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THE REACTION OF ALKYNES WITH I_2 ON UNACTIVATED ALUMINA

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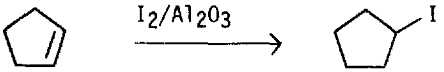
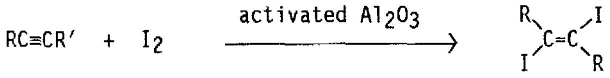
Abstract: Alkynes react with I_2 on unactivated alumina under mild conditions to form (E)-diiodoalkenes. Terminal alkynes also afford 1,1,2-triiodo-1-alkenes in low yield. These latter products were not observed on activated alumina.

Previous work from our laboratory has shown that many synthetically useful reactions, some of which are unique, occur on the surface of alumina which has been activated by heating under a vacuum.[1-9] Alkenes, for example, react with HI, generated in the reaction I_2 with surface hydroxyl groups, to form alkyl iodides under mild conditions (eq.1).[7,9] These reactions would be even more useful if out-of-the-bottle, unactivated alumina could be used because the time and expense required for activation would be eliminated. In the aforementioned addition of HI to alkenes, for example, the reaction does occur on unactivated solid, although at a somewhat slower rate.[7]



(1)

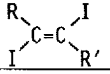
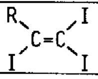
Alkynes reacts differently with I_2 on activated alumina, forming (E)-diiodoalkenes by the stereospecific addition of I_2 to the triple bond (eq.2).[8,9] We now wish to report our results for this reaction on out-of-the-bottle alumina. Although the reactions occur readily, internal and terminal alkynes exhibit different chemical behavior



(2)

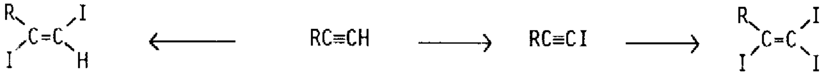
The product distribution obtained from the reaction of I_2 with representative alkynes on unactivated alumina, slurried in low boiling (bp 35-36°) petroleum ether for 6 hr at room temperature, is shown in Table 1. The first four alkynes are internal and the results are comparable to those obtained on activated alumina; (E)-vicinal diiodoalkenes are the only products in all cases. A second, minor product, readily separated from the major product by chromatography on silica gel or alumina, was also formed with terminal alkynes. These products were identified as 1,1,2-triiodo-1-alkenes by spectroscopic characterization and, in several instances, by independent synthesis (Table 1, entry 10). Triiodoalkenes were not formed on activated alumina.

Table 1. **Addition of I_2 to RC≡CR′ on Unactivated Alumina**

ENTRY	ALKYNE (RC≡CR′) R	 R′	% YIELD OF PRODUCTS 	 
1	Et	Et	98	-
2	Pr	Pr	63	-
3	$\mathrm{MeO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}$	$\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OMe}$	60^{a}	-
4	$CH_3CHOHCH_2$	Me	50	-
5	$CH_3(CH_2)_3$	H	75	10
6	Ph	H	87	0
7	$HOCH_2$	H	68	3
8	Pr	H	76.5	9.5
9	$CH_3(CH_2)_5$	H	72	14
10	Pr	I	-	43

a) This reaction was run for 10 hr.

It is presently unclear why terminal alkynes yield tiiodoalkenes on unactivated alumina. It is clear, however, that they arise by iodination of 1-iodo-1-alkynes, which can be detected spectroscopically during the course of the course of the reaction (see also Table 1, entry 10) (eq.3). In any event the addition of I_2 to alkynes on unactivated alumina is the best method available for making (E)-vicinal diiodoalkenes. It also represents a simple method for the preparation of certain 1,1,2-triiodo-1-alkenes, albeit in low yields.



(3)

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