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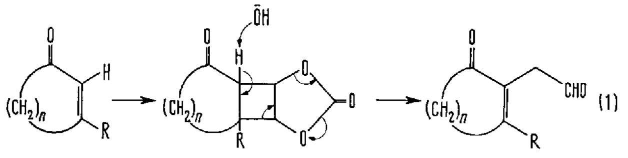
SPECIALIA

Fragmentation of Photoadducts between Vinylene Carbonate and Unsaturated Ketones

A procedure for the preparation of unsaturated 1,4-dicarbonyl compounds, which involved an oxidative fragmentation of a suitably substituted cyclobutane derivative has been described recently[1]. We now wish to report a shorter and more convenient method for the synthesis of the same kind of derivatives, which appears to be quite general.

The simple procedure consists in the hydrolysis (by water or dilute alkali) of the photoadduct between an α, β-unsaturated ketone and vinylene carbonate. The process is illustrated in equation (1) and it gives the final products in a good overall yield.

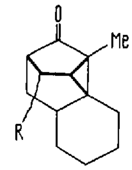


R = H, alkyl group $n = 2,3$

In a typical reaction, irradiation of isophorone (III) (276 mg) and vinylene carbonate (1.30 g) in distilled tetrahydrofuran (8 ml) with an 100 W Hanovia Mercury lamp through a Pyrex filter under nitrogen at $-10\,°C$ for 14 h resulted in the isolation of 2 crystalline adducts (IIIA), *cis*-anti-*cis* and *cis*-syn-*cis* (ratio 2:1) in an 85% yield[2]. Anti-isomer of (IIIA): [mp 98°; IR cm^{-1}: 1800, 1700; NMR: quadruplet (ABX, $J_{AB} = 6$ cps, $J_{AX} = 3.6$ cps, 1H) $\tau = 4.95$, doublet ($J = 6$ cps, 1H) $\tau = 5.23$, doublet ($J = 3.6$ cps, 1H) $\tau = 7.13$]. Syn-isomer of (IIIA): [mp 90°; IR cm^{-1}: 1800, 1700; NMR: triplet (ABX, $J_{AB} = 6$ cps, $J_{AX} = 7$ cps, 1H) $\tau = 4.74$, doublet ($J = 6$ cps, 1H) $\tau = 5.27$, doublet ($J = 7$ cps, 1H) $\tau = 7.14$]. On treatment with water or potassium hydroxide in methanol at room temperature, the anti-isomer of (IIIA) was readily converted to an oily unsaturated ketoaldehyde (IIIB) [IR cm^{-1}: 1670, 1725, 1640; NMR: triplet (1H) $\tau = 0.42$, broad singlet (2H) $\tau = 6.53$, broad singlet (4H) $\tau = 7.70$, singlet (3H) τ 8.07, singlet (6H $\tau = 8.95$; UV λ_{max}^{EtOH} nm (log ε): 243 (4.10)], in a yield of 90% (2,4-dinitrophenylhydrazone mp 131°). The conversion of the syn-isomer into (IIIB) proceeded in a lower yield. In a similar manner, a series of unsaturated ketones shown in Chart I has been studied and the spectral data of the products are assembled in the Table.

In all cases the outcome was the same, except in the case of compound (IV) which differs from the others by possessing a fully substituted double bond. On treatment with dilute alkali, (IVA) gave the cyclopropyl aldhyde (IVB). Further treatment of (IVB) with 10% methanolic potassium hydroxide gave quantitatively the hydroxyketone (VI) which was oxidized at low temperature in acetone with Jones' reagent to the diketone (VII) [mp 49°; IR cm^{-1}: 1720, 1750; NMR: multiplet (1H) $\tau = 7.44$, singlet (1H) $\tau = 7.60$, singlet (3H) $\tau = 8.60$]. The IR-spectrum of (VII) which had the typical cyclopropyl ketone carbonyl absorption at 1720 cm^{-1} [2] and a five-membered ketone at 1750 cm^{-1} supports the structure shown.

