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REACTIONS OF KETENES—IX

REACTIONS BETWEEN KETENE ACETALS AND DIPHENYLKETENE[1,2]

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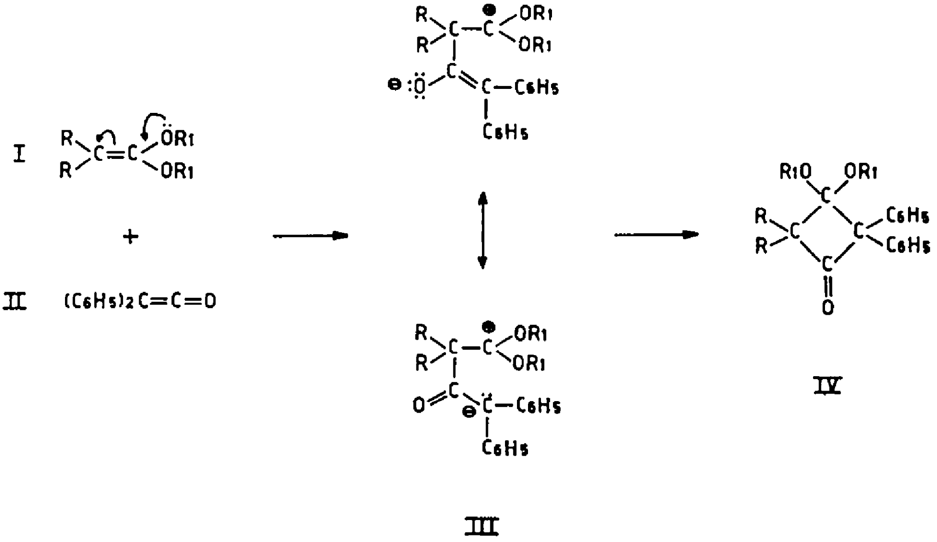
Abstract—Monoalkylketene acetals and monoarylketene acetals react with diphenylketene to give acylketene acetals (VII). These compounds can further react with diphenylketene to give 2,4-pyronone 4-acetals (IX), which, by mild acid hydrolysis, yields 2,4-pyronones (X).

Reaction of methylketene diethylacetal with two equivalents of diphenylketene yields 3,3-diphenyl-5-methyl-6-diphenylmethylentetrahydropyran-2,4-dione 4-diethylacetal (XIV) in addition to small quantities of the pyronone acetal IXb.

IT HAS already been shown[3] that dialkylketene acetals (I) react with diphenylketene (II) to give monoacetals of cyclobutane-1,3-diones according to Scheme I.

Scheme I:



In a preliminary communication on the chemical behaviour of monosubstituted ketene acetals, we reported on the reaction between phenylketene dimethylacetal and diphenylketene.[4] Although the reaction product was not isolated in a pure state, we formulated the hypothesis that it must have the structure of acylketene acetal.

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[1] This investigation was supported in part by Shell Internationale Research Maatschappij N.V. The Hague, Holland.

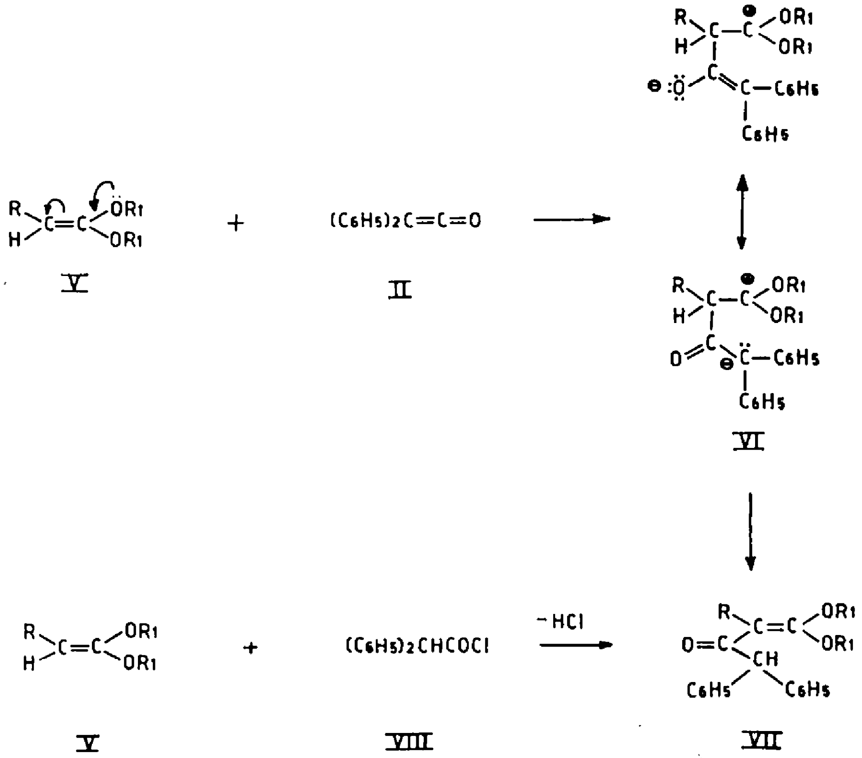
[2] Part VIII. R. Scarpati and D. Sica, *Gazz. Chim. Ital.* **93**, 942 (1963).

