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COPPER(I)-CATALYZED REACTION OF ISOPRENE BROMOHYDRIN WITH ORGANOLITHIUM REAGENT

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The reaction of isoprene bromohydrin (1-bromo-2-methyl-3-buten-2-ol) (1) with ethyl-, propyl- and butyllithium in the presence of copper(I) iodide leads to the exclusive formation of the vinyl group migrated 2-alkyl-4-penten-2-ols (3d-3f), in contrast to the reaction with methyl-, phenyl- and benzyllithium, which yields the corresponding 2-methyl-4-substituted-2-buten-1-ols (2a-2c).

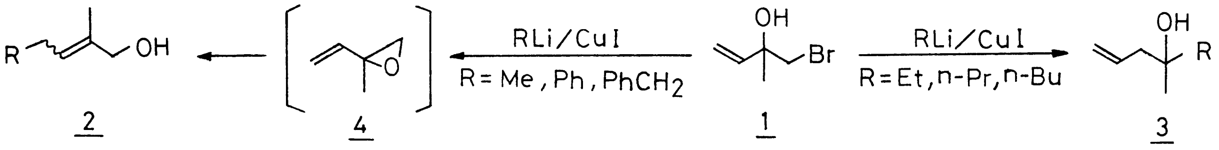
We have recently reported the copper(I)-catalyzed reaction of isoprene bromohydrin (1) with allylic Grignard reagents which involves the highly selective rearrangement of vinyl group.[1)] As an extension of this study, we have examined the reaction of 1 with a variety of organolithium reagents and recognized the striking differences in the reaction behavior of 1 toward Grignard reagents and organolithium reagents. Furthermore, the bromohydrin 1 has been found to give two quite different types of product (2 and 3) depending on the kinds of the organolithium reagents used.

In the presence of copper(I) iodide (0.5 eq), 1 (1 eq) was added to an ethereal solution of methyllithium (5 eq) at 0°, and the mixture was stirred overnight at room temperature. The reaction mixture was poured into a saturated ammonium chloride solution, and the product was extracted with ether. The extract was dried over anhydrous sodium sulfate and the solvent was removed. The residue was chromatographed on silica gel to afford 2-methyl-2-penten-1-ol (2a) in 83% yield.[2)] The E/Z ratio (70/30) was estimated based on the integration of the methylene protons ($-CH_2OH$) in the ^{1}H-nmr spectrum.[3)] Similar results were obtained for the reaction with phenyl- and benzyllithium (Table). It has been reported[4)] that

Table. Reaction of isoprene bromohydrin (1) and organolithium reagents in the presence of copper(I) iodide

entry	RLi	solvent	product	yield
a	MeLi	Et_2O	2a (E/Z=70/30)	83%
b	PhLi	Et_2O	2b (E/Z=81/19)	89
c	$PhCH_2Li$	THF	2c (E/Z=94/ 6)	61
d	EtLi	Et_2O	3d	75
e	n-PrLi	Et_2O	3e	89
f	n-BuLi	Et_2O	3f	85

isoprene oxide (4) reacts with various vinyllithiums in the presence of a copper(I) salt to give the allylic alcohols of the type 2 (R=vinyl). The intermediacy of the epoxide 4 in the catalytic reaction of the bromohydrin 1 was proved by the following experimental evidence. Thus, the epoxide 4 (1 eq) was treated with excess (3 eq) phenyllithium in the presence of copper(I) iodide (0.3 eq) in ether. After stirring overnight at room temperature, the reaction mixture was worked-up to give 2b (E/Z=72/28) in 92% yield.[5] Surprisingly, the copper(I)-catalyzed reaction of 1 with the excess (5 eq) alkyllithium which has β-hydrogen atoms, e.g., ethyl-, propyl- and butyllithium, gave the corresponding 2-alkyl-4-penten-2-ol (3d-3f)[2] exclusively (Table). No evidence of the formation of the alcohols of the type 2 was found. In the absence of the catalyst, the reaction gave a complicating product mixture. The possibility of the epoxide 4 being the intermediate of the reaction with the alkyllithiums was excluded by the fact that the treatment of 4 with ethyllithium in the presence of copper(I) iodide afforded 2-methyl-2-hexen-1-ol (2d; E/Z=47/53)[2] in 87% yield, and the formation of 3d was not found.



The reaction mechanism of this interesting process is not yet clear, however, it should be noted that the pentenols 3 are the products of the copper(I)-catalyzed reaction of 1 with allylic Grignard reagents (R=allyl).[1] Further evidence on the nature of this reaction is currently being sought.

References and Notes

1) Y.Butsugan, I.Kadosaka, and S.Araki, Chem.Lett., 527 (1979).

2) Structures were proved by ir, ^{1}H- and ^{13}C-nmr and/or comparison with authentic samples: 2a: see ref.3; 2b: see ref.5; 2c: ir(neat) 3340, 1603, 1500, 1458, 1000, 746, 698 cm^{-1}, ^{1}H-nmr(CCl_4) δ 7.03(5H,m,Ph), 5.27(1H,m,olefin), 4.43(0.1H,s,[Z]-$C\underline{H}_2OH$), 3.77(1.9H,s,[E]-$C\underline{H}_2OH$), 3.00(1H,s,OH), 2.8-2.0(4H,m,$-CH_2CH_2-$), 1.65(0.2H,m,[Z]-CH_3), 1.49(2.8H,s,[E]-CH_3); 2d: ir(neat) 3340, 1644, 1382, 1008, 888 cm^{-1}, ^{1}H-nmr(CCl_4) δ 5.14(1H,m,olefin), 4.60(1H,s,OH), 3.96(1.1H,s,[Z]-$C\underline{H}_2OH$), 3.82(0.9H,s,[E]-$C\underline{H}_2OH$), 1.98(2H,m,$-CH_2-$), 1.70(1.6H,m,[Z]-CH_3), 1.58(1.4H,s,[E]-CH_3), 1.24(2H,m,$-CH_2-$), 0.87(3H,m,$-CH_3$); 3c and 3d: J.Huet, Bull.Soc.Chim.Fr., 2677 (1964); 3e: ir(neat) 3400, 1646, 1478, 1389, 1001, 918 cm^{-1}, ^{1}H-nmr(CCl_4) δ 6.2-4.7(3H,m,olefin), 2.08(2H,d,J=7Hz,$-C\underline{H}_2CH=CH_2$), 1.69(1H,s,OH), 1.30(6H,m,$-CH_2-$), 1.04(3H,s,$-CH_3$), 0.86(3H,m,$-CH_2C\underline{H}_3$), ^{13}C-nmr($CDCl_3$) 134.7($CH_2=\underline{C}H-$), 118.5($\underline{C}H_2=CH-$), 72.6($-\overset{|}{\underset{|}{C}}-OH$), 46.8, 42.0, 26.5, 23.7($-CH_2-$), 27.0, 14.5($-CH_3$).

3) K.C.Chan, R.A.Jewell, W.H.Nutting, and H.Rapoport, J.Org.Chem., 33, 3382 (1968).

4) G.Cahiez, A.Alexakis, and J.F.Normant, Synthesis, 528 (1978).

5) Non-catalytic reaction of 4 with phenyllithium has been reported: G.C.M.Aithie and J.A.Miller, Tetrahedron Lett., 4419 (1975).

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