Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 1992, **2(1)**, 8–10

Mendeleev Communications

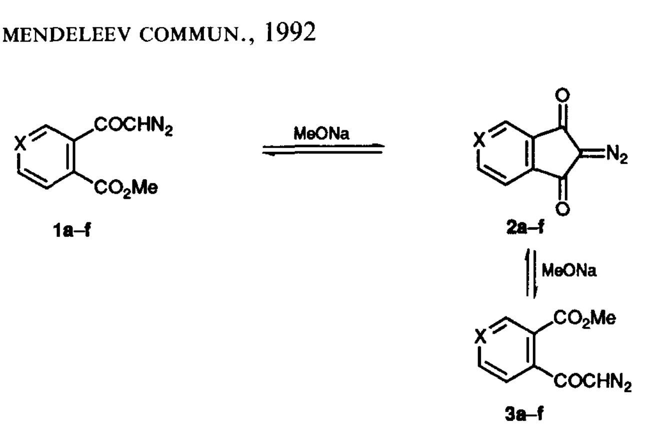
New Rearrangement in the *o*-Methoxycarbonyl-ω-diazoacetophenone Series

Sergei V. Chapyshev and Victor G. Kartsev*

Institute of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russia.
Fax: +7 095 938 2156

Correlation analysis has been used to study a new ring–chain rearrangement in the *o*-methoxycarbonyl-ω-diazoacetophenone series.

For some years we have been investigating the intramolecular reactions of *o*-methoxycarbonyl-ω-diazoacetylquinolines[1] and *o*-methoxycarbonyl-ω-diazoacetylquinolines.[2] We have found that on reaction with sodium methoxide these compounds undergo a previously unknown ring–chain rearrangement, leading to the formation of an equilibrium mixture of isomeric *o*-methoxycarbonyldiazoacetylazines corresponding to the 2-diazo-1,3-dicarbonyl compounds. In this communication, using the series of unsymmetrical *o*-methoxycarbonyl-ω-diazoacetophenones **1a–f**, we have examined both the possibility of a similar ring–chain rearrangement occurring in these compounds and the influence of electronic factors on the ratio of products obtained.



a; $X = COMe$
b; $X = CH$
c; $X = CCl$
d; $X = CCO_2Me$
e; $X = CHO_2$

Scheme 1

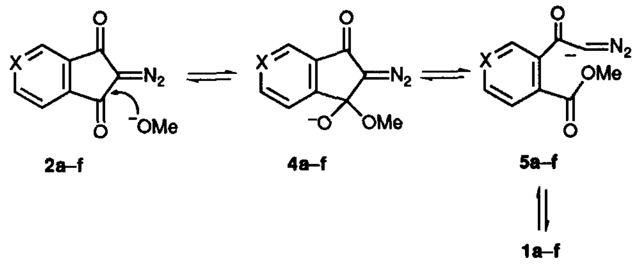
Diazoketones **1a–f** have been prepared by acylation of diazomethane with the acyl chlorides of the appropriate 2-methoxycarbonylbenzoic acids.[3,4] It has been found that on reaction between a 5% solution of MeONa in MeOH and diazoketones **1a–f** an intramolecular rearrangement takes place, leading to the formation of an equilibrium mixture of the starting diazoketones **1a–f** and their isomeric derivatives **3a–f**, and also the 2-diazoindan-1,3-diones **2a–f** (25 °C, 48 h) (Scheme 1). However, in contrast to similar reaction with *o*-methoxycarbonyldiazoacetylazines,[1,2] the main products of the transformation of diazoketones **1a–e** were compounds **2a–e**. The mechanism of the reaction presumably involves initial deprotonation of the diazocarbonyl fragment of diazoketones **1a–f** and intramolecular condensation with the formation of diazoindandiones **2a–f**. Subsequent nucleophilic attack of the methoxide on the carbon atom of one of the carbonyl groups of compounds **2a–f** leads to acyl cleavage and to the formation of an equilibrium mixture of isomeric diazoketones **1a–f** and **3a–f**. Thus, it should be noted that similar equilibrium mixtures were also obtained on reaction with a solution of 5% MeONa on both diazoketones **3a–f** and diazoindandiones **2a–f**.

In order to determine the molar ratio of the rearrangement products in the equilibrium mixture, compounds **1a–f**, **2a–f** and **3a–f** were separated by TLC on Silufol plates, eluted with methanol, and the concentration of the compounds was measured spectrophotometrically using the known molar extinction coefficients.† The ratios of the rearrangement products of diazoketones **1a–f** were also determined from ^1H NMR spectra of the reaction mixture. It has been found that the presence of more strongly electron-donating substituents in the aromatic ring of diazoketones leads to an increase in the molar contents of diazoindandiones **2a–f** in the equilibrium mixture so that the rearrangement is already complete at the stage of formation of the cyclic products.‡

In order to quantify the effect of the substituent on the ratio of the products formed during the rearrangement we used the Jaffé equation,[5] which allows for the electronic effect of a substituent in compounds having two reaction centres [eqn. (1)].

