UTILIZATION OF 2-BROMO-3, 3-DICHLOROPROPENAL IN THE SYNTHESIS OF 3-BROMO-2-PYRONES

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3-Bromo-2-pyrones are usually obtained by bromination of the corresponding 2-pyrones (see, for example, [1]). We have shown that the condensation of 2-bromo-3,3-dichloropropenal (I) with ketones IIa-c, which contain an active methylene group, gives 1,2-dialkyl-4-bromo-5,5-dichloropentadien-2,4-ones (IIIa-c), which undergo cyclization in an acidic medium with the liberation of hydrogen chloride to give 3-bromo-2-pyrones (IVa-c) via the scheme



11 **a**  $R=CH_3$ ; **b**  $R=C_6H_5$ ; **c**  $R=CH_2COOC_2H_5$ ; 111, IV a  $R=CH_3$ ; **b**  $R=C_6H_5$ ; **c**  $R=CH_3$ ; IV **a**, **b**  $R^1=H$ ; **c**:  $R^1=COOC_2H_5$ 

Compounds I and IIa-c in a ratio of 1:2 (1:5 in the case of acetone) were stirred at room temperature for 1-7 days in the presence of catalytic amounts of sulfuric acid. The course of the reaction was monitored by thin-layer chromatography (TLC) on Silufol UV-254 plates (benzene). At the end of the reaction the dark viscous oil was poured over ice, and the aqueous mixture was extracted with ether. The extract was washed with saturated NaHCO<sub>3</sub> solution and water and dried with MgSO<sub>4</sub>. The solvent was removed by distillation, and the residue was chromatographed with a column and crystallized to give the following unsaturated ketones: IIIa, bp 52°C (1 mm),  $n_D^{2°}$  1.5455, 57% yield; IIIb, mp 44-45°C, 51% yield; IIIc, mp 75-76°C (from CH<sub>3</sub>OH), 54% yield. The structures and compositions of the compounds obtained were converted to the corresponding 3-bromo-2-pyrones (IVa,c) by cyclization in an acidic medium in the presence of strong acids. The yields of 2-pyrones ranged from 75 to 85%. Ketones IIIa-c were refluxed in glacial acetic acid in the presence of hydrochloric acid for 15-20 h to give cream-colored crystals, which were purified by crystallization: IVa, mp 101-103°C (from hexane), 75% yield; IVb, mp 137°C [1] (from ethanol), 80% yield; IVc, 87°C (from ethanol), 85% yield. The structures and compositions of pyrones IVa-c were confirmed by the IR spectra and the results of pyrones IVa-c were confirmed by the IR spectra and compositions of pyrones IVa-c were confirmed by the IR spectra and compositions of pyrones IVa-c were confirmed by the IR spectra and compositions of pyrones IVa-c were confirmed by the structures and compositions of pyrones IVa-c were confirmed by the IR spectra and the results of elemental analysis.

## LITERATURE CITED

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