[3] R. Scarpati and D. Sica, *Gazz. Chim. Ital.* **92**, 1073 (1962).

[4] R. Scarpati and D. Sica, *Rend. Ac. Sci. fis. e mat. Napoli* [IV], Vol. XXVIII, 70 (1961).

Now, the characterization of the products of the reaction between diphenylketene and an increased number of ketene acetals with at least one hydrogen atom at position 2 has confirmed that the reaction takes place according to Scheme II. Diphenylketene (II), by reaction with an excess of ketene dimethylacetal (Va), yielded diphenylacetylketene dimethylacetal (VIIa), identified by comparison (mixed m.p. and IR spectra) with an authentic sample prepared by reaction of diphenylacetyl chloride (VIII) with ketene dimethylacetal (Va).[5] Methylketene diethylacetal (Vb) and phenylketene dimethylacetal (Vc), by reaction with diphenylketene (II), yielded two oily products to which the structures of 2-methyl-2-diphenylacetylketene diethylacetal (VIIb) and 2-phenyl-2-diphenylacetylketene dimethylacetal (VIIc) have been assigned by comparison (IR spectra) with the products obtained from diphenylacetyl chloride (VIII) by the unequivocal reactions with methylketene diethylacetal and phenylketene dimethylacetal respectively.

Scheme II:



Va, VIa, VIIa : R = H, $R_1 = CH_3$

Vb, VIb, VIIb : $R = CH_3$, $R_1 = C_2H_5$

Vc, VIc, VIIc : $R = C_6H_5$, $R_1 = CH_3$

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[5] S. M. McElvain and G. R. McKay, Jr., *J. Amer. Chem. Soc.* 78, 6086 (1956).

The above results confirm the previous hypothesis,[4] according to which intermediate VI, deriving from the reaction of an unsubstituted or a monoalkyl or a monoaryl ketene acetal, rearranges to acylketene acetal (VII) (Scheme II). In the case of the reaction of dialkylketene acetals, intermediate III, which cannot undergo this rearrangement, yields cyclobutanedione acetals by cyclization,[3] (Scheme I).

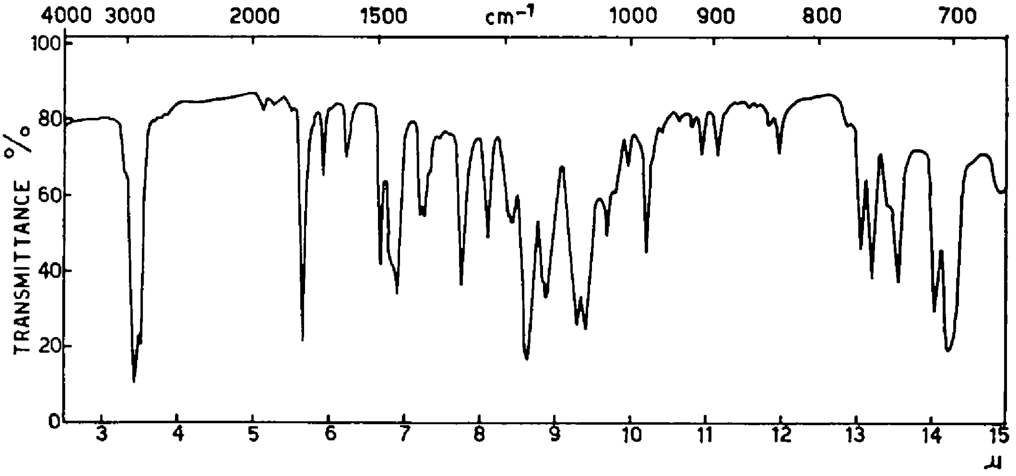


FIG. 1. IR spectrum of 3,3-diphenyl-5-methyl-6-diphenylmethyl-2,4-pyronone 4-diethylacetal (IXb).