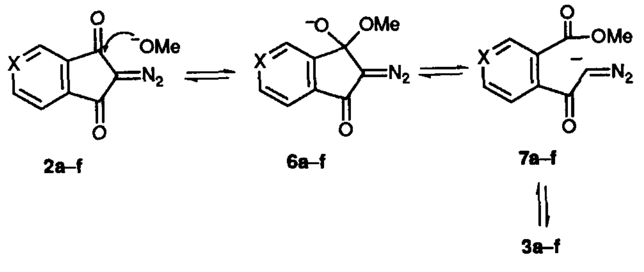
$$\lg K = \rho_p \sigma_p + \rho_m \sigma_m \qquad (1)$$

Using Hammett's σ-values[6] for compounds **2a–e** and the aza-substituent σ-values[7] for compound **2f** ($\sigma_p = 1.105$, $\sigma_m = 0.74$), two equations have been obtained describing the acyl cleavage reactions of compounds **2a–f** to give diazoketones **1a–f** [eqn. (2)] and diazoketones **3a–f** [eqn. (3)], where K_1 and K_2 are the equilibrium constants [**1**]/[**2**] and [**3**]/[**2**], respectively.



$$\lg K_1 = 0.477\sigma_p + 0.919\sigma_m \qquad (2)$$

$$R = 0.954,\ r_{xy} = 0.918,\ r_{xz} = 0.946,\ r_{yz} = 0.919.$$



$$\lg K_2 = 1.235\sigma_p + 0.183\sigma_m \qquad (3)$$

$$R = 0.999,\ r_{xy} = 0.953,\ r_{xz} = 0.946,\ r_{yz} = 0.999.$$

Taking into account the fact that a high magnitude of the ρ-constant indicates a high polarity of the reaction transition state,[6] and on the basis of a comparison of the magnitudes of the ρ_p- and ρ_m-constants in eqns. (2) and (3) [for eqn. (2) the ratio $\rho_m/\rho_p \approx 2$; for eqn. (3) $\rho_p/\rho_m \approx 7$] it may be assumed that the negative charge is preferentially located on the diazocarbonyl fragment of intermediates **5a–f** and **7a–f**. Subtraction of eqn. (3) from eqn. (2) gives eqn. (4), describing the ratio of isomers **3** and **1** during the rearrangement, where K_4 is the equilibrium constant [**3**]/[**1**].

$$\lg K_3 = 0.758\sigma_p - 0.739\sigma_m \qquad (4)$$

It can be seen from eqn. (4) that the greater the difference between the magnitudes of σ_p- and σ_m-values for substituents in the aromatic ring of diazoketones, the greater is the extent to which they may be expected to isomerise.

Received: Moscow, 31st July 1991
Cambridge, 11th October 1991; Com. 1/04126F

---

† All compounds gave satisfactory elemental analyses and were characterized by mass, IR, UV and ^1H NMR spectra. Characteristic data for compounds **1a–f**, **3a–f** and **2f** are given in refs. 1, 3, 4. **2a**: m.p. 120–121 °C; UV (MeOH) λ_{max}/nm (lg ε) 252 (4.29), 260 sh (4.11), 310 (3.91), 323 (3.97); IR ν_{max}/cm^{-1} 2120, 2105 (N_2), 1670 (C=O), 1600 (C=C); ^1H NMR ($CDCl_3$) δ 3.90 (s, 3H, OMe), 7.12–7.64 (m, 3H, C_6H_3). **2b**: m.p. 146–147 °C; UV (MeOH) λ_{max}/cm^{-1} (lg ε) 248 (4.50), 288 (3.70), 310 (3.45), 317 (3.45); IR ν_{max}/cm^{-1} 2130 (N_2), 1680 (C=O), 1590 (C=C); ^1H NMR ($CDCl_3$) δ 7.70–7.78 (m, 3H, C_6H_4). **2c**: m.p. 126–128 °C; UV (MeOH) λ_{max}/cm^{-1} (lg ε) 252 (4.60), 289 (3.87), 308 (3.70), 318 (3.17); ^1H NMR ($CDCl_3$) δ 7.69–7.78 (m, 3H, C_6H_3). **2d**: m.p. 95–96 °C; UV (MeOH) λ_{max}/cm^{-1} (lg ε) 210 (4.37), 251 (4.59), 290 sh (3.83), 308 (3.54), 320 (3.47); IR ν_{max}/cm^{-1} 2125 (N_2), 1725, 1680 (C=O), 1620 (C=C); ^1H NMR ([$^2H_6$]acetone) δ 3.98 (s, 3H, CO_2Me), 7.92–8.40 (m, 3H, C_6H_3). **2e**: m.p. 143–144 °C; UV (MeOH) λ_{max}/cm^{-1} (lg ε) 233 (4.50), 260 (4.47), 294 sh (4.03), 313 (3.81), 320 (3.73); IR ν_{max}/cm^{-1} 2130 (N_2), 1685 (C=O), 1595 (C=C); 1530 (NO_2); ^1H NMR ($CDCl_3$) δ 8.04–8.64 (m, 3H, C_6H_3).

‡ The ratios of the rearrangement products were **1a:2a:3a** 4.5:93.5:2; **1b:2b:3b** 4:92:4; **1c:2c:3c** 10:82:13; **1d:2d:3d** 11:76:13; **1e:2e:3e** 24.5:50:25.5; **1f:2f:3f** 25:32:43. Maximum error ± 1%.

References

1 S. V. Chapyshev and V. G. Kartsev, *Dokl. Akad. Nauk SSSR*, 1983, **272**, 125.
2 S. V. Chapyshev and V. G. Kartsev, *Khim. Geterotsikl. Soedin.*, 1987, 959.
3 S. V. Chapyshev, L. I. Kirkovskii and V. G. Kartsev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 837.
4 S. V. Chapyshev, A. M. Sipyagin and V. G. Kartsev, *Khim. Geterotsikl. Soedin.*, 1983, 1098.
5 H. H. Jaffë, *Chem. Rev.*, 1953, **53**, 191.
6 Yu. A. Zhdanov and V. I. Minkin, *Korrelyatsionnyi analiz v organicheskoi khimii* (Correlation analysis in organic chemistry), Izd. RGU, Rostov, 1966, p. 191 (in Russian).
7 D. M. Dimitrijewič, Z. D. Dadič, M. M. Mašič-Vukovič and M. Muškatirovič, *J. Chem. Soc., Perkin Trans. 2*, 1974, 1051.