Tetrahedron Letters,Vol.25,No.8,pp 817-820,1984
Printed in Great Britain

0040-4039/84 $3.00 + .00

THERMAL AND PHOTOCHEMICAL REACTIONS OF BIACETYL WITH 1,1-DIETHOXYETHENE."UMPOLUNG" OF THE REACTIVITY OF BIACETYL BY PHOTOCHEMICAL INDUCED ELECTRON TRANSFER.

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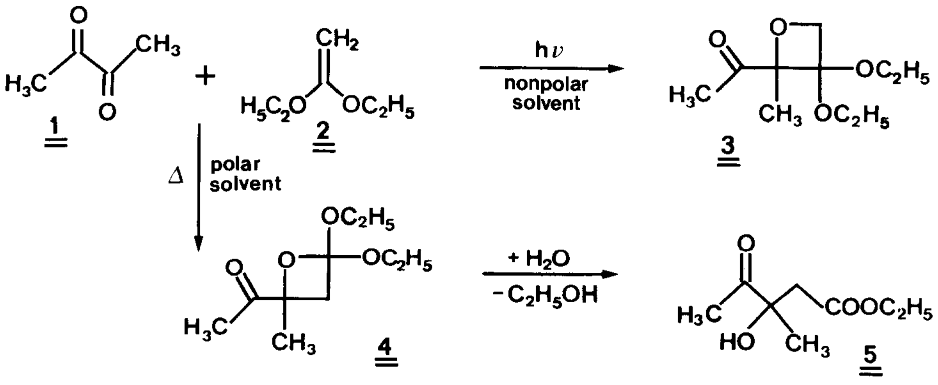
Summary: The thermal and photochemical reactions of biacetyl 1 and 1,1-diethoxyethene 2 are totally complementary: 1 and 2 exclusively form the 2,2-diethoxyoxetane 4 in polar solvents at room temperature. Contrary to the literature this thermal cycloadditon proceeds uncatalyzed. 1 and 2 react photochemically under exclusive formation of the regioisomer oxetane 3 - preferably in nonpolar solvents. The inversion ("Umpolung") of the reactivity of 1 is caused by the photoinduced electron transfer.

Introduction: Oxetane formation from electronically excited carbonyl compounds and olefins belongs to the most extensively studied photoreactions[1,2]. A recently reported investigation of chiral induction in the Paterno-Büchi reaction again demonstrated its importance both as a synthetic route to natural products and their precursors, respectively, and as a tool for mechanistic studies[3]. Generally, the relatively low regioselectivity of these reactions, at least for enol ethers and ketene acetals is explained by the involvement of exciplexes of some CT-character and biradicals as intermediates[2,4]. Exclusive formation of one regioisomer is observed only in thermal cycloadditons between electron-poor carbonyl compounds and electron-rich olefins[5,6]. In most cases these reactions are catalyzed by Lewis acids.

In recent papers we reported studies on the influcence of charge (electron) transfer on the addition-substitution-ionic photodissociation pattern of photoreactions of biacetyl 1 and 1,3-dioxoles[7,8]. For example the decreasing oxidation potential $E^{ox}_{1/2}$ of the olefin results in increasing substitution product formation including the possibility of dissociation into free radical ions in polar solvents. In extension of these studies we investigated photochemical and thermal reactions of biacetyl 1 with 1,1-diethoxyethene 2 in order to clarify the effect of charge transfer (CT) on the regioselectivity of this photoreaction and on the relation to its thermal counterpart.

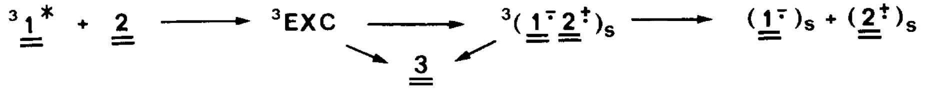
Products: Preparative irradiation[9,10] of 1:1 mixtures containing 1 and 2 in cyclohexane or benzene (0.01-0.1 M) with λ=400-500 nm results in formation of only one cycloadduct 3 in 69 % isolated yield identified as 2-acetyl-2-methyl-3,3-diethoxy-oxetane[11,12] (scheme 1).



(1)

