Synthesis and Dimroth Rearrangement of 6-Cyano-1,2,4-triazolo-[4,3-*a*]pyrimidin-5- and 7-ones. A Novel Alkylation with Orthoesters and a New Participation of the Cyano Group in the Rearrangement

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The cyclization products of 5-cyano-2-hydrazino-6-phenyl-3,4-dihydropyrimidin-4-one (**6**) with one carbon inserting agents have been confirmed to be of the 1,2,4-triazolo[4,3-*a*]pyrimidin-5(8*H*)-ones type and not the respective 7-ones, by comparing their alkylated derivatives **10a**, **11a**, **27** and **28** with the product from the cyclization of the 3-methyl and 3-benzyl derivatives of **6**. A novel alkylation process was found when triethyl orthoformate was used as a cyclizing agent. Dimroth rearrangement of **8**, **14**, **15**, **24**, **34** and **36** with 2% ethanolic KOH gave the respective triazolo[1,5-*a*]pyrimidinone **13**, **18**, **19**, **25**, **38** and **40,** respectively. Using 10% ethanolic KOH led to a novel participation of the cyano group in the rearrangement whereby **8a** gave 7-imino-5-phenyl-1,2,4-triazolo[1,5-*a*]pyrimidine **22**.

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