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Products of the Reactions of 1-Aroyl-2,2-dimethylhydrazines with Propargyl and Allyl Bromides

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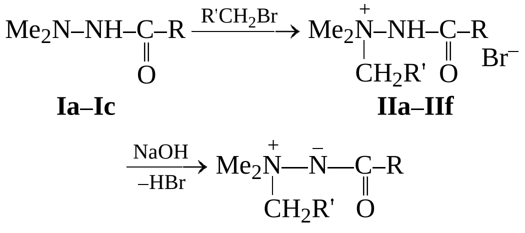
Abstract—1-Aroyl-2,2-dimethylhydrazines react with propargyl and allyl bromides to form, respectively, 1,1-dimethyl-1-(2-propyn-1-yl)- and 1,1-dimethyl-1-(2-propen-1-yl)-2-aroylhydrazinium bromides. Treatment of these compounds with an NaOH solution yielded, respectively, *N*-[dimethyl(2-propyn-1-yl)ammonio]- and *N*-[dimethyl(2-propen-1-yl)ammonio]aroylimides.

Among diverse transformations of 1,1-dimethylhydrazine and its derivatives, quaternization with alkenyl and alkynyl halides is still poorly studied. The reaction of 1,1-dimethylhydrazine with propargyl bromide in diethyl ether gave 1,1-dimethyl-1-(2-propyn-1-yl)hydrazinium bromide in 59% yield [1]. The reactions of 1,1-dimethylhydrazine with allyl and propargyl chlorides in MeCN gave, respectively, 1,1-dimethyl-1-allylhydrazinium chloride (yield 90%) and 1,1-dimethyl-1-(2-propyn-1-yl)hydrazinium chloride (yield 55%) [2]. 1-Aroyl-2-bromoacetylenes react with 1,1-dimethylhydrazine in MeCN at 20°C to form 1-(1-bromo-2-aroylvinyl)-1,1-dimethylhydrazinium bromides [3]. The reactions of 1,1-dimethylhydrazones with propargyl bromide and 1,3-dibromopropyne in diethyl ether, MeCN, or benzene at 20°C gave the bromides of the corresponding 1,1-dimethyl-1-(2-propyn-1-yl)hydrazones and 1,1-dimethyl-1-(3-bromo-2-propyn-1-yl)hydrazones [4] in 30–72% yields [4].

With the aim to further study alkylation of 1,1-dimethylhydrazine derivatives, we examined the reaction of 1-benzoyl-2,2-dimethylhydrazine **Ia**, 1-(4-bromobenzoyl)-2,2-dimethylhydrazine **Ib**, and 1-(2-chlorobenzoyl)-2,2-dimethylhydrazine **Ic** with propargyl and allyl bromides.

The starting compounds **Ia**–**Ic** were prepared by the reactions of the corresponding acid chlorides with 1,1-dimethylhydrazine in absolute diethyl ether, benzene, and THF at 20°C or with weak heating (35–40°C), following the procedure described in [5].

We found that hydrazines **Ia**–**Ic** react with propargyl bromide in absolute methanol on heating (50°C) to form 1-aroyl-2,2-dimethyl-2-(2-propyn-1-yl)hydrazinium bromides **IIa**–**IIc** in 30–59% yield, i.e., alkylation occurs at the tertiary nitrogen atom.



Ia–**Ic** **IIa**–**IIf** **IIIa**–**IIIf**

$$\mathrm{Me_2N{-}NH{-}\underset{\displaystyle \overset{\|}{O}}{C}{-}R} \xrightarrow{\mathrm{R'CH_2Br}} \mathrm{Me_2\underset{\displaystyle CH_2R'}{\overset{+}{N}}{-}NH{-}\underset{\displaystyle \overset{\|}{O}}{C}{-}R}\ \mathrm{Br^-}$$

$$\xrightarrow[\mathrm{-HBr}]{\mathrm{NaOH}} \mathrm{Me_2\underset{\displaystyle CH_2R'}{\overset{+}{N}}{-}\overset{-}{N}{-}\underset{\displaystyle \overset{\|}{O}}{C}{-}R}$$

R = Ph, R' = HC≡C (**a**); R = 4-BrC_6H_4, R' = HC≡C (**b**); R = 2-ClC_6H_4, R' = HC≡C (**c**); R = Ph, R' = CH_2=CH (**d**); R = 4-BrC_6H_4, R' = CH_2=CH (**e**); R = 2-ClC_6H_4, R' = CH_2=CH (**f**).

