Dependence of Product on Catalyst in the Transition-metal-catalysed Decomposition of Ethyl 2-Allyl-4-diazoacetoacetate
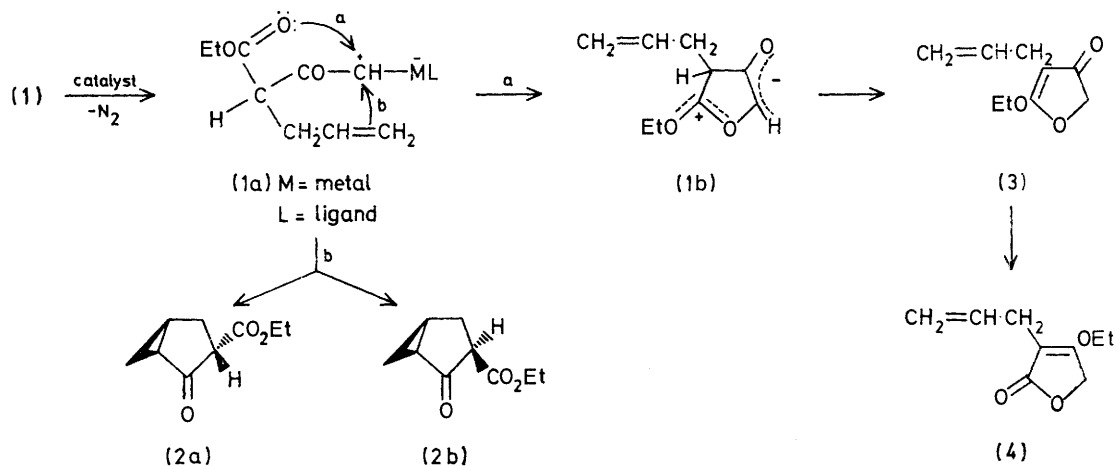
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Competitive formation of the epimeric ethyl 2-oxobicyclo[3.1.0]hexane-3-carboxylates (2a and b) and 4-allyl-5-ethoxyfuran-3(2*H*)-one (3) in the thermal decomposition of ethyl 2-allyl-4-diazoacetoacetate has been observed. The decomposition could be controlled by use of transition metal catalysts: highly selective formation of (2) or (3) could be achieved by appropriate choice of catalyst.

RECENTLY we described the copper-induced formation of the furan-3(2*H*)-one system from monosubstituted 4-diazoacetoacetates, both under homogeneous and under heterogeneous conditions.[1] The reaction represents a rarely observed [2,3] pathway in the catalytic

(1a) M = metal
L = ligand

(2a)   (2b)

(1b)   (3)

(4)

decomposition of α-diazo-ketones involving intermediate carbonyl ylide formation from an electrophilic oxocarbenoid species and a carbonyl group oxygen atom. A successful isolation of such a carbonyl ylide has been reported recently.[4]

Although copper derivatives are some of the most efficient catalysts, there is increasing interest in the use of other transition metal compounds.[5-12] Recent publications have pointed to the differences in activity of various of these catalysts, *e.g.* in cyclopropane formation from olefins,[9,13] in insertion of a carbenoid species into O–H bonds,[10] and in oxazole formation from α-diazo-carbonyl compounds and nitriles.[12]

In our search for evidence of the product-determining role of the catalyst, we have investigated the catalytic decomposition of ethyl 2-allyl-4-diazoacetoacetate (1).

In this compound the olefinic double bond and the ester carbonyl group compete for the intermediate α-oxo-carbenoid species (1a), and production of the bicyclohexanone (2) and/or the furan-3(2*H*)-one (3) is expected.