(VI) R = -OH
(VII) R = =O



Product	IR (cm^{-1})	NMR (τ, ppm)[a]
(IB)	2740	0.32 (1H) t
	1725	3.12 (1H) t
	1670	6.72 (2H) d
(IIB)	1730	0.40 (1H) t
	1670	6.57 (2H) d
	1640	8.07 (3H) s
(IVB)	2740	0.39 (1H) d
	1700	8.50 (3H) s
(VB)	1728	0.40 (1H) t
	1650	3.60 (1H) t
		6.80 (2H) d

[a] s = singlet, d = doublet, t = triplet.

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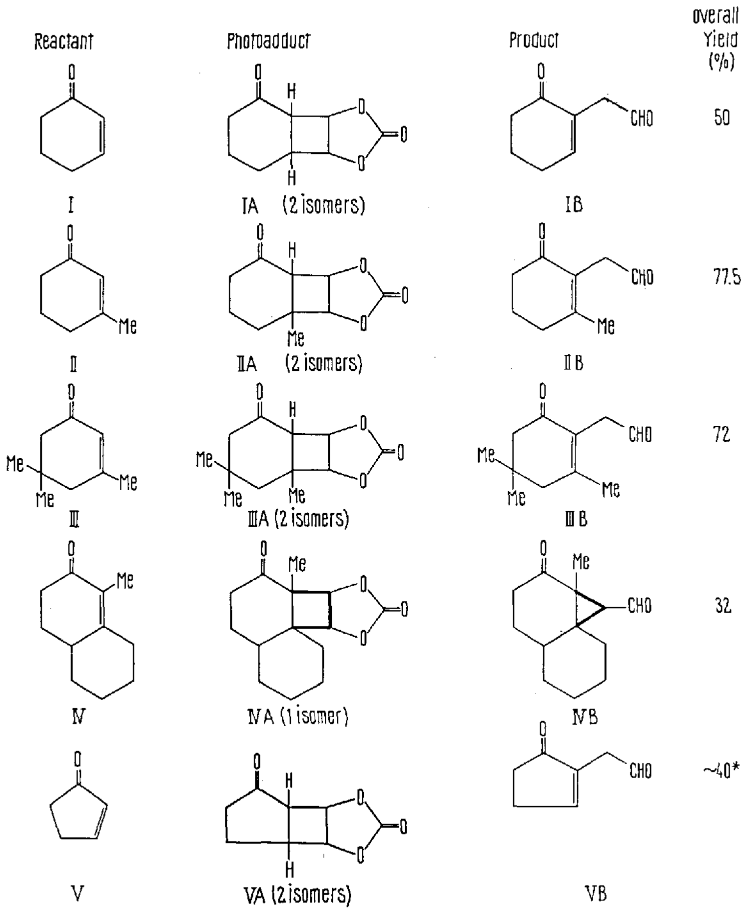
[1] N. R. HUNTER, G. A. MACALPINE, H. J. LIU and Z. VALENTA, Can. J. Chem. *48*, 1436 (1970).

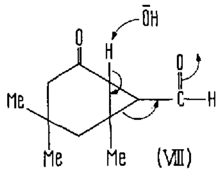
[2] Satisfactory analytical data were obtained for all new compounds reported.

[3] H. DUTLER, C. GANTER, H. RYF, E. C. UTZINGER, K. WEINBERG, K. SCHAFFNER, D. ARIGONI and O. JEGER, Helv. chim. Acta *45*, 2346 (1962). – P. J. KROPP and W. F. ERMAN, J. Am. chem. Soc. *85*, 2456 (1963).



In all cases shown in Chart I our procedure represents a very simple and efficient method to replace an α-hydrogen in an α, β-unsaturated ketone by an acetaldehyde side chain. The reaction mechanism which we believe may be responsible for the reported fragmentations is portrayed by the arrows in equation (1).

