intensity) 191 (M^+ + H, 100). Anal. Calcd for $C_7H_{10}O_6$: C, 44.21; H, 5.30. Found: C, 43.99; H, 5.37.

The triacetate of **8** was prepared under standard conditions (Ac_2O/py/room temperature). A sample for elemental analysis was obtained by recrystallization from hexane–ethyl acetate: mp 124–126 °C; ^1H NMR ($CDCl_3$) δ 2.07 (9 H, s), 4.60 (3 H, dd, J = 4.4, 3.0 Hz), 5.37 (3 H, dd, J = 4.4, 3.0 Hz), 5.57 (1 H, s). Anal. Calcd for $C_{13}H_{16}O_9$: C, 49.37; H, 5.10. Found: C, 49.26; H, 5.21.

Bis Ortho Ester Preparation from Monoorthoformate 8. The monoorthoformate **8** (38 mg, 2 mmol) and triethyl orthoacetate (73 L, 4 mmol) were dissolved in 2 mL of THF, and a catalytic amount of *p*-TSH·H_2O was added. The reaction mixture was stirred at room temperature for 5 h, and then 1 mL of 10% aqueous $NaHCO_3$ solution was added. The reaction mixture was evaporated to dryness in vacuo, and the residue was partitioned between CH_2Cl_2 and water. The organic layer was washed with 10% aqueous $NaHCO_3$ solution, water, and brine. The organic layer was dried over Na_2SO_4 and evaporated to dryness, to give the desired bis ortho ester **10** (42.1 mg, 98% yield). A sample for elemental analysis was prepared by recrystallization from hexane–ethyl acetate: mp 177–178 °C; ^1H NMR ($CDCl_3$) δ 1.47 (3 H, s), 4.54 (6 H, s), 5.51 (1 H, s). IR (KBr disk) 2960, 1420, 1400, 1310, 1280, 1180, 1138, 1098, 1045, 958, 870; MS, *m/e* (relative intensity) 215 (M^+ + H, 100). Anal. Calcd for $C_9H_{10}O_6$: C, 50.47; H, 4.71. Found: C, 50.49; H, 4.76.

Bis ortho ester **9**[9] was similarly obtained by treatment with triethyl orthoformate.

Acknowledgment. Financial support from the National Institutes of Health (Grant No. CA22215) is gratefully acknowledged. The Bruker AM300 NMR instrument used in this research was purchased through the NIH instrument Grant No. S10 RR01748 to Harvard University.

Registry No. **2**, 98510-20-4; **2** (triacetate), 98510-21-5; **3**, 98510-22-6; **3** (diacetate), 98510-23-7; **4**, 98510-24-8; **5**, 98510-25-9; **5** (monoacetate), 98510-26-0; **6**, 98510-27-1; **7**, 98575-46-3; **7** (monoacetate), 98575-47-4; **8**, 98575-48-5; **8** (triacetate), 98575-49-6; **9**, 4922-14-9; **10**, 98510-28-2; *myo*-inositol, 87-89-8; triethyl orthoformate, 122-51-0; triethyl orthoacetate, 78-39-7.

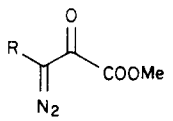
Photolysis of Methyl 3-Diazo-2-oxopropionate. Wolff Migration of the Carbomethoxy Group[1]

Robert R. Gallucci and Maitland Jones, Jr.*

Department of Chemistry, Princeton University, Princeton, New Jersey 08544

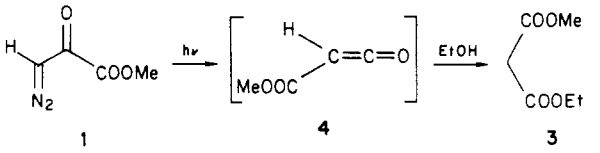
Received March 8, 1985

In 1977 Bien and Segal[2] reported an unusual palladium-catalyzed Wolff rearrangement of ethyl 3-diazo-2-oxopropionate. Here we describe our results on the photolysis of the related methyl ester **1**[3] and of other diazo-2-oxopropionates (**2a**, **2b**).