The decomposition of (1) was effected by use of the various transition metal catalysts listed in the Table. Each reaction mixture, after filtration and removal of

Distribution (%) of compounds (2) and (3) from the decomposition of the diazo-ketone (1) with various catalysts [a,b]

Catalyst	Temp. (°C)	(2)	(3)
$Pd_2Cl_2(C_3H_5)_2$	Room	53	3
$Pd(OAc)_2$	Room	53	<1
$Pd(PhCO \cdot CH \cdot COMe)_2$	80	54	<1
$Cu(PhCO \cdot CH \cdot COMe)_2$	80	50	13
$(EtO)_3PCuCl$	Room	3	32
$(MeO)_3PCuI$	Room	3	35
$Rh_2(OAc)_4$	Room	1	58
None	80	15	54

[a] Yields are based on the crude diazo-ketone (1). [b] Some variation in product distribution was observed in repeated runs and the figures are representative yields showing the trend in the catalytic action.

the solvent, was distilled rapidly, and yielded approximately the same amount of distillable product (*ca.*

[1] S. Bien and A. Gillon, *Tetrahedron Letters,* 1974, 3073.

[2] M. S. Kharasch, T. Rudy, W. Nudenberg, and G. Buchi, *J. Org. Chem.,* 1953, **18**, 1030.

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[9] R. Paulissen, A. J. Hubert, and Ph. Teyssie, *Tetrahedron Letters,* 1972, 1465.

[10] R. Paulissen, H. Reimlinger, E. Hayez, A. J. Hubert, and Ph. Teyssie, *Tetrahedron Letters,* 1973, 2233.

[11] R. Paulissen, E. Hayez, A. J. Hubert, and Ph. Teyssie, *Tetrahedron Letters,* 1974, 607.

[12] K. Kitatani, T. Hiyama, and H. Nozaki, *Tetrahedron Letters,* 1974, 1531.

[13] S. Bien and D. Ovadia, *J. Org. Chem.,* 1970, **35**, 1028; *J.C.S. Perkin I,* 1974, 333.

75—80%), except in the decompositions with the copper–phosphite complexes, which produced only 50—60% of volatile material. The higher-proportion of pot residue obtained in repeated runs of the copper(I)-complex-catalysed decomposition indicates a higher degree polymerization under the influence of these catalysts as compared with the others. The product distribution in the distillates (see Table) was determined by g.l.c. from retention times and coinjections with authentic samples, isolated by column chromatography from a bis(chloro-π-allylpalladium)-catalysed reaction.*

The data clearly reflect control of product distribution by the catalyst: cyclopropane formation was induced with high selectivity by palladium catalysts of various types, but was almost completely suppressed with rhodium acetate and with copper(I)–phosphite complexes. These last two catalysts, on the other hand, led to selective formation of the dihydrofuranone.†

No satisfactory explanation has yet been given for the metal-catalysed decomposition of diazo-carbonyl compounds. The model originally postulated by Skell,[14] suggesting primary co-ordination of the diazo-compound or the derived carbene to the metal is now generally accepted [see (1a)]. Experimental evidence has been accumulated [15-18] indicating participation of the metal ion, the diazo-compound, and the substrate in the transition state of the reaction.

In our case the thermal decomposition data show that the developing carbene reacts preferentially with the carbonyl oxygen atom rather than the allylic double bond. Presumably the intermediate carbonyl ylide (1b) is not only resonance-stabilized but its formation is sterically favoured, in comparison with the necessarily more strained transition state involved in cyclopropane ring formation.

The product distribution data from the catalysed reactions, compared with those for the thermal reactions, suggest that the decomposition is indeed co-ordination-controlled and thus would be influenced by the nature of the metal and/or the steric demands of the catalyst.

In this work we have tried to evaluate the influence of some steric properties of the catalysts. The results obtained with bis(benzoylacetonato)-palladium and -copper, which are identical in ligand and stereochemistry but differ in the metal component, suggest that the steric requirements of these catalysts have some influence on product. This argument, however, cannot be used in a general way. A high, but different

* In each distillate compounds (2) and (3) were accompanied by ethyl 2-(chloroacetyl)pent-4-enoate (5) and ethyl methyl allylmalonate (6), isolated in small quantities and identified by spectral data.

$$CH_2{:}CH{\cdot}CH_2{\cdot}CH(CO_2Et){\cdot}CO{\cdot}CH_2Cl$$
(5)
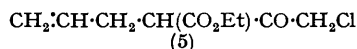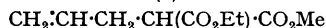
$$CH_2{:}CH{\cdot}CH_2{\cdot}CH(CO_2Et){\cdot}CO_2Me$$
(6)

† This conclusion is not a generalization but is strictly relevant only to the decomposition of the diazo-ketone (1), and presumably to other structurally similar 4-diazoacetoacetates.

