Formal C—H insertion of diketocarbene generated by rhodium(II)-catalyzed decomposition of diazodimedone into a benzene molecule

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Diketocarbene generated by rhodium(II) acetate-catalyzed decomposition of diazodimedone reacts with benzene at room temperature to give 5,5-dimethyl-2-phenylcyclohexane-1,3-dione in 88 % yield.

Key words: rhodium(II) acetate, diazodimedone, carbenes, C—H insertion.

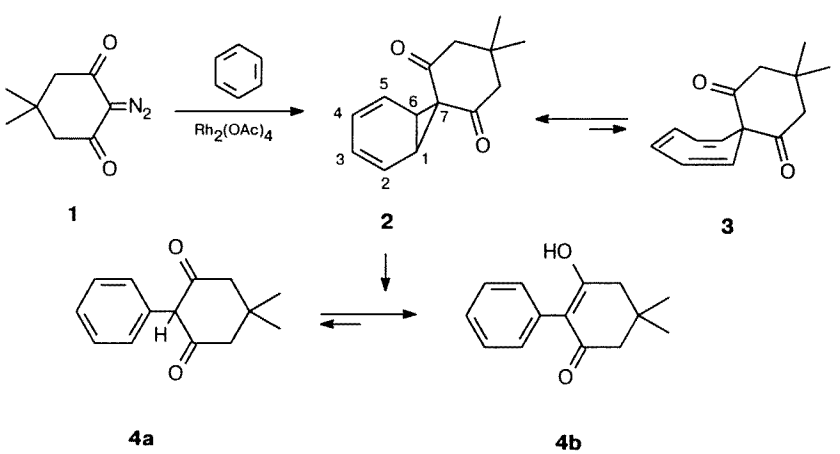
Reactions of benzene with carbenes generated by decomposition of aliphatic diazo compounds in the presence of Rh(II) are widely used for synthesis of cyclohepta-1,3,5-trienes (CHT).[1,2] However, literature data on this type of reactions involving 2-diazo-1,3-dicarbonyl compounds are lacking. It has only been shown[3] that the use of $Rh_2(OCOCF_3)_4$ is inefficient for the catalytic decomposition of diazodimedone (**1**), which is stable in the presence of this catalyst and does not participate in carbenoid insertion reactions into aromatic compounds.

It has been found in this work that compound **1** readily undergoes catalytic decomposition in benzene in the presence of $Rh_2(OAc)_4$ to give 5,5-dimethyl-2-phenylcyclohexane-1,3-dione (**4**) as the sole product.

The reaction of compound **1** with benzene in the presence of $Rh_2(OAc)_4$ was carried out at room temperature in a nitrogen atmosphere and controlled by TLC. The TLC analysis shows that the catalytic decomposition of compound **1** is completely ended in 0.5 h, resulting in the formation of a sole product. According to spectral and elemental analysis data, the product obtained is compound **4** (88 % yield).

It is known[1,2] that one of the initial stages of the rhodium(II)-catalyzed reactions of aliphatic diazo compounds with benzene involves the formation of bicyclo[4.1.0]hepta-2,4-dienes (norcaradienes, NCD), which under the reaction conditions usually undergo electrocyclic synchronic opening of the cyclopropane

Scheme 1



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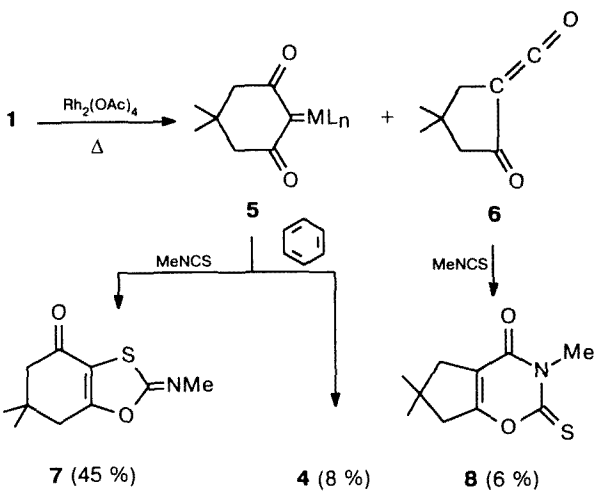
ring to form the corresponding CHT. An interesting specific feature of these reactions is valence tautomerism between CHT and NCD. It is established[4] that the presence of unsaturated electron-accepting groups, especially of the carbonyl group, in substituents at position 7 of NCD and CHT shifts the equilibrium between these tautomers to a great extent toward the NCD side. Upon the action of acids, the latters readily undergo opening of the cyclopropane ring at the C(1)—C(7) bond to form benzylketones.[5] It can be assumed that the $Rh_2(OAc)_4$-catalyzed reaction of compound **1** with benzene also involves the formation of NCD **2**. The presence of the spiran moiety and two carbonyl groups in intermediate **2** most probably exerts a decisive effect on the subsequent course of the reaction. As a result, the main direction of the further transformation of NCD **2** becomes the opening of its C(1)—C(7) bond to give compound **4a** rather than the opening of the C(1)—C(6) bond of NCD **2** followed by the formation of CHT **3**. It is of interest that the irreversible opening of the cyclopropane ring of **2** to form compound **4a** can occur under the conditions of autocatalysis, when final compound **4** formed in the reaction serves as an acid catalyst. The previous study[6] of the series of 2-aryl-substituted derivatives of dimedone has shown that all these compounds are classified as strong C—H acids. Another peculiarity of 2-aryl-substituted derivatives of dimedone is the fact that the majority of these compounds exist predominantly in the form of enols.[6,7] Since ^1H and ^{13}C NMR spectra of compound **4** are lacking in the literature, and all conclusions about the existence of 2-aryl-substituted derivatives of dimedone in the form of enols were based only on the data of IR spectra,[6,7] it seems interesting to discuss the ^1H and ^{13}C NMR spectra of compound **4**, which also provide valuable information for determining the enol forms of 2-aryl-substituted derivatives of dimedone. Thus, the ^1H NMR spectrum of compound **4b** indicates its enol form by nonequivalence of the protons of two CH_2 groups, which are manifested as two equally intense singlets at 2.47 and 2.37 ppm. By analogy, in the ^{13}C NMR spectrum of **4b**, carbon atoms of two CH_2 groups manifest as two signals at 50.8 and 41.8 ppm, while carbon atoms of carbonyl groups exhibit two signals at 196.7 and 169.2 ppm. At the same time, the position of the signal at 169.2 ppm, which better corresponds to those of carbon atoms of strongly conjugated carbonyl groups, allows one to suppose that the enolization of **4a** is not complete and only shifted noticeably toward enol **4b**.