The acylketene acetals (VII) may react further with the diphenylketene (II).[4] In a preliminary research on the reaction between diphenylketene and crude 2-phenyl-2-diphenylacetylketene dimethylacetal (VIIc), a product was obtained whose chemical behaviour proved insufficient for a reliable delucidation of its structure; therefore, by analogy with the behaviour of the dialkylketene acetals, the structure 2,2,4-triphenyl-4-diphenylacetylcyclobutane-1,3,dione 1-dimethylacetal was suggested for it.[4] In pursuing our work on the reaction between diphenylketene and acylketene acetals, we have investigated the reaction of 2-methyl-2-diphenylacetylketene diethylacetal (VIIb) with one equivalent of diphenylketene. The C, H, —OC_2H_5 analyses of the reaction product indicated the formula $C_{31}H_{24}O_2(OC_2H_5)_2$ (IXb). When this product was heated in a dioxane solution containing 5% conc. HCl, a crystalline compound (Xb) was obtained which had the empirical formula $C_{31}H_{24}O_3$. The IR spectrum of the compound IXb showed bands at 1767 cm^{-1} (δ-enol lactone) and at 1686 cm^{-1} (C—C double bond); the bands at 1000–1200 cm^{-1} are indicative of an acetal structure (Fig. 1). The IR spectrum of Xb (Fig. 2) was consistent with a lactone structure (band at 1776 cm^{-1}), and its conspicuous feature was a peak at 1683 cm^{-1} which suggested the presence of a carbonyl group conjugated with a C—C double bond (band at 1639 cm^{-1}). The UV spectrum ($\lambda_{max} = 283$ mμ, $\varepsilon = 8850$) supports this view.

The NMR spectra of IXb (Table 1) and of Xb (Table 2) show singlets at τ 4·95 and τ 4·68 respectively, arising from the allylic proton $\left(\rangle CH—\overset{|}{C}=\right)$. The peaks at τ 8·05 (IXb) and τ 8·03 (Xb) corresponds to the 3 protons of the methyl group $\left(CH_3—\overset{|}{C}=\right)$.

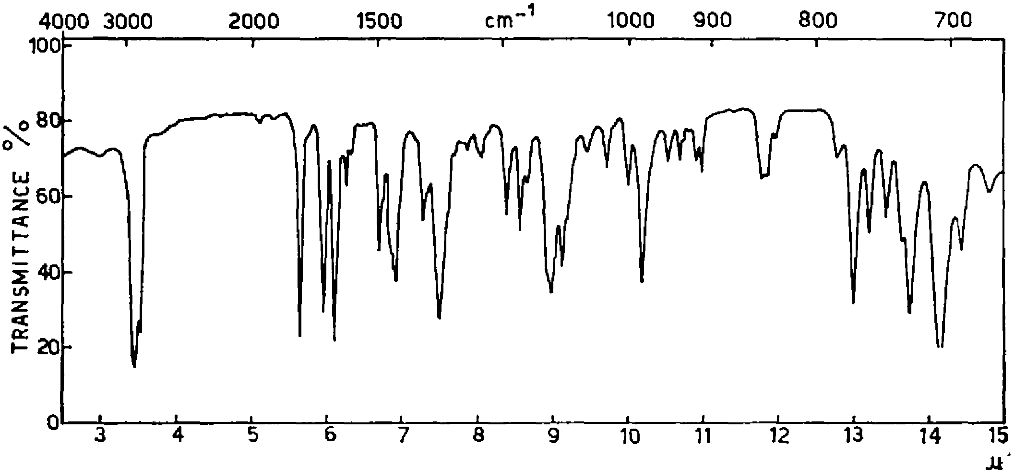


FIG. 2. IR spectrum of 3,3-diphenyl-5-methyl-6-diphenylmethyl-2,4-pyronone (Xb).

TABLE 1. NMR DATA ON 3,3-DIPHENYL-5-METHYL-6-DIPHENYLMETHYL-2,4-PYRONONE 4-DIETHYLACETAL (IXb)