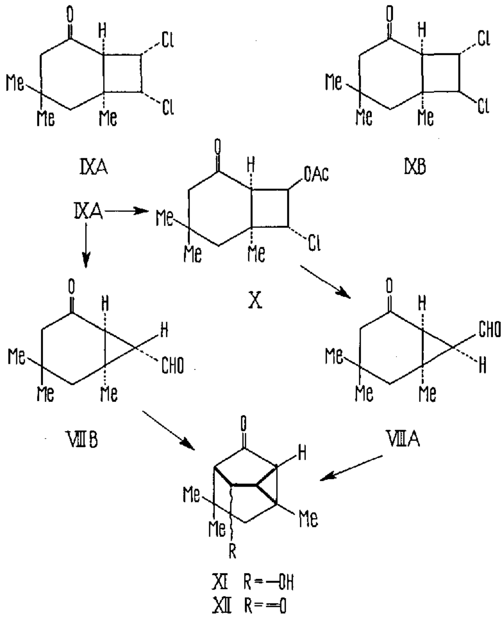
We have also considered the following mechanistic possibility. It would be conceivable that all the fragmentations proceed via cyclopropyl aldehyde intermediates such as (VIII). These intermediates could then open by a reverse Michael reaction (indicated by the arrows in formula (VIII)) provided there is an α-hydrogen present. In the absence of an α-hydrogen, the cyclopropyl aldehyde would be the final product (cf. IVB). However, this path does not seem to be correct. We have succeeded to prepare compound (VIII) and we have found that it does not yield the fragmentation product (IIIB) on treatment with water or dilute alkali.



(VIII)

Irradiation of (III) with *cis*-1,2-dichloroethylene in tetrahydrofuran gave two isomeric adducts, IXA and IXB (ratio 12:1) in a yield of 73%. Compound (IXA): [mp 99°; IR cm^{-1}: 1700; NMR: triplet (ABX, $J_{AB} = 8.5$ cps, $J_{AX} = 8$ cps, 1H) $\tau = 5.68$, doublet (J = 8.5 cps, 1H) $\tau = 5.96$, doublet (J = 8 cps, 1H) $\tau = 7.35$]. Compound (IXB): [mp 89°; IR cm^{-1}: 1700; NMR: triplet (ABX, $J_{AB} = 6$ cps, $J_{AX} = 8$ cps, 1H) $\tau = 5.15$, doublet (J = 6 cps, 1H) $\tau = 5.57$, doublet (J = 8 cps, 1H) $\tau = 6.96$].

Treatment of (IXA) with zinc dust in boiling glacial acetic acid gave the chloroacetate (X), which on metha-



* Because the product VB was unstable the yield varied from run to run.

nolysis in dilute alkali at pH 9 yielded the oily cyclopropyl aldehyde (VIIIA) [IR cm^{-1}: 1700, 1716; NMR: doublet (1H) $\tau = 0.20$, singlet (3H) $\tau = 8.57$, singlet (6H) $\tau = 8.95$]. Reaction of (IXA) with lithium carbonate and lithium chloride in anhydrous dimethylformamide gave quantitatively the crystalline cyclopropyl aldehyde (VIIIB), isomer of (VIIIA) [mp 56°; IR cm^{-1}: 1700, 1716; NMR: doublet (1H) $\tau = 0.54$, singlet 3H) $\tau = 8,60$, singlet (6H) $\tau = 9.00$]. The mass spectra of compound (VIIIA) and (VIIIB) were identical. Both (VIIIA) and (VIIIB) on treatment with 10% methanolic potassium hydroxide gave exclusively the hydroxy ketone (XI) which was oxidized with Jones' reagent to the diketone (XII) [mp 109°; IR cm^{-1}: 1724, 1750; NMR: singlet (1H) $\tau = 7.35$, singlet (1H) $\tau = 7.96$, singlet (2H) $\tau = 8.10$, singlet (3H) $\tau = 8.70$, singlet (6H) $\tau = 8.91$][4].

Zusammenfassung. Einfache photochemische Methode für die Substitution von α-H-Atomen eines α, β-ungesättigten Ketons durch eine Acetaldehyd-Seitenkette.

Pak-Tsun Ho, S.F. Lee, D. Chang,
and K. Wiesner

Natural Products Research Center,
University of New Brunswick,
Fredericton (N.B., Canada), 28 June 1971.

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[4] We wish to thank the National Research Council, Ottawa, and Hoffmann-La Roche, Nutley, New Jersey, for financial support of these studies.

