

Homogeneous Catalysis of the Decomposition of Dimethyl Diazomalonate in Alcohols

By Roberto Pellicciari * and Pietro Cogolli, Istituto di Chimica Farmaceutica e Tossicologica dell'Università, Perugia, Italy

Decomposition of dimethyl diazomalonate in alcohols catalysed by trimethyl phosphite-copper(I) iodide leads to dimethyl alkoxy-malonates.

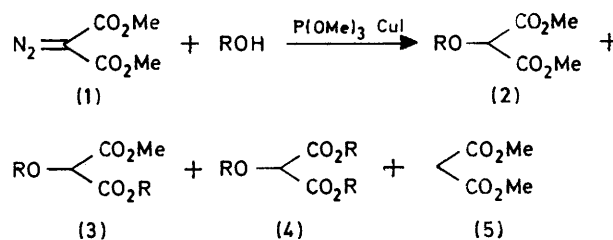
We have previously¹ reported the synthesis of diethyl ethoxymalonate by decomposition of diethyl diazomalonate in the presence of the homogeneous trimethyl phosphite-copper(I) iodide catalyst in ethanol. Since diazomalonate esters are now readily accessible *via* the diazo transfer reaction,² this procedure could be usefully employed for the introduction of an ether function into malonic esters under mild, neutral conditions. Alkoxy-esters of the general structure $RO \cdot C(CO_2R')_2$ are otherwise not readily accessible.³ We have carried out this reaction in a number of representative alcohols, following the procedure previously described,¹ *i.e.* dropwise addition of dimethyl diazomalonate (1) to a stirred solution of the catalyst in the alcohol. Once the evolution of nitrogen had ceased, the excess of alcohol was evaporated off and the oily residue analysed by g.l.c. The results are summarized in Table 1.

Only the decomposition of the diazo-ester (1) in methanol gave the corresponding dimethyl alkoxy-malonate (2a) in high yield. With the other alcohols, the major products were those arising from either partial or complete ester interchange. We were thus unable to isolate the pure alkoxy-malonates (2b—d) from the respective reaction mixtures. These products, however, were obtained pure by a reverse transesterification, achieved by refluxing the crude product in an excess of methanol in the presence of a catalytic amount of toluene-*p*-sulphonic acid. Analytical and n.m.r. data

for the dimethyl alkoxy-malonates (2a—f) are given in Table 2.

Dimethyl malonate (5) was another, unexpected by-product of the reaction of the diazo-ester (1) with

TABLE 1



| R | Yields (%) ^a | | | | Reaction time temp. | |
|----------------------|-------------------------|-----|-----|-----|---------------------|------|
| | (2) | (3) | (4) | (5) | (h) | (°C) |
| a; Me | 80 (77) ^b | | | | 15 | 50 |
| b; Et | — (65) ^c | 14 | 55 | 8 | 16 | 50 |
| c; Pr ⁿ | 11 (60) ^d | 20 | 34 | 13 | 42 | 100 |
| d; Pr ⁱ | 23 (45) ^e | 25 | | 18 | 30 | 70 |
| e; Bu ^t | 30 (23) ^b | 10 | | 8 | 24 | 75 |
| f; PhCH ₃ | 43 (40) ^b | 17 | | 10 | 22 | 100 |

^a The figures refer to product distribution determined by g.l.c. analysis of the oily residue from the reaction mixture. ^b Obtained by fractional distillation at reduced pressure of the oily residue from the reaction mixture. ^c Obtained by fractional distillation at reduced pressure of the oily residue from the transesterification reaction. ^d Obtained by silica gel column chromatography (eluant 90 : 10 hexane-diethyl ether) of the oily residue from the transesterification reaction.

alcohols. Hydrogen abstraction from the solvent has been observed in the benzophenone-sensitized photolysis⁴ and in the diethyl peroxodicarbonate-promoted

⁴ (a) A. P. Padwa and R. Layton, *Tetrahedron Letters*, 1965, 2167; (b) S. Julia, H. Ledon, and G. Linstrumentelle, *Compt. rend.*, 1971, 272, 1898.

¹ R. Pellicciari and P. Cogolli, *Synthesis*, 1975, 269.

² M. Regitz, *Angew. Chem. Internat. Edn.*, 1967, 6, 733.