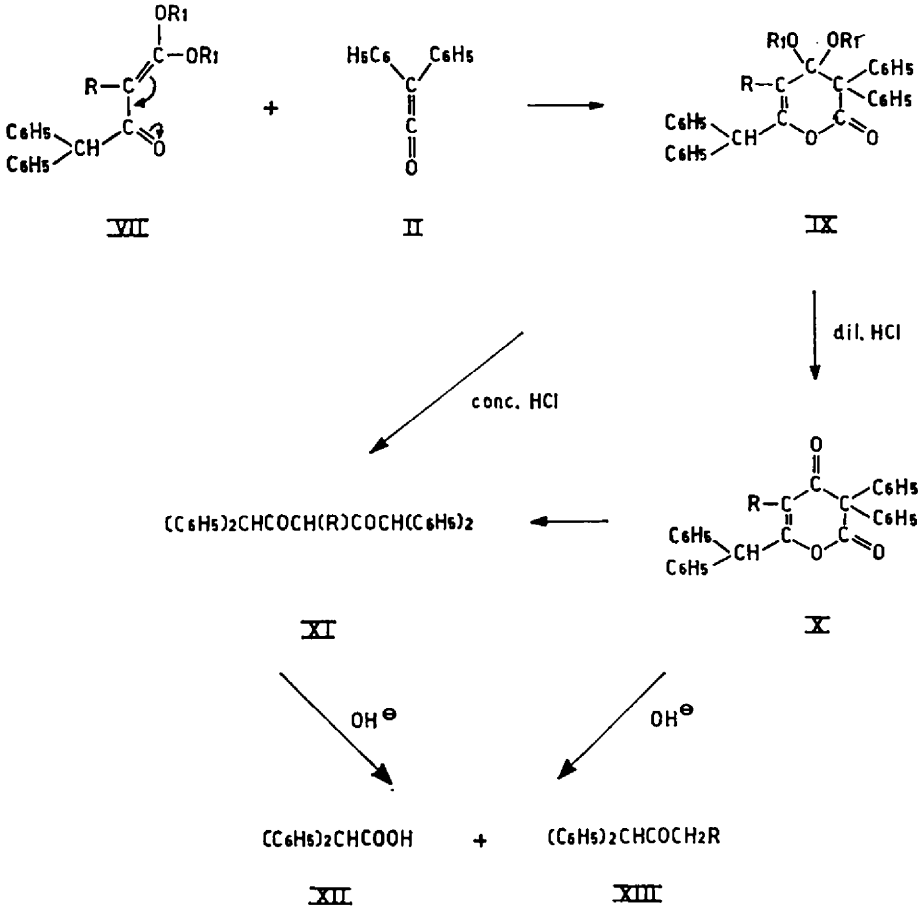
τ	Multiplicity	Relative number of protons	Assignment
9·09	(t)(J:7 c/s)	3	$CH_3-C(H_2)-$
8·89	(t)(J:7 c/s)	3	$CH_3-C(H_2)-$
8·05	(s)	3	$CH_3-\overset{\vert}{C}=$
7·05	(m)	4	$C(H_2)-CH_2-O-$
4·95	(s)	1	$\begin{matrix}C_6(H_5)\\C_6(H_5)\end{matrix}\!>\!CH-\overset{\vert}{C}=$
3·10	(m)	20	C_6H_5-

TABLE 2. NMR DATA ON 3,3-DIPHENYL-5-METHYL-6-DIPHENYLMETHYL-2,4-PYRONONE (Xb)

τ	Multiplicity	Relative number of protons	Assignment
8·03	(s)	3	$CH_3-\overset{\vert}{C}=$
4·68	(s)	1	$\begin{matrix}C_6(H_5)\\C_6(H_5)\end{matrix}\!>\!CH-\overset{\vert}{C}=$
2·85	(m)	20	C_6H_5-

These results demonstrate that acylketene acetals do not react with diphenylketene according to Scheme I but form enolic δ-lactones by 1,4-cycloaddition (Scheme III).

Scheme III:



VII b, IX b, X b, XI b, XIII b : $R = CH_3, R_1 = C_2H_5$

VII c, IX c, X c, XI c, XIII c : $R = C_6H_5, R_1 = CH_3$

According to this mechanism, acylketene acetal VIIb gives 3,3-diphenyl-5-methyl-6-diphenylmethyl-2,4-pyronone 4-diethylacetal (IXb), which, by mild acid hydrolysis, yields 3,3-diphenyl-5-methyl-6-diphenylmethyl-2,4-pyronone (Xb) and, in more drastic conditions (dioxane with 40% conc. HCl), yields 1,1,5,5-tetraphenyl-3-methylpentane-2,4-dione (XIb). The structure of this latter compound was determined on the basis of elementary analyses and chemical data (splitting by alkalies into diphenylacetic acid (XII) and 1,1-diphenylbutan-2-one (XIIIb). It is to be noted that lactone IXb is fairly resistant to alkaline hydrolysis and its corresponding ketoacid could not be obtained. This is probably because of the sterical hindrance by the two phenyls and the diphenylmethyl group.

Ketolactone Xb yielded diketone XIb by acid hydrolysis under drastic conditions. When hydrolysed with alkalies it gave diphenylacetic acid (XII) and ketone XIIIb.

The IR spectrum of the compound IXc obtained by reaction between acylketene acetal VIIc and diphenylketene and that of the corresponding ketone Xc are shown in Figs. 3 and 4, respectively; Table 3 summarizes the NMR data of the compound IXc. On the basis of these physical data, the cyclobutanedione structures proposed[4] can be discarded in favour of the 6-membered lactone structures 3,3,5-triphenyl-6-diphenylmethyl-2,4-pyronone 4-dimethylacetal (IXc) and 3,3,5-triphenyl-6-diphenylmethyl-2,4-pyronone (Xc).