High efficiency of the C—H insertion reaction of diketocarbenoid formed upon the Rh^{II}-catalyzed decomposition of **1** into a benzene molecule promped us to repeatedly study the reaction of **1** with methyl isothiocyanate in benzene in the presence of $Rh_2(OAc)_4$. We have previously established[8] that this reaction in boiling benzene includes two competing processes. 1,3-Dipolar cycloaddition of intermediately formed diketocarbenoid **5** to a methyl isothiocyanate molecule

Scheme 2



results in the formation of the main product, cycloadduct **7**. On the other hand, the Wolff rearrangement of initial compound **1** produces ketoketene **6** that adds to methyl isothiocyanate to form cycloadduct **8**. The repeated study of this reaction in boiling benzene shows that compound **4** is the third reaction product formed in 8 % yield along with compounds **7** (45 % yield) and **8** (6 % yield) described previously (Scheme 2).[8] The formation of the product of the Wolff rearrangement in the reaction of **1** with methyl isothiocyanate in the presence of $Rh_2(OAc)_4$ confirms to a certain extent the previous conclusions[3] that the interaction of diazodimedone with the Rh^{II} compounds is relatively weak, because $Rh_2(OCOCF_3)_4$ was inefficient for the catalytic decomposition of initial compound **1**.

The revealed capability of compound **1** of readily reacting with benzene in the presence of $Rh_2(OAc)_4$ at room temperature can be used as the new efficient method for the synthesis of various 2-aryl-substituted derivatives of dimedone. In addition, a possibility of this type reactions should be taken into account, when heterocycles are synthesized on the basis of the $Rh_2(OAc)_4$-catalyzed reactions of compound **1** with weak dipolarophiles.

Experimental

NMR spectra were recorded on a JEOL EX-270 instrument (working frequencies of 270 and 67.8 MHz were used for ^1H and ^{13}C, respectively, and TMS was used as an internal standard). $Rh_2(OAc)_4$ (Aldrich) was used.

Reaction of compound 1 with benzene. A solution of 332 mg (2.0 mmol) of **1** in anhydrous benzene (10 mL) was added dropwise with stirring to a solution of 13.3 mg (0.03 mmol) of rhodium(II) acetate in benzene in a nitrogen atmosphere at

room temperature, and then the reaction mixture was stirred for 0.5 h until initial compound **1** completely decomposed (control by TLC). The reaction mixture obtained was concentrated by evaporation at a reduced pressure, and the residue was chromatographed on a column filled with silica gel. An ethyl acetate—hexane (1 : 2) mixture was used as the eluent. Compound **4** (381 mg, 88 % yield) was obtained, m.p. 199—200 °C (*cf.* Ref. 11: m.p. 192—193 °C). ^{1}H NMR ($CDCl_3$), δ: 7.44 (t, 2 H, H arom); 7.34 (t, 1 H, H arom); 7.19 (d, 2 H, H arom); 6.40 (br.s, 1 H, CH); 2.47 (s, 2 H, CH_2); 2.37 (s, 2 H, CH_2); 1.12 (s, 6 H, 2Me). ^{13}C NMR ($CDCl_3$), δ: 196.7 (C(1)); 169.2 (C(3)); 130.9 (C′(1)); 130.6 (C′(3)); 129.2 (C′(2)); 128.1 (C′(4)); 116.9 (C(2)); 50.8 (C(6)); 41.8 (C(4)); 31.5 (C(5)); 28.3 (Me).

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