ISSN 0012-5008, Doklady Chemistry, 2012, Vol. 445, Part 2, pp. 150–151. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © E.K. Kurbankulieva, A.N. Kazakova, S.S. Zlotskii, 2012, published in Doklady Akademii Nauk, 2012, Vol. 445, No. 4, pp. 419–420.

CHEMISTRY

Reaction of 2-Bromo-2-phenyl-1,1-dichlorocyclopropane with Phenols and Alcohols

E. K. Kurbankulieva, A. N. Kazakova, and S. S. Zlotskii

Presented by Academician A.A. Berlin December 5, 2011

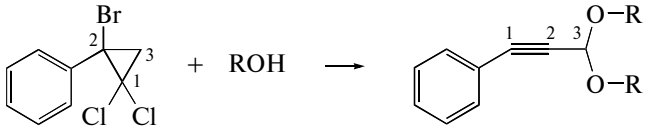
Received March 28, 2012

DOI: 10.1134/S0012500812080022

We showed recently that substituted *gem*-dichlorocyclopropanes in the reactions with monohydric and dihydric phenols convert at the first stage to compounds with exocyclic double bond. The latter, owing to the presence of the reactive chloroallyl moiety, readily react with hydroxy groups to form the corresponding cyclopropanone ketals [1].

It was interesting to study the transformations under these conditions of 2-bromo-2-phenyl-1,1-dichlorocyclopropane (**I**), which readily forms via the reaction of available α-bromostyrene with dichlorocarbene [2].

We have found that compound **I** reacts with phenols **IIa**–**IIc** under phase transfer catalysis conditions to yield acetals of phenylpropargyl aldehyde **IIIa**–**IIIc**.



I **IIa–IIc, IVa, IVb** **IIIa–IIIc, Va, Vb**

R = Ph (**IIa**, **IIIa**); 2-$CH_3C_6H_4$ (**IIb**, **IIIb**); 4-ClC_6H_4 (**IIc**, **IIIc**); *n*-C_4H_9 (**IVa**, **Va**); CH_2=CH–CH_2 (**IVb**, **Vb**).

Endocyclic elimination of HBr is likely to lead to intermediate cyclopropenes in which the chloroallyl fragments react rapidly with phenols **IIa**–**IIc**. The reaction is accompanied by ring opening to form the acetylene bond.

Allyl alcohol (**IVa**) and butyl alcohol (**IVb**) do not react under these conditions with compound **I**. We managed to accomplish this reaction using as a catalyst sodium metal in excess of the initial alcohol. The yields of resultant acetals in the reaction with alcohols are much lower than in the reactions with phenols, while conditions are more severe (table).

A nonselective formation of acetylene structures was noted previously in the condensation of polysubstituted *gem*-dibromocyclopropanes with alkanols [3]. We established for the first time that *gem*-dichlorocyclopropanes containing bromine atom in the ring can participate in similar transformations.

Ufa State Oil Technical University, ul. Kosmonavtov 1, Ufa, 450062 Russia

EXPERIMENTAL

Qualitative and quantitative analysis of the initial compounds and reaction products were performed on an LKhM-8D chromatograph equipped with a catharometer, helium as a carrier gas (column 2000 × 5 mm with 5% SE-30). ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer (operating at 300.13 and 75.47 MHz, respectively) in $CDCl_3$

Reaction of phenols **IIa**–**IIc** and alcohols **IVa** and **IVb** with 2-bromo-2-phenyl-1,1-dichlorocyclopropane **I**

Reactant	Reaction conditions	Reaction product (yield, %)
IIa	A	**IIIa** (78)
IIb		**IIIb** (69)
IIc		**IIIc** (33)
IVa	B	**Va** (11)
IVb		**Vb** (30)

Note: System A: molar ratio NaOH : **IIa**–**IIc** : **I** = 0.02 : 0.007 : 0.003, 3.5 mL of DMF, 20°C, reaction time 4 h (2 h for phenol **IIa**). System B: molar ratio Na : **IVa**, **IVb** : **I** = 0.1 : 0.012 : 0.005, 100°C, reaction time 8 h (12 h for alcohol **IVb**).

using Me_4Si as an internal reference. GC-MS analysis was performed with the use of a Focus instrument with a Finnigan DSQ II mass-spectral detector (EI, 70 eV; ionizing chamber temperature, 200°C; direct inlet temperature, 50–270°C; heating rate, 10 K/min).

