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Photolysis of 1,4-Dichlorobutane Sensitized by the n,π^* Singlet State of Acetone

Sir:

We wish to report the photodecomposition of 1,4-dichlorobutane (1,4-DCB) sensitized by the $[n,\pi^*]^1$ state of acetone, a reaction that may be the first example in which this particular state photosensitizes a chemical, rather than a physical, process. Although much interest has been shown in photosensitization of the $[n,\pi^*]^3$ state of acetone and other carbonyl compounds,[1-6] apparently the only cases of photosensitization by the corresponding $[n,\pi^*]^1$ state involve sensitization of biacetyl fluorescence,[7] or quenching of type II photoelimination from aliphatic ketones,[8] through singlet–singlet energy transfer to biacetyl. The acetone photosensitized decomposition of 1,4-DCB is of added interest since it offers photo*chemical* indications for the occurrence of excimer and monomer forms of the $[n,\pi^*]^1$ state, complementing recently reported photo*physical* evidence, based on fluorescence measurements.[9]

Degassed 1,4-DCB–acetone solutions, with and without isooctane as inert diluent, were sealed in tubes with optically flat quartz or Pyrex windows and irradiated at 3130 Å in a merry-go-round apparatus.[10] The major products were hydrogen chloride and 1,3-dichlorobutane (1,3-DCB). This communication is concerned only with the former product, and detailed results will be presented later.[11] The initial quantum yields for HCl formation[12] ($\lesssim$1% photolysis) are all acetone *photosensitization* values; the yields, for quartz tubes, represent only the energy-transfer contribution after subtracting the calculated contribution due to direct absorption by 1,4-DCB at 2537 Å[13] (using Φ(HCl) = 0.032 for the direct photolysis[11]). The data obtained with Pyrex and quartz[14] windows show that it is immaterial if the radiation is $\lesssim$3100 Å, so long as it lies within the acetone n → π^* band. This implied wavelength independence of Φ(HCl) was confirmed by runs in quartz tubes using monochromatic 2537-Å radiation.[15]

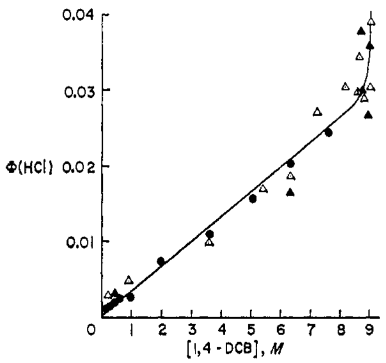

Figure 1. Effect of 1,4-dichlorobutane concentration on the quantum yield of hydrogen chloride at 3130 Å. The circles correspond to 1,4-DCB–acetone–isooctane solutions at constant acetone concentration (0.544 *M*), and the triangles correspond to 1,4-DCB in acetone alone. The open symbols denote runs in quartz tubes and the closed symbols denote those in Pyrex; △ represents a typical run in quartz at 2537 Å.

Figure 1 shows Φ(HCl) to be essentially a linear function of 1,4-DCB concentration over almost the entire concentration range. This is so whether the samples contain only 1,4-DCB and acetone, or contain a fixed acetone concentration in various 1,4-DCB–isooctane solutions. At the highest substrate concentrations (neat 1,4-DCB = 9.13 *M*), where [acetone] $\lesssim$ 0.2 *M*, there is a significant departure from a straight line because Φ(HCl) is then markedly dependent on acetone concentration (see Figure 2). The absence of a sharp rise in yield with leveling off at low substrate concentration, characteristic of triplet–triplet energy transfer (*e.g.*, acetone[2,4] or benzene[16] photosensitized *cis–trans* isomerization of an olefin), suggests that the $[n,\pi^*]^3$ state is not involved here. This view is supported by the fact that irradiation in the presence of dissolved oxygen, or a simple olefin, both efficient triplet quenchers,[4] did not suppress the photosensitized reaction. Furthermore, although the benzene triplet sensitizes the photolysis (and radiolysis) of chloroform[17,18] or carbon tetrachloride,[17] triplet sensitization of the radiolysis[17] of ethyl and propyl chlorides is not observed; hence, it probably does not occur in the photolysis of 1,4-DCB either. On the other hand, quenching of acetone fluorescence (at 340 mμ) by 1,4-DCB, though inefficient, was definitely observed, with a Stern–Volmer plot showing a slight upward curvature and an initial slope of ~0.05 M^{-1}. These facts all indicate that the $[n,\pi^*]^1$ state of acetone is the probable source for the photosensitized decomposition of 1,4-DCB. The possibility that acetone sensitization in-

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(1) G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962); G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964).

