Reactions of $(Me_2N)_3P$ with functionalized di- and trichlorocyclopentenones

*R. R. Akhmetvaleev, T. A. Belogaeva, G. M. Karimova, and M. S. Miftakhov**

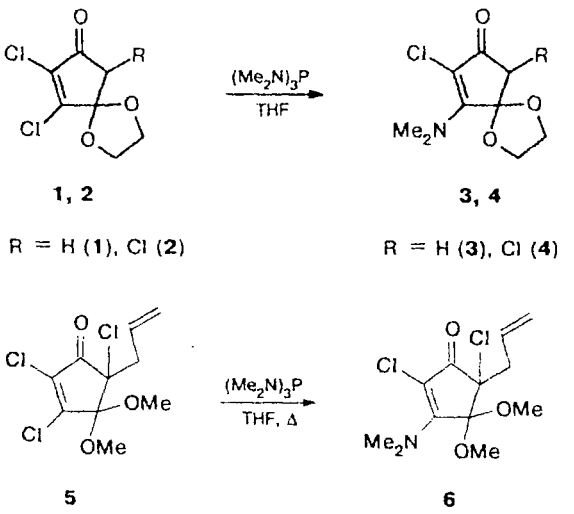
Institute of Organic Chemistry, Ufa Research Center of the Russian Academy of Sciences, 71 prosp. Octyabrya, 450054 Ufa, Russian Federation. Fax: +7 (347 2) 35 6066

2,3-Dichloro-4,4-ethylenedioxycyclopent-2-enone, its 5-chloroderivative, and 5-allyl-2,3,5-trichloro-4,4-dimethoxycyclopent-2-enone react with $(Me_2N)_3P$ to give the corresponding products of substitution of the NMe_2 group for the vinylic Cl atom at C(3).

Key words: 3-chlorocyclopent-2-enones, hexamethylphosphorous triamide, 3-dimethylaminocyclopent-2-enones.

The reaction of equimolar amounts of dichlorocyclopentenedione monoketal (**1**)[1] and $P(NMe_2)_3$ in boiling THF (Scheme 1) gives compound **3** in 80% yield. Under the same conditions, trichlorocyclopentenedione monoketal (**5**)[2] yields 3-dimethylamino derivative (**6**). Similar reaction of trichlorocyclopentenedione monoketal (**2**)[3] proceeds under milder conditions (THF, 20 °C) to give 2,5-dichloro-3-dimethylaminocyclopent-2-ene-1,4-dione 4-ethylene ketal (**4**) (85%). To the best of our knowledge, such a transformation is unprecedented.

Scheme 1



Experimental

IR spectra were recorded on a UR-20 spectrometer (thin film or suspension in Nujol). NMR spectra were recorded on a Bruker AM-300 spectrometer (^1H, 300 MHz and ^{13}C, 75.47 MHz) in $CDCl_3$ with $SiMe_4$ as the internal standard.

Reaction of di- and trichlorocyclopentenedione ketals 1, 2, and 5 with $P(Me_2N)_3$ (general procedure). A solution of the corresponding chloride (5 mmol) and $P(Me_2N)_3$ (5 mmol) in 10 mL of THF was refluxed (in the case of compound **2**, the solution was stirred at 20 °C) in an atmosphere of argon until the initial compounds disappeared (3—4 h, monitoring by TLC). The reaction mixture was cooled, diluted with 50 mL of ethyl acetate, washed with a saturated aqueous solution of NaCl, dried with $MgSO_4$, and concentrated. The residue was purified by column chromatography on SiO_2 (hexane—ethyl acetate, 1 : 2, as the eluent).

2-Chloro-3-dimethylamino-4,4-ethylenedioxycyclopent-2-enone (3). Yield 80%, m.p. 92—94 °C. IR, ν/cm^{-1}: 1705, 1600. ^1H NMR, δ: 2.47 (s, 2 H, C(5)H_2); 3.20 (s, 6 H, 2 Me); 3.95—4.20 (m, 4 H, 2 CH_2O). ^{13}C NMR, δ: 41.52 (2 Me); 45.76 (C(5)); 64.02 (2 CH_2O); 104.78 (C(3)); 109.12 (C(4)); 159.65 (C(2)); 189.55 (C=O). Found (%): C, 43.3; H, 4.05; Cl, 28.43; N, 5.19. $C_9H_{12}ClNO_3$. Calculated (%): C, 43.05; H, 4.01; Cl, 28.24; N, 5.58.

2,5-Dichloro-3-dimethylamino-4,4-ethylenedioxycyclopent-2-enone (4). Yield 85%, m.p. 149—151 °C. IR, ν/cm^{-1}: 1600, 1610, 1705. ^1H NMR, δ: 3.31 (s, 6 H, 2 Me); 4.15—4.45 (m, 5 H, C(5)H, 2 CH_2O). ^{13}C NMR, δ: 42.04 (2 Me); 62.89 (C(5)H); 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, 49.61; H, 5.10; Cl, 16.23; N, 6.18. $C_9H_{11}Cl_2NO_3$. Calculated (%): C, 49.90; H, 5.12; Cl, 16.36; N, 6.47.

5-Allyl-2,5-dichloro-3-dimethylamino-4,4-dimethoxycyclopent-2-enone (6). Yield 90%, m.p. 72—73 °C. IR, ν/cm^{-1}: 1740, 1695, 1620. ^1H NMR, δ: 2.58 (d, 2 H, CH_2, J = 7.0 Hz); 3.13 (s, 3 H, OMe); 3.50 (s, 3 H, OMe); 3.28 (s, 6 H, Me_2N); 4.67—5.01 (m, 2 H, CH_2=); 5.30—6.01 (m, 1 H, —CH=). ^{13}C NMR, δ: 187.84 (C=O); 159.62 (C(3)); 133.35 (—CH=); 117.23 (CH_2=); 106.84 (C(2)); 102.55 (C(4)); 75.15 (C(5)); 52.38 (OMe); 51.55 (OMe); 45.13 (CH_2); 42.35 (Me_2N). Found (%): C, 49.16; H, 5.76; Cl, 24.10; N, 4.73. $C_{12}H_{17}Cl_2NO_3$. Calculated (%): C, 48.98; H, 5.82; Cl, 24.10; N, 4.76.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 12, pp. 2555—2556, December, 1998.

1066-5285/98/4712-2473 $20.00

This work was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-33247a).

References

1. R. R. Akhmetvaleev, L. R. Imaeva, T. A. Belogaeva, and M. S. Miftakhov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1699 [*Russ. Chem. Bull.*, 1997, **46**, 1622 (Engl. Transl.)].
2. S. A. Ismailov, *Zh. Org. Khim.*, 1989, **25**, 2238 [*J. Org. Chem. USSR*, 1989, **25** (Engl. Transl.)].
3. O. M. Kuznetsov, R. R. Akhmetvaleev, N. S. Vostrikov, and M. S. Miftakhov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 1027 [*Russ. Chem. Bull.*, 1996, **45**, 982 (Engl. Transl.)].

Received April 24, 1998;
in revised form June 26, 1998