[14] P. S. Skell and R. M. Etter, *Chem. and Ind.*, 1958, 624; *Proc. Chem. Soc.*, 1961, 443.

selectivity was observed with rhodium and palladium acetates, both of which are known to have a similar acetate-bridged crystal structure [19,20] and an approximately square-planar co-ordination at the metal atom. For our discussion, however, it may be meaningful, that, in contrast to the dimeric structure of the rhodium acetate $[Rh(OAc)_2]_2$, containing an Rh–Rh bond, a recent X-ray investigation [20] of palladium acetate has shown a trimeric crystal structure, $([Pd(OAc)_2]_3)$ with no metal–metal bonding. This structure is retained in benzene solution at ambient temperature.[21] Even so, it is not to be expected that the resulting difference in steric crowding of the acetate bridges around the metal in the two catalysts would be large enough to reverse completely the selectivity in the carbenoid–substrate interaction.

Alternatively, an initial catalyst–olefin co-ordination, prior to carbenoid formation, can be considered to be preferred for the palladium catalysts. Pd^{II}–olefin complexation is well established, but Rh^{II}–olefin complexes are rare and unstable.[22]

It is clear that further studies are necessary to elucidate the nature of the diazo-ketone–catalyst interaction and the influences of the electronic and steric properties of the catalysts on the course of the decomposition.

EXPERIMENTAL

I.r. spectra were determined for solutions in chloroform unless otherwise stated, with a Perkin-Elmer Infracord spectrophotometer. N.m.r. spectra were recorded on either a Varian A-60 or a Varian T-60 spectrometer for solutions in $CDCl_3$ unless otherwise stated, with Me_4Si as internal reference. G.l.c., unless otherwise specified, was carried out on a Varian Aerograph 90-P gas chromatograph [¼ in × 6 ft column packed with 3% SE-30 on GasChrom Q(100—120 mesh) (column A) or 3/8 in × 6 ft column of 3% SE-30 on 60—80 mesh Chromosorb W (column B)]. Molecular weights were determined with a Varian MAT 711 high-resolution mass spectrometer.

Ethyl 2-Allyl-4-diazoacetoacetate (1).—A cooled solution of potassium hydroxide (7.8 g, 0.14 mol) in anhydrous ethanol (100 ml) was added to diethyl allylmalonate (28 g, 0.14 mol) in anhydrous ethanol (150 ml) and the mixture was kept at room temperature overnight. The ethanol was then removed (water pump), water was added, and the cooled solution was washed twice with ether in order to recover starting material. The aqueous layer was then acidified with cold 10% hydrochloric acid and extracted several times with ether. From the combined, dried (Na_2SO_4) extracts the oily monoacid was isolated (21.2 g,

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[18] R. G. Salomon and J. K. Kochi, *J. Amer. Chem. Soc.*, 1973, **95**, 3300.

[19] M. J. Bennett, K. G. Caulton, and F. A. Cotton, *Inorg. Chem.*, 1969, **8**, 1.

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[21] T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, and G. Wilkinson, *J. Chem. Soc.*, 1965, 3632.

[22] S. E. Livingstone in 'Comprehensive Inorganic Chemistry,' ed. E. F. Trotman-Dickenson *et al.*, Pergamon, Oxford and New York, 1973, vol. 3, p. 1245.

88%); $\nu_{max.}$ 1 730 (C=O) and 3 000—3 600 cm^{-1} (OH); δ 1.29 (3 H, t, CO$_2$CH$_2$·CH$_3$), 2.65 (2 H, m, CH$_2$·CH), 3.48 (1 H, t, CH$_2$·CH), 4.22 (2 H, q, CO$_2$CH$_2$·CH$_3$), 4.90—5.33 (2 H, m, CH$_2$=CH), 5.48—6.19 (1 H, m, CH$_2$=CH), and 8.05 (1 H, s, CO$_2$H).