(2) R. F. Borkman and D. R. Kearns, *ibid.*, **88**, 3467 (1966).

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(5) H. Morrison, *J. Am. Chem. Soc.*, **87**, 932 (1965).

(6) N. C. Yang, J. I. Cohen, and A. Shani, *ibid.*, **90**, 3264 (1968).

(7) See F. Wilkinson, *Advan. Photochem.*, **3**, 241 (1965), for a review of this topic.

(8) J. L. Michel and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **85**, 1027 (1963); N. C. Yang and S. P. Elliott, *ibid.*, **90**, 4194 (1968).

(9) M. O'Sullivan and A. C. Testa, *ibid.*, **90**, 6245 (1968); their findings have been verified by the present author.

(10) Rayonet reactor, equipped with 16 fluorescent lamps with emission peaked at 3130 Å, and calibrated with uranyl oxalate actinometry. The tubes had a 4-mm light path, and the absorption properties of the solutions were calculated from measured uv spectra.

(11) M. A. Golub, submitted for publication.

(12) Potentiometric titration with NaOH of methanol–water extracts of the frozen contents of irradiated tubes.

(13) Although most of the emission from this source[10] is centered at 3130 Å, ~15% is at 2537 Å.

(14) The quartz windows were used to enhance acetone absorption at ~2850 Å, thereby increasing the likelihood of observing effects from the *monomer* form of the $[n,\pi^*]^1$ state, as opposed to the excimer.[9]

(15) The Rayonet reactor[10] equipped with low-pressure mercury resonance lamps.

(16) R. B. Cundall and A. S. Davies, *Trans. Faraday Soc.*, **62**, 1151 (1966).

(17) W. Van Dusen, Jr., and W. H. Hamill, *J. Am. Chem. Soc.*, **84**, 3648 (1962).

(18) S. H. Ng, G. P. Semeluk, and I. Unger, *Can. J. Chem.*, **46**, 2459 (1968).

volved some methyl radicals generated in its photolysis was dismissed since vpc analysis revealed negligible formation of products arising from acetone.[11]

The sharp increase in Φ(HCl) with acetone dilution (Figure 2) points to the *monomer* form of the $[n,\pi^*]^1$ state as the effective photosensitizer.[19a] Thus, for example, just as the acetone monomer fluorescence yield is approximately doubled in going from 1.1×10^{-2} to 2.7×10^{-3} *M* in hexane,[9] also is Φ(HCl) doubled for the same concentrations. However, at [acetone] $\gtrsim$ 0.1 *M*, the $[n,\pi^*]^1$ state is mainly in the excimer form, so that Φ(HCl) will reflect the concentration of singlet monomer in equilibrium with its excimer.[19b] In fact, according to the kinetics of energy transfer involving successive excimer formation and dissociation,[20] the energy-transfer efficiency, and hence Φ(HCl), should be independent of the sensitizer concentration (*i.e.*, independent of isooctane dilution) at a given concentration of 1,4-DCB, so long as [acetone] $\gtrsim$ 0.1 *M*. As Figure 1 shows, this is indeed the case, as is also the expected linearity of this plot.[21]

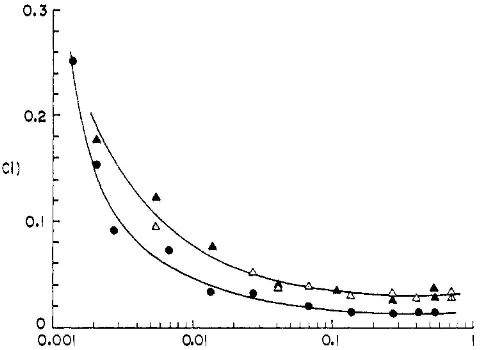

Figure 2. Effect of acetone concentration on the quantum yield of hydrogen chloride at 3130 Å. The circles correspond to 1,4-DCB–acetone–isooctane solutions at constant 1,4-DCB concentration (5.1 *M*) irradiated in Pyrex, while the triangles have the same significance as in Figure 1.

The mechanism for HCl formation, as well as rearrangement to 1,3-DCB, ensuant on sensitized C–Cl cleavage in 1,4-DCB, is presumed to be that depicted for the analogous processes in the photolysis and radiolysis of *n*-propyl chloride.[22]

Further work on sensitizing the photolysis of 1,4-DCB[23] using various excimer-forming compounds besides acetone is currently in progress.

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[19] (a) Sensitization presumably entails collisional deactivation by 1,4-DCB, the energy of the monomer $[n,\pi^*]^1$ state ($\gtrsim$92 kcal/mole) being ample to promote rupture of the C–Cl bond (bond strength $\simeq$ 80 kcal/mole). (b) Dissociation of 1,4-DCB through collisional deactivation of the excimer is probably unimportant since the excimer energy ($\sim$71 kcal/mole)[9] is less than the C–Cl bond strength.

