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ETHYLIDYNE ALKYNES FROM ISOPROPYLIDENE OLEFINS

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Summary: A number of isopropylidene olefins was reacted with sodium nitrite in AcOH-H_2O to give the corresponding ethylidyne alkynes with net loss of a CH_4 unit.

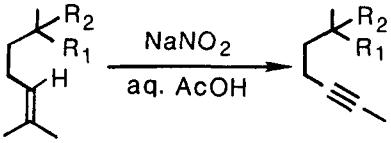
Several studies on reactions of olefins with sodium nitrite in aqueous acetic acid have appeared in the literature[1,2,3]. Very recently Marchesini and co-workers[4] reported formation of substituted acetylenes from diazotization of some 5-aminoisoxazoles. Our continuing interest in nitrosative elimination of terpenyl alkanolamines[5] led us to examine the scope of the title reaction. This unique alkene-alkyne transformation observed under normal nitrosation conditions[6] is believed to involve an unprecedented carbon-carbon bond rupture by removal of one methyl group from the isopropylidene moiety resulting in apparent elimination of a CH_4 unit from the double bond of the 2-methyl-propenyl group(a → b, Table I; c → d, Table II). Preliminary results of our current investigation on terpene derivatives(1a-11a) and other isopropylidene olefins (12c-20c) are summarized in Table I and Table II, respectively.

The general procedure for reactions listed in the tables is outlined as follows: To a well-stirred solution of an olefinic reactant(7 mmol) in acetic acid(20 ml) and water(13 ml), sodium nitrite(13 g) was added portionwise at 0°C. The mixture was heated at 60°C for 0.5 hours. It was then poured into ice water(60 ml) and extracted with CH_2Cl_2(3 x 10 ml). Flash chromatography[7] (silica gel) of the crude product followed by distillation under reduced pressure afforded the pure product whose structure was determined by ^{13}CNMR spectrometry. Further structural confirmation was performed on the pure sample by high-resolution mass spectrometry and by comparison with an authentic compound.

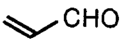
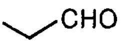
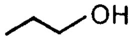
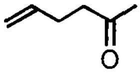
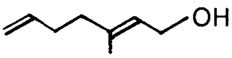
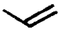
Reactions carried out under conditions described above normally provided alkyne products in moderate to high yield. In our earlier studies, numerous attempts were made to evaluate the formation potential of alkynes in nonaqueous systems using either butyl nitrite-benzene[1] or $AgNO_2$-DMF[8]. Essentially no alkene-alkyne conversion was observed in these systems. However, in the presence of acetic acid and water, 4a reacted with butyl nitrite in benzene to give 4b in 50% yield. Likewise, treatment of 3a with $AgNO_2$ in DMF and AcOH-H_2O produced 1b(40%) as the sole alkyne product. In view of our previous finding that 3a was oxidized quantitatively to 1a by $AgNO_2$ in DMF, it was not unexpected to note the formation of 1b from 3a in the aqueous medium via obvious intermediacy of 1a.

For compounds containing isomerizable double bonds, the formation of an alkyne from a pure cis(or trans) isomer of a terpene(1a, 3a, 5a, or 6a) was found to be accompanied by isomerization of the double bond involved. It is presumed that the isomerization process occurred prior to the elimination reaction as the cis/trans ratio observed in 1b, 3b, 5b, or 6b was identical

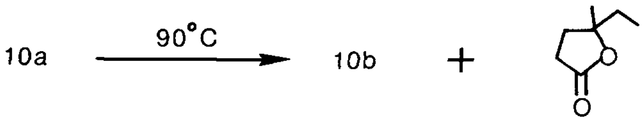
Table I. Conversion of Terpene Olefins to Related Alkynes



a b

Entry	R_1	R_2	Yield(%)	Carbon-13 NMR, δ (ppm)*		
				$\underline{C}H_3C\equiv$	$CH_3\underline{C}\equiv$	$CH_2\underline{C}\equiv$
1		H	64	3.34	77.1	77.3
2		H	70	3.36	76.8	77.4
3		H	98	2.76	75.4	78.3
4		H	95	3.39	75.3	79.2
5		H	91	3.39	75.6	79.4
6		H	30	3.13	75.9	78.2
7		OH	72	3.42	76.2	79.3
8		OAc	80	2.93	75.0	78.2
9		OCH_3	89	3.43	76.6	79.3
10		OH	66	3.41	75.3	80.2
11		OCH_3	79	3.27	75.4	79.2

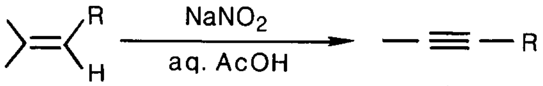
*Solvent, $CDCl_3$; internal reference, $(CH_3)_4Si$; data are for trans isomers.



