6-nonadiyn-5-one (VI) was obtained from alcohol (V) by oxidation with pyridinium chlorochromate [8] or standing in the light by oxidation with atmospheric oxygen, mp 67°C (from pentane).

2,2-Dimethyl-6-nonen-4-yn-6-ol (VII) was obtained by analogy to alcohol (V) from t-$BuCH_2CH$=CHCl, lithium (with ~2% Na) and crotonaldehyde. The yield of this product was 8.19 g (98.7%), bp 60°C (8 mm).

Trimethylsilyl Ether of 2,5-Hepten-4-ol (VIII). A sample of 2.5 ml of a 1:2 mixture of crotonaldehyde and bromopropene was added to 4.07 g (0.582 g-atom) Li in 100 abs. THF under argon at –40°C with cooling by dry ice–acetone. After some time, the mixture warmed and the lithium surface became silvery. Then, the remaining amount of the component mixture was added such that the reaction temperature was maintained at from –38° to –40°C. A total of 26 ml (36.6 g, 0.303 mole) 1-bromo-1-propene and 19 ml (16.3 g, 0.233 mole) CH_3CH=CHCHO was added. At the end of the addition, the mixture was stirred for an additional 0.5 h and then 30 ml (25.3 g, 0.233 mole) Me_3SiCl was added. The LiCl precipitate was filtered off. The organic layer was washed twice with brine and dried over $MgSO_4$. Distillation gave 27.8 g (65%) ether (VIII) with bp 45-48°C (8 mm). Gas–liquid chromatography gave two isomers since the starting bromopropene is a mixture of cis and trans isomers.

CONCLUSIONS

1. Vinyl halides with a bulky substituent at the β-carbon atom react with metallic lithium to give acetylenides.

2. The undesired formation of acetylenides in the reaction of vinyl halides RCH=CHX (where R = CH_3 or C_2H_5) with lithium may be blocked by the simultaneous addition of the vinyl halide and carbonyl component to lithium.

LITERATURE CITED

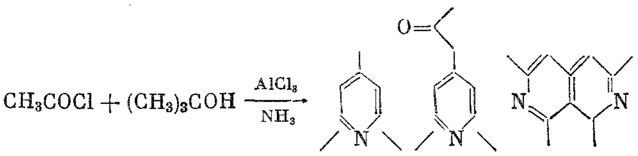
1. E. A. Braude and J. A. Coles, J. Chem. Soc., 2078 (1951).
2. D. Y. Curtin and J. W. Grump, J. Am. Chem. Soc., 80, 1922 (1958).
3. D. Seyferth and L. G. Vaughan, J. Am. Chem. Soc., 86, 883 (1964).
4. D. J. Nelson, J. Org. Chem., 49, 2059 (1984).
5. E. A. Mistryukov and I. K. Korshevets (Korshevetz), Synthesis, 947 (1984).
6. P. J. Pearce, D. H. Richards, and N. F. Scilly, J. Chem. Soc., Perkin Trans, 1, 1655 (1972).
7. K. G. Migliorese, Y. Tanaka, and S. I. Miller, J. Org. Chem., 39, 739 (1974).
8. E. J. Corey and J. W. Suggs, Tetrahedron Lett., 2647 (1975).

A HIGHLY SELECTIVE METHOD FOR THE SYNTHESIS OF SYMMETRICAL TRISUBSTITUTED PYRIDINES USING TRANSITION AND NON-TRANSITION METAL SALTS

F. A. Selimov, O. G. Ruttan,
and U. M. Dzhemilev

UDC 542.97:547.82

Erre et al. [1] have recently reported the preparation of alkylpyridines by the reaction of AcCl with t-BuOH in the presence of $AlCl_3$ with subsequent treatment of the condensation products by aqueous or gaseous NH_3 to give a mixture of 2,4,6-trimethylpyridine (I), 4-acetonyl-2,6-dimethylpyridine (II), and 1,3,6,8-tetramethyl-2,7-naphthyridine (II) with ~85% total yield; the content of pyridines (I) and (II) in the product was ~35-70% [1].



(I) (II) (III)

Attempts to increase the selectivity of this reaction relative to (I) by changing the reagent ratio, conditions and concentration of the Lewis acid were unsuccessful.

A study was carried out on the reaction of C_2-C_6 aliphatic acid chlorides with t-BuOH, isobutylene and NH_3 by the action of transition and non-transition metal salts ($AlCl_3$, $ZnCl_2$, $InCl_3$, $TiCl_4$, $TiCl_3$, WCl_6, $FeCl_3$, $CoCl_2$, $NiCl_2$ and $PdCl_2$) and bimetallic systems $AlCl_3$–$NiCl_2$ and $AlCl_3$–$PdCl_2$ in a search for new catalysts for this reaction which provide for the formation of (I), which has practical importance, and to determine the possibility of using other acid chlorides and isobutylene in this reaction.

The use of isobutylene gives some increase in the total yield of (I)-(III) but with a predominance of (III). The use of bimetallic Lewis acids containing $AlCl_3$, $NiCl_2$ and $PdCl_2$ significantly increased the yield of (I)-(III) and the selectivity relative to (I). Thus, for example, a 1.6:0.1 mixture of acetyl chloride and isobutylene in the presence of 7:3 $AlCl_3$–$NiCl_2$ or $AlCl_3$–$PdCl_2$ with subsequent treatment of the reaction products with NH_4OH gave a mixture of (I)-(III) with total yield of 97%, in which the content of (I) was 88%. In addition to (I), a slight amount of (III) and unidentified higher isobutylene oligomers are formed under these conditions. Among the transition and non-transition metal salts tested, the highest yields of (I) were obtained upon using $InCl_3$ or $ZnCl_2$ as the Lewis acid. The selectivity relative to (I) in the presence of these salts is 97%, while the isobutylene conversion in these experiments was 99%. In light of the availability and ease of obtaining $ZnCl_2$, all the subsequent experiments on the synthesis of substituted alkylpyridines were carried out in the presence of $ZnCl_2$.

Institute of Chemistry, Bashkir Branch, Academy of Sciences of the USSR, Ufa. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 688-690, March, 1986. Original article submitted May 21, 1985.

0568-5230/86/3503-0629$12.50