Brief Communications

New reaction of mononitroarenes: condensation with two acetophenone molecules *via* the nitro group

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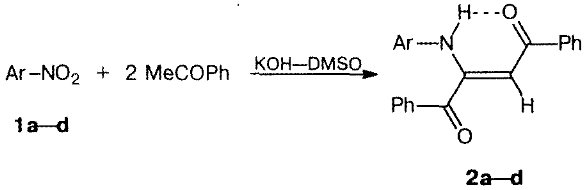
Nitrobenzene, *p*-bromonitrobenzene, *N,N*-diethyl-*p*-nitroaniline, and 9-methyl-3-nitrocarbazole undergo condensation with two moles of acetophenone in a DMSO—KOH system to form the corresponding (*Z*)-1,4-diphenyl-2-arylamino-2-butene-1,4-diones.

Key words: mononitroarenes, nucleophilic addition, acetophenone, condensation, dehydroisomerization.

Previously, intramolecular nucleophilic addition of CH acids to the nitro group was used in the synthesis of a number of heterocycles.[1,2] It was believed that it is impossible to perform intermolecular aldol condensation with CH acids *via* the nitro group.[1,3] However, in the preliminary communication[4] we reported the first and only example of intermolecular condensation of nitrobenzene **1a** with CH acid (acetophenone) *via* the nitro group with the formation of noncyclic product **2a**. In some sense, this condensation may be considered as an analog of crotonization. In this work, we present new results, which demonstrate the general character of this reaction for a series of different mononitroarenes, and the results of X-ray structural analysis of product **2a**.

It has been established that in reactions with acetophenone, *p*-substituted nitrobenzenes **1b,c** and carbazole derivative **1d** exhibit behavior similar to that of **1a** and give analogous products **2b—d**.



Ar = Ph (**a**), 4-BrC$_6$H$_4$ (**b**), 4-Et$_2$NC$_6$H$_4$ (**c**), 9-methylcarbazol-3-yl (**d**)

A low yield of product **2b** is attributable to a competitive replacement of the halogen atom with the enolate

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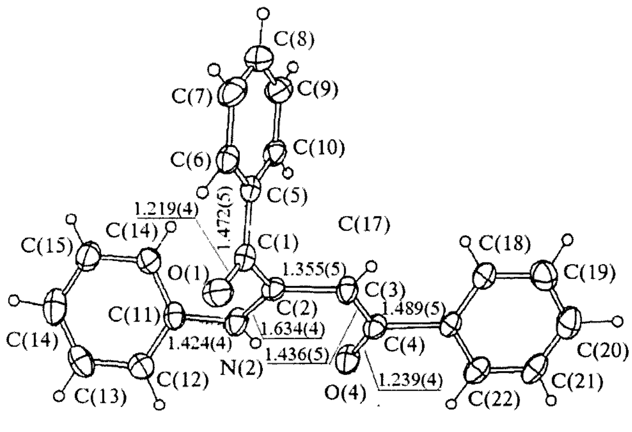

Fig. 1. Structure of molecule **2**.

anion.[5] Judging from the concentration of bromine ions in washing water, the total replacement of bromine with enolate and, presumably, with OH^- is ~20 %. Donor substituents in *para* positions of nitroarene hamper the reaction because compounds **1c,d** do not react with MeCOPh at 20 °C. However, the reaction occurs upon slight heating of the mixture to provide products **2c,d** in high yields. Previously, compounds of type **2** were obtained by the addition of amines to dibenzoylacetylene; in this case, it was believed that the *E* configuration of adducts is more favorable.[6] We have established that adducts **2a—d** have exclusively a *Z* configuration, which is stabilized by an intramolecular hydrogen bond.