To a stirred and ice-cooled mixture of the monoacid (21 g, 0.12 mol), dry benzene (100 ml), and anhydrous pyridine (1 ml) a solution of freshly distilled oxalyl chloride (26 ml, 0.3 mol) in dry benzene (50 ml) was added dropwise. The ice-bath was then removed and the mixture was slowly heated to 40 °C, kept at this temperature for 2 h, and then kept at 60 °C for an additional 2 h. The excess of oxalyl chloride and benzene were removed under reduced pressure and the residue was washed several times with dry ether. From the combined ethereal extracts the pure acid chloride was isolated by distillation at 50—54° and 0.2 mmHg (17.5 g, 75%), $\nu_{max.}$ (CCl$_4$) 1 749 and 1 806 cm^{-1}; δ (CCl$_4$) 1.32 (3 H, t, CO$_2$CH$_2$·CH$_3$), 2.69 (2 H, m, CH$_2$·CH), 3.76 (1 H, t, CH$_2$·CH), 4.25 (2 H, q, CO$_2$CH$_2$·CH$_3$), 4.95—5.38 (2 H, m, CH$_2$=CH), and 5.47—6.18 (1 H, m, CH$_2$=CH).

A solution of the acid chloride (17.2 g, 90.3 mmol) in dry ether (ca. 500 ml) was added dropwise with swirling to ice-cold ethereal diazomethane [from nitrosomethylurea (54 g) and aqueous 40% potassium hydroxide (200 ml) in ether (500 ml)]. After 2 h, the solution was filtered and the solvent was removed under reduced pressure to give crude, oily diazo-ketone (1) (17 g) [contaminated with ca. 10% chloro-ketone (5)], $\nu_{max.}$ 1 645, 1 730, and 2 100 cm^{-1}; δ 1.30 (3 H, t, CO$_2$CH$_2$·CH$_3$), 2.47 (2 H, m, CH$_2$·CH), 3.43 (1 H, t, CH$_2$·CH), 4.23 (2 H, q, CO$_2$CH$_2$·CH$_3$), 4.90—5.33 (2 H, m, CH$_2$=CH), 5.53 (1 H, s, CO·CHN$_2$), and 5.47—6.20 (1 H, m, CH$_2$=CH).

The oily diazo-ketone was characterized by conversion into the hydrazonotriphenylphosphine derivative. Mixing the diazo-ketone (1) (1.0 g, 5.1 mmol) with triphenylphosphine (1.34 g, 5.1 mmol) in dry ether (5 ml) gave a crystalline precipitate (1.45 g), which was purified by trituration with dry ether to yield the *hydrazonotriphenylphosphine*, m.p. 92—93° (decomp.) (Found: C, 70.2; H, 5.8; N, 6.1. C$_{27}$H$_{27}$N$_2$O$_3$P requires C, 70.7; H, 5.9; N, 6.1%).

Decomposition of the Diazo-ketone (1) *with Bis(chloro-π-allylpalladium)*.—A cold solution of crude diazo-ketone (1) (7.0 g, 35.7 mmol) in dry benzene (400 ml) was added dropwise during ca. 5 h to a stirred solution of the π-allylic palladium complex (0.13 g, 0.37 mmol) in benzene (1 100 ml) at 5 °C. Stirring was then continued overnight at room temperature. Complete decomposition of the diazo-ketone was shown by the disappearance of the i.r. band at 2 110 cm^{-1}. The solution was filtered and concentrated and the residue (6.1 g) was distilled; the fraction boiling at 60—70° and 0.05 mmHg was collected (4.6 g). Chromatography on Florisil (60—100 mesh; 230 g) [column prepared in light petroleum (b.p. 60—70°)] gave the chloro-ketone (5) [eluted with light petroleum (b.p. 60—70°)–benzene (1 : 1)] (0.65 g) and small amounts of the diester (6) [eluted with light petroleum–benzene (4 : 6)]. Benzene eluted a mixture of the isomers bicyclohexanone (2a and b) (3.15 g), and the furanone (3) (0.4 g) was obtained by elution with benzene–chloroform (3 : 7).* Some mixed fractions were obtained with eluants of intermediate polarity.

