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CONVENIENT PREPARATION OF 1,2-CYCLOHEXANEDIONES

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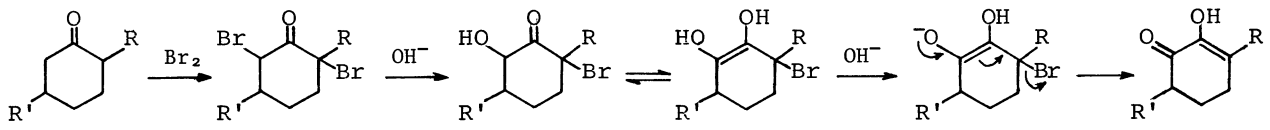
1,2-Cyclohexanedione and 3-alkyl-1,2-cyclohexanediones were prepared in good to excellent yields from the corresponding 2,6-dibromocyclohexanones by treatment with aqueous NaOH.

1,2-Cyclohexanedione (1a) has hitherto been prepared by the oxidation of cyclohexanone using SeO_2.[1] However, this method suffers several disadvantages: the yield is not satisfactory, that is, 60% based on SeO_2 and 12% based on cyclohexanone used; rather expensive and toxic SeO_2 should be recovered and/or reused with a tedious procedure; elimination of all selenium from the reaction mixture is not easy. Recently an improved method by the base-catalyzed autoxidation in dimethoxyethane–*t*-butyl alcohol using potassium *t*-butoxide as a base has been reported to give crude 1a in 44% yield.[2]

Here we report that Wallach's method,[3] which was published in 1924 but once abandoned in 1945 for the reason of poor yield,[4] actually provides satisfactory yields with easiness in operation. Since Wallach mentioned neither the reaction conditions nor the yield in his paper, our successful procedure is described in details as follows.

In 30 ml of anhydrous ether, 6.0 g (61 mmol) of cyclohexanone was brominated at -10 °C by adding 19.5 g (122 mmol) of bromine dropwise with stirring. The reaction mixture was washed with saturated aqueous NaCl then twice with saturated aqueous $NaHCO_3$, and finally with saturated aqueous NaCl. The organic layer was dried over $MgSO_4$ and the ether was evaporated to give 14.4 g of 2,6-dibromocyclohexanone in 92% yield. A colorless oily product crystallized partly. The IR and ^1H NMR spectra[5] were satisfactory. To 14.2 g (55.5 mmol) of the dibromoketone dissolved in 30 ml of tetrahydrofuran was added 33.5 g (838 mmol) of NaOH dissolved in 280 ml of ice-cold water with stirring. The resulting homogeneous solution was stirred magnetically for 2 h in an ice bath under a nitrogen atmosphere.[6] The slightly yellow solution was evaporated under reduced pressure to remove about half the tetrahydrofuran added,



	a	b	c	1a–c
R =	H	Me	*i*-Pr	
R'=	H	H	Me	

and the solution was adjusted to pH 7 with concentrated hydrochloric acid. The neutral solution was extracted with 300 ml of ethyl acetate in five portions. After drying over $MgSO_4$, the solvent was evaporated under reduced pressure to give 4.4 g of slightly brown needles of 1a in 71% (65% overall) yield. The ^1H NMR spectrum of the crude crystals indicated the small amount of the impurity at δ 1.3–1.7. Bulb-to-bulb distillation of 1.02 g of the crude crystals gave 0.87 g of a colorless oil (76–103 °C/10 torr), which crystallized on standing: mp 35.7–38 °C (lit.[2] 36–38 °C). The IR and ^1H and ^{13}C NMR spectra were satisfactory.[2]

According to the present procedure, 2-methylcyclohexanone was converted to 3-methyl-1,2-cyclohexanedione (1b), which was isolated as white needles (mp 58.5–60 °C, lit.[7] 62–63 °C) in 75% overall yield.[8] The compound 1b is known to have a flavor of burnt sugar[9] and somewhat complicated methods for the preparation with or without SeO_2 have recently been reported.[7] Menthone was also converted to the corresponding α-diketone, being isolated as 2-hydroxy-3-isopropyl-6-methyl-2-cyclohexen-1-one (isodiosphenol)[10] (1c) (bp 93–98 °C/5 torr) in 94% overall yield.[11] Interestingly, 2-hydroxy-3-methyl-6-isopropyl-2-cyclohexen-1-one (diosphenol) was not obtained, in contrast to the fact that diosphenol was always the major product from other oxidations of menthone.[12] Such selective formation of 1c indicates versatility of the present procedure and suggests the mechanism of the reaction.

A possible mechanism of the reaction is shown in the Scheme. Work is in progress to investigate the application of the present method to other systems as well as the reaction mechanism.

References and Notes

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