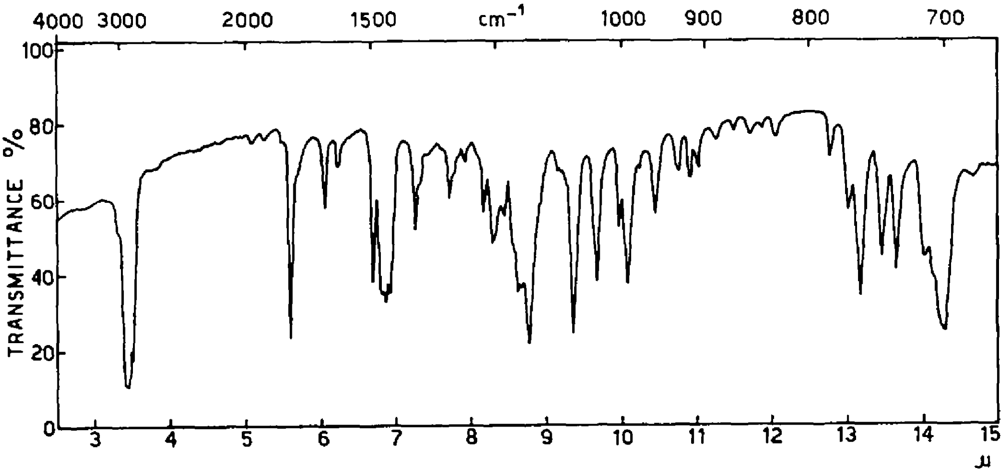


FIG. 3. IR spectrum of 3,3,5-triphenyl-6-diphenylmethyl-2,4-pyronone 4-dimethylacetal (IXc)

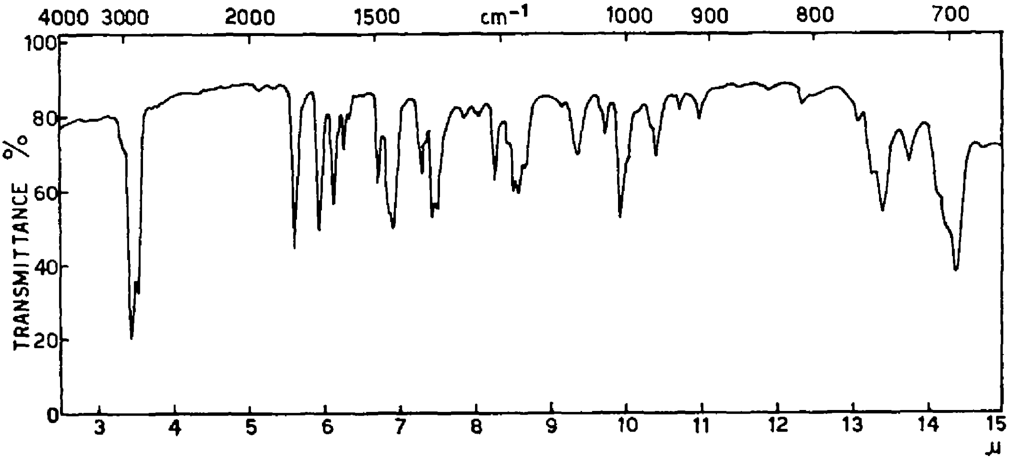
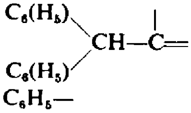


FIG. 4. IR spectrum of 3,3,5-triphenyl-6-diphenylmethyl-2,4-pyronone (Xc).

TABLE 3. NMR DATA ON 3,3,5-TRIPHENYL-6-DIPHENYLMETHYL-2,4-PYRONONE 4-DIMETHYLACETAL (IXc)

τ	Multiplicity	Relative number of protons	Assignment
7·42	(s)	3	CH_3—O—
6.64	(s)	3	CH_3—O—
5·28	(s)	1	 $(C_6(H_5))_2CH-\overset{\vert}{C}=$
2·95	(m)	25	C_6H_5—

In an attempt to prepare acetal IXb in a single stage without isolating acetylketene acetal VIIb, two equivalents of diphenylketene were heated with one equivalent of methylketene diethylacetal (Vb). By using this procedure which had been successfully used for the preparation of acetal IXc,[4] a mixture of acetal lactone IXb and an isomeric compound (XIV) was obtained. Compound XIV, which was the main component of the mixture, gave ketolactone Xb by treatment with HCl under the same conditions adopted for hydrolysis of IXb. The IR spectrum of acetal XIV (Fig. 5) shows bands

