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Synthesis, Structure and Facile Rearrangement of a (Bromomethylene)-cyclopropane–Dichloroketene Adduct

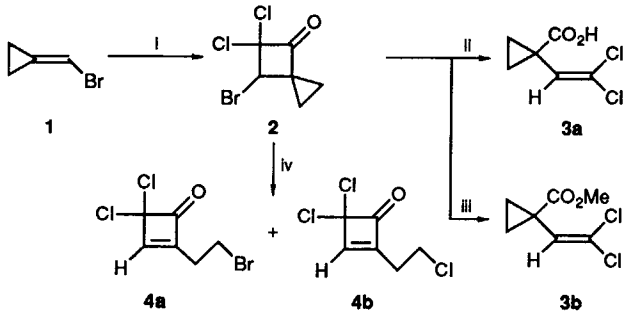
Nadezhda A. Donskaya* and Boris A. Lukovskii

Department of Chemistry, M. V. Lomonosov Moscow State University, 119899 Moscow, USSR. Fax: 095 939 0126

5,5-Dichloro-6-bromospiro[2.3]hexan-4-one **2** is produced by the reaction of (bromomethylene)cyclopropane **1** with dichloroketene and rearranges readily at 0°C into 2-(2-bromoethyl)-4,4-dichlorocyclobut-2-enone **4a**; reaction of **2** with basic reagents leads to the formation of 1-vinylcyclopropanecarboxylic acid derivatives.

In continuation of our studies on the reactivity of substituted methylenecyclopropanes with halogenated ketenes,[1] we report here a cycloaddition reaction, involving (bromomethylene)-cyclopropane **1**[2] and dichloroketene. Although cycloaddition of dichloroketene to alkenes is well known,[3] to our knowledge, all attempts to effect its reaction with electron deficient alkenes have failed.[4] We believed that this reaction should proceed, owing to the greater reactivity of the methylenecyclopropane double bond in [2 + 2] cycloaddition.

Indeed, the interaction of **1** with dichloroketene, generated under standard conditions[5] from trichloroacetyl chloride and activated zinc, affords only adduct **2** in 37% yield (separated by distillation) (Scheme 1).†



Scheme 1 *Reagents and conditions*: i, Cl_3CCOCl, Zn, diethyl ether, reflux, 10 h; ii, 2% KOH, H_2O, room temp., 30 min.; iii, MeONa, MeOH, room temp., 2.5 h; iv, $AlCl_3$, CCl_4, room temp., 2 h

Spirohexanone **2** was characterized by its ^1H and ^{13}C NMR and IR spectra. However, these data were not sufficient to establish unequivocally the mutual disposition of substituents in molecule. In our previous publication[6] we demonstrated that the carbonyl carbon in the ^{13}C NMR spectra of spiro[2.3]hexan-4-ones is more deshielded than that in spiro[2.3]hexan-5-ones (δ 200 and 190, respectively). The carbonyl resonance of compound **2** is situated near δ 196.5 and it was difficult to assign one of the two possible structures. We obtained additional information regarding the structure of adduct **2** from its behaviour upon the action of basic reagents.

Spirohexanone **2** reacted with 2% aqueous potassium hydroxide (25°C; 30 min) to produce 1-(2,2-dichlorovinyl)-cyclopropanecarboxylic acid **3a**‡ in 92% yield. Interaction of **2** with a ten-fold excess of sodium methoxide in methanol (25°C; 2.5 h) gives methyl 1-(2,2-dichlorovinyl)cyclopropanecarboxylate **3b**‡ in 95% yield.

The dichlorovinylic group is present in both compounds **3a** and **b**, *i.e.* opening of the cyclobutanone ring has been accompanied by debromination. These results allow us to conclude that the bromine atom is in position 6 of spirohexanone **2**.

We have found that **2** rearranges upon prolonged standing (about 2 months at 0°C). It is evident from the spectral data (^1H, ^{13}C NMR, IR and mass spectral) of the new compound, that it is 2-(2-bromoethyl)-4,4-dichlorocyclobut-2-enone **4a**.§

† Calculated on the basis of the amount of (bromomethylene)cyclopropane which underwent the reaction; 20% of **1** was recovered.

‡ *Selected spectral data*, for **2**: 5,5-dichloro-6-bromospiro[2.3]hexan-4-one, IR ν/cm^{-1} 1810 (C=O); ^1H NMR ($CDCl_3$) δ 1.66 (m, 4H, AA'BB') 5.05 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.6, 21.9 (C-1, C-2), 43.7 (C-3), 196.5 (C-4), 86.38 (C-5), 58.31 (C-6).

For **3a**: 1-(2,2-dichlorovinyl)cyclopropanecarboxylic acid, IR ν/cm^{-1} 1620 (C–C), 1685 (C–O); ^1H NMR ($CDCl_3$) δ 1.21 and 1.62 (m, 4H, AA'BB'), 6.1 (s, 1H), 9.68 (w.s, 1H); ^{13}C NMR ($CDCl_3$) δ 23.3 (C-1) 18.9 (C-2, C-3), 179.0 (-4), 126.1 (C-5), 127.4 (C-6).

For **3b**: methyl 1-(2,2-dichlorovinyl)cyclopropanecarboxylate, IR ν/cm 1625 (C–C), 1740 (–O); ^1H NMR ($CDCl_3$) δ 0.85–1.6 (m, 4H); 3.6 (s, 3H); 6.0 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 23.1 (C-1), 17.9 (C-2, C-3), 172.5 (C-4), 126.7 (C-5), 126.4 (C-6), 52.2 (C-7).

§ *Selected spectral data* for **4a**: 2-(2-bromoethy)-4,4-dichlorocyclobut-2-enone, IR ν/cm^{-1} 1660 (C–C), 1800 (C–O); ^1H NMR ($CDCl_3$) δ 3.17 (t, 2H, *J* 8 Hz), 3.87 (t, 2H, *J* 8 Hz), 8.57 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 181.6 (C-1), 89.4 (C-2), 163.3 (C-3), 154.6 (C-4), 26.6 (C-5), 28.0 (C-6); MS *m/z* 242 (M^+).

For **4b**: 2-(2-chloroethyl)-4,4-dichlorocyclobut-2-enone, IR ν/cm^{-1} 1550 (C–C), 1800 (C–O); ^1H NMR ($CDCl_3$) 2.62 (t, 2H, *J* 7 Hz), 3.57 (t, 2H, *J* 7 Hz), 8.5 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 182.3 (C-1), 81.8 (C-2), 163.5 (C-3), 136.3 (C-4), 26.7 (C-5), 39.3 (C-6); *m/z* 198 (M^+).

Mendeleev Commun., 1991, 1(4), 127–128

The rearrangement is accelerated by Lewis acids. Spirohexanone **2** is transformed into a mixture of **4a** and **b** when treated with $AlCl_3$ (25°C, CCl_4, 2 h). Compounds **4a** and **b**§ were separated by means of column chromatography [SiO_2 40/100, eluent hexane: ethylacetate (5:1)] in 50% and 30% yields, respectively. These results suggest a mechanism involving cyclopropylmethyl–homoallyl rearrangement[7] of the spirocyclopropane moiety of the molecule. This is the first example of cyclopropylmethyl–homoallyl rearrangement in spiroketones, that allows dichlorocyclobutenones with functional substituents in the side chain to be obtained.

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