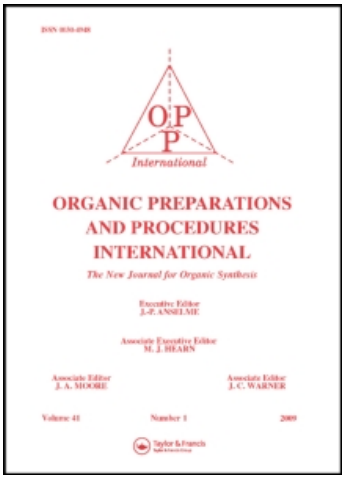

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REACTION OF THIONYL BROMIDE WITH KETONES

S. M. Al-Mousawi[a]; I. Bhatti[a]; S. D. Saraf[a]
[a] Department of Chemistry, Kuwait University, Kuwait City, Kuwait

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8. With benzyl and *tert*-butyl alcohol as substrates, treatment with $POCl_3$ (with or without a tertiary amine) led to the formation of the corresponding chloroalkane as the only isolable organic product. With cyclohexanol, high yield of cyclohexene was obtained. We believe that the spontaneous decomposition of the product **1** involves fragmentation to the corresponding carbonium ion and of the metaphosphate species, $ClPO_2$.[9]

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REACTION OF THIONYL BROMIDE WITH KETONES

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S. M. Al-Mousawi,* I. Bhatti and S. D. Saraf†

Department of Chemistry, Kuwait University, Kuwait City, KUWAIT

Thionyl bromide reacts with aromatic aldehydes to yield either the acid bromides, the benzalbromides or the corresponding acid in the case of 2-anisaldehyde.[1] It has also been reported that benzoin (**1**) reacts with thionyl bromide to produce α,α-dibromodesoxybenzoin (**2**) as the major product along with small amounts of benzil.[2] We now report that thionyl bromide reacts with

$$\underset{\mathbf{1}}{PhCOCHOHPh} + SOBr_2 \longrightarrow \underset{\mathbf{2}}{PhCOCBr_2Ph} + PhCOCOPh$$

aromatic ketones bearing α-protons or active methylene groups, producing either α-bromoketones or α,α-dibromoketones. This method is superior to the other methods of obtaining α,α-bromoketones where the yields in general vary between 60-70%.

Acetophenone (**3**) reacted with thionyl bromide at room temperature over a period of 10 hrs to give α,α-dibromoacetophenone (**4**) in 82% yield. Upon warming the reaction mixture, the product polymerized. Similarly *p*-methyl and *p*-methoxyacetophenone afforded the corresponding α,α-dibromo compounds in nearly quantitative yields. Propiophenone and isobutyrophenone also reacted

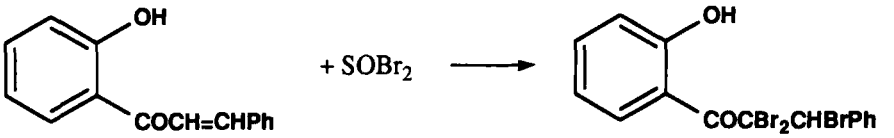
$$\underset{\mathbf{3}}{PhCOCH_3} + SOBr_2 \longrightarrow \underset{\mathbf{4}}{PhCOCHBr_2}$$

with thionyl bromide to produce α-bromopropiophenone and α-bromo-α-methylpropiophenone, respectively. Similarly, desoxybenzoin was converted into α,α-dibromodesoxybenzoin. Conversion of anthrone to anthrone dibromide by thionyl bromide is another somewhat different application of this reagent.

