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SHORT COMMUNICATIONS

Iron Pentacarbonyl, Efficient Promoter of Aromatic Compounds Alkylation with Bromoadamantane

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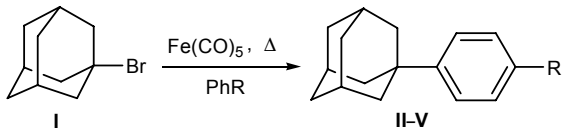
We have repeatedly demonstrated the large opportunities of iron pentacarbonyl $Fe(CO)_5$ application [1–7] as initiator of versatile organic reactions leading to the formation of bonds C–C, C–O, C–Hlg, etc. $Fe(CO)_5$ is a promoter of addition of α-halocarboxylic acids esters and nitriles to aldehydes and ketones along the Reformatsky type reaction [2, 3]; the reaction proceeds especially successful with polyfluorinated aldehydes and ketones [3, 4]. Using $Fe(CO)_5$ we succeeded to perform a diastereoselective hydrodimerization of aromatic aldehydes with transition to diols [5], and also to carry out the addition of C_4F_9I [6] and benzyl bromide [7, 8] to pentafluorobenzaldehyde by the type of Zaitsev–Barbier reaction. However it was established that iodohexane under similar conditions did not react with pentafluorobenzaldehyde and formed dihexyl ketone [6].

In this study we have continued the investigation of the initiating effect of $Fe(CO)_5$ using as a halogen-containing addend the sterically hindered 1-bromoadamantane (**I**) that is often utilized in alkylation [9–11] and cross-coupling [12, 13] reactions for the introduction of bulky adamantly fragment providing the final products with special physicochemical properties [14] and modifying their physiological action [11, 15, 16].

The attempt to add 1-bromoadamantane (**I**) to pentafluorobenzaldehyde by the type of Zaitsev–Barbier reaction in the presence of $Fe(CO)_5$ in benzene at 80°C was unsuccessful, but here the alkylation occurred of usually inert solvent with the formation of 1-phenyladamantane (**II**).



I **II–V**

R = H (**II**, 80°C), Me (**III**, 80°C), Cl (**IV**, 110°C), Br (**V**, 110°C).

Since a new reaction direction was discovered, we carried out the alkylation of a series of typical aromatic compounds under similar conditions. In all cases the arenes alkylation products **II–V** were obtained in good yields. Thus we discovered for the first time the ability of $Fe(CO)_5$ to initiate alkylation with 1-bromoadamantane in Friedel–Krafts reaction. These reactions do not occur without initiator, besides, the yield of compounds **II–V** does not virtually decrease at reducing the amount of $Fe(CO)_5$ to 0.5 mol per 1 mol of 1-bromoadamantane. Under similar conditions nitrobenzene, dichlorobenzene, and cyclohexane do not undergo alkylation. The alkylation with 1-bromoadamantane under the action of Friedel–Krafts catalysts is known [9, 10], but metal carbonyls have not been used in these processes. Besides in the known examples the alkylation product yields in some cases were lower, and higher temperature was required along with prolonged stirring, inert environment and as a rule larger (1–2 mol) amounts of initiator. Therewith the reactions catalyzed with Lewis acids occurred mainly in heterogenic conditions [9, 10], and the use of $FeCl_3$ and $SbCl_5$, for instance, resulted in a partial chlorination of adamantane [17].

The mechanism of the process may be presented as follows: $Fe(CO)_5$ forms an intermediate complex with bromoadamantane activating the haloalkane. We formerly observed the result of such interaction manifested in the shift of the absorption bands in the UV spectrum to the longwave region in the mixtures of $Fe(CO)_5$ with a haloalkane [18]. As a result of this activation the haloalkane may suffer a dimerization as in the case of benzyl bromide [7, 8], or form an active radical as has been suggested for iodohexane [6]. The formation of ion-radical is also possible [19, 20] with subsequent aldehyde alkylation to give the corresponding alcohol (like the cases described in [2–4, 7, 8]), yet this is hardly probable for the bulky adamantine fragment. In the reaction conditions under consideration apparently a sterically hindered electrophilic species appears or an ion-radical [19, 20]. It is presumable that the formed electrophile is unable to attack the "hard" carbonyl site of the pentafluorobenzaldehyde [3, 4] but efficiently alkylates the aromatic compound present in the mixture along the type of Friedel–Krafts reaction [9, 10].

