

Reaction of Ketenes. Part 18.¹ Catalysed Reactions between α -Diazocarbonyl Compounds and Ketene Acetals

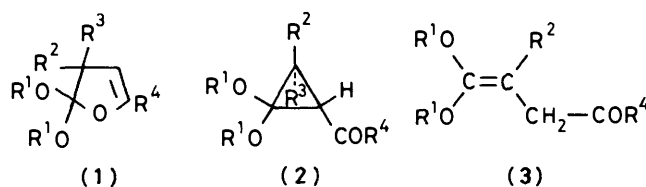
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In the presence of copper powder or $\text{Cu}(\text{acac})_2$, ethyl diazoacetate reacts with dialkylketene acetals to give cyclopropanes (**2**) whilst with ketene acetals having at least one hydrogen atom at position 2 both cyclopropanes (**2**) and butenoates (**3**) are formed. Noteworthy in these reactions is the fact that the α -diazooester fails to give dihydrofurans (**1**), which are the only reaction products when α -diazoketones are the employed α -diazocarbonyl compounds. The results can be rationalized on the basis of the intermediacy of a species in which α -diazocarbonyl compound, catalyst, and ketene acetal are involved.

Several years ago we described the synthesis² and the chemical behaviour^{3,4} of the 2,2-dialkoxy-2,3-dihydrofurans (**1**), which were obtained by copper powder-catalysed reaction of α -diazoketones with ketene acetals in generally good yields. This route has been recently extended to the synthesis of the ethyl 2,2-dialkoxy-2,3-dihydrofuran-5-carboxylates (**1**; $\text{R}^4 = \text{CO}_2\text{Et}$) by the bis(acetoacetonato)copper(II) [$\text{Cu}(\text{acac})_2$]-catalysed reaction of ethyl diazopyruvate.⁵ In that paper ethyl 2,2-dimethoxycyclopropane-1-carboxylate (**2a**) was reported as the only product formed from the $\text{Cu}(\text{acac})_2$ -catalysed reaction of ethyl diazoacetate with ketene dimethyl acetal.^{5,†} This result is in contrast with the previous reported results that the reaction of ethyl diazoacetate, ketene diethyl acetal, and copper powder or copper(I) bromide leads to ethyl 4,4-diethoxybut-3-enoate (**3b**).⁷ In an attempt to rationalize the aforementioned results, we have carried out a systematic investigation of the reactions between ethyl diazoacetate and ketene dimethyl acetals or ketene diethyl acetals using copper powder or $\text{Cu}(\text{acac})_2$ as catalyst.

Reactions catalysed by copper powder (Method A) were carried out as previously described^{2,7} and are reported in the Experimental section. ¹H N.m.r. spectra of the crude reaction mixture let us establish the absence of dihydrofurans (**1**), confirmed that disubstituted ketene acetals lead to cyclopropane derivatives (**2**),^{6,‡} and showed that monosubstituted and unsubstituted ketene acetals lead to mixtures of two compounds. In particular, methylketene dimethyl acetal yielded a mixture from which the major product was isolated by distillation under reduced pressure and identified as ethyl *trans*-2,2-dimethoxy-3-methylcyclopropane-1-carboxylate (**2c**) on the basis of spectral and analytical data reported in Table 1. When heated at 130 °C under strictly anhydrous conditions, the cyclopropane (**2c**) led quantitatively to a product which was identified as butenoate (**3c**) on the basis of spectral and analytical data (Table 1). Comparison of the ¹H n.m.r. spectrum of this compound with those of the reaction mixture showed the butenoate (**3c**) as the minor reaction product. The rearrangement of (**2c**) into (**3c**) occurs very slowly at room temperature. In order to examine the possibility that the only reaction product of ethyl diazoacetate with methylketene dimethyl acetal in the presence of copper powder is the cyclopropane (**2c**),



- a; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{R}^3 = \text{H}$, $\text{R}^4 = \text{OEt}$
 b; $\text{R}^1 = \text{Et}$, $\text{R}^2 = \text{R}^3 = \text{H}$, $\text{R}^4 = \text{OEt}$
 c; $\text{R}^1 = \text{R}^2 = \text{Me}$, $\text{R}^3 = \text{H}$, $\text{R}^4 = \text{OEt}$
 d; $\text{R}^1 = \text{Et}$, $\text{R}^2 = \text{Me}$, $\text{R}^3 = \text{H}$, $\text{R}^4 = \text{OEt}$
 e; $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{Me}$, $\text{R}^4 = \text{OEt}$
 f; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{R}^3 = \text{H}$, $\text{R}^4 = \text{Ph}$

