SHORT
COMMUNICATIONS

Rhodium(II)-Catalyzed Intramolecular Reactions of Methyl 4-Diazo-5-oxo-3-trifluoromethylalk-2-enoates in the Presence of 2,5-Dimethylfuran

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Reaction paths of vinyl oxo carbenoids generated by rhodium-catalyzed decomposition of vinyl diazo esters in the presence of unsaturated substrates are determined mainly by the structure of initial diazo compounds and, correspondingly, intermediate Rh(II)-carbenoids [1, 2].

The goal of the present study was to estimate the effect of perfluoroalkyl substituent on C^3 in methyl 4-diazo-5-oxo-3-trifluoromethylalk-2-enoates **I** (which were synthesized by us for the first time in [3]) on the direction of Rh(II)-catalyzed reactions with substituted furans and other unsaturated compounds. An analogous study was recently reported by Wang et al. [4]; the authors used fluorine-containing vinyl diazo esters [5] that are structurally related to diazo ketones **I**. It was found [4] that catalytic decomposition of these compounds in the presence of dirhodium tetraacetate and 2,5-dimethylfuran or other furans involves initial cyclopropanation of the double bond in the furan ring by intermediate vinyl carbenoid and subsequent Cope rearrangement leading to bicyclooctadienes like **A**, as in similar reactions with nonfluorinated vinyl diazo esters [6]. The authors also succeeded in isolating cyclopropene derivatives like **B** in the above reactions.
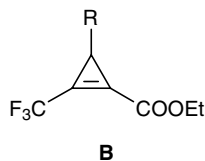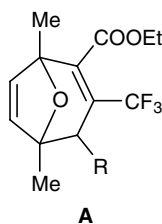
R = CO2Me, CO2Et, COMe.

Unlike the data of [4], catalytic decomposition of diazo ketones **Ia** and **Ib** with dirhodium tetraacetate in benzene at 80°C in the presence of 2,5-dimethylfuran gave tricyclooctenes **IIa** and **IIb** together with 2,3,5-trisubstituted furans **IIIa** and **IIIb** (Scheme 1). The structure of compounds **II** and **III**, as well as the *exo* configuration of adducts **II** was reliably determined by ^{1}H and ^{13}C NMR spectroscopy and X-ray analysis of tricyclooctene **IIa** and 3-(trifluoromethyl)-substituted furan **IIIa**.
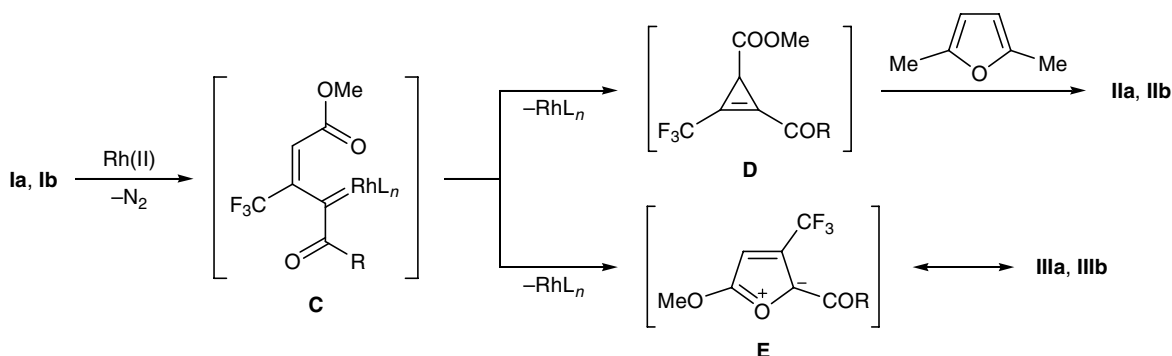
Scheme 1.
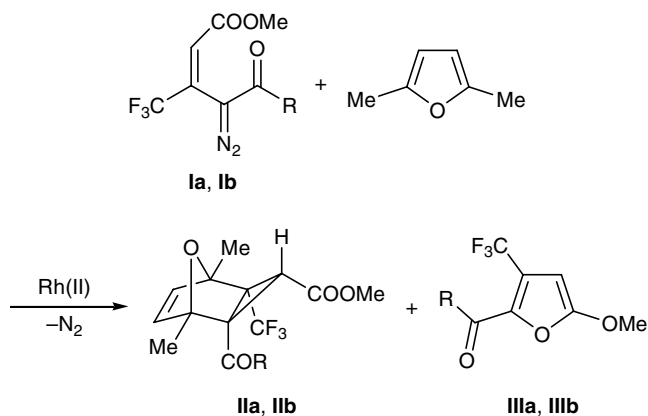
R = Me (**a**), *p*-ClC$_6$H$_4$ (**b**).