1, R = H
2a, R = COMe
2b, R = COOMe

Photolysis of a dilute solution of **1** in benzene and a fourfold molar excess of ethanol (relative to **1**) led to a single major product in 37% yield, ethyl methyl malonate (**3**). The clear inference is that Wolff rearrangement to

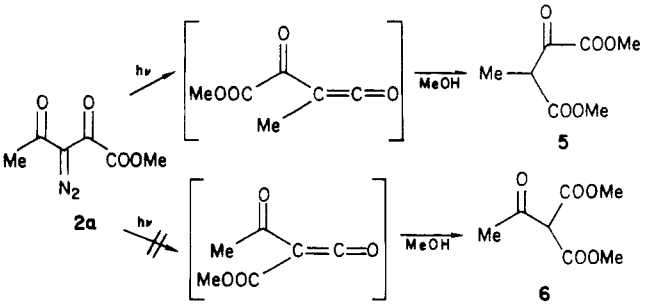


1 **4** **3**

4 was followed by capture of the ketene by alcohol. When the photolysis was carried out in benzene alone, and the excess ethanol added immediately afterwards, the yield of **3** declined to 14%. Thus **3** is not produced by any *direct* reaction of **1** with ethanol. When no alcohol was added, an 8% yield of dimethylmalonate was isolated. The precise source of the required methyl alcohol is obscure, but it must be derived from the carboalkoxy group of **1**.

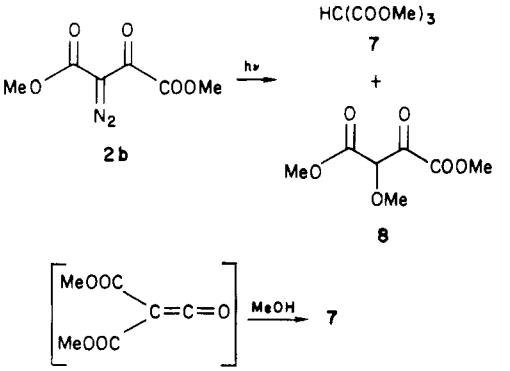
Although an example of ester migration in the Wolff rearrangement was described as early as 1917,[4] the migration remains an unusual one, and the ester group is not well placed on the scale of migratory aptitudes.

We have synthesized diazo esters **2a** and **2b** in order to compare the migratory aptitude of carboalkoxy with a relatively efficient migrating group, methyl, and an inefficient group, methoxy.[5] Irradiation of **2a** in a dilute benzene solution containing a fourfold excess of methanol led to the isolation of a single major product **5**, the product of methyl migration. No trace of **6**, the product of ester migration, was found. Thus methyl migrates to the exclusion of carbomethoxy.



2a **5** **6**

Irradiation of **2b** in a benzene/methanol solution led to three products. The major product, trimethyl methanetricarboxylate (**7**) (83% relative yield), was accompanied by 9% of **8** and 8% of an unidentified product.



2b **8**

(1) Support for this work through grants from the Van't Hoff Fund and the National Science Foundation (MPS 74-05690, CHE-8318345) is gratefully acknowledged.

(2) Bien, S.; Segal, Y. *J. Org. Chem.* **1977**, *42*, 1685.

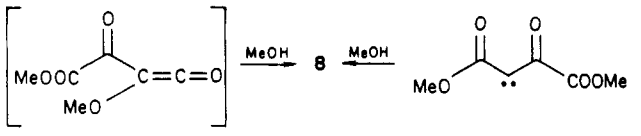
(3) A copper-catalyzed addition reaction of **1** has been previously described by us: Gallucci, R. R.; Jones, M., Jr. *J. Am. Chem. Soc.* **1976**, *98*, 7704.

(4) Staudinger, H.; Hirzel, H. *Chem. Ber.* **1916**, *49*, 2522.

(5) For a comparison of various groups, see: Meier, H.; Zeller, K.-P. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 32. Roedig, A.; Fahr, E.; Aman, H. *Chem. Ber.* **1964**, *97*, 77. Zeller, K.-P.; Meier, H.; Müller, E. *Tetrahedron* **1972**, *28*, 5831. Heyes, G.; Holt, G. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1206. Buu, N. T.; Edward, J. T. *Can. J. Chem.* **1972**, *50*, 3719, 3730.