which subsequently rearranges in part to the butenoate (**3c**), the reaction mixture was refluxed for an additional period equal to the reaction time. Comparison of the ¹H n.m.r. spectrum of the reaction mixture with those of the mixture obtained after the additional heating showed the molar ratio (**2c**):(**3c**) to be little or not at all affected. This result was confirmed on carrying out the reaction and the additional heating at 40 °C. Therefore at least part of the butenoate (**3c**) is directly formed during the addition of reactants. The characterization of the products of the copper powder-catalysed reaction between ethyl diazoacetate and a suitable number of ketene acetals with at least one hydrogen atom at position 2 has confirmed that in all cases cyclopropanes (**2a—d**) and butenoates (**3a—d**) are the reaction products. Physical, spectral, and analytical data of the new products and of the butenoate (**3b**)§ are summarized in Table 1. The structure of the cyclopropanes (**2b**) and (**2d**), which turned out to be too unstable to be isolated by distillation,¶ were deduced from ¹H n.m.r. spectra and elemental analyses of mixtures containing butenoate (**3b**) and (**3d**) respectively. The already known cyclopropanes (**2a**) and (**2e**) were identified by straightforward comparison of their i.r. and ¹H n.m.r. spectra with those of authentic samples.^{5,6} In Table 1 is also reported the ¹H n.m.r. spectrum of the known cyclopropane (**2a**), recorded on a spectrometer operating at 270 MHz, in order to estimate the values of the coupling constants J_{cis} , J_{trans} , and J_{gem} .

† The cyclopropane derivative was also obtained when ethyl diazoacetate was treated with dimethylketene dimethyl acetal in the presence of copper-bronze.⁶

‡ Owing to the poor reactivity of disubstituted ketene acetals,⁸ ethyl diazoacetate partly led to diethyl fumarate and maleate. Interestingly these compounds were formed only in trace amounts when mono- or un-substituted ketene acetals were employed.

§ The correctness of the structure (**3b**) for the reaction product of ketene diethyl acetal with ethyl diazoacetate was questioned (see footnote 6 of ref. 5 and footnote 40 of ref. 6).

¶ The isomerization rate is higher for 2,2-diethoxy- than for 2,2-dimethoxy-cyclopropanes. The high hydrolytic reactivity of the acetals (**2a—d**) and (**3a—d**) makes quantitative measurements very difficult. However, the results reported in the Experimental section are meaningful.

Table 1. Physical, spectral, and analytical data of the products derived from the reaction between α -diazocarbonyl compounds and ketene acetals