[20] J. B. Birks, J. M. de C. Conte, and G. Walker, *IEEE Trans. Nucl. Sci.*, *NS*, 13, 148 (1966); J. B. Birks and J. C. Conte, *Proc. Roy. Soc.*, A303, 85 (1968), and references cited therein.

[21] In view of the low quantum yields, and hence high rates of competing decay processes.[20]

[22] H. L. Benson, Jr., and J. E. Willard, *J. Am. Chem. Soc.*, **83**, 4672 (1961); **88**, 5689 (1966).

[23] Preliminary data indicate that toluene and benzophenone are two other singlet sensitizers for this reaction.

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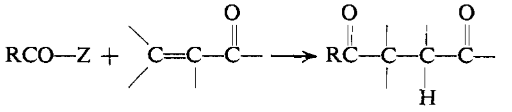
A Method for 1,4 Addition of Acyl Groups to Conjugated Enones

Sir:

This communication reports a new reaction which leads to the formation of a 1,4-dicarbonyl unit by the combination of acyl and conjugated enone moieties as depicted in eq 1. The direct formation of such 1,4-dicarbonyl structures by *intermolecular* coupling is not possible using classical synthetic reactions,[1] and consequently indirect approaches have been required, *e.g.*, a sequence employing the conjugate addition of nitro-stabilized carbanions to enones.[2] The reaction of conjugated enones with 2-lithio-1,3-dithianes, which are synthetically equivalent to C-nucleophilic carbonyl groups,[3] leads only to 1,2 addition to the enone system,[4] and other potentially useful and general reagents (*e.g.*, acetylide anions[5]) suffer from the same limitation.



$$\mathrm{RCO{-}Z} + \;\gt C{=}\underset{|}{C}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-} \longrightarrow \mathrm{R}\overset{\overset{\displaystyle O}{\|}}{C}{-}\underset{|}{\overset{|}{C}}{-}\underset{\underset{\displaystyle H}{|}}{\overset{|}{C}}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-} \qquad (1)$$

We chose to investigate the unstable intermediates formed by the reaction of metal carbonyls with organolithium reagents[6–9] as potential nucleophilic acyl equivalents. Complexes from nickel carbonyl[8] seemed especially promising in view of the recently discovered alkoxy- and aminocarbonylation reactions of halides.[10] Three reasonable mechanistic pathways by which conjugate addition of acyl could occur from such complexes are outlined in eq 2. Path a involves preliminary electron transfer, path b, direct acyl anion transfer, and path c, cycloaddition of acyl anion as though it were an

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[1] The cyclization of 4-methyl-4-(β-ethoxycarbonylethyl)-2-cyclohexenone to *cis*-9-methylindene-1,6-dione by lithium–ammonia reagent, an *intramolecular* enone acylation, has been reported recently by R. G. Carlson and R. G. Blecke, *Chem. Commun.*, 93 (1969); see also M. Tanabe, J. W. Chamberlin, and P. Nishiura, *Tetrahedron Lett.*, 601 (1961); B. J. Majerlein and J. A. Hogg, *J. Am. Chem. Soc.*, 80, 2220 (1958).

[2] See E. J. Corey, I. Vlattas, N. H. Andersen, and K. Harding, *ibid.*, 90, 3247 (1968), for an illustration.

[3] E. J. Corey and D. Seebach, *Angew. Chem. Intern. Ed. Engl.*, 4, 1075, 1077 (1965).

[4] E. J. Corey and D. Crouse, *J. Org. Chem.*, 33, 298 (1968); N. H. Andersen, unpublished work in these laboratories.

[5] For the synthesis of 1,4-dicarbonyl compounds from γ,δ-acetylenic ketones, see G. Stork and R. Borch, *J. Am. Chem. Soc.*, **86**, 935 (1964).

[6] M. Ryang, I. Rhee, and S. Tsutsumi, *Bull. Chem. Soc. Jap.*, 37, 341 (1964).

[7] S. Kwang-Myeong, Y. Sawa, M. Ryang, and S. Tsutsumi, *ibid.*, **38**, 330 (1965).

[8] M. Ryang, S. Kwang-Myeong, Y. Sawa, and S. Tsutsumi, *J. Organometal. Chem.*, 5, 305 (1966).

[9] E. O. Fischer and A. Maasböl, *Chem. Ber.*, 100, 2445 (1967), and references cited therein.

[10] E. J. Corey and L. S. Hegedus, *J. Am. Chem. Soc.*, **91**, 1233 (1969).