0022-3263/85/1950-4404$01.50/0

Ester 7 is the ultimate product of ester migration, but the source of 8 is ambiguous. It might be the result of methanolysis of 9, the ketene formed by methoxy migration. However, it is possible that 8 arises by direct insertion of the carbene into the O–H bond of methanol.[6] In either event, migration of the ester is greatly preferred. Thus the order of migratory aptitudes in the Wolff rearrangement is $CH_3 > COOR > OCH_3$.



9

Experimental Section

Proton nuclear magnetic resonance spectra were recorded at 60 MHz with a Varian A-60A spectrometer. All chemical shifts are measured in ppm from Me_4Si (δ). Infrared spectra were taken on a Perkin-Elmer 237-B grating spectrophotometer. Gas chromatographic collections and analyses were performed on a Varian Aerograph A-90P chromatograph with the following columns: (A) 6 ft × $^1/_4$ in., 10% Carbowax 20M on 60/80 mesh Chromosorb P; (B) 6 ft × $^1/_4$ in., 10% DEGS on 60/80 mesh Chromosorb P. Absolute yields determined gas chromatographically are corrected for relative detector response. All photolyses were carried out with a Hanovia 450-W medium-pressure mercury arc shielded with Pyrex filters unless otherwise stated. Samples were cooled to ca. 15 °C. Unless further purification is indicated, material was used as received from the commercial sources.

Preparation of Methyl 3-Diazo-2-oxopropionate (1). The reaction of methyloxalyl chloride with an ether solution of diazomethane has been described elsewhere.[7] A pale yellow powder precipitated from solution and was usually used without further purification. The diazo compound may be recrystallized from CCl_4 [mp 102.5–104 °C (lit.[7] 103–105 °C)]. Yields ranged from 67–73% (lit. 90%): ^1H NMR (C_6D_6) δ 3.28 (s, 3), 5.37 (s, 1).

Photolysis of 1. The diazo compound (0.2 mM) was dissolved in 5 mL of benzene, 80 μL of ethanol was added, and the sample was irradiated for 20 h through a Pyrex filter with a medium-pressure Hanovia lamp. Solvent was removed on a rotary evaporator, and the products were analyzed by gas chromatography using column A at 120 °C. The major compound was identified as ethyl methyl malonate; other minor components were not identified.

In order to test the method of ketene trapping, two photolyses were conducted. In one system in which an internal trap was used, 0.084 g of diazo ester and 0.123 g of ethanol (1:4) were dissolved in 6 mL of dry benzene, and 0.1008 g of tetradecane was added as an internal standard. After 1.25 h of irradiation, the solvent was removed and the sample analyzed on column B at 125 °C. The major product, ethyl methyl malonate, was formed in 37% yield (corrected for relative detector response). In a second photolysis 0.140 g of diazo compound and 0.079 g of tetradecane were dissolved in 10 mL of benzene. The sample was irradiated for 1.25 h. Immediately after photolysis, a large excess of ethanol was added. The corrected yield of ethyl methyl malonate, identified by comparison with an authentic sample, was only 14%.

Methyl 2,4-Dioxo-3-diazopentanoate (2a). A solution of 3.06 g (0.025 M) of methyloxalyl chloride in 30 mL of absolute ether was added dropwise to a solution of 0.063 M diazoacetone[8] in 75 mL of absolute ether at 0 °C and the reaction stirred for 3 h at 0 °C. Solvent was removed on a rotary evaporator, and excess diazoacetone and chloroacetone were removed by distillation [room temperature (~1.0 mmHg)]. The product was distilled twice by using a short-path column, 35 °C (0.03 mmHg), yield 1.62 g (38%). The diazo compound was often contaminated with a small amount of methyl 3-chloro-2,4-dioxopentanoate. *Caution*! Higher temperatures must be avoided since the diazo compound tends to form azine and may explode (~120 °C).[7] ^1H NMR (C_6D_6) δ 3.41 (s, 3), 2.23 (s, 3).