Product	B.p. (°C/mmHg)	$\nu_{\max.}(\text{CCl}_4)/\text{cm}^{-1}$	$\delta_{\text{H}}(\text{CDCl}_3) (J/\text{Hz})$	Formula	Found (%) (Required)	
					C	H
(1f)	100—102/1	1 648m	2.83 (2 H, d, J 2.9, CH_2), 3.39 (6 H, s, $2 \times \text{OCH}_3$), 5.31 (1 H, t, J 2.9, CH), 7.28 (3 H, m, Ar 3-, 4-, and 5-H), 7.56 (2 H, m, Ar, 2- and 6-H)	$\text{C}_{12}\text{H}_{14}\text{O}_3$	70.0 (69.88)	6.5 (6.84)
(2a)	52—54/2 ^a	1 735s ^b	1.27 (t, J 7.0, X part of ABX_3 system, CH_3) and 1.33 (dd, J_{gem} 5.9, J_{cis} 9.6, 3- H_{cis}) (together 4 H), 1.65 (1 H, dd, J_{gem} 5.9, J_{trans} 7.0, 3- H_{trans}), 2.06 (1 H, dd, J_{cis} 9.6, J_{trans} 7.0, 1-H), 3.38 and 3.39 (6 H, 2 s, $2 \times \text{OCH}_3$), 4.12 and 4.13 (2 H, 2 q, J 2.3 and 7.0, AB part of ABX_3 system, OCH_2) ^c			
(2b)	48—54/0.1 ^d	1 734s	1.24 and 1.26 (2 t, J 7.0, $2 \times \text{CH}_3$), 1.27 (t, J 7.0, X part of ABX_3 system, CH_3) and 1.32 (dd, J_{gem} 5.9, J_{cis} 9.6, 3- H_{cis}) (together 10 H), 1.66 (1 H, dd, J_{gem} 5.9, J_{trans} 7.0, 3- H_{trans}), 2.06 (1 H, dd, J_{cis} 9.6, J_{trans} 7.0, 1-H), 3.71 and 3.73 (4 H, 2 q, J 7.0, $2 \times \text{OCH}_2$), 4.12 and 4.13 (2 H, 2 q, J 2.3 and 7.0, AB part of ABX_3 system, CO_2CH_2) ^{c,e}	$\text{C}_{10}\text{H}_{18}\text{O}_4$ ^d	59.6 (59.38)	9.1 (8.97)
(2c)	33/0.1	1 734s	1.17 (3 H, d, J 6.2, 3- CH_3), 1.27 (3 H, t, J 7.0, X part of ABX_3 system, CH_2CH_3), 1.63 (1 H, d, J 6.6, 1-H), 1.96 (1 H, dq, J 6.6 and 6.2, 3-H), 3.35 and 3.41 (6 H, 2 s, $2 \times \text{OCH}_3$), 4.12 and 4.13 (2 H, 2 q, J 2.3 and 7.0, AB part of ABX_3 system, OCH_2) ^f	$\text{C}_9\text{H}_{16}\text{O}_4$	57.5 (57.43)	8.55 (8.57)
(2d)	48—53/0.3 ^g	1 734s	1.17 (3 H, d, J 6.2, 3- CH_3), 1.24 and 1.26 (2 t, J 7.0, $2 \times \text{CH}_3$) and 1.27 (t, J 7.0, X part of ABX_3 system, CH_3) (together 9 H), 1.62 (1 H, d, J 6.6, 1-H), 1.96 (1 H, dq, J 6.6 and 6.2, 3-H), 3.72 and 3.74 (4 H, 2 q, J 7.0, $2 \times \text{OCH}_2$), 4.12 and 4.13 (2 H, 2 q, J 2.3 and 7.0, AB part of ABX_3 system, CO_2CH_2) ^{f,h}	$\text{C}_{11}\text{H}_{20}\text{O}_4$ ^g	61.4 (61.09)	9.05 (9.32)
(3a)	108—109/35	1 734s 1 645w	1.25 (3H, t, J 7.0, CH_3), 3.01 (2 H, d, J 7.0, $\text{CH}_2\text{C}=\text{C}$), 3.58 and 3.59 (6 H, 2 s, $2 \times \text{OCH}_3$), 3.67 (1 H, t, J 7.0, CH), 4.12 (2 H, q, J 7.0, CO_2CH_2)	$\text{C}_8\text{H}_{14}\text{O}_4$	55.0 (55.16)	8.1 (8.10)
(3b) ⁱ	64—66/0.5 ^j	1 735s 1 645w	1.22, 1.25, and 1.29 (9 H, 3 t, J 7.0, $3 \times \text{CH}_3$), 3.04 (2 H, d, J 7.0, $\text{CH}_2\text{C}=\text{C}$), 3.75 (t, J 7.0, CH) and 3.79 (q, J 7.0, OCH_2) (together 3 H), 3.93 (2 H, q, J 7.0, OCH_2), 4.12 (2 H, q, J 7.0, CO_2CH_2)	$\text{C}_{10}\text{H}_{18}\text{O}_4$	59.0 (59.38)	9.1 (8.97)
(3c)	106—107/30	1 734s 1 650w	1.25 (3 H, t, J 7.0, CH_3), 1.63 (3 H, s, $\text{CH}_3\text{C}=\text{C}$), 2.99 (2 H, s, $\text{CH}_2\text{C}=\text{C}$), 3.52 and 3.54 (6 H, 2 s, $2 \times \text{OCH}_3$), 4.12 (2 H, q, J 7.0, CO_2CH_2)	$\text{C}_9\text{H}_{16}\text{O}_4$	57.5 (57.43)	8.3 (8.57)
(3d)	78—79/1	1 734s 1 650w	1.23, 1.25, and 1.27 (9 H, 3 t, J 7.0, $3 \times \text{CH}_3$), 1.64 (3 H, s, $\text{CH}_3\text{C}=\text{C}$), 3.02 (2 H, s, $\text{CH}_2\text{C}=\text{C}$), 3.78 and 3.80 (6 H, 2 q, J 7.0, $2 \times \text{OCH}_3$), 4.12 (2 H, q, J 7.0, CO_2CH_2)	$\text{C}_{11}\text{H}_{20}\text{O}_4$	61.0 (61.09)	9.2 (9.32)

