ISSN 1070-3632, Russian Journal of General Chemistry, 2006, Vol. 76, No. 7, pp. 1176–1177. © Pleiades Publishing, Inc., 2006.
Original Russian Text © M.B. Gazizov, R.K. Ismagilov, L.P. Shamsutdinova, R.F. Karimova, O.G. Sinyashin, 2006, published in Zhurnal Obshchei Khimii, 2006, Vol. 76, No. 7, pp. 1224–1225.

LETTERS
TO THE EDITOR

Reactions of 4-Hydroxy-3,5-di-*tert*-butylbenzylidene Chloride with Aminals

M. B. Gazizov[a], R. K. Ismagilov[a], L. P. Shamsutdinova[a], R. F. Karimova[a], and O. G. Sinyashin[b]

[a] *Kazan State Technological University,*
ul. K. Marksa 68, Kazan, Tatarstan, 420015 Russia
e-mail: mukattisg@mail.ru

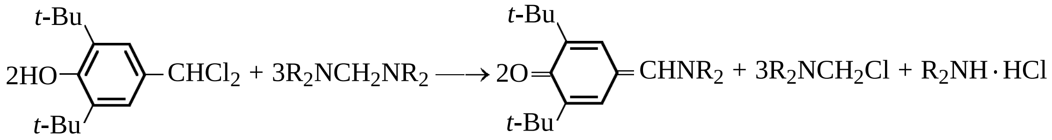
[b] *Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center,*
Russian Academy of Sciences, Kazan, Tatarstan, Russia

Received December 30, 2005

DOI: 10.1134/S1070363206070322

It is known that the C–N bond in aminals is cleaved under the action of carboxylic and inorganic acid halides [1, 2].

We found that this bond is also cleaved with 4-hydroxy-3,5-di-*tert*-butylbenzylidene chloride **I**. Reactions of **I** with aminals **II** occur with a heat release upon mixing the reactants (neat or in solvents such as ether or hexane). Irrespective of the structure of the aminal and reactant ratio, *gem*-dichloride **I** undergoes dehydrochlorination and dechloroamination with the formation of 4-(dialkylamino- or piperidino)methylene-3,5-di-*tert*-butylcyclohexa-2,5-dienones **III**. The dialkylamine formed in the dehydrochlorination step, as found in additional experiments, further reacts with **I** to form salt **V** [3, 4]. When the reaction of **I** with **IIa** was performed in diethyl ether, a crystalline mass consisting of **IVa** and **Va** was obtained. By its treatment with ethyl diphenylphosphinite, we obtained individual products: (dimethylamino)methyldiphenylphosphine oxide **VI** and dimethylammonium chloride **Va**.



I **II** **III** **IV** **V**

II–**V**, R = Me (**a**), Et (**b**), R + R = $(CH_2)_5$ (**c**).

$$\textbf{IVa} + \textbf{Va} + Ph_2POEt \longrightarrow \underset{\textbf{VI}}{Ph_2P(O)CH_2NMe_2} + EtCl + \textbf{Va}.$$

The structure of 4-(dialkylamino- or piperidino)-methylene-3,5-di-*tert*-butylcyclohexa-2,5-dienones **III** was confirmed by elemental analysis, spectroscopic methods, and independent synthesis from 4-hydroxy-3,5-di-*tert*-butylbenzenecarbaldehyde and the corresponding amines [5].

Reaction of 4-hydroxy-3,5-di-*tert*-butylbenzylidene chloride I with *N*,*N*,*N*',*N*'-tetramethylmethanediamine IIa. *a*. A solution of 2.89 g of *gem*-dichloride **I** in 30 ml of diethyl ether was added dropwise to a solution of 1.53 g of aminal **IIa** in 120 ml of diethyl ether at 5 to 0°C with stirring. In the process, a colorless crystalline compound precipitated. The mixture was allowed to stand for 18 h at 20°C. After filtration and washing the crystalline product with ether, 1.55 g (83%) of a mixture of chloromethyldimethylamine and dimethylammonium chloride was obtained. After removal of volatiles from the filtrate in a vacuum, 1.80 g (69%) of 4-(dimethylamino)methylene-3,5-di-*tert*-butylcyclohexa-2,5-dienone **IIIa** was obtained; mp 169–170°C (ether) (published data [4]: mp 171–173°C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.32 s [18H, $C(CH_3)_3$], 3.32 s (6H, CH_3N), 6.95 d (1H, CH, $^4J_{HH}$ 2 Hz), 7.05 s (1H, CHN), 7.60 d (1H, CH, $^4J_{HH}$ 2 Hz). Found N, %: 5.48, 5.61. $C_{17}H_{27}NO$. Calculated N, %: 5.36.