Photolysis of Methyl 2,4-Dioxo-3-diazopentanoate (2a). Diazo compound **2a** (0.27 g, 1.8 mM) was dissolved in 6 mL of benzene, and 300 μL (7.2 mM) of methanol was added. The solution was placed in a Pyrex tube and irradiated for 6 h with a 450-W medium-pressure Hg arc Hanovia lamp. After irradiation, the solvent was removed on a rotary evaporator and the oily residue analyzed by gas chromatography using column A at 128 °C. The only major product was identified by ^1H NMR, mass spectrometry, and IR spectroscopy as methyl 2-oxo-3-methylbutanedioate (**5**): ^1H NMR (CCl_4) δ 4.09 (q, 1, J = 7.0 Hz), 3.87 (s, 3), 3.73 (s, 3), 1.37 (d, 3, J = 7.0 Hz).

Dimethyl 2-Oxo-3-diazobutanedioate (2b). Methyloxalyl chloride (4.67 g, 0.038 M) in 25 mL anhydrous ether was added dropwise to a 100-mL solution of 11.4 g of methyl diazoacetate[9] in ether at 0 °C. The mixture was stirred for 2 h, solvent was removed by rotary evaporation, and the lower boiling components were removed by distillation [room temperature (~1.0 mmH)]. The product, a viscous yellow oil, was distilled twice by using a short-path column, bath temperature 95 °C, still head temperature 80 °C (0.2 mmHg; lower pressure would have been much better, and safer). The NMR spectrum often showed small amounts of an impurity which arose from HCl addition to the diazo compound:[10] ^1H NMR (CCl_4) δ 3.9 (2 s, separation 2 Hz).

Photolysis of Dimethyl 2-Oxo-3-diazobutanedioate (2b). Diazo compound **2b** (0.56 g, 0.003 M) was dissolved in 4 mL of benzene and 0.50 mL (0.012) of methanol. The sample was placed in a Pyrex tube and irradiated in a water-cooled bath with a Hanovia lamp for 4 h. After irradiation, the solvent was removed by rotary evaporation and the residue analyzed by gas chromatography on column A at 130 °C. Three major products were isolated. The first component off the gas chromatograph was identified by ^1H NMR, mass spectrometry, and IR spectroscopy as dimethyl 2-oxo-3-methoxybutanedioate (**8**), the second component was tricarbomethoxymethane (**7**),[12] and the third component was not identified. Relative yields were 9.3%, 82.8%, and 7.9%, respectively: ^1H NMR (**8**, CCl_4) δ 4.32 (s, 1), 3.79 (s, 6), 3.48 (s, 3); (**7**, CCl_4) δ 4.50 (s, 1), 3.81 (s, 9).

Irradiation of a more dilute sample of the diazo compound (0.125 M vs. 0.75 M) resulted in the same set of products; however, the relative amount of the third peak was reduced. Irradiation of a sample of diazo compound in the absence of a trapping reagent gave dimethyl malonate.

Registry No. **1**, 56023-96-2; **2a**, 98268-20-3; **2b**, 17094-36-9; **5**, 63921-06-2; **7**, 1186-73-8; **8**, 36797-93-0; methyloxalyl chloride, 5781-53-3; ethyl methyl malonate, 6186-89-6; diazoacetone, 2684-62-0; methyl diazoacetate, 6832-16-2.

(6) Kirmse, W.; Loosen, K.; Sluma, H.-D. *J. Am. Chem. Soc.* **1981**, *103*, 5935.

(7) Eistert, B.; Regitz, M.; Heck, G.; Schwall, H. "Methoden der Organische Chemie (Houben–Weyl)"; Georg Thieme Verlag: Stuttgart, 1968; Vol I, Band 10/4, pp 589–598.

(8) Arndt, F.; Amende, J. *Chem. Ber.* **1928**, *61*, 1122.

(9) Searle, N. E. "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. IV, p 424.

(10) A much easier synthesis of dimethyl 2-oxo-3-diazobutanedioate should be available through the reaction of dimethyl oxalacetate and a tosylazide exchange reagent.[11]

(11) Hendrickson, J. B.; Wolf, W. A. *J. Org. Chem.* **1968**, *33*, 3610.

(12) Corson, B. B.; Sayre, J. L. Organic Syntheses"; New York, Collect. Vol. II, p 596.