^a Lit.,⁵ b.p. 80—85/0.5 mmHg. ^b Lit.,⁵ $\nu_{\max.}(\text{neat})$ 1 720s cm^{-1} . ^c The values 9.6 and 7.0 Hz of the coupling constants are consistent with J_{cis} and J_{trans} assignments in agreement with the literature data.⁹ ^d Mixture of (2b) and (3b) in ca. 8:1 molar ratio by ¹H n.m.r. spectrometric analysis. ^e The data were obtained from those of a mixture of (2b) and (3b), and rejecting the signals of (3b). ^f The *trans* configuration was assigned on the basis of the low value of the coupling constant at 1-H⁹ and by its comparison with J_{cis} and J_{trans} in (2a) and (2b). ^g Mixture of (2d) and (3d) in ca. 16:1 molar ratio by ¹H n.m.r. spectrometric analysis. ^h The data were obtained from those of a mixture of (2d) and (3d), by rejecting the signals of (3d). ⁱ Known product,⁷ but ¹H n.m.r. data were unreported. ^j Lit.,⁷ b.p. 87—90/1.7 mmHg.

Table 2. Catalysed reactions between α -diazocarbonyl compounds and ketene acetals

Diazocarbonyl	Ketene acetal	Method ^a	Reaction time (min)	Products	Yield (%)		
					(1)	(2)	(3)
$\text{EtO}_2\text{C}-\text{CHN}_2$	$\text{H}_2\text{C}=\text{C}(\text{OMe})_2$	A	140	a	—	50	13
$\text{EtO}_2\text{C}-\text{CHN}_2$	$\text{H}_2\text{C}=\text{C}(\text{OEt})_2$	A	140	b	—	40	20
$\text{EtO}_2\text{C}-\text{CHN}_2$	$\text{MeCH}=\text{C}(\text{OMe})_2$	A	140	c	—	44	6
$\text{EtO}_2\text{C}-\text{CHN}_2$	$\text{MeCH}=\text{C}(\text{OEt})_2$	A	140	d	—	48	8
$\text{EtO}_2\text{C}-\text{CHN}_2$	$\text{Me}_2\text{C}=\text{C}(\text{OMe})_2$	A	280	e	—	25	—
$\text{PhCO}-\text{CHN}_2$	$\text{H}_2\text{C}=\text{C}(\text{OMe})_2$	A	120	f	85	—	—
$\text{EtO}_2\text{C}-\text{CHN}_2$	$\text{H}_2\text{C}=\text{C}(\text{OMe})_2$	B	150	a	—	62	5
$\text{EtO}_2\text{C}-\text{CHN}_2$	$\text{H}_2\text{C}=\text{C}(\text{OEt})_2$	B	150	b	—	62	8
$\text{EtO}_2\text{C}-\text{CHN}_2$	$\text{MeCH}=\text{C}(\text{OMe})_2$	B	150	c	—	53	3
$\text{EtO}_2\text{C}-\text{CHN}_2$	$\text{MeCH}=\text{C}(\text{OEt})_2$	B	150	d	—	63	4
$\text{EtO}_2\text{C}-\text{CHN}_2$	$\text{Me}_2\text{C}=\text{C}(\text{OMe})_2$	B	210	e	—	61	—
$\text{PhCO}-\text{CHN}_2$	$\text{H}_2\text{C}=\text{C}(\text{OMe})_2$	B	130	f	80	—	—

^a A: Copper powder as catalyst, dry benzene as solvent, under reflux. B: $\text{Cu}(\text{acac})_2$ as catalyst, dry benzene as solvent, under reflux.

ethyl diazoacetate is the α -diazocarbonyl compound, an S_E2 -type substitution would lead to the cyclopropanes (**2**) as shown by transition state (**5**). The alternative mechanism postulated, *via* (**6**), would lead to the butenoates (**3**) *via* enol tautomers (**7**).^{*} This interpretation could account for the obtained *trans* isomers (**2**) when monosubstituted ketene acetals are used; in fact in these cases the formation of (**4**) could yield the diastereoisomers (**8**) and (**9**), represented in their preferred conformation. Conformation (**8**) is favoured for the S_E2 -type substitution which, with inversion at the front carbon atom, would lead exclusively to the *trans*-substituted cyclopropanes (**2c**) and (**2d**). For diastereoisomer (**9**) to follow a similar pathway, the more crowded conformation (**10**) would be required. Therefore, (**9**) *via* eclipsed conformation (**11**) would lead to butenoates (**3c**) and (**3d**). The behaviour of α -diazoketones towards ketene acetals in the presence of copper powder or $\text{Cu}(\text{acac})_2$ as catalysts can also be explained by, first, formation of the intermediate (**4**). In this case the more electrophilic character of the carbonyl carbon would favour formation of the carbon-carbon double bond and carbonyl oxygen acetal carbon bond, as suggested in transition state (**12**). Dihydrofurans (**1**) would form by this route also when ethyl diazopyruvate is the diazoketone.⁵