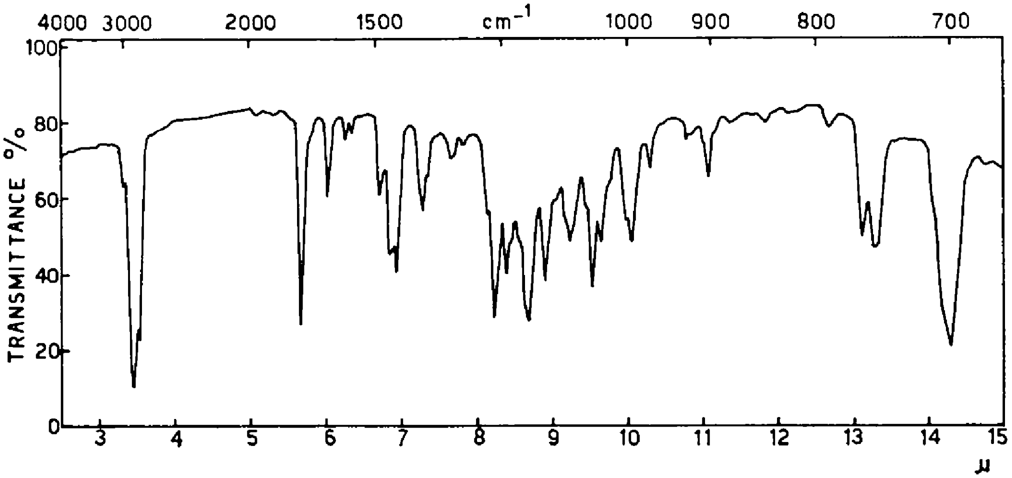


FIG. 5. IR spectrum of 3,3-diphenyl-5-methyl-6-diphenylmethylentetrahydropyran-2,4-dione 4-diethylacetal (XIV).

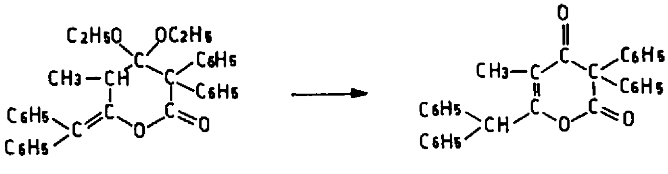
at 1760 cm^{-1} (δ-enol lactone), 1650 cm^{-1} (C—C double bond) and 1000–1200 cm^{-1}, indicative of an acetal structure. These absorption bands were also observed in the IR spectrum of IXb. It is to be noted, however, that the band due to the C—C double bond is shifted slightly towards the lower frequencies. This shift indicates that this double bond is more conjugated in XIV than in IXb. Further evidence of this was afforded by comparing the UV spectra of XIV (λ_{max} = 252 mμ; ε = 12850) and of IXb (λ_{max} = 260 mμ, shoulder; ε = 2000).

On the basis of above data, the structure of the compound under investigation may be assumed to be 3,3-diphenyl-5-methyl-6-diphenylmethylentetrahydropyran-2,4-dione 4-diethylacetal (XIV), differing from IXb on account of its double bond position as well as the position of the methynic hydrogen. Comparison of the NMR spectrum of XIV with that of the lactone IXb bears this out (cf. Table 1 and Table 4).

Table 4. NMR data on 3,3-diphenyl-5-methyl-6-diphenylmethylen-tetrahydropyran-2,4-dione 4-diethylacetal (XIV)

τ	Multiplicity	Relative number of protons	Assignments
8·95	(d)	3	$CH_3—\overset{\vert}{C}(H)—$
8·92	(t)	3	$CH_3—C(H_2)—$
8·83	(t)	3	$CH_3—C(H_2)—$
6·70	(m)	5	$2\ C(H_2)—CH_2—O—$ $C(H_3)—\underset{\vert}{CH}—$
3·00	(m)	20	$C_6H_5—$

Acetal XIV yields, by hydrolysis, the same ketolactone as acetal IXb, because an allylic rearrangement takes place and the double bond conjugates with the ketonic >C=O.



XIV Xb

In conclusion, from the above data it can be deduced that ketene acetals behave as nucleophylic reagents with diphenylketene, just as with other compounds, the reaction pathway depending on the number and type of the groups at position 2 of specific ketene acetal. Dialkylketene acetals lead to formation of the monoacetals of cyclobutanediones[3] (Scheme I); monoalkyl and monoaryl ketene acetals lead, under suitable conditions, to acylketene acetals (Scheme II); these acylketene acetals lead to the monoacetals of 2,4-pyronones (Scheme III).