This example once again shows wide opportunities of $Fe(CO)_5$ application [1] as the initiator of versatile organic reaction of C–C bond formation not only in aliphatic [2], but also in aromatic series.

Arenes alkylation with 1-bromoadamantane in the presence of iron pentacarbonyl. In a flask equipped with a reflux condenser and gas-washing bottle for monitoring CO liberation to a mixture of 0.1 g (0.5 mmol) of reagent **I** and 1 mL of arene was added 0.135 mL (1 mmol) of $Fe(CO)_5$ and a drop (~1%) of benzene solution of $CBrCl_3$ as activator. The mixture was stirred for 5 h at the necessary temperature till the end of gas liberation and the pressure decrease. Then the reaction mixture was treated with 30 mL of 1N HCl, thrice washed with water, the organic layer was dried with Na_2SO_4, evaporated in a vacuum, the residue was chromatographed on a column packed with silica gel (eluent benzene).

1-Phenyladamantane (II). Yield 0.0883 g (92%), mp 79–80°C [21]. At using 0.5 and 0.25 mmol of $Fe(CO)_5$ the yield decreased to 84%. ^{1}H NMR spectrum, δ, ppm: 1.87 s (6H, CH_2, Ad), 2.02 s (6H, CH_2, Ad), 2.19 s (3H, CH, Ad), 7.25–7.40 m ($5H_{arom}$). Mass spectrum, *m/z* (I_{rel}, %): 212 (80) $[M]^+$, 169 (13) $[M - C_3H_7]^+$, 155 (100) $[M - C_4H_9]^+$, 135 (2) $[Ad]^+$.

1-(4-Tolyl)adamantane (III). Yield 0.1 g (95%), mp 102°C [10]. ^{1}H NMR spectrum, δ, ppm: 1.97 s (6H, CH_2, Ad), 2.10 s (6H, CH_2, Ad), 2.28 s (3H, CH, Ad), 2.51 s (3H, CH_3), 7.33–7.45 m ($4H_{arom}$). Mass spectrum, *m/z* (I_{rel}, %): 226 (95) $[M]^+$, 169 (100) $[M - C_4H_9]^+$, 183 (25) $[M - C_3H_7]^+$, 91 (25) $[M - Ad]^+$.

1-(4-Chlorophenyl)adamantane (IV). Yield 0.0696 g (62%), mp 89°C (mp 90–91°C [22]). ^{1}H NMR spectrum, δ, ppm: 1.85 s (6H, CH_2, Ad), 1.99 s (6H, CH_2, Ad), 2.17 s (3H, CH, Ad), 7.35 m ($4H_{arom}$). Mass spectrum, *m/z* (I_{rel}, %): 246 (100) $[M]^+$, 189 (80) $[M - C_4H_9]^+$, 153 (25) $[M - C_4H_9 - HCl]^+$, 135 (100) $[Ad]^+$.

1-(4-Bromophenyl)adamantane (V). Yield 0.0863 g (64%), mp 99–100°C [10]. ^{1}H NMR spectrum, δ, ppm: 1.86 s (6H, CH_2, Ad), 2.0 м (6H, CH_2, Ad), 2.17 s (3H, CH, Ad), 7.30–7.50 m ($4H_{arom}$). Mass spectrum, *m/z* (I_{rel}, %): 290 (100) $[M]^+$, 233 (30) $[M - C_4H_9]^+$, 154 (75) $[M - Ad]^+$, 135 (40) $[Ad]^+$.

Mass spectra were recorded on a mass spectrometer Finnigan SSQ-700 (ionizing electrons energy 70 eV). ^{1}H NMR spectra were registered on spectrometers Bruker Avance 300 and Bruker Avance 400 (300 and 400 MHz respectively) in $CDCl_3$ at 30°C, chemical shifts measured with respect to TMS. The melting points were measured in a sealed capillary with a melting point indicator Electrothermal IA 9000. GLC was performed on a chromatograph LKhM-80, steel column (1300 × 3 mm), statiorary phase SKTFT-50X on Chromaton N-AW, carrier gas helium, detector katharometer, ramp in the range 50–250°C, heating rate 6 deg min^{-1}.

All organic reagents were purified by distillation or recrystallization. Bromoadamantane (**I**) was purchased from Aldrich. $Fe(CO)_5$ of Fluka (98%) was used without additional purification.

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