In contrast to ketene acetals, hydrocarbon alkenes react with α -diazoketones in the presence of copper salts¹⁴ to give acyl-cyclopropanes. Probably in this case a different mechanism operates.[†]

Experimental

I.r. spectra were measured with carbon tetrachloride as solvent on a Perkin-Elmer 399 spectrophotometer. ¹H N.m.r. spectra were recorded with deuteriochloroform as solvent on a Bruker WH 270 spectrometer with tetramethylsilane as internal standard. Dimethylketene dimethyl acetal,¹⁵ methylketene dimethyl acetal,¹⁶ methylketene diethyl acetal,¹⁷ ketene dimethyl acetal,¹⁸ ketene diethyl acetal,¹⁷ and diazoacetophenone¹⁹ were prepared as previously reported.

General Procedure for the Reactions Between Ethyl Diazoacetate and Ketene Acetals Catalysed by Copper Powder (Method A).—The reactions were carried out as previously reported^{2,7} by the dropwise addition of a 30% solution of ethyl diazoacetate (20 mmol) in dry benzene to a stirred suspension of copper powder (228 mg) and ketene acetal (30 mmol) heated at 95 °C (oil-bath). Upon completion of the addition, the mixture was heated for a further 45 min. The solvent and the unchanged ketene acetal were removed under reduced pressure at room temperature. The reaction time (inclusive of the 45 min) and the yields of cyclopropane (**2**) and butenoate (**3**) are reported in Table 2. In no case was spectral evidence obtained to support the presence of dihydrofurans (**1**) in the crude reaction mixtures.

Reaction Between Ethyl Diazoacetate and Dimethylketene Dimethyl Acetal Catalysed by Copper Powder.—Inspection of the ¹H n.m.r. spectrum of the crude reaction mixture showed the presence of cyclopropane (**2c**) and diethyl fumarate and maleate. The cyclopropane (**2c**) was isolated from the reaction mixture according to the previously reported procedure⁶ and identified by comparison of its i.r. and ¹H n.m.r. spectra with those of an authentic sample.⁶ The lack of signals at δ 3.9–4.3 in the ¹H n.m.r. spectrum of the tarry residue of the distillation confirmed that the dihydrofuran (**1c**) was not present.

Reaction Between Ethyl Diazoacetate and Methylketene Dimethyl Acetal Catalysed by Copper Powder, and Cyclopropane (2c) Rearrangement.—Inspection of the ¹H n.m.r. spectrum of the crude reaction mixture showed the presence of the cyclopropane (**2c**) and butenoate (**3c**) in *ca.* 7:1 molar ratio on the basis of the relative areas of the multiplet at δ 1.96 [CHCH_3 of (**2c**)] and of the singlet at δ 2.99 [$\text{CH}_2\text{C}=\text{}$ of (**3c**)]. In addition very small quantities of diethyl fumarate and maleate were detected. The crude reaction mixture was rapidly distilled under reduced pressure to give, first, the cyclopropane (**2c**) and, further, a mixture composed of the cyclopropane (**2c**) and butenoate (**3c**) (¹H n.m.r.). The lack of signals at δ 2.9–3.1 in the ¹H n.m.r. spectrum of the tarry residue of the distillation confirmed that the dihydrofuran (**1c**) was not present. When a sample of the reaction mixture, drawn before the catalyst was filtered and the solvent and unchanged ketene acetal were removed, was refluxed for 140 min, ¹H n.m.r. spectroscopy showed that the molar ratio (**2c**):(**3c**) was still *ca.* 7:1.

Cyclopropane (**2c**) was heated at 130 °C in a sealed ampoule; after 10 h the ¹H n.m.r. spectrum showed that (**2c**) was quantitatively converted into butenoate (**3c**). When cyclopropane (**2c**) was kept in a sealed ampoule at room temperature, after 40 d the ¹H n.m.r. spectrum showed a molar ratio (**2c**):(**3c**) *ca.* 30:1. All attempts to isolate (**2c**) or (**3c**) by chromatographic methods failed since they undergo hydrolysis to methyl 2-methyl-3-ethoxycarbonylpropionate on contact with the adsorbents.