A 2.30-g portion of ethyl diphenylphosphinite was added to 1.21 g of the isolated mixture of chloromethyldimethylamine and dimethylammonium chloride. The reaction was accompanied by heat release and evolution of ethyl chloride; the mixture became crystalline. After 30 min, the mixture was treated with refluxing toluene (2 × 15 ml). The fraction insoluble in toluene consisted of dimethylammonium chloride {yield 0.24 g (93%); mp 172–175°C (published data [6]: mp 171°C}. On cooling the toluene solution, 1.47 g (57%) of (dimethylamino)methyldiphenylphosphine oxide was isolated; mp 186–188°C (toluene). ^{1}H NMR spectrum (CCl_4 + $CDCl_3$), δ, ppm: 2.40 s (6H, CH_3N), 3.20 d (2H, CH_2P, $^2J_{PH}$ 7.5 Hz), 7.55 m, 7.87 m (10H, C_6H_5). Found, %: N 5.95, 5.95; P 12.15, 12.2. $C_{15}H_{18}NOP$. Calculated, %: N 5.41; P 11.97.

b. A 2.89-g portion of **I** was added to 3.06 g of aminal **IIa**. The mixture warmed up, and restructurization of the crystalline mass occurred. After 3 h, this mass was treated with a refluxing mixture of 40 ml of isooctane and 5 ml of toluene. The solution was decanted from a dark tar. After cooling the solution, 1.99 g (76%) of **IIIa** was isolated; mp 166–167.5°C (hexane).

4-(Diethylamino)methylene-3,5-di-*tert*-butylcyclohexa-2,5-dienone IIIb. *a*. A 1.45-g portion of **I** was added to 2.37 g of aminal **IIb**. Compound **IIIb** was obtained; yield 0.98 g (68%), mp 138–139°C (heptane) (published data [4]: mp 134–135°C). ^{1}H NMR spectrum (CCl_4 + $CDCl_3$), δ, ppm: 1.28 s [18H, $C(CH_3)_3$], 1.35 t (6H, CH_3, $^3J_{HH}$ 7.5 Hz), 3.50 q (4H, CH_2, $^3J_{HH}$ 7.5 Hz), 6.82 d (1H, CH, $^4J_{HH}$ 2 Hz), 6.90 s (1H, CHN), 7.37 d (1H, CH, $^4J_{HH}$ 2 Hz). Found N, %: 5.15, 5.25. $C_{19}H_{31}NO$. Calculated N, %: 4.84.

b. A 3.65-g portion of diethylamine was added to 2.34 g of 4-hydroxy-3,5-di-*tert*-butylbenzenecarbaldehyde. The mixture warmed up, and restructurization of the crystalline mass occurred. After 18 h, the mixture was treated with hexane; 2.35 g (81%) of **IIIb** was obtained, mp 137–139°C (heptane).

4-Piperidinomethylene-3,5-di-*tert*-butylcyclohexa-2,5-dienone IIIc. *a*. A 1.45-g portion of **I** was added to 2.73 g of aminal **IIc**. Compound **IIIc** was obtained; yield 0.95 g (63%), mp 165–166°C (heptane) (published data [4]: mp 169–170°C [4]). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.22 s [18H, $C(CH_3)_3$], 1.70 br.s (6H, CH_2), 3.62 br.s (4H, CH_2N), 6.82 br.s (1H, CH), 6.95 s (1H, CHN), 7.37 br.s (1H, CH). Found N, %: 4.75, 4.90. $C_{20}H_{31}NO$. Calculated N, %: 4.65.

b. A 4.30-g portion of piperidine was added to 2.34 g of 4-hydroxy-3,5-di-*tert*-butylbenzenecarbaldehyde. Compound **IIIc** was obtained; yield 2.80 g (93%), mp 168–169°C (heptane).

The structures of **IIIa**–**IIIc** were confirmed by comparison with authentic samples (identity of the ^{1}H NMR spectra and no depression of the melting point of the mixed samples).

The ^{1}H NMR spectra were recorded on a Tesla BS-567A spectrometer (100 MHz); the proton chemical shifts are given relative to $(CH_3)_4Si$.

ACKNOWLEDGMENTS

The study was financially supported by the Russian Foundation for Basic Research (project no. 03-03-32 547).

REFERENCES

1. *Comprehensive Organic Chemistry. The Synthesis and Reactions of Organic Compounds*, Barton, D. and Ollis, W.D., Eds., Oxford: Pergamon, 1979. Translated under the title *Obshchaya organicheskaya khimiya*, Moscow: Khimiya, 1982, vol. 3, p. 148.
2. Böhme, H. and Hartke, K., *Chem. Ber.*, 1960, vol. 93, no. 6, p. 1305.
3. Popov, L.K., Egidis, F.M., and Ershov, V.V., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1968, no. 4, p. 902.
4. Egidis, F.M., Popov, L.K., Volod'kin, A.A., Ershov, V.V., and Volkotrub, M.N., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1970, no. 11, p. 2580.
5. Volod'kin, A.A., Ershov, V.V., and Ostapets-Sveshnikova, G.D., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1969, no. 3, p. 647.
6. *Spravochnik khimika* (Chemist's Handbook), Nikol'skii, B.P., Ed., Moscow: Khimiya, 1964, vol. 2.