Ethyl 2-*(chloroacetyl)pent*-4-*enoate* (5) was obtained by g.l.c. on column A at 155 °C (helium flow rate 80 ml min^{-1},

t_R 2.2 min) (Found: C, 53.4; H, 6.8; Cl, 17.0. C$_9$H$_{13}$ClO$_3$ requires C, 52.9; H, 6.4; Cl, 17.15%); $\nu_{max.}$ 1 728 cm^{-1} (C=O); δ 1.27 (3 H, t, CO$_2$CH$_2$·CH$_3$), 2.64 (2 H, t, with further allylic splitting, J 7 and 1.5 Hz, CH$_2$=CH·CH$_2$), 3.86 (1 H, t, CO·CH·CO$_2$Et), 4.23 (2 H, q, CO$_2$CH$_2$·CH$_3$), 4.26 (2 H, s, CO·CH$_2$Cl), 4.85—5.32 (2 H, m, CH$_2$=CH), and 5.48—6.18 (1 H, m, CH$_2$=CH).

Ethyl methyl allylmalonate (6) was purified by g.l.c. on column A at 140 °C (helium flow rate 92 ml min^{-1}, t_R 1.5 min); insufficient was obtained for analysis. The diester showed $\nu_{max.}$ 1 735 cm^{-1}; δ 1.25 (3 H, t, CO$_2$CH$_2$·CH$_3$), 2.74 (2 H, q, CH$_2$=CH·CH$_2$), 3.45 (1 H, t, MeO$_2$C·CH·CO$_2$Et), 3.77 (3 H, s, CO$_2$Me), 4.20 (2 H, q, CO$_2$CH$_2$·CH$_3$), 4.90—5.33 (2 H, m, CH$_2$=CH), and 5.46—6.22 (1 H, m, CH$_2$=CH); M^+ 186.

Bulb-to-bulb distillation of a sample of the major fraction from the column chromatography, at 85 °C (bath temp.) and 0.03 mmHg, gave *ethyl* 2-*oxobicyclo*[3.1.0]*hexane*-3-*carboxylate* as a mixture of stereoisomers (2a and b) (Found: C, 64.2; H, 7.3. C$_9$H$_{12}$O$_3$ requires C, 64.3; H, 7.2%); $\nu_{max.}$ 1 718 (ketone C=O) and 1 740 cm^{-1} (ester C=O); δ 0.82—1.50 (5 H, m overlapped by t, cyclopropyl CH$_2$ and CO·CH$_2$·CH$_3$), 1.71—2.94 (4 H, m, cyclopropyl protons and ring CH$_2$), 3.19 (1 H, t, CO·CH·CO$_2$Et), and 4.21—4.24 (2 H, q, CO$_2$CH$_2$·CH$_3$); M^+ 168. The mixture (2a and b) was analysed by g.l.c. on a Packard Gas Chromatograph (1/8 in × 5 ft column packed with 15% DEGS on 60—80 mesh Chromosorb W; column temperature 150 °C; nitrogen rate 50 ml min^{-1}). Two peaks with relative areas 30 : 70 and retention times 14.0 and 16.6 min, respectively, were observed. On the basis of our previous work on decomposition of similar allyl- and but-3-enyl-substituted diazo-ketones,[13] the structures (2a and b) are suggested for the major and the minor isomer, respectively.

The last fraction from the column chromatography was further purified by preparative g.l.c. on column B at 170 °C yielding 4-*allyl*-5-*ethoxyfuran*-3(2H)-*one* (3). Sample collected from g.l.c. on column A at 155 °C (helium flow rate 80 ml min^{-1}, t_R 3.5 min) (Found: M^+, 168.0790. C$_9$H$_{12}$O$_3$ requires M, 168.0786) showed $\nu_{max.}$ 1 594 and 1 690 cm^{-1}; δ 1.43 (3 H, t, CH$_3$·CH$_2$·O), 2.85 (2 H, m, CH$_2$=CH·CH$_2$), 4.48 (2 H, q, CH$_3$·CH$_2$·O), 4.59 (2 H, s, CO·CH$_2$·O), 4.85—5.27 (2 H, m, CH$_2$=CH), and 5.55—6.25 (1 H, m, CH$_2$=CH).