The brominating action of thionyl bromide on certain unsaturated ketones such as benzalacetone does not proceed by replacement of α-hydrogens or methylene groups, but instead results in the less useful addition of bromine to the olefinic bond. In this respect, the behaviour of thionyl bromide parallels that of N-bromosucinimide in combination with benzoyl peroxide, producing chiefly benzalacetone dibromide (**5**) from benzalacetone in higher yield (92%) than with N-bromosuccinimide

$$\underset{\mathbf{5}}{PhCHBrCHBrCOCH_3}$$

(46%). Benzalacetone likewise gave the corresponding dibromide in 81% yield, while 2-hydroxychalcone (**6**) yielded the tribromide (**7**) evidently by a sequence of addition and substitution.[4]



6 **7**

EXPERIMENTAL SECTION

CAUTION: *These compounds are lachrymators and vesicants and due caution should be exercised in their handling.*

All mps were determined by electrothermal apparatus and are uncorrected. The IR spectra were obtained as KBr pellets using a Perkin Elmer-850B Spectrophotometer. The NMR spectra were recorded with a Varian T60 MHz instrument using TMS as internal standard.

α,α-Dibromoacetophenone.- Thionyl bromide (15 mL from Fluka Chemicals) was added over a period of 30 min. to magnetically stirred solution of acetophenone (24 g, 0.2 mole) in benzene (250 mL) at room temperature. The yellow-red reaction mixture was stirred for a period of 10 hrs. The dark brown solution thus obtained was washed with cold aqueous sodium bicarbonate solution and dried ($MgSO_4$). Removal of the solvent left an oil which solidified; it was crystallized from petroleum ether (40-60°) to give 45 g (81%) of white needles, mp. 35-36°, lit.[5] mp. 36-37°. IR (KBr): 1680 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): δ 6.55 (1H, s, $CHBr_2$), 7.6 (3H, m, ArH), 8.2 (2H, m, Ar-H).

Anal. Calcd. for $C_8H_6Br_2O$: C, 34.53; H, 2.15; Br, 57.55. Found: C, 34.37; H, 2.02; Br, 57.68

α,α-Dibromo-*p*-methylacetophenone.- Thionyl bromide (8 mL) was added to a solution of *p*-methylacetophenone (13.4 g, 0.1 mol) in benzene (200 mL) and the mixture was refluxed for 1 hr. Work-up in the usual manner left white solid, which was crystallized from alcohol to afford 28.3 g (97%) of white needles, mp. 97-98°. IR (KBr): 1690 cm^{-1} (C=O) ^1H NMR ($CDCl_3$): δ 2.5 (3H, s, CH_3), 6.65 (1H, s, $CHBr_2$), 7.3 (2H, m, ArH), 8.0 (2H, m, ArH).

Anal. Calcd. for $C_9H_8Br_2O$: C, 36.98, H, 2.73, Br, 54.79. Found: C, 37.15; H, 2.63; Br, 54.92

α,α-Dibromo-*p*-methoxyacetophenone.- *p*-Methoxyacetophenone (7.5 g, 0.05 mol) reacted with thionyl bromide to produce 15 g (91%) of α,α-dibromo-*p*-methoxyacetophenone as white solid, mp. 73-74°. IR (KBr): 1680 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): δ 3.95 (3H, s, OCH_3), 6.65 (1H, S, $CHBr_2$), 7.0 (2H, m, ArH), 8.2 (2H, m, ArH).

Anal. Calcd. for $C_9H_8Br_2O_2$: C, 35.06; H, 2.59; Br, 51.92. Found: C, 35.25, H, 2.67; Br, 52.03

α-Bromopropiophenone.- Thionyl bromide (10 mL) was added to a solution of propiophenone (13.4 g, 0.1 mol) in benzene (250 ml) and the mixture was refluxed for 1 hr. Workup in the usual manner left 15 g (70%) of an oil, bp. 135-137°/20 mm, lit.[6] bp. 136-137°/18 mm. IR (film): 1685 cm^{-1} (C=O); ^1H NMR ($CDCl_3$): δ 1.9 (3H, d, H_{AB}, 7 Hz, CH_3), 5.2 (lH, q, J_{BA}, 7Hz., CHBr), 7.4 (3H, m, ArH), 8.0 (2H, m, ArH).

α-Bromo-α-methylpropiophenone.- In a similar reaction, isobutyrophenone gave 17.3 g (76%) of α-bromo-α-methylpropiophenone as yellow liquid, bp. 146-148°/20 mm, lit.[7] bp. 146-148°/30 mm. ^1H NMR ($CDCl_3$): δ 2.0 (6H, s, CH_3), 7.4 (3H, m, Ar-H), 8.2 (2H, m, ArH).