Polarographic Determination of the Reaction Rate of the Second Step in an SN1 Displacement

We wish to disclose the first direct determination of the rate of the second 'very fast' step in an SNI displacement by a novel application of polarographic kinetic currents.

Since the discovery of polarographic kinetic currents[1] this method has been frequently used for the determination of fast reaction rates mainly in an 'equilibrium situation'.

$$\mathrm{N} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R \qquad (1)$$

If a nonreducible species N is in equilibrium with a reducible species R, then under certain conditions, which result in 'complete kinetic control', the polarographic wave of R is controlled by the rate of formation k_1 and the rate of decay k_2 of this species.

Equation (2) gives the value of the kinetic current $\bar{i}_k$ as a function of the concentration of N, the two rate constants k_1 and k_2, the diffusion constant of the reducible species D and the average surface of the electrode q[2-4].

$$\bar{i}_k = n\ \mathrm{F}\ 10^{-3}\ q\ D^{1/2}\ k_1 \sqrt{1/k_2}\ [\mathrm{N}] \qquad (2)$$

Since equation (2) contains two unknowns (k_1 and k_2), we must have at our disposal a second relationship between them, in order to be able to solve the system. Such a relationship is mostly provided by the determination of the equilibrium constant $\mathrm{K} = k_1 / k_2 = [R] / [\mathrm{N}]$.

Consider now an irreversible system undergoing SN1 displacement.

$$RX \xrightarrow{k_1} R^{(+)} \xrightarrow{k_2} RS \qquad (3)$$

The starting material RX ejects the leaving group X^- in the rate – determining first step and yields the carbonium ion $R^{(+)}$. This species reacts 'extremely rapidly' with the solvent S and yields the end product RS. The reaction is first order and the overall rate is identical with the rate of the first step k_1. Let us assume that both RX and RS are polarographically nonreducible and $R^{(+)}$ yields a well defined polarographic wave.

Equation (2) is immediately applicable to this system and may be written in the form (4)

$$\bar{i}_{k(t)} = n\ \mathrm{F}\ 10^{-3}\ q\ D^{1/2}\ k_1 \sqrt{1/k_2}\ [RX]_t \qquad (4)$$

The kinetic current of the carbonium ion, $\bar{i}_{k(t)}$ is directly proportional to the concentration of the starting material RX. Since RX decreases by a first order reaction, the kinetic current is time dependent and from this time dependence it is possible to evaluate simply the overall reaction rate k_{exp}.

Now the overall reaction rate k_{exp} is identical with the rate of the first step k_1.

Consequently, if we introduce into the equation (4) the kinetic current at time zero $\bar{i}_{ko}$ obtained by extrapolation, the initial concentration of the starting material $[RX]_o$ and substitute the known k_{exp} for k_1 the rate constant for the second fast step k_2 may be calculated.

Since diffusion coefficients are difficult to determine, it is convenient to eliminate from equation (4) the diffusion coefficient D by introducing the concept of 'theoretical diffusion current' $\bar{i}_d$. This may be defined as the height of the diffusion controlled polarographic wave given by a reducible compound which has the same diffusion coefficient as RX in the same solvent system and is present in the same concentration as RX. It is clear that $\bar{i}_d$ may be determined by recording a polarogram of a reducible compound of very approximately the same size and shape as RX. Thus, we obtain the equation (5) which contains besides k_2 only readily measurable quantities.

$$\bar{i}_{k_0} / \bar{i}_d = 0.886 \sqrt{[\text{drop time}]}\ k_{exp} / \sqrt{k_2} \qquad (5)$$

In acetone water mixtures which contain less than 10% v/v water the chloride I has been reported[5] to undergo an SN1 displacement and yield the alcohol III via the carbonium ion II.

We now find that this system gives a clear polarographic wave ($\mathrm{E}_{1/2} = -0.37$ V vs S.C.E.) which decreases with time as a first order reaction. The wave is independent of mercury pressure[1], surfactants, linearly dependent on the concentration of I and it gives smooth '*i–t*' parabolas

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