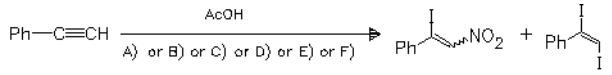
addition reactions

O 0060

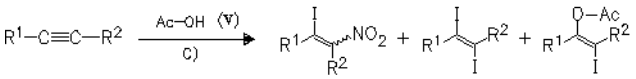
38 - 037

Reactions of Alkynes with Iodine and Potassium Iodide in Acetic Acid in the Presence of Nitrates. Simple Synthesis of 1-Iodo-2-nitroalkenes. — Reaction of aryl- and alkylacetylenes with iodine (or potassium iodide) and nitrates proceeds at the acetylene moiety to furnish vic-iodonitroalkenes. Side products are diiodoalkenes as well as acetoxyiodoalkenes. The influence of reaction conditions and acetylene substitution on the reaction outcome is studied. A possible reaction mechanism, involving addition of in situ generated INO_2 to the acetylene, is discussed. — (YUSUBOV, M. S.; PEREDERINA, I. A.; KULMANAKOVA, YU. YU.; FILIMONOV, V. D.; CHI, KI-WHAN; Russ. J. Org. Chem. 35 (1999) 9, 1264-1272; Dep. Chem., Tomsk Polytech. Univ., Tomsk 634004, Russia; EN)



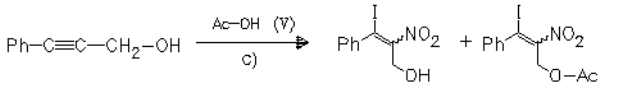
I II III

A): 1 equiv. I_2, 85°C	0%	90%
B): 0.75 equiv. I_2, 2 equiv. $NaNO_3$, 45°C	29% (m.i.)	40%
C): 0.75 equiv. I_2, 2 equiv. $NaNO_3$, 85°C	51% (E:Z=86:14)	5%
D): 0.75 equiv. I_2, 1 equiv. $NaNO_3$, 85°C	27% (m.i.)	12%
E): 1.5 equiv. KI, 3 equiv. $NaNO_3$, 85°C	67% (E:Z=83:17)	7%
F): 1.5 equiv. KI, 3 equiv. $NaNO_3$, 85°C, [argon]	0%	34%

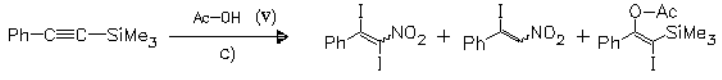


IV VI VII VIII

a R^1: —Ph ; R^2: —Me	51% (E:Z=88:12)	0%	16%
b R^1, R^2: —Ph	70% (E:Z=80:20)	traces	11%
c R^1, R^2: —Pr	13% (E:Z=67:33)	3%	–



IX X 22% (E:Z=72:28) XI 13% (E:Z=72:28)



XII XIII 27% II 9% XIV 13%

C): 0.75 equiv. I_2, 2 equiv. $NaNO_3$, 85°C