³ (a) W. Wislicenus and M. Munzsheimer, *Chem. Ber.*, 1898, 31, 552; (b) J. Pride and R. T. Williams, *J. Chem. Soc.*, 1933, 1627; (c) J. A. Vida, C. M. Samour, M. H. O'Dea, T. S. Wang, and J. F. Reinhard, *J. Medicin. Chem.*, 1974, 17, 1.

TABLE 2
Analytical and spectral data ^a

| Compd. | B.p. (°C) [mmHg] | $\delta(\text{CCl}_4)$ | Found (%) | | Formula | Required (%) | |
|--------|---------------------|--|-----------|------|--|--------------|------|
| | | | C | H | | C | H |
| (2a) | 76 [1.5] | 3.41 (3 H, s), 3.74 (6 H, s), 4.31 (1 H, s) | 44.2 | 6.1 | C ₆ H ₁₀ O ₅ | 44.45 | 6.2 |
| (2b) | 78 [0.7] | 1.25 (3 H, s), 3.50 (2 H, q), 3.67 (6 H, s), 4.30 (1 H, s) | 47.55 | 6.65 | C ₇ H ₁₂ O ₅ | 47.7 | 6.85 |
| (2c) | 80 [0.2] | 0.90 (3 H, t), 1.57 (2 H, m), 3.43 (2 H, t), 3.67 (6 H, s), 4.30 (1 H, s) | 50.4 | 7.1 | C ₈ H ₁₄ O ₅ | 50.5 | 7.4 |
| (2d) | 52 [0.06] | 1.17 (6 H, d), 3.70 (6 H, s), 3.80 (1 H, m), 4.33 (1 H, s) | 50.2 | 7.35 | C ₈ H ₁₄ O ₅ | 50.5 | 7.4 |
| (2e) | 90 [1.0] | 1.22 (9 H, s), 3.45 (3 H, s), 3.75 (3 H, s), 4.50 (1 H, s) | 52.85 | 7.95 | C ₉ H ₁₆ O ₅ | 52.95 | 7.9 |
| (2f) | 112 [0.08] | 3.67 (6 H, s), 4.22 (1 H, s), 4.40 (2 H, s), 7.23 (5 H, s) | 60.2 | 5.75 | C ₁₂ H ₁₄ O ₅ | 60.5 | 5.9 |

decomposition ⁵ of diazocarbonyl compounds, but this is the first example of this process in a catalysed decomposition reaction. Wolff rearrangement products, often formed by photolysis of diazocarbonyl compounds,⁶ were not observed in the present case.

EXPERIMENTAL

G.l.c. analyses were carried out with a Fractovap G 1 (Carlo Erba) chromatograph (6 ft column packed with Carbowax 20 M). Yields determined by g.l.c. were not corrected for thermal conductivities. N.m.r. spectra were recorded with a JEOL INM-C-60 HL spectrometer for solutions in carbon tetrachloride (internal tetramethylsilane as standard).

Dimethyl diazomalonate was prepared by treatment of a solution of dimethyl malonate and tosyl azide with triethylamine.² The trimethyl phosphite-copper(I) iodide complex was prepared as described.⁷ Reagent grade alcohols were employed. Column chromatography was performed with Merck silica gel (0.063–0.200 mm).

⁵ L. Horner and H. Schwarz, *Annalen*, 1971, **747**, 1.

⁶ W. Kirmse, 'Carbene Chemistry,' 2nd edn., Academic Press, New York, 1971, pp. 475 *et seq.*

Reactions of Dimethyl Diazomalonate with Alcohols.—To a solution of trimethyl phosphite-copper(I) iodide catalyst (0.6 mmol) in a large excess of the alcohol, a solution of dimethyl diazomalonate in the same alcohol was added from a dropping funnel at 5 drops per min, with stirring, at the temperature indicated in Table 1. The mixture was then maintained at constant temperature until evolution of nitrogen ceased, and filtered. The excess of alcohol was removed by use of a water aspirator and the oily residue was further purified (see Table 1).

Transesterification.—In a typical procedure, the oily residue (1.8 g) obtained by removal of the excess of alcohol from the product of the reaction of diethyl diazomalonate (1) with ethyl alcohol was refluxed at 65 °C for 6 h in methyl alcohol (50 ml) in the presence of toluene-*p*-sulphonic acid (0.1 g). The excess of methyl alcohol was then evaporated off (water pump) and the oily residue further purified by distillation at reduced pressure. Further experimental details are given in Tables 1 and 2.

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⁷ B. W. Peace, F. Carman, and D. S. Wulfman, *Synthesis*, 1973, 658.