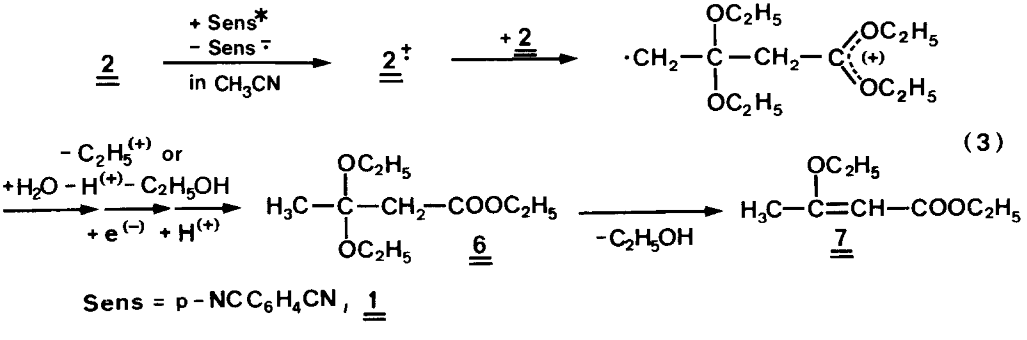
In contrast to this the thermal reaction[9,13] of 1 and 2 in acetonitrile (1.5M) at room temperature yields exclusively 2,2-diethoxy-4-acetyl-4-methyl-oxetane 4[14] in 34 % isolated yield[15]. 4 was also identified as 3-hydroxy-3-methyl-levulinic acid ethylester 5[16] (scheme 1). Two aspects are noteworthy in relation to thermal cycloadditions of electron-poor carbonyl compounds and electron-rich olefins reported by Scheeren and coworkers[5,6]: contrary to these authors (1) we were able to isolate and purify 2,2-dialkoxy oxetanes (especially from 1,1-dialkoxyethenes[17] under certain precautionary measures[9] (2) we could show that these cycloadditions proceed even in a non catalyzed reaction[18].

Mechanistic studies and discussion. Photoreaction: The Stern-Volmer data for luminescence quenching of 1 by 2 in benzene (K_{SV} = 3.36 ± 0.01 $lmol^{-1}$ for fluorescence, $\tau_F(1)$ = 9.15 ns; K_{SV} = 3940 ± 90 $lmol^{-1}$ for phosphorescence, $\tau_P(1)$ = 283.6 ± 15.4 μs) indicate that the photoreaction mainly occurs via T_1 at the chosen concentrations. This was further proofed by sensitization of 1 using benzophenone yielding exclusively 3 in presence of 2[19]. In a preceding paper[20] dealing with reactions of excitated 1 with electron-rich olefins we were able to differentiate between a primary step leading to a less polar intermediate ("exciplex") and a consecutive pathway yielding either products or free radical ions. Because of these results and because of the dependence of the product quantum yield on solvent polarity (table) we propose the following mechanism (scheme 2):



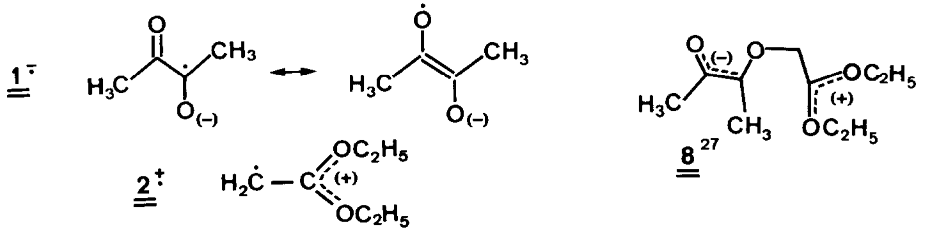
(2)

A more quantitative description of this competition between product formation and ionic photodissociation - according to Masuhara's method[21] - is described elswhere[8]. Additional evidence for this mechanism is obtained by isolation of 6 and 7[22] after photolysis of 1 and 2 in acetonitrile using HPLC. 6 and 7 are also formed by electron transfer sensitization [23] of 2 in polar solvents - like acetonitrile or tetrahydrofuran - via free radical ions (for the proposed mechanism in scheme (3) see ref. 23 and ref. there in).



(3)

Formation of 3 must involve intersystem crossing and therefore should proceed stepwise. In analogy to the exciplex-biradical mechanism of oxetane formation of simple ketones[2], but under consideration of the photoinduced electron transfer we further propose a zwitterionic intermediate 8 in the addition reaction pathway (scheme 4).

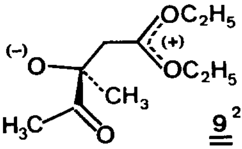


(4)

8 may be formed from the exciplex followed by e-transfer or from a contact ion pair (scheme 2). Evidence for a mechanism involving first e-transfer and secondly σ-bond formation is given by the most important VB-structures of $1^{\cdot-}$ and $2^{\cdot+}$ obtained from

ESR-measurements[24,25](scheme 4). 1,1-Dialkoxyethene radical ions with ca. 80 % of spin density at the 2-position[25] may couple with the ketyl-type structured semidione 1$^{\bullet-}$[24] via the radical centers at O and C,respectively, yielding the most efficiently stabilized zwitterion 8.

Thermal reaction: Contrary to the photoreaction the thermal cycloaddition to 4 works better in polar solvents (table). Based on a frontier MO treatment of cycloadditions by Houk[26] the HOMO(2)-LUMO(1) interaction (1_s^D + 1_s^A) should lead to 4 via a dipolar intermediate 9, stabilized in polar solvents.



9[27]

Our results indicate that the reactivity of a carbonyl compound in (2+2) cycloadditions can be totally reversed by photoinduced e-transfer. Further investigations dealing with other diketones are in progress.

Acknowledgement: The authors are very grateful to Prof. H.-D. Scharf (Aachen) both for his generous support of this work and for his stimulating and helpful discussions.