We have studied the reaction of 1-aroyl-2,2-dimethylhydrazines **Ia**–**Ic** with allyl bromide in MeCN at 20°C. As in the reaction with propargyl bromide, alkylation occurred at the tertiary nitrogen atom and yielded 1-aroyl-2,2-dimethyl-2-(2-propen-1-yl)hydrazinium bromides **IId**–**IIf**.

Treatment of **IIa**–**IIe** with 6 N NaOH at 20°C resulted in elimination of HBr and formation of *N*-[dimethyl(2-propyn-1-yl)ammonio]aroylimides **IIIa**–**IIIc** and *N*-[dimethyl(2-propen-1-yl)ammonio]aroylimides **IIId**–**IIIf**; their compositions and structures were confirmed by elemental analysis and by ^{1}H and ^{15}N NMR and IR spectroscopy.

EXPERIMENTAL

The IR spectra were taken on a Specord IR-75 spectrometer in KBr. The ^{1}H, ^{13}C, and ^{15}N NMR spectra were recorded at 20°C on a Bruker DPX-400

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spectrometer (400.13, 100.62, and 40.54 MHz, respectively); HMDS was used as internal reference.

All the compounds are colorless crystals or powders.

1-Benzoyl-2,2-dimethylhydrazine Ia was prepared according to [5] from 3 g of 1,1-dimethylhydrazine and 7.1 g of benzoyl chloride in benzene at 20°C. Yield 1.7 g (21%), mp 106–107°C (from CCl_4). IR spectrum, ν, cm^{-1}: 3190 (NH), 1640 (C=O). Found, %: C 65.63; H 7.31; N 16.95. $C_9H_{12}N_2O$. Calculated, %: C 65.83; H 7.37; N 17.06.

1-(4-Bromobenzoyl)-2,2-dimethylhydrazine Ib was prepared from 4.4 g of 4-bromobenzoyl chloride and 2.4 g of 1,1-dimethylhydrazine in THF at 40°C. Yield 3.7 g (77%), mp 148–150°C (from MeCN). IR spectrum, ν, cm^{-1}: 3200 (NH), 1640 (C=O). Found, %: C 44.12; H 4.82; Br 32.74; N 11.23. $C_9H_{11}BrN_2O$. Calculated, %: C 44.47; H 4.56; Br 32.87; N 11.52.

1-(2-Chlorobenzoyl)-2,2-dimethylhydrazine Ic was prepared from 7.2 g of 1,1-dimethylhydrazine and 10 g of 2-chlorobenzoyl chloride in THF at 40°C. Yield 6.9 g (58%), mp 150–152°C (from CCl_4). IR spectrum, ν, cm^{-1}: 3180 (NH), 1640 (C=O). Found, %: C 54.30; H 6.01; Cl 18.20; N 14.52. $C_9H_{11}ClN_2O$. Calculated, %: C 54.42; H 5.58; Cl 17.85; N 14.10.

1-Benzoyl-2,2-dimethyl-2-(2-propyn-1-yl)hydrazinium bromide IIa. A solution of 0.7 g of propargyl bromide in 10 ml of absolute methanol was added slowly with stirring to a solution of 1 g of 1-benzoyl-2,2-dimethylhydrazine **Ia** in 15 ml of absolute methanol. The mixture was stirred at 50°C for 6 h. The solvent was vacuum-evaporated, and the remaining oily residue was dissolved in a small amount of methanol. Bromide **IIa** was precipitated by adding cold diethyl ether. The precipitate was filtered off and vacuum-dried. Yield 1.1 g (59%), mp 125–126°C (from MeCN). IR spectrum, ν, cm^{-1}: 3280 (NH), 2920 (N^+CH_2), 2140 (C≡C), 1680 (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.95 s (6H, $2CH_3$), 4.04 m (1H, ≡CH), 5.37 d (2H, CH_2), 7.29–7.52 m (5H, C_6H_5), 8.13 t (1H, NH). Found, %: C 50.68; H 5.51; Br 28.09; N 9.75. $C_{12}H_{15}BrN_2O$. Calculated, %: C 50.90; H 5.34; Br 28.22; N 9.89.

