# Carboxylic Anhydrides and Diphenylketen, a New Reaction Mode of Ketens

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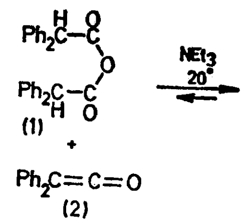
*Summary* Carboxylic anhydrides are converted into keten acylals or naphthalene-1,3-diol esters *via* base-catalysed *O*- or *C*-acylation by diphenylketen.

Diphenylacetic anhydride (**1**) combines with 1 equiv. of (**2**) in the presence of a trace of triethylamine (1 month, 25°) to give the keten acylal (**3**) (80%)[†] m.p. 128—129; ν (KBr) C=O 1792, 1770, C=C 1664 cm$^{-1}$; $\tau$ ($CDCl_3$) 2·86 (s, broad, 6 Ph) and 5·07 (s, 2 benzhydryl H). On distillation at 140—160°/0·0001 Torr, (**3**) cleaves to give (**1**) and (**2**) and can thus be used as an *in situ* generator for diphenylketen. *E.g.*, heating of (**3**) in hex-1-ene (5 days, 100°) produces 3-butyl-2,2-diphenylcyclobutanone (63%)[1] and (**1**) (73%).

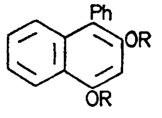


Scheme 1

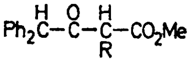
The formation of (**3**) is attributed to deprotonation of (**1**) by the tertiary amine and *O*-acylation of the enolate anion by (**2**). *C*-Acylation of carboxylic anhydride anions is preferred if not sterically prevented as in the enolate from (**1**). This is borne out by the behaviour of acetic anhydride which reacts with (**2**) and triethylamine (21 days, 50°, ethyl acetate) according to the stoichieometry:

$$\mathrm{Ac_2O} + 8\,\underset{(2)}{\mathrm{Ph_2C{=}C{=}O}} \rightarrow 2\,\underset{60\%}{\mathrm{C_{44}H_{32}O_4}} + \underset{(1)\ 21\%}{\mathrm{(Ph_2CH{-}CO)_2O}}$$

The n.m.r. spectrum of the compound $C_{44}H_{32}O_4$, m.p. 158—159°, reveals two diphenylacetyl-H as singlets at $\tau$ 4·55 and 5·02; the C=O frequency of 1758 cm$^{-1}$ is that of a phenyl ester. Formula (**4**) is confirmed by degradation and independent synthesis. Methanolic potassium hydroxide converts (**4**) into 2 equiv. of diphenylacetic acid and 4-phenylnaphthalene-1,3-diol (**5**) which gives a blue $FeCl_3$ reaction and was synthesised *via* (**6**) and (**7**).



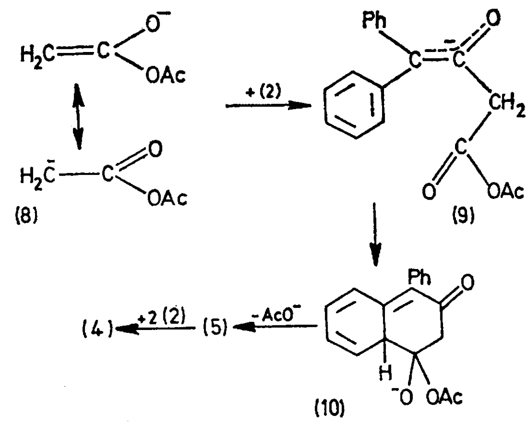
(4) R = CO•CHPh$_2$
(5) R = H



$$\mathrm{Ph_2\overset{H}{C}{-}\overset{O}{\overset{\|}{C}}{-}\underset{R}{\overset{H}{C}}{-}CO_2Me}$$

(6) R = CO$_2$CMe$_3$
(7) R = H

With the assumption of *C*-acylation of the acetic anhydride anion (**8**) by (**2**) as the key step, the mode of formation shown in Scheme 2 appears plausible.

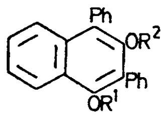


Scheme 2

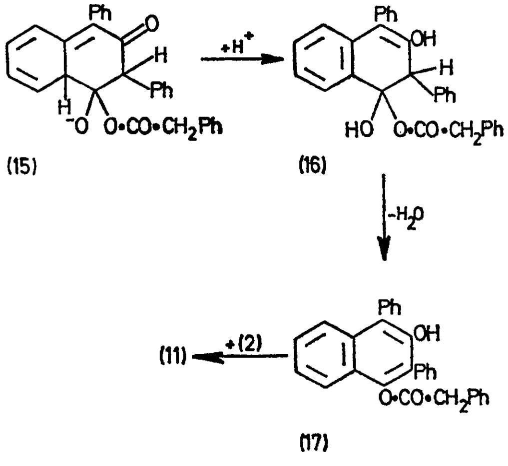
Surprisingly, the reaction of phenylacetic anhydride with (**2**) under triethylamine catalysis (7 days, 20°, ethyl acetate) yields an *isomer of* (**4**) in accordance with:

$$\mathrm{(PhCH_2{-}CO)_2O} + 4\,\underset{(2)}{\mathrm{Ph_2C{=}C{=}O}} \rightarrow \underset{41\%}{\mathrm{C_{44}H_{32}O_4}} + \underset{(1)\ 79\%}{\mathrm{(Ph_2CH{-}CO)_2O}}$$

The n.m.r. spectrum of the new isomer (**11**), m.p. 156—158°, reveals 29 aromatic protons, 1 benzhydryl-H at $\tau$ 5·45 (s) and 2 benzyl protons at 6·35 (s). The u.v. spectrum of (**11**) is similar to that of (**4**).



| | R$^1$ | R$^2$ |
|---|---|---|
| (11) | CO•CH$_2$Ph | CO•CHPh$_2$ |
| (12) | H | CO•CHPh$_2$ |
| (13) | H | H |



Scheme 3

Refluxing methanolic potassium hydroxide hydrolyses only the phenylacetate ester group of (**11**) giving the monoester (**12**), m.p. 153·5—154·5°.[2] Hydrolysis of the second,

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[†] All new compounds gave satisfactory CH analyses; mol.-weights with vapour pressure osmometer or mass spectrometer.

highly-screened ester group is effected by potassium hydroxide in ethylene glycol at 150° producing (**13**)[3] and diphenylacetic acid.

Up to the cyclization product (**15**), the formation pathway of (**11**) may parallel that of the acetic anhydride reaction as far as (**10**). Though (**10**) loses the acetate anion on aromatization, the phenylacetate residue in (**15**) is retained and hydroxide is instead eliminated. The sequence (**15**) → (**16**) → (**17**) (Scheme 3) illustrates one of many conceivable schemes for the prototropic shifts. The reason for the mechanistic divergence starting at (**10**) and (**15**) could be, that the relative configurations at the positions 3 and 4 of (**16**) allow a *trans*-elimination of water only.

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[1] R. Huisgen and L. A. Feiler, *Chem. Ber.*, 1969, **102**, 3391.

[2] D. S. Breslow, E. Baumgarten, and C. R. Hauser, *J. Amer. Chem Soc.*, 1944, **66**, 1286.

[3] H. Guesten, G. Kirsch, and D. Schulte-Frohlinde, *Tetrahedron*, 1968, **24**, 4393.