Physical, spectral, and analytical data of the cyclopropane (**2c**) and butenoate (**3c**) are listed in Table 1.

To a stirred mixture of methylketene dimethyl acetal (39 mmol), dry benzene (8 ml), and copper powder (250 mg) heated at 40 °C, after being flushed with dry nitrogen, was added ethyl diazoacetate (22 mol). The reaction vessel was connected to a measuring burette (filled with water) *via* a drying tube. After an induction period of 12 h, evolution of nitrogen (*ca.* 95% of the theoretical amount) was observed during 72 h. After having been checked for the absence of any absorption at 2175 cm^{-1} (ν_{max} , diazo group), the mixture was filtered and the solvent and the unchanged ketene acetal were removed under reduced pressure at room temperature. The ¹H n.m.r. spectrum of the residue showed the presence of the cyclopropane (**2c**) and butenoate (**3c**) in *ca.* 3.2:1 molar ratio. In addition diethyl fumarate and maleate were present. The residue was rapidly distilled under reduced pressure to afford a distillate [b.p. 45–51 °C/0.3 mmHg] composed of (**2c**) and (**3c**) (¹H n.m.r.). Yield of the cyclopropane (**2c**) was 30%. Yield of butenoate (**3c**) was 10%. The acetals (**2c**) and (**3c**) were identified by comparison (i.r. and ¹H n.m.r.) with those of the pure compounds. No spectral evidence was obtained to support the presence of the dihydrofuran (**1c**) in the crude reaction mixture or in the tarry residue of the distillation. When a sample of the reaction mixture, drawn before the catalyst was filtered and the solvent and the unchanged ketene acetal were removed, was stirred and heated at 40 °C for 84 h, the molar ratio (**2c**):(**3c**) was *ca.* 3.1:1.

Reaction Between Ethyl Diazoacetate and Methylketene Diethyl Acetal Catalysed by Copper Powder, and Cyclopropane (2d) Rearrangement.—Inspection of the ¹H n.m.r. spectrum of the crude reaction mixture showed the presence of the cyclopropane (**2d**) and butenoate (**3d**) in *ca.* 6:1 molar ratio on the basis of the relative areas of the multiplet at δ 1.96 [CHCH_3 of (**2d**)] and singlet at δ 3.02 [$\text{CH}_2\text{C}=\text{}$ of (**3d**)]. In addition very small quantities of diethyl fumarate and maleate were present. The crude reaction mixture was rapidly distilled under reduced pressure to afford a distillate composed of the cyclopropane (**2d**) and butenoate (**3d**) (¹H n.m.r.). The spectral data of (**2d**) listed in Table 1 were obtained by recording the ¹H n.m.r. spectrum of the mixture and rejecting the signals of the

* The ratio of products (**2**):(**3**) would be a reflection of the position of co-ordination of the copper.

† We acknowledge the help of one of the referees whose comments made possible an improvement of the discussion.

butenoate (**3d**). Analytical data of (**2d**) were obtained by elemental analysis of the mixture of the two isomers. The lack of a multiplet at δ 2.8–3.1 (CH_3CH) in the ^1H n.m.r. spectrum of the tarry residue of the distillation confirmed that the dihydrofuran (**1d**) was not present.

The distillate composed of the acetals (**2d**) and (**3d**) was heated at 130°C in a sealed ampoule; after 5 h the ^1H n.m.r. spectrum showed that cyclopropane (**2d**) was quantitatively converted into butenoate (**3d**). Physical, spectral, and analytical data of (**3d**) are listed in Table 1. A mixture of acetals (**2d**) and (**3d**) in *ca.* 3:1 molar ratio was kept in a sealed ampoule at room temperature; after 40 d the ^1H n.m.r. spectrum showed that the molar ratio (**2d**):(**3d**) was *ca.* 3:2. All attempts to isolate acetals (**2d**) and (**3d**) by chromatographic methods failed since they undergo hydrolysis to ethyl 2-methyl-3-ethoxycarbonylpropionate on contact with the adsorbents.