Synthesis of compound I. A 50% solution of NaOH (320 g) was added dropwise for 2 h to a vigorously stirred mixture of 0.1 mol of α-bromostyrene and 0.2 g of triethylbenzylammonium chloride as the phase transfer catalyst in 300 mL of chloroform at 40°C. After that, the mixture was stirred for another 1 h at 40°C. Then, the reaction mixture was washed with water, the solvent was evaporated, and the residue was distilled in a vacuum.

2-Bromo-2-phenyl-1,1-dichlorocyclopropane I. Bp 125–127°C (4 mmHg).

^{1}H NMR ($CDCl_3$, δ, ppm, *J*, Hz): 2.06 (d, 1H, C^3H_a, ^2J 9.0), 2.09 (d, 1H, C^3H_b, ^2J 9.0), 7.17–7.39 (m, 4H, Ph).

^{13}C NMR ($CDCl_3$, δ, ppm): 35.4 (CH_2), 43.0 (CBr), 62.9 (CCl_2), 128.7, 128.9, 129.3, 138.9 (Ph).

MS *m/z* (I_{rel}, %): 264/266/268/270 $[M]^{+\cdot}$ (1), 192/194 (5/5), 185/186/188 $[M - Br^{\cdot}]^+$ (10/6/1), 149/151 (100/30), 115 (47), 89 (28), 75 (18), 63 (22).

Synthesis of compounds IIIa–IIIc. A solution of 0.003 mol of 2-bromo-2-phenyl-1,1-dichlorocyclopropane (**I**) in 1 mL of DMF was added dropwise to a vigorously stirred mixture of 0.007 mol of phenol **IIa–IIc**, 0.02 mol of NaOH, and 2.5 mL of DMF. After 2–4 h, the reaction mixture was diluted with water, extracted with chloroform, and washed with water, the solvent was removed, and the residue was chromatographed on silica gel (hexane–ethyl acetate, 9 : 1, as an eluent).

(1-Phenylprop-1-yn-3,3-diyl)bis(hydroxybenzene), IIa. R_f 0.22.

^{1}H NMR ($CDCl_3$, δ, ppm, *J*, Hz): 7.05–7.40 (m, 15H, Ph; 1H, CH).

^{13}C NMR ($CDCl_3$, δ, ppm): 85.32 (C^2), 95.10 (C^1), 103.39 (C^3), 126.58, 127.61, 128.10, 128.35, 129.00, 131.02, 158.37 (Ph).

MS *m/z* (I_{rel}, %): 300 $[M]^{+\cdot}$ (<1), 207 $[M - {}^{\cdot}OC_6H_5]^+$ (2), 175 (100), 158 (91), 144 (13), 131 (15), 116 (28), 102 (19), 91 (12), 77 (10), 63 (11).

(1-Phenylprop-1-yn-3,3-diyl)bis(hydroxy-2-methylbenzene), IIIb. R_f 0.27.

^{1}H NMR ($CDCl_3$, δ, ppm, *J*, Hz): 2.2 (s, 6H, CH_3), 6.7–7.5 (m, 13H, Ph; 1H, CH).

MS *m/z* (I_{rel}, %): 328 $[M]^{+\cdot}$ (<1), 175 (100), 158 (87), 144 (12), 131 (15), 116 (29), 102 (21), 91 (12), 77 (10), 63 (12), 51 (4).

(1-Phenylprop-1-yn-3,3-diyl)bis(hydroxy-4-chlorobenzene), IIIc. R_f 0.24.

^{1}H NMR ($CDCl_3$, δ, ppm, *J*, Hz): 6.90–7.48 (m, 13H, Ph; 1H, CH).

