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ALKYLATION OF 1-CHLORO-3,4-EPOXY-1*E*-BUTENE BY ALKYNYLLITHIUM

Anne PAJU, M. LOPP, Ü. LILLE. 1-KLORO-3,4-EPOKSÜ-1*E*-BUTEENI ALKÜLEERIMINE ALKÜNÜÜLLIITIUMIGA

Анне ПАЮ, М. ЛОПП, Ю. ЛИЛЛЕ. АЛКИЛИРОВАНИЕ 1-ХЛОР-3,4-ЭПОКСИ-1*E*-БУТЕНА АЛКИНИЛЛИТИЕМ

Recently we have demonstrated the application of the ketale derivative of 1-chloro-3-keto-4-bromo-1*E*-butene (1) in constructing the conjugated *E,Z* double bond system by copper mediated alkynylation of (1) followed by the reduction of the triple bond [1]. Now we have investigated how the epoxy derivative of (1) 1-chloro-3,4-epoxy-1*E*-butene (2) can be used in constructing the compounds (4)—(6) with non-conjugated double-triple (double-double) bonds.

Epoxybutene (2) was treated with alkynyllithium (3) ($R=C_2H_5$; C_3H_7; C_6H_{13}) in the presence of HMPA in Et_2O, THF, toluene and hexane, yielding the epoxide opening product (4) (30—55% yield) together with a certain amount of the elimination product (6) (the (4):(6) ratio varied from 3:1 to 9:1). The best yield of (4) was gained at a 3:1 hexane/HMPA mixture at 0 °C for 14h. Alkynyllithium in the presence of $BF_3 \cdot OEt_2$ in THF at −78 °C in the reaction with (2) gave the addition product (5) as the main product together with allylic alcohol (4) at a ratio of 2:1. The elimination product (6) was not detected in this case. The triple bond in (4) was reduced by the zinkcopper couple [2] to yield *E,Z* diene (7). The reaction products were identified by IR and ^{13}C NMR spectra.

(2) IR: 1640(−C=C−); 935(−C=C−); 850(C−C); 1250(C−C); bp= =40—42 °C (30 mmHg);
C% requires 45.93, found 45.84; H% requires 4.78, found 4.71

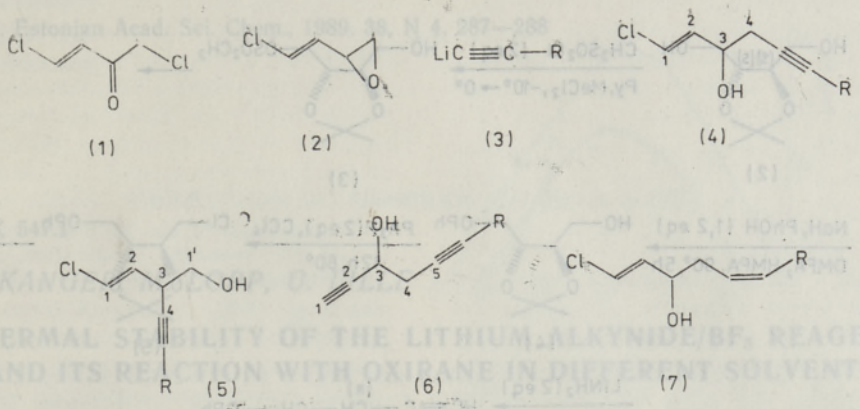
(4) $R=C_2H_5$; C_3H_7; C_6H_3 IR: 3500(OH); 1100(OH); 935(−C=C−); 1635(−C=C−)
^{13}C NMR (TMS, $CDCl_3$) C_1 120.6 (d); C_2 134.5 (d); C_3 69.5 (d); C_4 28.1 (t); C_5 74.8 (s); C_6 84.3 (s); C_7 18.18 (t); C_9 28.6 (t); C_{10} 29.0 (t); C_{11} 31.4 (t); C_{12} 22.6 (t); C_{13} 14.0 (q)

(5) C_6H_{13} IR: 3500(OH); 1050(OH); 1630(−C=C−); 935(−C=C−)

^{13}C NMR (TMS, $CDCl_3$) C_1 120.9 (d); C_2 130.3 (d); C_3 37.2 (d); C_4 86.1 (s); C_5 76.3 (s); C_6 18.8 (t); C_7 28.6 (t); C_9 28.9 (t); C_{10} 31.9 (t); C_{11} 22.6 (t); C_{12} 14.0 (q); C'_1 65.5 (t)

(6) $R=C_2H_5$ IR: 3330(HC≡C−); 2260(−C≡C−); 3500(OH)
^{13}C NMR (TMS, $CDCl_3$) C_1 71.1 (d); C_2 87.7 (s); C_3 61.02 (d); C_4 28.89 (t); C_5 78.9 (s); C_6 79.8 (s); C_7 12.69 (t); C_8 13.69 (q)

(7) $R=C_2H_5$ IR: 3500(OH); 3050(−C=C−); 1665(−C=C−); 1645 (−C=C−); 935(−C=C−)
^{13}C NMR (TMS, $CDCl_3$) C_1 119.6 (d); C_2 135.4 (d); C_3 70.5 (d); C_4 34.9 (t); C_5 122.8 (d); C_6 135.6 (d); C_7 20.6 (t); C_8 12.3 (q).



(1) (2) (3) (4) (5) (6) (7)

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REFERENCES

1. *Лопп М., Паю А., Кангер Т., Вялимяэ Т., Лилле Ю.* Алкилирование этиленового кеталя 1-хлоро-4-бромо-1Е-бутен-3-она. Синтез иненовых и диеновых фрагментов лейкотриенов и феромонов // Ж. орг. хим., 1989, **25**, вып. 4, 869—870.
2. *Mäeorg, U.* Zink/copper as a reducing agent. 1. Reduction of some enyols and alkynols // Acta Comm. Univ. Tartuensis, 1982, N 616, 50—54.

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SYNTHESIS OF (R)-(-)-4-PHENOXY-3-HYDROXY-1-BUTYNE FROM TARTARIC ACID DERIVATIVES

Piret NIIDAS, T. KANGER, M. LOPP, Ü. LILLE. (R)-(-)-4-FENOKSÜ-3-HÜDROKSÜ-1-BUTÜÜNI SÜNTEES VIINHAPPE DERIVAATIDEST

Пиpет НИЙДАС, Т. КАНГЕР, М. ЛОПП, Ю. ЛИЛЛЕ. СИНТЕЗ (R)-(-)-4-ФЕНОКСИ-3-ГИДРОКСИ-1-БУТИНА ИЗ ПРОИЗВОДНЫХ ВИННОЙ КИСЛОТЫ

Tartaric acid is a readily available chiral natural product which can be used as a source of chiral building blocks for synthesis [1]. We have synthesized (R)-(-)-4-phenoxy-3-hydroxy-1-butyne (1), a ω-chain precursor in prostaglandin synthesis [2], starting from 2,3-O-isopropylidene-1.2(*S*), 3(*S*), 4- butane-tetraol (2) [3]. Monomesylate (3) was alkylated with sodium phenylate in DMFA to give phenoxy substituted butanol (4) (65%; $[\alpha]_D^{25} = -11.3°$, c 8.23 $CHCl_3$). After the chlorination by $CCl_4 - Ph_3P$ according to [4] (83%) and the elimination according to [5] (85%),