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Synthesis of Dibromoacetyl Derivatives by Use of Benzyltrimethylammonium Tribromide

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Synopsis. The reaction of acetyl derivatives with double the molar quantity of benzyltrimethylammoniun tribromide in dichloromethane-methanol solution at room temperature gave dibromoacetyl derivatives in fairly good yields.

Organic ammonium tribromides are considered to be mild and selective brominating agents.[1] These reagents have a merit in that they can be quantitatively treated, compared with liquid bromine, because of their solid character. Previous work in this series[2] has shown that monobromoacetyl derivertives are readily obtained from reactions of acetyl derivatives with tetrabutylammonium tribromide (TBA Br_3) under mild conditions. In the present paper, we wish to report the syntheses of dibromoacetyl derivatives (**1**) by the use of a new reagent, benzyltrimethylammonium tribromide (BTMA Br_3).

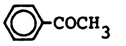
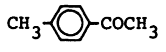
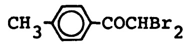
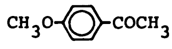
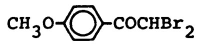
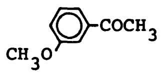
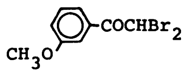
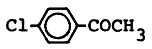
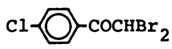
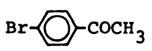
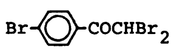
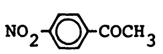
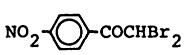
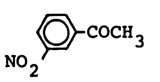
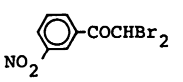
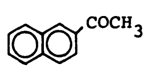
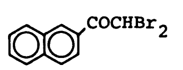
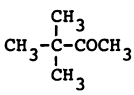
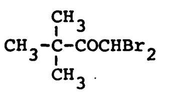
Results and Discussion

The reaction of benzyltrimethylammonium chloride with bromine in dichloromethane gave BTMA Br_3. BTMA Br_3 was also prepared by the addition of hydrobromic acid to an aqueous solution of benzyltrimethylammonium chloride and sodium bromate in good yield.

The reaction of acetyl derivatives (**2**) with double the molar quantity of BTMA Br_3 in a dichloromethane-methanol solution for 2—7 h at room temperature gave **1** readily. The results are summarized in the Table 1.

$$\underset{\mathbf{2}}{RCOCH_3} \xrightarrow[\text{in } CH_2Cl_2\text{-}CH_3OH \text{ rt}]{2PhCH_2(CH_3)_3N^+Br_3^-} \underset{\mathbf{1}}{RCOCHBr_2}$$

Table 1. Dibromoacetyl Derivatives (1) from Acetyl Derivatives (2)

	Starting material (2)	Product (1)	Reaction time/h	Yield[a] %	IR(KBr) ν(CO) cm^{-1}	Mp θ_m/°C	
						Found	Reported
a			2	86	1695	33.5—34.5	36[3]
b			2	88	1690	99—99	100[4]
c			2	87	1680	93—94	93—94[5]
d			2	89	1690	67—68	—
e			7	89	1695	92.5—93.5	92.5[6]
f			7	82	1700	92—93	92—93[7]
g			7	83	1700	63—65	67.4[8]
h			7	88	1710	56—57	59[9]
i			4	89	1695	100—101	101[10]
j	 $CH_3\text{-}C(CH_3)_2\text{-}COCH_3$	 $CH_3\text{-}C(CH_3)_2\text{-}COCHBr_2$	7	75	1725	73.5—74	74.5[11]

a) Yield of isolated product.

When an equimolecular amount of BTMA Br_3 was used with **2**, monobromoacetyl derivatives **3** were obtained in the same manner as when using TBA Br_3.[2] However, the reaction of **2**, with double the molar quantity of TBA Br_3 gave **1** as a byproduct, together with the main product **3**[12] Therefore, it turned out that the brominating effect of BTMA Br_3 is stronger than that of TBA Br_3. Nevertheless, BTAM Br_3 could not further brominate **1** to tribromoacetyl derivatives at room temperature.

Because the presence of methanol markedly facilitated the bromination of **2**, it can be presumed that active species which generate Br^+ is probably methyl hypobromite produced from the reaction of BTMA Br_3 with methanol. In fact, we confirmed the evolution of hydrogen bromide by the addition of methanol to BTMA Br_3 at room temperature.

$$\mathrm{PhCH_2(CH_3)_3N^+Br_3^- + CH_3OH}$$

$$\longrightarrow \mathrm{PhCH_2(CH_3)_3N^+Br^- + CH_3OBr + HBr}$$

$$\mathbf{2} + \mathrm{2CH_3OBr} \longrightarrow \mathbf{1} + \mathrm{2CH_3OH}$$

In general, derivatives **1** such as phenacylidene dibromide (a material for mandelic acid), were prepared from acyl derivatives and bromine.[3] By our method, **1** was easily obtained under mild conditions.

Experimental

Benzyltrimethylammonium Tribromide (BTMA Br_3). To a solution of benzyltrimethylammonium chloride (11.1 g, 60 mmol) and sodium bromate (4.5 g, 30 mmol) in water (100 ml) was added hydrobromic acid (47% , 180 mmol) under stirring at room temperature. A precipitated solid was extracted with dichlormethane (50 ml × 4). The organic layer was dried with magnesium sulfate and evaporated in vacuo to leave a residue which was recrystallized from dichloromethane-ether (10 : 1) to give BTMA Br_3 as orange crystals; yield 18.2 g (78%); mp 100—101 °C. Found: C, 30.69; H, 4.11; N, 3.76; Br, 61.44%. Calcd for $C_{10}H_{16}NBr_3$: C, 30.80; H, 4.14; N, 3.59; Br, 61.47%.

Phenacylidene Dibromide (1a): Typical procedure. To a solution of acetophenone (**2a**) (0.5 g, 4.16 mmol) in dichloromethane (50 ml)-methanol (20 ml) was added BTMA Br_3 (3.4 g, 8.74 mmol) at room temperature. The mixture was stirred for 2 hr until a decoloration of the orange solution took place. The solvent was distilled; the obtained precipitate was extracted with ether (40 ml × 4). The ether layer was then dried with magnesium sulfate and evaporated in vacuo to give a residue which was recrystallized from methanol-water (1 : 2) affording **1a** as colorless crystals; yield 1.0 g (86%); mp 33.5—34.5 °C (lit,[3] mp 36 °C).

2.2-Dibromo-3′-methoxyacetophenone (1d). Compound **1d** was obtained as colorless needles; mp 67—68 °C. ^{1}H NMR ($CDCl_3$) δ=3.82 (3H, s, OCH_3), 6.70 (1H, s, $CHBr_2$), and 6.9—7.75 (4H, m, H_{arom}). Found: C, 35.00; H, 2.78; Br, 51.80%. Calcd for $C_9H_8O_2Br_2$: C, 35.10; H, 2.62; Br, 51.89%.

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12) For example, the reaction of 4-methylacetophenone (**2b**) with double the molar quantity of TBA Br_3 in dichloromethane-methanol at room temperature gave a mixture of 2,2-dibromo-4′-methylacetophenone (**1b**) and 2-bromo-4′-methylacetophenone (**3b**) in the ratio of 1:2.5 on NMR spectra. The same treatment of 4-methoxyacetophenone (**2c**) afforded 2,2-dibromo-4′-methoxyacetophenone (**1c**) and 2-bromo-4′-methoxyacetophenone (**3c**) in the ratio of 1:2.