The structure of compound **2a** was unambiguously established by X-ray structural analysis. The PhC=O group is twisted about the C(1)—C(2) bond by 68.3(1)° with respect to the plane of the C(2)—C(3) double bond; the PhN group is twisted by 38.2(1)° about the C(2)—N(2) bond; the Ph group at the C(4) atom is twisted by 22.4(1)° about the C(4)—C(17) bond. The parameters of the intramolecular N(2)—H...O(4) H-bond are as follows: H...O 1.96(3) Å, N...O 2.661(4) Å, the N—H...O angle 141(3)° (Fig. 1).

In the ^1H NMR spectra of products **2a—d**, singlet signals of HC= protons at δ 5.95—6.3 and of HN protons at δ 12.7—13.1 were observed.

In the mass spectra of the products, the peak of the phenyl fragment had the maximum intensity. The elimination of the PhCO group is the main direction of decomposition of $M^{\cdot +}$. In the mass spectrum of compound **2c**, an intense peak of the corresponding metastable ion $m^* = 215.5$ was observed; for the process $398^+ \rightarrow 293^+ + 105$, it was calculated that $m^* = 215.70$.

As in the case of compound **2a**,[4] products **2b—d** readily undergo acid hydrolysis with the formation of 1,4-diphenylbutane-1,2,4-trione and the corresponding amines, which is in agreement with the behavior of compounds of this class.[6]

Preliminary experiments demonstrated that the reaction under consideration is typical of a number of other methylarylketones and can be used as a method of dehydroisomerization of these compounds with formation of 1,4-diarylbutane-1,2,4-triones. These results will be published elsewhere.

Experimental

The ^1H NMR spectra were recorded on a Tesla BS-576 instrument (100 MHz) with HMDS as internal standard. The IR spectra were obtained on a UR-20 instrument using KBr pellets; the mass spectra were recorded on an MKh-1310 instrument (direct introduction, electron impact, 70 eV); intensities of peaks are given relative to the maximum peak of Ph^+ (*m/z* 77).

(*Z*)-1,4-Diphenyl-2-(*p*-bromophenylamino)-2-butene-1,4-dione (2c). The yield was 0.6 g (30 %), m.p. 158—159 °C. Found (%): C, 65.05; H, 3.96; N, 3.49. $C_{22}H_{16}BrNO_2$. Calculated (%): C, 65.02; H, 3.94; N, 3.45. IR, ν/cm^{-1}: 1685 (C=O). ^1H NMR ($CDCl_3$), δ: 12.7 (m, 1 H, NH...O=C); 6.1 (s, 1 H, HC=). Mass spectrum, *m/z* (I_{rel} (%)): 405, 407 [M^+] (11); 300, 302 [M^+—PhCO] (77); 155, 157 [BrC_6H_4] (94).

(*Z*)-1,4-Diphenyl-2-[*p*-(*N,N*-diethylamino)phenylamino]-2-butene-1,4-dione (2c). The yield was 1.6 g (78 %), m.p. 112—113 °C. Found (%): C, 78.39; H, 6.43; N, 6.95. $C_{26}H_{26}N_2O_2$. Calculated (%): C, 78.39; H, 6.46; N, 7.04. IR, ν/cm^{-1}: 1700 (C=O). ^1H NMR ($CDCl_3$), δ: 12.75 (m, 1 H, NH...O=C); 5.95 (s, 1 H, HC=). Mass spectrum, *m/z* (I_{rel} (%)): 398 [M^+] (43); 293 [M^+—PhCO] (77); 250 [M^+—$Et_2C_6H_4$] (9).

(*Z*)-1,4-Diphenyl-2-(*N*-methylcarbazol-3-ylamino)-2-butene-1,4-dione (2d). The yield was 1.14 g (60 %), m.p. 190—192 °C. Found (%): C, 81.03; H, 5.19; N, 6.51. $C_{29}H_{22}N_2O_2$. Calculated (%): C, 80.93; H, 5.12; N, 6.51. IR, ν/cm^{-1}: 1700 (C=O). ^1H NMR ($CDCl_3$), δ: 12.75 (m, 1 H, NH...O=C); 6.1 (s, 1 H, HC=). Mass spectrum, *m/z* (I_{rel} (%)): 430 [M^+] (13); 325 [M^+—PhCO] (48); 296 (21); 180 [9-methylcarbazolyl] (57).