1-(4-Bromobenzoyl)-2,2-dimethyl-2-(2-propyn-1-yl)hydrazinium bromide IIb was prepared similarly to **IIa** from 5.81 g of **Ib** and 2.38 g of propargyl bromide in absolute methanol at 80°C. Yield 2.1 g (29%), mp 158–160°C (from MeOH). IR spectrum, ν, cm^{-1}: 3190 (NH), 2921 (N^+CH_2), 2130 (C≡C), 1680 (C=O). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.80 s (6H, $2CH_3$), 4.15 m (1H, ≡CH), 5.21 d (2H, CH_2), 7.81–7.86 m (4H, C_6H_4), 7.95 t (1H, NH). Found, %: C 40.10; H 4.21; Br 44.42; N 7.80. $C_{12}H_{14}Br_2N_2O$. Calculated, %: C 39.81; H 3.89; Br 44.14; N 7.74.

1-(2-Chlorobenzoyl)-2,2-dimethyl-2-(2-propyn-1-yl)hydrazinium bromide IIc was prepared similarly to **IIa** from 3 g of **Ic** and 1.8 g of propargyl bromide in absolute methanol at 60°C. Yield 1.42 g (30%), mp 142–144°C (from chloroform). IR spectrum, ν, cm^{-1}: 3275 (NH), 3082 (N^+CH_2), 2130 (C≡C), 1675 (C=O). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.72 s (6H, $2CH_3$), 4.18 m (1H, ≡CH), 5.12 d (2H, CH_2), 7.48–7.61 m (4H, C_6H_4), 8.12 t (1H, NH). Found, %: C 45.51; H 4.72; Br 25.32; Cl 11.23; N 8.74. $C_{12}H_{14}BrClN_2O$. Calculated, %: C 45.38; H 4.44; Br 25.16; Cl 11.16; N 8.82.

1-Benzoyl-2,2-dimethyl-2-(2-propen-1-yl)hydrazinium bromide IId was prepared similarly from 1.53 g of **Ia** and 1.21 g of allyl bromide. Yield 1.86 g (68%), mp 133–134°C (from MeCN). IR spectrum, ν, cm^{-1}: 3445 (NH), 3020, 2945 (CH_2), 1684 (C=O), 1582 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.91 s (6H, $2CH_3$), 4.97 d (2H, CH_2), 5.74 t (2H, $=CH_2$), 6.02 m (1H, CH), 7.26–8.05 m (5H, C_6H_5), 11.82 t (1H, NH). Found, %: C 50.88; H 5.65; Br 28.32; N 10.12. $C_{12}H_{17}BrN_2O$. Calculated, %: C 50.52; H 5.96; Br 28.07; N 9.82.

1-(4-Bromobenzoyl)-2,2-dimethyl-2-(2-propen-1-yl)hydrazinium bromide IIe was prepared similarly from 2.13 g of **Ib** and 1.6 g of allyl bromide in MeCN at 20°C. Yield 2.42 g (65%), mp 138–140°C (from acetone). IR spectrum, ν, cm^{-1}: 3452 (NH), 3019, 2951 (CH_2), 1695 (C=O), 1590 (C=C), 748 (C–Br). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.91 s (6H, $2CH_3$), 4.97 d (2H, NCH_2), 5.74 t (2H, CH_2), 5.99 m (1H, CH), 7.55–7.90 m (4H, C_6H_4), 7.94 t (1H, NH). Found, %: C 39.31; H 4.28; Br 43.93; N 8.05. $C_{12}H_{16}Br_2N_2O$. Calculated, %: C 39.69; H 4.42; Br 43.89; N 7.69.

1-(2-Chlorobenzoyl)-2,2-dimethyl-2-(2-propen-1-yl)hydrazinium bromide IIf was prepared similarly from 3.3 g of **Ic** and 2.42 g of allyl bromide in MeCN at 20°C. Yield 4.29 g (75%), mp 104–106°C. IR spectrum, ν, cm^{-1}: 3440 (NH), 3080, 2940 (CH_2), 1680 (C=O), 1620 (C=C), 620 (C–Cl). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.64 s (6H, $2CH_3$), 4.68 d (2H, NCH_2), 5.72 t (2H, CH_2), 6.07 m (1H, CH), 7.47–7.60 m (4H, C_6H_4), 12.24 t (1H, NH). Found, %: C 45.20; H 5.24; Br 25.31; Cl 11.32; N 8.86. $C_{12}H_{16}BrClN_2O$. Calculated, %: C 45.09; H 5.04; Br 25.00; Cl 11.09; N 8.76.