Decomposition of the Diazo-ketone (1) *with Other Organometallic Catalysts*.—For the decomposition of diazo-ketone (1) (2.5 g, 12.7 mmol) the following amounts of the various catalysts were used: Rh$_2$(OAc)$_4$, 20 mg, 0.045 mmol; Pd(OAc)$_2$, 10 mg, 0.049 mmol; (MeO)$_3$PCuI, 100 mg, 0.318 mmol; (EtO)$_3$PCuCl, 85 mg, 0.32 mmol; Cu-(PhCO·CH·COMe)$_2$, 163 mg, 0.42 mmol; Pd(PhCO·CH·COMe)$_2$, 181 mg, 0.42 mmol. The freshly prepared diazo-ketone (1) in dry benzene (100 ml) was added dropwise during ca. 3 h to a stirred suspension or solution of the catalyst in dry benzene (100 ml) at room temperature or at 80 °C (see Table). The mixture was then stirred overnight at room temperature or at 80 °C and complete decomposition of the diazo-ketone was evidenced by the disappearance of the i.r. band at 2 110 cm^{-1}. After filtration, the solvent was evaporated off and the oily residue was distilled † to give a reddish oil, collected at 80—100° and 0.15 mmHg. G.l.c. analysis of this oil was carried out on

* In parallel experiments the furanone (3) was isolated in yields of 0.1—0.4 g.

† The distillation should be fast at a temperature as low as possible in order to avoid conversion of (3) into (4). Details of this and similar reactions will be published elsewhere.

column A at 155 °C (helium flow rate 80 ml min⁻¹. Yields of compounds (2) and (3) are summarized in the Table (calculated from integration of the peaks with t_R 2.9 and 3.5 min, respectively).

Thermal Decomposition of the Diazo-ketone (1).—A solution of the diazo-ketone (1) (0.25 g) in dry benzene (40 ml) was heated under reflux. Decomposition, monitored by i.r. spectroscopy, was complete after 10 days. The solvent was removed under reduced pressure and the residual red oil was analysed by g.l.c. on column A.

3-*Allyl*-4-*ethoxyfuran*-2(5H)-*one* (4).—(*a*) The diazo-ketone (1) (2.3 g) was decomposed with (EtO)₃PCuCl as catalyst as described above. After filtration and evaporation the residual oil (*ca.* 2.1 g) was subjected to slow, bulb-to-bulb distillation at 110—140° and 0.3 mmHg to yield a mixture of the dihydrofuranone (3) (0.1 g) and the lactone (4) (0.85 g). The *lactone* (4) was separated by preparative g.l.c. on column B at 170 °C. A sample collected by g.l.c. on column A at 175 °C (helium flow rate 60 ml min⁻¹, t_R 2.5 min) (Found: M^+, 168.0795. $C_9H_{12}O_3$ requires M, 168.0786) had $\nu_{max.}$ 1 668 and 1 760 cm⁻¹; δ 1.41 (3 H, t, $CH_3\cdot CH_2\cdot O$), 3.04 (2 H, m, $CH_2{=}CH\cdot CH_2$), 4.26 (2 H, q, $CH_3\cdot CH_2\cdot O$), 4.68 (2 H, s, $CH_2\cdot O\cdot CO$), 4.87—5.31 (2 H, m, $CH_2{=}CH$), and 5.61—6.34 (1 H, m, $CH_2{=}CH$).

(*b*) The dihydrofuranone (3) was converted into the lactone (4) by heating in an oil-bath. Conversion was monitored by n.m.r. spectroscopy. Heating at 120 °C for 2 h resulted in a mixture of compounds (3) and (4), and after additional heating at 130—160 °C for 1 h the spectrum showed the presence of impure (4) only but no starting material.