Reaction Between Ethyl Diazoacetate and Ketene Dimethyl Acetal Catalysed by Copper Powder, and Cyclopropane (2a) Rearrangement.—Inspection of the ^1H n.m.r. spectrum of the crude reaction mixture showed the presence of the cyclopropane (**2a**) and butenoate (**3a**) in *ca.* 4:1 molar ratio on the basis of the relative areas of the multiplet at δ 2.06 [CHCO of (**2a**)] and of the doublet at δ 3.01 [$\text{CH}_2\text{CH}=\text{}$ of (**3a**)]. In addition small quantities of diethyl fumarate and maleate were present. The crude reaction mixture was rapidly distilled under reduced pressure to give, first, the cyclopropane (**2a**) and, further, a mixture composed of acetals (**2a**) and (**3a**) (^1H n.m.r.). The lack of a doublet at δ *ca.* 2.7–2.9 [$\text{CH}_2\text{CH}=\text{}$] in the ^1H n.m.r. spectrum of the tarry residue of the distillation confirmed that the dihydrofuran (**1a**) was not present. The cyclopropane (**2a**) was identified by comparison of its spectral data with those previously reported.⁵ In Table 1 is reported the ^1H n.m.r. spectrum of (**2a**) recorded on a spectrometer operating at 270 MHz.

The cyclopropane (**2a**) was heated in a sealed ampoule at 130°C ; after 4 h the ^1H n.m.r. spectrum showed that (**2a**) was quantitatively converted into butenoate (**3a**). Physical, spectral, and analytical data of (**3a**) are listed in Table 1. When the cyclopropane (**2a**) was kept at room temperature in a sealed ampoule, after 10 d the ^1H n.m.r. spectrum showed that the molar ratio of (**2a**):(**3a**) was *ca.* 30:1. All attempts to isolate (**2a**) and (**3a**) by chromatographic methods failed since they undergo hydrolysis to methyl 2-methyl-3-ethoxycarbonylpropionate on contact with the adsorbents.

Reaction Between Ethyl Diazoacetate and Ketene Diethyl Acetal Catalysed by Copper Powder, and Cyclopropane (2b) Rearrangement.—Inspection of the ^1H n.m.r. spectrum of the crude reaction mixture showed the presence of the cyclopropane (**2b**) and butenoate (**3b**) in *ca.* 2:1 molar ratio on the basis of the relative areas of the multiplet at δ 2.06 (CHCO of (**2b**)) and of the doublet at δ 3.04 [$\text{CH}_2\text{CH}=\text{}$ of (**3b**)]. In addition very small quantities of diethyl fumarate and maleate were present. The residue was rapidly distilled under reduced pressure to afford a distillate composed of the cyclopropane (**2b**) and butenoate (**3b**) (^1H n.m.r.). The spectral data of (**2b**), listed in Table 1 were obtained by recording the ^1H n.m.r. spectrum of the mixture and rejecting the signals of the butenoate (**3b**). The analytical data of (**2b**) were obtained by elemental analysis of the mixture of the two isomers. The lack of a doublet at δ *ca.* 2.7–2.9 [$\text{CH}_2\text{CH}=\text{}$] in the ^1H n.m.r. spectrum of the tarry residue of the distillation confirmed that the dihydrofuran (**1b**) was not present.

The distillate composed of the acetals (**2b**) and (**3b**) was heated at 130°C in a sealed ampoule; after 2 h ^1H n.m.r. spectroscopy showed that the cyclopropane (**2b**) was quantitatively converted into butenoate (**3b**). Physical, spectral, and

analytical data of (**3b**) are listed in Table 1. A mixture of the cyclopropane (**2b**) and a butenoate (**3b**) in *ca.* 2:1 molar ratio was kept at room temperature in a sealed ampoule; after 15 d the ^1H n.m.r. spectrum showed that the molar ratio (**2b**):(**3b**) was *ca.* 1:1. All attempts to isolate acetals (**2b**) or (**3b**) by chromatographic methods failed since they undergo hydrolysis to ethyl 2-methyl-3-ethoxycarbonylpropionate on contact with the adsorbents.

General Procedure for the Reaction Between Ethyl Diazoacetate and Ketene Acetals Catalysed by $\text{Cu}(\text{acac})_2$ (Method B).—As previously reported,⁵ a solution of ethyl diazoacetate (20 mmol) in dry benzene (22 ml) and a solution of ketene acetal (58 mmol) in dry benzene (20 ml) were simultaneously slowly added to a stirred, refluxed (oil-bath at 85°C) suspension of $\text{Cu}(\text{acac})_2$ (23 mg) and ketene acetal (12 mmol) in dry benzene (4 ml). Upon completion of the addition, the mixture was refluxed for a further 30 min. The solvent and the unchanged ketene acetal were removed under reduced pressure at room temperature. The $\text{Cu}(\text{acac})_2$, which dissolved in the course of the reaction, did not separate when the solvent and unchanged ketene acetal were removed. Quantification of the products in the reaction mixture was carried out as previously reported when copper powder was the catalyst. Reaction time and yields of the acetals (**2**) and (**3**) are reported in Table 2. Acetals (**2**) and (**3**) were identified by comparison (*i.r.* and ^1H n.m.r.) with the compounds obtained by copper powder-catalysed reactions. No spectral evidence was obtained to support the presence of dihydrofurans (**1**) in the crude reaction mixtures or in the tarry residue of the distillations. Small quantities of diethyl fumarate and maleate were present only in the reaction mixture of the dimethylketene dimethyl acetal.

