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A CONVENIENT SYNTHESIS OF α-BROMOKETONES FROM OLEFINS

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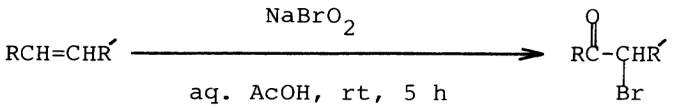
α-Bromoketones are prepared in good yields by the reaction of olefins with sodium bromite in aqueous acetic acid at room temperature.

α-Haloketones are very useful synthetic intermediates for acyclic or cyclic compounds including products via a Favorskii rearrangement.[1] Especially, a numerous kind of heterocycles have been prepared starting from α-haloketones. For example, the donor component of highly electrically conductive organic metals, i.e. tetrathiofluvalene has been synthesized using α-haloketones.[2]

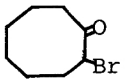
α-Haloketones are generally prepared by the careful halogenation of ketones,[3] the reaction of α-diazoketone with HCl,[4] and oxidation of olefins with CrO_2Cl_2 or other oxidizing agents.[5] These methods, however, often involve contamination of impurities such as polyhaloketones or halogenated regioisomers, or require hazardous reagents such as α-diazoketones or CrO_2Cl_2.

We wish to report here a synthetically useful method for the title compounds. Thus, we found olefins reacted with sodium bromite ($NaBrO_2$)[6] in aqueous acetic acid at room temperature for 5 h to give α-bromoketones in good yields.



The results are summarized in the Table 1. A controlled experiment revealed 6 molar amount of sodium bromite gave the best result.[7] Employment of a lesser amount of the reagent resulted in the formation of appreciable amount of bromohydrin, indicating a possible intermediacy of bromohydrin. In fact we observed the formation of α-bromocyclohexanone in 89% yield by the reaction of 2-bromocyclohexanol with sodium bromite (3 molar amount) under similar conditions. No regioisomers were isolated in the cases of unsymmetrical olefins studied here.

Table 1. Preparation of α-bromoketones.

Olefin	Product	Yield (%)	IR νC=O (cm^{-1})
		87	1740
		94	1725
$PhCH_2CH=CH_2$	$PhCH_2COCH_2Br$	78	1705
$n\text{-}C_6H_{13}CH=CH_2$	$n\text{-}C_6H_{13}COCH_2Br$	81	1730
$PhCH=CHCH_3$	$PhCOCH(Br)CH_3$	62	1720
$(CH_3)_3CCH=CHCH_3$	$(CH_3)_3CCOCH(Br)CH_3$	83	1720

The present straightforward synthesis of α-bromoketones may provide a most simple procedure. The reaction is characteristic to sodium bromite, since sodium hypobromite (NaBrO) is well known to give bromohydrins by the reaction with olefins, and sodium bromate ($NaBrO_3$) is inert towards olefins.[8)]

References

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3) R. Bloch, Synthesis, 1978, 140.
4) Y. Ueno, Y. Masuyama, and M. Okawara, Chem. Lett., 1978, 603.
5) K. B. Sharpless and A. Y. Teranishi, J. Org. Chem., 38, 185 (1973); E. Murayama A. Kohda, and T. Sato, Chem. Lett., 1978, 161.
6) Anhydrous sodium bromite; Concentration of commercial Brodisizer (aq. sodium bromite, Nippon Silica Industrial Co., Ltd.) under reduced pressure at less than 30°C leaves residual sodium bromite trihydrate which is recrystallized from aqueous 2 normal sodium hydroxide solution, and dried at 20°C/5 torr to give anhydrous sodium bromite. The purity is estimated by titration with Na_3AsO_3 to be 98%.[9)]
7) The reaction was carried out using 6 molar amount of $NaBrO_2$. The product was extracted with dichloromethane, and purified by column chromatography on silica gel eluting with dichloromethane. 1,2-Dibromides (olefin-bromine adducts) were also isolated in 5-10% yied in each case. The structures of α-bromoketones are fully confirmed by the comparison of spectral data with those of authentic samples prepared by the oxidation of known bromohydrins with the Jones reagent, or elemental analysis of the corresponding 2,4-dinitrophenylhydrazone.
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