***N*-[Dimethyl(2-propyn-1-yl)ammonio]benzoylimide IIIa.** To 0.57 g of **IIa** we added 2.5 ml of 6 N NaOH and stirred at 20°C for 2 h. The light yellow oily precipitate was extracted with chloroform, and the extract was dried over $MgSO_4$. The solvent was evaporated to dryness in a vacuum, and the white solid residue was ground in a mortar. Yield 0.21 g (51%), mp 94–95°C. IR spectrum, ν, cm^{-1}: 2980 (N^+CH_2), 2120 (C≡C). 1620 (C=O), no NH absorption band. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.32 s (6H, $2CH_3$), 3.68 t (1H, ≡CH), 4.74 d (2H, CH_2), 7.24–7.87 m (5H, C_6H_5). Found, %: C 70.71; H 7.04; N 13.44. $C_{12}H_{14}N_2O$. Calculated, %: C 71.29; H 6.93; N 13.86.

***N*-[Dimethyl(2-propyn-1-yl)ammonio](4-bromobenzoyl)imide IIIb** was prepared similarly to **IIIa** from 0.4 g of **IIb**. Yield 0.24 g (77%), mp 104–106°C. IR spectrum, ν, cm^{-1}: 3120 (N^+CH_2), 2110 (C≡C), 1580 (C=O), 760 (C–Br), no NH absorption band. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.67 t (1H, ≡CH), 3.52 s (6H, $2CH_3$), 4.71 d (2H, CH_2), 7.25–8.01 m (4H, C_6H_4). ^{15}N NMR spectrum (DMSO-d_6), δ_N, ppm: 93.8 (Me_2N^+), 247.0 (N^-–CO). Found, %: C 51.45; H 5.04; Br 27.99; N 9.59. $C_{12}H_{13}BrN_2O$. Calculated, %: C 51.27; H 4.66; Br 28.42; N 9.96.

***N*-[Dimethyl(2-propyn-1-yl)ammonio](2-chlorobenzoyl)imide IIIc** was prepared similarly from 1.13 g of **IIc**. Yield 0.22 g (24%), mp 118–120°C. IR spectrum, ν, cm^{-1}: 2980 (N^+CH_2), 2110 (C≡C), 1580 (C=O), 650 (C–Cl), no NH absorption band. ^1H NMR spectrum (acetone-d_6), δ, ppm: 3.28 t (1H, ≡CH), 3.48 s (6H, $2CH_3$), 4.80 d (2H, CH_2), 7.17–7.38 m (4H, C_6H_4). ^{15}N NMR spectrum (DMSO-d_6), δ_N, ppm: 94.5 (Me_2N^+), 248.5 (N^-–CO). Found, %: C 60.46; H 5.86; Cl 14.97; N 11.62. $C_{12}H_{13}ClN_2O$. Calculated, %: C 60.89; H 5.53; Cl 14.98; N 11.84.

***N*-[Dimethyl(2-propen-1-yl)ammonio]benzoylimide IIId** was prepared similarly from 2.85 g of **IId**. Yield 0.75 g (37%), mp 84–85°C. IR spectrum, ν, cm^{-1}: 3040, 2980 (CH_2), 1640 (C=O), 1590 (C=C), no NH absorption band. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.33 s (6H, $2CH_3$), 4.35 d (2H, N^+CH_2), 5.43 m (2H, $=CH_2$), 6.04 m (1H, CH=), 7.24–7.83 m (5H, C_6H_5). Found, %: C 70.74; H 8.66; N 13.68. $C_{12}H_{16}N_2O$. Calculated, %: C 70.59; H 7.84; N 13.72.

***N*-[Dimethyl(2-propen-1-yl)ammonio](4-bromobenzoyl)imide IIIe** was prepared similarly from 2.17 g of **IIe**. Yield 0.28 g (17%), mp 43–45°C. IR spectrum, ν, cm^{-1}: 3040, 2960 (CH_2), 1590 (C=O), 1550 (C=C), 760 (C–Br), no NH absorption band. ^1H NMR spectrum (acetone-d_6), δ, ppm: 3.36 s (6H, $2CH_3$), 4.41 d (2H, N^+CH_2), 5.45 m (2H, $=CH_2$), 6.11 m (1H, CH=), 7.39–7.89 m (4H, C_6H_4). ^{15}N NMR spectrum (DMSO-d_6), δ_N, ppm: 94.1 (Me_2N^+), 244.6 (N^-–CO). Found, %: C 50.54; H 5.62; Br 28.32; N 9.68. $C_{12}H_{15}BrN_2O$. Calculated, %: C 50.90; H 5.33; Br 28.22; N 9.89.

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