Reaction Between Ethyl Diazoacetate and Methylketene Dimethyl Acetal Catalysed by $\text{Cu}(\text{acac})_2$.—Inspection of the ^1H n.m.r. spectrum of the crude reaction mixture showed the presence of the cyclopropane (**2c**) and the butenoate (**3c**) in *ca.* 20:1 molar ratio which remained unchanged when a sample of the reaction mixture, drawn before the solvent and unchanged ketene acetal were removed, was refluxed for 150 min. Similar results were obtained when the reaction of ethyl diazoacetate (20 mmol) and methylketene dimethyl acetal (30 mmol) catalysed by $\text{Cu}(\text{acac})_2$ (23 mg) was carried under the experimental conditions which were used when copper powder was the catalyst.

Reaction of methylketene dimethyl acetal (31 mmol), ethyl diazoacetate (9 mmol), dry benzene (9 ml), and $\text{Cu}(\text{acac})_2$ (11 mg) was carried out at 40°C under the experimental conditions which were used when copper powder was the catalyst. After an induction period of 12 h, evolution of nitrogen was observed in *ca.* 98% of the theoretical amount during 20 h and the cyclopropane (**2c**) and butenoate (**3c**) were formed in *ca.* 7:1 molar ratio. Diethyl fumarate and maleate were also present. Quantification of compounds (**2c**) and (**3c**) was carried out as previously described. Yield: compound (**2c**) 37%, compound (**3c**) 5%. When a sample of the reaction mixture, drawn before the solvent and the unchanged ketene acetal were removed, was heated at 40°C for 32 h, the molar ratio (**2c**):(**3c**) was 6.9:1.

Reaction Between α -Diazoacetophenone and Ketene Dimethyl Acetal Catalysed by Copper Powder.—The reaction was carried out as described above (Method A). Inspection of the ^1H n.m.r. spectrum of the crude reaction mixture showed only the presence of the dihydrofuran (**1f**) which was distilled under reduced pressure. Percentage yields are reported in Table 2. Physical, spectral, and analytical data are reported in Table 1. No ^1H n.m.r. evidence was obtained to support the presence of the cyclopropane (**2f**) (lack of signals at δ 1.4–2.2 or of the

butenoate (**3f**) (lack of a triplet at δ 3.5—3.8) in the crude reaction mixture and in the tarry residue of the distillation.

Reaction Between α -Diazoacetophenone and Ketene Dimethyl Acetal Catalysed by $\text{Cu}(\text{acac})_2$.—The reaction was carried out as described above (Method B). Inspection of the ^1H n.m.r. spectrum of the crude reaction mixture showed only the presence of the dihydrofuran (**1f**) which was distilled under reduced pressure. Percentage yields are reported in Table 2. No ^1H n.m.r. evidence was obtained to support the presence of the cyclopropane (**2f**) or of the butenoate (**3f**).

Decomposition of Ethyl Diazoacetate at 40 °C Catalysed by $\text{Cu}(\text{acac})_2$.—To a stirred suspension of $\text{Cu}(\text{acac})_2$ (11 mg) in dry benzene (12 ml) heated at 40 °C, after having been flushed with dry nitrogen, was added ethyl diazoacetate (9 mmol). The reaction vessel was connected to a measuring burette (filled with water) *via* a drying tube. After an induction period of 1 h, evolution of nitrogen was observed in *ca.* the theoretical amount within 1 h. The ^1H n.m.r. spectrum of the decomposition mixture, recorded after evaporation of the solvent, showed only the presence of diethyl fumarate and maleate.

Decomposition of Ethyl Diazoacetate at 40 °C Catalysed by Copper Powder.—The decomposition of ethyl diazoacetate (22 mmol) in dry benzene (10 ml) catalysed by copper powder (250 mg) was carried out as described above. After an induction period of 6 h, evolution of nitrogen was observed in *ca.* the theoretical amount within 20 h. The ^1H n.m.r. spectrum of the decomposition mixture showed only the presence of diethyl fumarate and maleate.

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