Notes and References:

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9) Because of the sensitivity of 2 and the products (especially 4) all glass apparatuses should be free of acids which can be done by immersing all glass vessels in sodium hydroxide solution over night before use.
10) Philips HPK 125 W as light source; solution of copper sulphate, sodium nitrite, and concentrated ammonia as filter; complete conversion of 0.1 mol educts requires ca. 2o h irradiation under nitrogen.
11) 3: b.p. 39-40 °C/0.1 torr. IR (neat)$\tilde{\nu}$: 2981,2935,2893 (CH); 1717 (C=O); 1214,1120-1048 cm^{-1} (COC).^1H-NMR (CCl_4) δ=1.19 and 1.17 (2xt,J=7 Hz,OEt,6H); 1.40 (s,CH_3,3H); 2.21 (s,acetyl,3H); 3.41 and 3.45 (2xq,J=7 Hz,OEt,4H); 4.40 (s,CH_2O,2H).^{13}C-NMR (C_6D_6) δ=15.06 and 15.56 (CH_3 from OEt); 18.80 (CH_3); 26.39 (CH_3 from acetyl), 58.12 and 58.61 (CH_2 from OEt); 76.10 (CH_2O); 97.88 (C-2); 102.17 (C-3); 208.68 (C=O).
12) Spectroscopic (NMR) and chromatographic (VPC, HPLC) analyses of the reaction mixture clearly showed that traces of 4 are only formed at higher educt concentrations due to a thermal reaction between 1 and 2 caused by the higher polar reaction medium (see text). This was proved by comparable experiments both under irradiation and under absence of light: e.g. the 3/4 ratio amounts to 97/3 at c= 0.2 M after 2d irradiation time.
13) See table for reaction conditions.
14) 4: b.p. 58 °C/2.5 torr. IR (neat)$\tilde{\nu}$ = 2980,2935,2899 (CH); 1720 (C=O); 1273,1213,1095, 1050 cm^{-1} (COC). ^1H-NMR ($CDCl_3$) δ = 1.20 and 1.24 (2xt,J=7Hz,OEt,6H); 1.53 (s,CH_3, 3H); 1.97 (s,acetyl,3H); 2.50 and 2.80 (AB,J=12Hz,CH_2,2H); 3.39 and 3.44 (2xq,OET, 4H); ^{13}C-NMR (C_6D_6) δ = 15.23 and 15.33 (CH_3 from OEt); 23.42 (CH_3); 24.25 (CH_3 from acetyl); 57.42 and 57.49 (CH_2 from OEt); 41.62 (C-3); 78.31 (C-4); 113.22 (C-2); 210.00 (C=O).
15) The relatively low isolated yield of 4 is caused by its sensitivity against traces of water. Ethyl acetate, ethyl orthoacetate, and the levulinic acid derivative 5 were detected as byproducts in the reaction mixture indicating partly hydrolysis of 2 and 4.
16) 5: 60 % yield after hydrolysis in acetone-water at room temperature according to Schroeter (ref. 4). b.p. 100 °C/12 torr (Kugelrohr). IR (neat) $\tilde{\nu}$ = 3470 (OH); 1735, 1715 cm^{-1} (C=O). ^1H-NMR ($CDCl_3$) δ = 1.33 (s,CH_3,3H); 1.26 (t,J=7Hz,OEt,3H); 2.31 (s,acetyl,3H); 2.56 and 3.05 (AB,J=17 Hz, CH_2, 2H); 4.16 (q,J=7 Hz,OEt,2H).

17) Photochemical and thermal reactions of 1 and 1,1-dimethoxyethene yield analogous products as obtained with 2.

18) A self-catalyzed thermal reaction (e.g. by the acidic enol of 1)may be excluded just like in the non-catalyzed cycloaddition of benzil and 2.

19) Appropriate concentrations for benzophenone, 1 and 2 were chosen according to absorption and emission quenching measurement to ensure excitation of benzophenone only and triplet energy transfer to 1 only.

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27) Only one conformer of 8 and 9, respectively, is drawn.

Table: Dependence of the photochemical (to 3) and thermal reaction (to 4) on solvent polarity at 20 °C.

Solvent	ε a)	$\phi(3)$ b)	$1 + 2 \rightarrow 4$ c)	
			conversion [%]	yield [%]
n-Hexane	1.88	0.099		
Cyclohexane	2.02	0.110		
Benzene	2.28	0.095	19	16
Diethyl ether	4.34	0.070	46	26
Chloroform	4.81	0.065	91	55
Tetrahydrofuran	7.58	0.045	63	36
Dichloromethane	8.93	0.051		
Acetonitrile	37.5	0.04	82	38

a) Dielectric constants from C. Reichardt in "Solvent Effects in Organic Chemistry" (H.F. Ebel, Ed.) Verlag Chemie, Weinheim 1977.

b) Potassium ferri-oxalate as actinometer; quantitative product formation was determined by VPC on silicone OV 17 - column using α-methylnaphthalene as internal standard.

c) c(1) = c(2) = 1.5 M in deuterated solvents; monitored by ^{1}H-NMR using C_6H_6 as internal standard; reaction time (under abscence of light) = 70 h.

d) The faster reaction may be caused by acid catalysis.

(Received in Germany 14 September 1983)