X-Ray structural study of compound 2a. $C_{22}H_{17}NO_2$, M = 327.37, monoclinic crystals, a = 5.973(1) Å, b = 13.636(3) Å, c = 21.267(4) Å,[3] space group $P2_1/n$, Z = 4, D_c = 1.259 g cm^{-3}, (Cu-Kα) = 0.641 mm^{-1}, F(000) = 688. The data set was collected on a Syntex $P2_1$ diffractometer with the use of graphite-monochromated Cu-Kα radiation using the θ/2θ scanning technique. Analytical absorption correction was applied. The structure was solved by direct methods and refined with anisotropic and isotropic temperature factors; R = 0.0563 for 1260 independent observed reflections [$|F_0| > 4\sigma|F_0|$], $2\theta < 120°$. Positions of hydrogen atoms were located from the difference Fourier synthesis.

Condensation was performed starting from nitroarene (1 g) and acetophenone (175 g) in the DMSO—KOH system using a procedure similar to that reported previously.[4] Compounds **2c** and **2d** were prepared at 50 °C. The products were recrystallyzed from heptane.

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Reaction of D_2 with palladium fulleride $C_{60}Pd_{4.9}$

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Fullerene deuteride was obtained by the reaction of deuterium with solid palladium fulleride $C_{60}Pd_{4.9}$ under fairly mild conditions. The compound was identified by FD-MS, UV-Vis and IR spectroscopies, and TLC.

Key words: fullerene, fullerene deuteride, palladium fulleride; mass spectrometry; UV-Vis and IR spectroscopies.

Hydrogenation of fullerenes is an important problem from both scientific and practical viewpoints.[1] The direct solid-phase noncatalytic hydrogenation of fullerenes occurs at high hydrogen pressures (500—850 bar) and temperatures (573—623 K).[2]

The preliminary results of the study of the reaction of D_2 with palladium fulleride, resulting in the formation of fullerene deuteride $C_{60}D_x$, are presented in this work.

Palladium fulleride $C_{60}Pd_{4.9}$ was prepared by the reaction of C_{60} with $Pd_2(dba)_3 \cdot CHCl_3$ (dba is dibenzylidene acetone) in toluene by the known procedure.[3] The synthesis of $C_{60}Pd_{4.9}$ is characterized by a specific feature: the molar fraction of Pd in the initial solution is 10-fold higher than that of C_{60}. The precipitate formed was multiply washed with toluene to remove unreacted initial reagents and the dba formed. The precipitate was characterized by chemical analysis and XPS, and its composition corresponds to the formula $C_{60}Pd_{4.9}$. Palladium is homogeneously distributed in the sample, *i.e.*, no clusterization of metal atoms typical of Pd/C catalysts occurs.

The reaction of D_2 with $C_{60}Pd_{4.9}$ in the solid phase was carried out for 2 h at 473—673 K and 20 atm of deuterium pressure. The reaction mixture was cooled to room temperature, then toluene was added, and the brown solution formed was separated from the precipitate by filtration. The filtrate was evaporated to dryness, and a brown residue obtained was dried for several hours *in vacuo* at 373 K.

The reaction product was analyzed by mass spectrometry (field desorption, the current of heating of the emitter was 30 mA) on a MAT-731 mass spectrometer. Unlike the electron impact mode, the mass spectrum of fullerene hydrides in the field desorption mode consists mainly of monocharged molecular ions.[4] The mass spectrum obtained (see Fig. 1) exhibits the peaks corresponding to the products of addition of different numbers of deuterium atoms to a fullerene molecule. The most intense peaks correspond to the addition of 2, 4, 18, and 26 deuterium atoms. In addition, the peaks corresponding to the compounds containing 1, 3, 8, 11, 16, and 33 deuterium atoms are observed. Products with different

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