Anal. Calcd. for $C_{10}H_{11}BrO$: C, 52.86; H, 3.93; Br, 34.90. Found: C, 52.92; H, 3.67; Br, 35.21

Benzalacetone Dibromide.- Thionyl bromide (10 mL) was added to benzalacetone (14.6 g, 0.1 mol) in benzene (250 mL) and the mixture was refluxed for 1 hr. Workup in the usual manner gave 22 g (92%) of benzalacetone dibromide as white needles, mp. 124-125°, lit.[3] mp. 124-125°. ^1H NMR ($CDCl_3$): δ 2.5 (3H, s, CH_3); 4.95 (lH, d, CBrCH, J_{AB}, 4 Hz) 5.33 (lH, d, CHCHBr, J_{AB} 4 Hz), 7.4 (5H, s, ArH).

Anal. Calcd. for $C_{10}H_{10}Br_2O$: C, 39.21; H, 3.26; Br, 52.28. Found: C, 39.03; H, 3.29; Br, 52.61

Benzalacetophenone Dibromide.- In a similar reaction, benzalacetophenone (10.4 g, 0.05 mol) gave 15 g (81%) of benzalacetophenone dibromide as yellow needles, mp. 156-157°, lit.[3] mp. 157-

158°. ^{1}H NMR ($CDCl_3$): δ 5.65 (lH, d, CBrCH, J_{AB} = 4 Hz) 5.85 (lH, d, CHCBr, J_{BA} = 4 Hz), 7.5 (8H, m, ArH), 8.1 (2H, m, ArH).

Anal. Calcd. for $C_{15}H_{12}Br_2O$: C, 48.93; H, 3.20; Br, 43.47. Found: C, 48.96; H, 3.46; Br, 43.32

2'-Hydroxychalcone Tribromide.- Thionyl bromide (7 mL) was added to a solution of 2'-hydroxychalcone (11.2 g, 0.05 mol) in benzene (200 mL), and the mixture was refluxed for 1 hr. Workup in the usual manner gave 19 g (83%) of 2'-hydroxychalcone tribromide, mp. 160-161°. ^{1}H NMR ($CDCl_3$): δ 5.3 (1H, s, CBr_2CHBr), 7.0-8.2 (10H, m, ArH, PhOH).

Anal. Calcd. for $C_{15}H_{11}Br_3O_2$: C, 38.87; H, 2.37; Br, 51.83. Found: 38.56; H, 2.23; Br, 52.01

Anthrone Dibromide.- Thionyl bromide (8 mL) was added to anthrone (9.7g, 0.05 mol) in benzene (150 mL). Workup in the usual manner gave anthrone dibromide as light yellow crystals, mp. 157-158°, lit.[8] mp. 157°. Recrystallization from alcohol hydrolyzed the product to yield 5.6 g (54%) anthraquinone, mp. 285° (dec.), lit.[9] mp. 285°. ^{1}H NMR ($CDCl_3$): δ 7.7 (4H, m, ArH) 8.3 (4H, m, ArH).

Anal. Calcd. for $C_{14}H_8O_2$: C, 80.75; H, 3.84. Found: C, 80.91; H, 3.65

α,α-Dibromodesoxybenzoin.- In a similar reaction, desoxybenzoin (9.8 g, 0.005 mol) reacted with thionyl bromide to produce 15 g (85%) of α,α-bromodesoxybenzoin, mp. 112-113°, lit.[2] mp. 112-113°. ^{1}H NMR ($CDCl_3$): δ 7.65 (2H, dd, J 2 Hz and 8.5 Hz ArH), 7.60 (2H, m, ArH), 7.45-7.13 (6H, m, remaining ArH).

Anal. Calcd. for $C_{14}H_{10}Br_2O$: C, 47.45; H, 2.82; Br, 45.16. Found: C, 47.30; H, 2.82; Br, 45.10

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