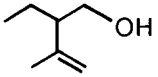
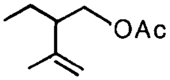
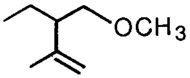
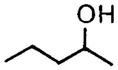
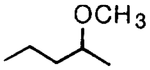
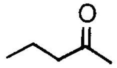
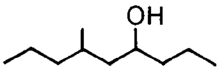
10e

43% 57%

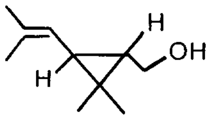
Table II. Conversion of Isopropylidene Olefins to Related Alkynes



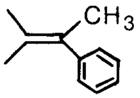
c d

Entry	R	Yield(%)	Carbon-13 NMR, δ (ppm)*		
			$\underline{C}H_3\equiv$	$CH_3\underline{C}\equiv$	$CH_2\underline{C}\equiv$
12		23	3.07	72.5	77.0
13		54	3.18	72.4	77.4
14		68	3.20	73.0	77.8
15		61	2.65	76.6	79.0
16		87	3.43	76.0	79.0
17		92	3.25	76.0	78.0
18		76	2.98	75.2	79.4
19		67	3.00	75.3	78.3
20		0	-	-	-

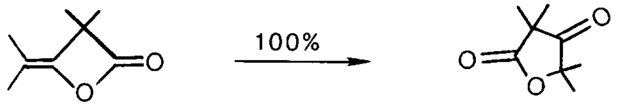
* See footnote to Table I



21



22



23 24

with that in the isomerized starting material. Our experimental data indicate that although yields of alkynes were highly dependent on the conditions employed and the structures of R_1, R_2, and R groups, studies conducted with compounds in the geranyl series(3a, 4a, 5a, and their O-acetyl- and O-methyl-analogues) as well as some ketones such as 5a and 17c showed little effect of these reaction variables on yields and were of greater success in their conversion to alkynes (91-98%). In other cases, especially where the hydroxy group of an alkene is separated from the isopropylidene double bond by three or four carbons as in 7a, 10a, 12c, and 15c, lowering of the reaction temperature invariably led to better yields of alkyne products. At an elevated temperature, the alkene-alkyne conversion for these alkenes could be complicated by concomitant oxidation and cyclization giving rise to a lactone. This became evident when 10e was isolated in 57% yield from reaction of 10a and sodium nitrite in $AcOH-H_2O$ at 90^oC for 0.5 hours; along with the lactone, 10b was also obtained as the minor product(43%). Similar results were observed with other alkenes of analogous structure. As illustrated in entries 8, 9, 11, 13, 14, and 16, yields of alkynes were significantly improved by use of acetylated and methylated compounds. The conversion of 12c to 12d was relatively less efficient because of the lability of both reactant and product under the conditions of reaction. Analysis of the crude product revealed the presence of intractable polymeric materials. Of all compounds studied in the control experiments without sodium nitrite, 1a, 2a, and 6a were found to cyclize, to some extent, forming known terpenes. This may partly be accounted for the comparatively lower yields of 1b, 2b, and 6b.

The results of this study clearly suggest that the prerequisite structure of an alkene must contain a 3-methyl-2-butenyl group for its favorable conversion to a related alkyne(1a-19a). Under standard nitrosation conditions, experiments with certain isopropylidene olefins devoid of $(CH_3)_2C=CHCH_2$- structure failed to produce alkynes of any type. Thus, 20d was not detected in the product obtained from 20c, but the product was benzaldehyde(100%). Pulegone isomerized to isopulegone(75%) without alkyne formation. Compound 21(and ethyl chrysanthemumate) yielded no products other than rearrangement products as result of ring opening. Furthermore, 22 was quantitatively transformed to acetophenone(100%) with no trace of alkynes detected, while a 100% yield of γ-lactone 24 was realized from β-lactone 23. The preceding examples represent reactions that appeared to involve initial hydroxylation[1] and subsequent oxidation and rearrangement.

Further studies on the mechanistic details of the title reaction are in progress.

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