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Mechanoactivation of solid-phase iodochlorination of olefins with potassium dichloroiodate(1)

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Mechanoactivation of iodochlorination of olefins with a new reagent, potassium dichloroiodate(1), was studied.

Key words: potassium dichloroiodate(1), iodochlorination; reactivity, mechanoactivation.

Solid-phase methods are promising in the development of techniques of organic synthesis¹ and chemical technology.² Much attention is being given to the study of the mechanisms of mechanoactivated chemical reactions.² The mechanical properties of reagents are likely to significantly influence the results of these processes, and hence solid-phase procedures are quite promising for the study of the action of solid reagents on solid organic substrates. We have found that stilbene (1), which almost does not react with potassium dichloroiodate(1), KICl₂, on stirring in CCl₄, undergoes preparative iodochlorination under the action of this reagent in a ball vibrational mill. This process is probably mechanoactivated by the energy that is released locally during the mechanical destruction of the hard and brittle stilbene crystals in the vibrational mill.



In contrast, methyl cinnamate (2), which easily undergoes iodochlorination under the same conditions in solution, remains unchanged when treated with $KICl_2$ in the ball vibrational mill. This can be explained by the fact that during mechanical treatment of the soft and low-melting crystals of ester 2 mechanical energy is consumed to melt it, and there is no mechanoactivation of iodochlorination. Thus, the data obtained by us suggest that solid-phase iodochlorination of olefins with potassium dichloroiodate(1) is decisively influenced by the mechanical properties of the olefin.

Experimental

The solid-phase syntheses were carried out in a plastic chamber 20 cm³ in volume (working agents were steel balls: 44 with a diameter of 4 mm and 27 with a diameter of 2 mm) rotating at a frequency of 5–7 Hz and with a vibrational amplitude of 2 cm along the vertical axis and 2 cm along the horizontal axis. The ¹H NMR spectrum was recorded on a Bruker FT-80 instrument (80 MHz) in CCl₄ with HMDS as the internal standard. Chromatographic analysis was performed using Silufol UV-254 plates.

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lodochlorination of stilbene (1). A. Stilbene (257 mg, 1.42 mmol) and K1Cl₂ (370 mg, 1.56 mmol) were treated in a ball vibrational mill for 1 h, and the mixture was extracted with benzene (3×5 mL), washed successively with an aqueous sodium thiosulfate solution and water, and dried with sodium sulfate. After the solvent was removed, 2-chloro-1-iodo-1,2-diphenylethane (413 mg) was obtained, yield 85%, m.p. 131 °C (decomp.) (cf. Ref. 3: m.p. 131 °C).

B. Stilbene (180 mg, 1 mmol) ground in a mortar and KICl₂ (260 mg, 1.1 mmol) in 5 mL of CCl₄ were stirred with a magnetic stirrer for 7.5 h and allowed to stand overnight. After treatment similar to that of procedure A the initial compound 1 was isolated (180 mg, 100%), m.p. 123-124 °C (from benzene) (cf. Ref. 4: m.p. 124 °C).

Iodochlorination of methyl cinnamate (2). *A.* Methyl cinnamate (162 mg, 1 mmol) and KICl₂ (260 mg, 1.1 mmol) were treated in a ball vibrational mill for 4 h and allowed to stand overnight. After the usual treatment the initial ester 2 was isolated (123 mg, 76%), m.p. 32-33 °C (*cf.* Ref. 5: m.p. 33-34 °C).

B. A solution of methyl cinnamate (162 mg, 1 mmol) and KICl₂ (260 mg, 1.1 mmol) in 5 mL of CCl₄ was stirred with a magnetic stirrer for 4 h and treated analogously to the above procedure. A mixture was obtained (276 g) that contained,

according to the data of ¹H NMR spectroscopy, 263 mg of methyl 2-chloro-1-iodo-2-phenylpropionate (yield 81%) and 13 mg (8%) of the initial ester 2. Pure iodochloroester (120 mg, 34%) was obtained by triple recrystallization öf the mixture from petroleum ether, m.p. 98–99 °C (from petroleum ether) (cf. Ref. 6: m.p. 97–98 °C). ¹H NMR, δ : 3.7 (s, 3 H, Me); 4.7 (d, 1 H, CH1, ³J = 11.7 Hz); 5.1 (d, 1 H, CHC1); 7.1 (m, 5 H, Ph).

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Synthesis of new bis[p-(phenylethynyl)phenyl]hetarylenes and bis[p-(phenylglyoxalyl)phenyl]hetarylenes

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A series of new bis[p-(phenylethynyl)phenyl]hetarylenes was obtained by cross-coupling between heteroaromatic dibromides and phenylacetylene catalyzed by phosphine complexes of palladium in the presence of Cul and an organic base. Bis[p-(phenylethynyl)phenyl]hetarylenes were oxidized to the corresponding bis[p-(phenylglyoxalyl)phenyl]hetarylenes using the l_2 -DMSO system.

Key words: phenylacetylene, cross-coupling reaction; bis[*p*-(phenylethynyl)phenyl]hetarylenes, bis[*p*-(phenylglyoxalyl)phenyl]hetarylenes; palladium, catalysis.

Bis[*p*-(phenylethynyl)phenyl]arylenes and bis[*p*-(phenylglyoxalyl)phenyl]arylenes have attracted attention of researchers as monomers for the preparation of phenylsubstituted polyphenylenes¹ and polyphenylquinoxalines.² Numerous representatives of both the former and the latter classes of monomers are known; however, their analogs containing divalent residues of aromatic heterocycles instead of arylene fragments have been poorly studied.

In the present work, we synthesized bis[p-(phenylethynyl)phenyl]hetarylenes and bis[p-(phenylglyoxalyl)phenyl]hetarylenes with quinoxal-2,3-diyl and

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