MS *m/z* (I_{rel}, %): 368/370/372 $[M]^{+\cdot}$ (<1), 175 (76), 158 (100), 144 (17), 131 (18), 116 (28), 102 (28), 91 (18), 77 (15), 63 (16), 51 (17).

Synthesis of compounds Va and Vb. Sodium metal (0.012 mol) was gradually added to 0.1 mol of alcohol **IVa**, **IVb**. 2-Bromo-2-phenyl-1,1-dichlorocyclopropane **I** (0.005 mol) was added to the prepared alcoholate and heated to 100°C for 8–12 h. The reaction mixture was diluted with water, extracted with ether, and washed with water, and the solvent was evaporated. TLC analysis was performed on Silufol plates (Merk) using hexane–ethyl acetate, 9 : 1, as an eluent. Preparative separation was accomplished by column chromatography on silica gel (hexane with ethyl acetate gradient from 5 to 100% as an eluent).

(3,3-Dibutoxyprop-1-yn-1-yl)benzene, Va. R_f 0.27.

^{1}H NMR ($CDCl_3$, δ, ppm, *J*, Hz): 0.95–1.01 (m, 6H, $C^{4'}H_3$, $C^{4''}H_3$), 1.38–1.49 (m, 4H, $C^{3'}H_a$, $C^{3'}H_b$, $C^{3''}H_a$, $C^{3''}H_b$), 1.72–1.81 (m, 4H, $C^{2'}H_a$, $C^{2'}H_b$, $C^{2''}H_a$, $C^{2''}H_b$), 3.43–3.50 (m, 2H, $C^{1'}H_a$, $C^{1'}H_b$), 3.66–3.72 $C^{1''}H_a$, $C^{1''}H_b$), 5.29 (c, 1H, C^3H), 7.25–7.48 (m, 5H, Ph).

MS *m/z* (I_{rel}, %): 260 $[M]^{+\cdot}$ (<0.1), 203 $[M - C_4H_8]^{+\cdot}$ (1), 187 (17), 159 (3), 147 (6), 131 (100), 102 (36), 91 (6), 77 (22), 57 (36).

(3,3-Diallyloxyprop-1-yn-1-yl)benzene], Vb. R_f 0.30.

^{1}H NMR ($CDCl_3$; δ, ppm, *J*, Hz): 4.13–4.32 (m, 4H, $C^{1''}H_a$, $C^{1''}H_b$, $C^{1'''}H_a$, $C^{1'''}H_b$), 5.21–5.39 (m, 4H, $C^{3'}H_a$, $C^{3'}H_b$, $C^{3''}H_a$, $C^{3''}H_b$), 5.56 (c, 1H, C^3H), 5.91–6.04 (m, 2H, $C^{2'}H$, $C^{2''}H$), 7.27–7.50 (m, 5H, Ph).

^{13}C NMR ($CDCl_3$, δ, ppm): 66.29 ($C^{1'}H_2$, $C^{1''}H_2$), 83.97 (C^2), 85.78 (C^1), 91.02 (C^3H), 117.50 ($C^{3'}H_2$, $C^{3''}H_2$), 121.82, 128.29, 128.89, 131.96 (Ph), 134.05 ($C^{2'}H$, $C^{2''}H$).

MS *m/z* (I_{rel}, %): 228 $[M]^{+\cdot}$ (<0.1), 171 $[M - {}^{\cdot}OC_3H_5]^+$ (18), 142 (78), 128 (100), 115 (40), 102 (58), 91 (22), 77 (27), 63 (13), 51 (19).

REFERENCES

1. Kazakova, A.N., Bogomazova, A.A., and Zlotskii, S.S., *Dokl. Chem.*, 2011, vol. 441, part 2, pp. 371–373.
2. Newman, M.S., Dhawan, B., Hashem, M.M., et al., *Org. Chem.*, 1976, vol. 41, no. 24, p. 3925.
3. Fedoryński, M., *Chem. Rev.*, 2003, vol. 103, no. 4, pp. 1099–1132.