The chemical shifts of protons on C^3 in **IIa** and C^4 in **IIIa** are very similar to the corresponding parameters of compounds **A** and **B** [4] (δ 3.18, 3.22 and 5.99, 5.47–6.32 ppm, respectively. The 3-H proton in 1,2,3-trisubstituted cyclopropene ring resonates usually at δ 2.25–2.45 ppm [7, 8], whereas δ values of 5.47–6.32 ppm were given in [4] for compounds **B**; such

Scheme 2.

chemical shifts are typical of furans [8, 9] rather than cyclopropenes. Therefore, the structure assignments made in [4] for compounds **A** and **B** are likely to be erroneous, and the products obtained in [4] are in fact tricyclooctenes like **II** and 2,3,5-trisubstituted furans like **III**.

Presumably, the scheme of formation of cycloadducts **II** and furans **III** from fluorine-containing diazo ketones **I**, as well as from nonfluorinated analogs [1, 2, 6], includes initial generation of vinyl oxo carbenoids **C** which undergo intramolecular [1,3]-electrocyclization to give quite reactive cyclopropenes **D**. The latter contain two electron-withdrawing groups (CF$_3$ and CO$_2$Me) at the double bond, which favor Diels–Alder reaction with 2,5-dimethylfuran present in the reaction mixture to produce cycloadducts **II** (Scheme 2). An alternative stabilization path of intermediate carbenoid **C** via intramolecular [1,5]-electrocyclization leads to 2,3,5-trisubstituted furans **III** through ylide **E**. This path is likely to be favored by *E* configuration of initial diazo ketones **I**, which facilitates intramolecular cyclization of intermediate **C** [3].

Thus, the presence of a trifluoromethyl group in diazo carbonyl compound almost completely suppresses intermolecular reactions of Rh(II)-carbenoids derived therefrom, and transformations of the latter follow exclusively intramolecular [1,3]- and [1,5]-electrocyclizations.

Catalytic decomposition of methyl 4-diazo-5-oxo-3-trifluoromethylhex-2-enoate (Ia) with dirhodium tetraacetate in the presence of 2,5-dimethylfuran. A solution of 9 mg (0.002 mmol) of Rh$_2$(OAc)$_4$ in a mixture of 0.96 g (10 mmol) of 2,5-dimethylfuran and 5 ml of benzene was heated to the boiling point, and a solution of 0.24 g (1 mmol) of diazo ketone **Ia** in 1.5 ml of benzene was added dropwise over a period of 4 h. The mixture was heated under reflux for 8 h until initial diazo compound **Ia** disappeared (TLC), the

solvent and excess 2,5-dimethylfuran were distilled off under reduced pressure, and the residue was separated by chromatography on silica gel (gradient elution with petroleum ether–diethyl ether mixtures) to isolate 0.11 g (36%) of **IIa** and 0.07 g (32%) of **IIIa**.

Methyl 2-acetyl-1,5-dimethyl-4-trifluoromethyl-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene-3-carboxylate (IIa). Colorless crystalline substance, mp 48–50°C. ^{1}H NMR spectrum, δ, ppm: 1.56 s (3H, CH$_3$), 1.62 s (3H, CH$_3$), 2.27 s (3H, COCH$_3$), 3.18 s (1H, CH), 3.73 s (3H, COOCH$_3$), 6.48 d (1H, CH=, J = 6 Hz), 6.55 m (1H, CH=). ^{13}C NMR spectrum, δ$_C$, ppm: 15.2 (CH$_3$), 15.6 (CH$_3$), 30.8 (COCH$_3$), 34.0 (CH), 50.6 q (C^4, $^2J_{CF}$ = 33.9 Hz), 52.6 (OCH$_3$), 58.7 (C^2), 87.2 (C^1 or C^5), 88.2 (C^5 or C^1), 124.7 (CF$_3$, $^1J_{CF}$ = 274.9 Hz), 140.9 (CH=), 142.4 (CH=), 166.8 (COOCH$_3$), 199.7 (C=O). Found, %: C 55.27; H 4.97. C$_{14}$H$_{15}$F$_3$O$_4$. Calculated, %: C 55.38; H 4.89.