EXPERIMENTAL

M.ps and b.ps are uncorrected. UV spectra were measured with a Beckmann DK2 spectrophotometer in methanol solution. IR spectra were taken with a Perkin-Elmer model 137 spectrophotometer; the IR spectra of liquid products were taken as such, those of solid products were taken in nujol. NMR spectra were recorded with a Varian NMR spectrophotometer at 60 Mc in $CDCl_3$ with TMS as internal reference. Light petroleum has a boiling range of 80–100°.

Diphenylacetylketene dimethylacetal (VIIa)

Diphenylketene[6] (8 g, 41·4 mmoles) was added to ketene dimethylacetal[7] (7·2 g, 81·7 mmoles);[8] the yellow-orange mixture became warm and gradually turned pale yellow. When the temp fell, the mixture was heated at 80° and kept at this temp for 30 min. After ice-cooling, it gave a crystalline precipitate, which was collected by filtration and washed with a little ether (yield 6·6 g, 56·8 %). On recrystallization from light petroleum, the product had m.p. 101–102°, undepressed by admixture with an authentic sample of diphenylacetylketene dimethylacetal (VIIa) obtained from reaction

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[6] Organic Syntheses, Coll. Vol. III, p. 356. J. Wiley, London (1955).

[7] S. M. McElvain, H. I. Anthes and S. H. Shapiro, *J. Amer. Chem. Soc.* **64**, 2525 (1942).

[8] When the reactants are used in 1:1 molar ratio lower yields of VII are obtained.

between diphenylacetyl chloride and ketene dimethylacetal.[5] Comparison of IR spectra further confirmed the identity of the two compounds.

2-*Methyl-2-diphenylacetylketene diethylacetal* (VIIb)

(a) *From diphenylketene and methylketene diethylacetal.* Reaction between diphenylketene[6] (5 g, 25·7 mmoles) and methylketene diethylacetal[9] (6·6 g, 50·7 mmoles)[8] was carried out as described for the preparation of VIIa. Distillation of the reaction mixture afforded a yellow oil b.p. 165–170°/0·8 mm (yield 6 g, 71·8%). (Found: C, 77·47; H, 6·94; OC_2H_5, 26·94; $C_{21}H_{24}O_3$ requires: C, 77·75; H, 7·46; OC_2H_5, 27·78%).

(b) *From diphenylacetyl chloride and methylketene diethylacetal.* Diphenylacetyl chloride (3·5 g, 15·2 mmoles) was slowly added to methylketene diethylacetal[9] (5·9 g, 45·3 mmoles); after heating for 1 hr at 60°, the resulting solution was distilled yielding a yellow oil b.p. 162–168°/0·8 mm (3·8 g, 77·2%) identified (IR spectra) as VIIb described under (a) above.

2-*Phenyl-2-diphenylacetylketene dimethylacetal* (VIIc)

(a) *From diphenylketene and phenylketene dimethylacetal.* Diphenylketene[6] (5 g, 25·7 mmole) and phenylketene dimethylacetal[10] (8·5 g, 51·7 mmoles)[8] were mixed; when the initial exothermic reaction had subsided, the mixture was heated at 80° for 30 min and then distilled at 0·8 mm. The fraction b.p. 212–216° was collected as an oily product (3·7 g, 40%). (Found: C, 80·47; H, 6·16; OCH_3, 16·52; $C_{24}H_{22}O_3$ requires: C, 80·42; H, 6·19; OCH_3, 17·31%).

(b) *From diphenylacetyl chloride and phenylketene dimethylacetal.* A mixture of phenylketene dimethylacetal[10] (8·5 g, 51·7 mmoles) and diphenylacetyl chloride (3 g, 13 mmoles) was heated at 60° for 8 hr. Distillation of the reaction afforded an oily product b.p. 210–216°/0·6 mm (2·4 g, 51·4%) identified (IR spectra) as VIIc described under (a) above.

3,3-*Diphenyl-5-methyl-6-diphenylmethyl-2,4-pyronone 4-diethylacetal* (IXb)

A mixture of diphenylketene[6] (5·1 g, 26·2 mmoles) and 2-methyl-2-diphenylacetylketene diethylacetal (8·5 g, 26·2 mmoles) was heated at 120° for 10 hr. The resulting partly crystalline product, upon treatment with dry ether (12 ml), yielded a colourless product (2·1 g, 15·4%) which, on recrystallization from ethanol, had m.p. 174–175°. The IR spectrum is reported in Fig. 1. The NMR data are summarized in Table 1. UV λ_{max} = 260 mμ (s); ε = 2000. (Found: C, 81·12; H, 6·70; OC_2H_5, 17·07; $C_{35}H_{34}O_4$ requires: C, 81·05; H, 6·61; OC_2H_5, 17·38%).

