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SHORT COMMUNICATIONS

Reactions of *N*,*N*-Dimethylformamide with Functionalized Di- and Trichlorocyclopentenones*

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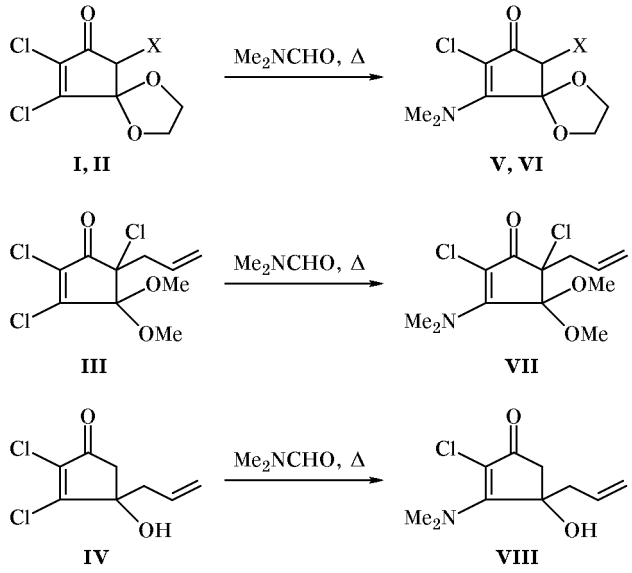
We have found that 2,3-dichloro-4,4-ethylenedioxy-2-cyclopentenone (**I**) [1], its 5-chloro derivative **II** [2], 5-allyl-2,3,5-trichloro-4,4-dimethoxy-2-cyclopentenone (**III**) [3], and 4-allyl-2,3-dichloro-4-hydroxy-2-cyclopentenone (**IV**) [4] react with DMF on heating under reflux to give in high yield products of replacement of the vinylic 3-chlorine atom by dimethylamino group (Scheme 1).

Scheme 1.



I, **V**, X = H; **II**, **VI**, X = Cl.

While interpreting the results of the above reactions and discussing their possible mechanisms, we must take into account published data on the related reactions such as dealkylation of tertiary amines R_3N by the action of R′OCOCl (CH_2=CHOCOCl, PhOCOCl, Cl_3CCH_2OCOCl) which involve intermediate formation of carbamates R_2NCO_2R' [5, 6] and substitution of the halogen atom in *p*-nitrohalobenzenes by dimethylamino group of DMF [7]. In our case, chlorocyclopentenones **I**–**IV** and DMF can be regarded as equivalents of chloroformate and tertiary amines, so that a transformation course analogous to *N*-dealkylation may be assumed. Thus the reaction of chlorocyclopentenones with DMF involves rupture of the weakest amide bond and yields aminomethylation products **V**–**VIII** and chloroformate.

Reaction of chlorocyclopentenones I–IV with DMF (*general procedure***).** A solution of 1 mmol of cyclopentenone **I**–**IV** in 3 ml of DMF was refluxed under argon until the initial compound disappeared (3–4 h; TLC data). The mixture was cooled, diluted with 50 ml of ethyl acetate, washed with a saturated aqueous solution of NaCl, dried over $MgSO_4$, and evaporated, and the residue was purified by column chromatography on silica gel using hexane–ethyl acetate (1 : 2) as eluent.

2-Chloro-3-dimethylamino-4,4-ethylenedioxy-2-cyclopentenone (V). Yield 50%, mp 92–94°C. IR spectrum, ν, cm^{-1}: 1705, 1600. ^1H NMR spectrum, δ, ppm: 2.47 s (2H, 5-H), 3.20 s (6H, $2CH_3$), 3.95–4.20 m (4H, $2CH_2O$). ^{13}C NMR spectrum, δ_C, ppm: 41.52 ($2CH_3$), 45.76 (C^5), 64.02 ($2CH_2O$), 104.78 (C^3), 109.12 (C^4), 159.65 (C^2), 189.55 (C=O). Found, %: C 49.3; H 5.55; Cl 16.43; N 6.29. $C_9H_{11}ClNO_3$. Calculated, %: C 49.67; H 5.56; Cl 16.29; N 6.44.

2,5-Dichloro-3-dimethylamino-4,4-ethylenedioxy-2-cyclopentenone (VI). Yield 70%, mp 149–151°C. IR spectrum, ν, cm^{-1}: 1705, 1610, 1600.

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^{1}H NMR spectrum, δ, ppm: 3.31 s (6H, $2CH_3$), 4.15–4.45 m (5H, 5-H, $2CH_2O$). ^{13}C NMR spectrum, δ_C, ppm: 42.04 ($2CH_3$), 62.89 (C^5), 65.11 (CH_2O), 65.66 (CH_2O), 104.46 (C^3), 108.73 (C^4), 158.29 (C^2), 184.08 (C=O). Found, %: C 42.61; H 4.20; Cl 28.23; N 5.48. $C_9H_{11}Cl_2NO_3$. Calculated, %: C 42.88; H 4.40; Cl 28.13; N 5.56.

5-Allyl-2,5-dichloro-3-dimethylamino-4,4-dimethoxy-2-cyclopentenone (VII). Yield 75%, mp 72–73°C. IR spectrum, ν, cm^{-1}: 1740, 1695, 1620. ^{1}H NMR spectrum, δ, ppm: 2.58 d (2H, CH_2, J = 7.0 Hz), 3.13 s (3H, OMe), 3.28 s (6H, Me_2H), 3.50 s (3H, OMe), 4.67–5.01 m (2H, CH_2=), 5.30–6.01 m (1H, CH=). ^{13}C NMR spectrum, δ_C, ppm: 42.35 (CH_3N), 45.13 (CH_2), 51.55 (OCH_3), 52.38 (OCH_3), 75.15 (C^5), 102.55 (C^4), 106.84 (C^2), 117.23 (CH_2=), 133.35 (CH=), 159.62 (C^3), 187.84 (C=O). Found, %: C 49.16; H 5.76; Cl 24.10; N 4.73. $C_{12}H_{17}Cl_2NO_3$. Calculated, %: C 48.99; H 5.82; Cl 24.10; N 4.76.

4-Allyl-2-chloro-3-dimethylamino-4-hydroxy-2-cyclopentenone (VIII). Yield 53%, mp 110–112°C. IR spectrum, ν, cm^{-1}: 3300, 1670, 1630, 1590. ^{1}H NMR spectrum, δ, ppm: 2.45 d (1H, 5-H, J = 17.5 Hz), 2.64 d (1H, 5-H, J = 17.5 Hz), 3.40 s (6H, $2CH_3$), 5.05–5.20 m (2H, CH_2=), 5.55–5.7 m (1H, CH=). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 42.35 (CH_3N), 43.65 (CH_2), 47.96 (C^5), 77.05 (C^4), 102.05 (C^2), 119.69 (CH_2=), 131.57 (CH=), 169.69 (C^3), 192.52 (C=O). Found, %: C 55.57; H 6.49; Cl 16.19; N 6.31. $C_{10}H_{14}ClNO_2$. Calculated, %: C 55.69; H 6.54; Cl 16.44; N 6.49.

The IR spectra were taken on a UR-20 instrument from samples prepared as thin films or mulls in Nujol. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AM-300 spectrometer (300 and 75.47 MHz, respectively) in $CDCl_3$ using tetramethylsilane as internal reference.

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