5-Acetyl-2-methoxy-4-(trifluoromethyl)furan (IIIa). Colorless crystalline substance, mp 58–60°C. ^{1}H NMR spectrum, δ, ppm: 2.41 s (3H, CH$_3$), 4.10 s (3H, OCH$_3$), 5.99 s (1H, CH). ^{13}C NMR spectrum, δ$_C$, ppm: 26.9 (CH$_3$), 58.8 (OCH$_3$), 84.2 q (C^4, $^3J_{CF}$ = 4.0 Hz), 121.4 q (CF$_3$, $^1J_{CF}$ = 269.0 Hz), 124.4 q (C^3, $^2J_{CF}$ = 39.6 Hz), 140.1 (C^2), 161.8 (C^5), 185.3 (C=O). Found, %: C 46.17; H 3.39. C$_8$H$_7$F$_3$O$_3$. Calculated, %: C 46.06; H 3.17.

Catalytic decomposition of methyl 5-(4-chlorophenyl)-4-diazo-5-oxo-3-trifluoromethylpent-2-enoate (Ib) with dirhodium tetraacetate in the presence of 2,5-dimethylfuran. The reaction was carried out as described above for compound **Ia** using 0.33 g (1 mmol) of diazo ketone **Ib**. Chromatographic separation of the product mixture gave 0.27 g (68%) of compound **IIb** and 0.58 g (19%) of **IIIb**.

Methyl 2-(4-chlorobenzoyl)-1,5-dimethyl-4-trifluoromethyl-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene-3-carboxylate (IIb). Colorless crystalline substance,

mp 85–89°C. ^{1}H NMR spectrum, δ, ppm: 1.45 s (3H, CH$_3$), 1.65 s (3H, CH$_3$), 3.51 s (3H, COOCH$_3$), 3.61 s (1H, CH), 6.41 d (1H, CH=, J = 6 Hz), 6.64 m (1H, CH=), 7.55 m (2H, H$_{arom}$), 8.07 m (2H, H$_{arom}$). ^{13}C NMR spectrum, δ$_C$, ppm: 15.4 (CH$_3$), 17.1 (CH$_3$), 36.6 (CH), 49.8 q (CCF$_3$, $^2J_{CF}$ = 34.0 Hz), 52.5 (OCH$_3$), 56.3 (C^2), 87.8 (C^1 or C^5), 89.5 (C^5 or C^1), 125.9 q (CF$_3$, $^1J_{CF}$ = 274.8 Hz), 129.3 (2C, C$_{arom}$), 132.0 (2C, C$_{arom}$), 137.0 (C$_{arom}$), 139.8 (C$_{arom}$), 141.6 (CH=), 142.7 (CH=), 167.0 (COOCH$_3$), 190.4 (C=O). Found, %: C 55.94; H 4.02. C$_{19}$H$_{16}$ClF$_3$O$_4$. Calculated, %: C 55.79; H 4.05.

5-(4-Chlorobenzoyl)-2-methoxy-4-(trifluoro-methyl)furan (IIIb). Colorless crystalline substance, mp 67–70°C. ^{1}H NMR spectrum, δ, ppm: 4.13 s (3H, OCH$_3$), 6.11 s (1H, CH), 7.60 m (2H, H$_{arom}$), 8.02 m (2H, H$_{arom}$). ^{13}C NMR spectrum, δ$_C$, ppm: 59.6 (OCH$_3$), 85.0 q (C^4, $^3J_{CF}$ = 4.0 Hz), 121.4 q (CF$_3$, $^1J_{CF}$ = 268.2 Hz), 124.2 q (C^3, $^2J_{CF}$ = 39.4 Hz), 129.6 (2C, C$_{arom}$), 131.9 (2C, C$_{arom}$), 136.3 (C$_{arom}$), 139.4 (C$_{arom}$), 143.8 (C^2), 163.3 (C^5), 179.4 (C=O). Found, %: C 51.25; H 2.65. C$_{13}$H$_{18}$ClF$_3$O$_3$. Calculated, %: C 51.23; H 2.69.

The ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 instrument at 300 and 75.45 MHz, respectively, using CDCl$_3$ as solvent and tetramethyl-silane as internal reference. The elemental compositions were determined on a Heraeus CHNO Rapid Analyser.

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