3,3-*Diphenyl-5-methyl-6-diphenylmethyl-2,4-pyronone* (Xb)

By hydrolysis of IXb. A mixture of IXb (1 g), dioxane (10 ml) and conc. HCl (0·5 ml) was heated at 80° for 2 hr and the solvent was removed under red. press. The solid residue was washed with water and collected by filtration; on recrystallization from ethanol, white needles (0·52 g, 60·6%) m.p. 156–157° were obtained. The IR spectrum is reported in Fig. 2. The NMR data are summarized in Table 2. UV λ_{max} = 283 mμ; ε = 8850. (Found: C, 83·64; H, 5·52; $C_{31}H_{24}O_3$ requires: C, 83·76; H, 5·44%).

1,1,5,5-*Tetraphenyl-3-methylpentan-2,4-dione* (XIb)

(a) *By hydrolysis of* IXb. A mixture of the acetal IXb (1 g), dioxane (15 ml) and conc. HCl (15 ml) was refluxed for 6 hr. After cooling, the solution was taken to dryness and the solid residue dissolved in ether. The ether solution was washed with 2N Na_2CO_3 and with water and finally dried. After removal of the solvent a solid (0·6 g, 74·4%) was obtained. Recrystallization from ethanol gave colourless needles m.p. 87°. (Found: C, 86·02; H, 6·44; $C_{30}H_{26}O_2$ requires: C, 86·09; H, 6·26%). This compound developed red colour with $FeCl_3$.

(b) *By hydrolysis of* Xb. Acid hydrolysis of Xb, performed in the experimental conditions used for the hydrolysis of IXb, gave XIb in good yields.

1,1-*Diphenylbutan-2-one and diphenylacetic acid*

(a) *By hydrolysis of* Xb. A solution of Xb (0·2 g) in 4% ethanolic KOH (6ml) was refluxed for 45 min. The solvent was removed under red. press., the residue was poured into water and extracted with ether. On evaporation, the dried ethereal extracts yielded a colourless oil. The identification of

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[9] P. M. Walters and S. M. McElvain, *J. Amer. Chem. Soc.* **62**, 1482 (1940).

[10] S. M. McElvain and J. T. Venerable, *J. Amer. Chem. Soc.* **72**, 1668 (1950).

this compound as 1,1-diphenyl-butan-2-one was made by mixed m.p. determination of its semicarbazone with an authentic sample.[11] The aqueous layer was acidified with dil. HCl and the precipitate (0·07 g), after crystallization from ethanol, identified (mixed m.p. and IR spectra) as diphenylacetic acid.

(b) *By hydrolysis of* XIb. Alkaline hydrolysis of XIb, performed in the experimental conditions described under (a) above, also yielded 1,1-diphenylbutan-2-one and diphenylacetic acid.

3,3-*Diphenyl-5-methyl-6-diphenylmethylentetrahydropyran-2,-4-dione 4-diethylacetal* (XIV) and 3,3-*diphenyl-5-methyl-6-diphenymethyl-2,4-pyronone 4-diethylacetal* (IXb)

From diphenylketene and methylketene diethylacetal in a ratio of 2:1. Diphenylketene[6] (4 g, 20·6 mmoles) and methylketene diethylacetal[9] (1·3 g, 10·3 mmoles) were heated at 100° for 16 hr. The reaction mixture was washed with light petroleum (10 ml) to remove the oily products, and the residue (2·5 g) was treated with boiling light petroleum (105 ml); while the resulting solution was still hot, a little insoluble material was filtered off. The solution was kept at room temp for 12 hr; the precipitate obtained (1·04 g) was collected by cautious decanting and recrystallized from light petroleum (m.p. 171–172°). The IR spectrum of this compound (XIV) is reported in Fig. 5. The NMR data are summarized in Table 4. UV $\lambda_{max} = 252$ mμ; $\varepsilon = 12850$. (Found: C, 80·80; H, 6·63; OC_2H_5, 16·67; $C_{35}H_{34}O_4$ requires: C, 81·05; H, 6·61; OC_2H_5, 17·38%).

By scratching, the decanted solution yielded a crystalline product (0·29 g) which upon recrystallization had m.p. 174–175° undepressed by admixture with the compound IXb obtained by reaction between 2-methyl-2- diphenylacetyketene diethylacetal (VIIb) and diphenylketene. The IR spectra were also identical.

3,3-*Diphenyl-5-methyl-6-diphenylmethyl-2,4-pyronone* (Xb)

By hydrolysis of XIV. The compound XIV by mild acid hydrolysis (experimental conditions described for the hydrolysis of IXb) yielded pyronone Xb.

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[11] W. Wilson, *J. Chem. Soc.* 6 (1952).