Tetrahedron. Vol. 27, pp. 5307 to 5313 Pergamon Press 1971. Printed in Great Britain

PHOTOCHEMICAL GENERATION OF IMINES FROM AZASUCCINIC ANHYDRIDES

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(*Received in the USA* 17 *June* 1971; *Received in the UK for publication* 26 *July* 1971)

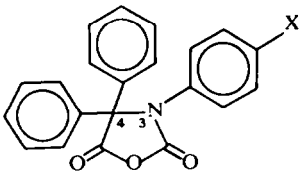
Abstract—Triarylazasuccinic anhydrides have been prepared and found to efficiently decompose photochemically by two pathways to give either the corresponding triarylimine, carbon dioxide and carbon monoxide or a diarylcarbenoid intermediate, carbon dioxide and an arylisocyanate. The type of photocleavage appears to be dependent on the position in the molecule of the chromophore with the lowest excited singlet state.

INTRODUCTION

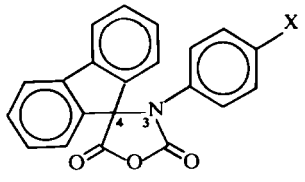
THERE ARE SEVERAL reports in the literature of the photocleavage of succinic anhydrides to give, *inter alia*, olefins, carbon dioxide and carbon monoxide.[1] It was of interest to see whether azasuccinic anhydrides would react in the same way to give imines, carbon dioxide and carbon monoxide.

DISCUSSION AND RESULTS

Several representatives of the hitherto unknown class of triarylazasuccinic anhydrides were synthesized by the addition of phosgene to the appropriate amino acid or amino acid ester. The first reaction afforded **1**, X = H and NMe_2. By the latter reaction, **2**, X = H, OMe and NMe_2 were obtained. Both methods afforded the desired anhydride analytically pure and in good yield.



1, X = H
NMe_2
NO_2

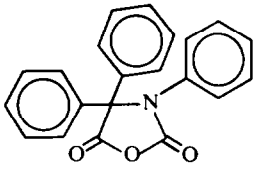


2, X = H
OMe
NMe_2
NO_2

Unlike the alkyl substituted Leuch's Anhydrides,[2] the triaryl anhydrides are exceedingly stable. They decompose with gas evolution and color formation only at temperatures above 200°C, and are solvolytically stable for months at room temperature in a variety of solvents including aqueous EtOH. Compounds **1**, X = H and **2**, X = H were cleanly nitrated by fuming HNO_3 in AcOH-Ac_2O to give the mononitro compounds **1**, X = NO_2 and **2**, X = NO_2, respectively.

On irradiation with 254 mμ light in MeOH, EtOH, benzene, ether or hexane, the

anhydride **1**. X = H is converted smoothly to the yellow anil of benzophenone **3**.* † In EtOH with oxygen present, the anil is formed in 61% yield (eq. 1) together with a trace of the cyclization product 6-phenylphenanthridine.[3] The formation of imine in hexane is not sensitized by acetone, nor is it quenched by perylene. Hence, decomposition probably occurs from the singlet excited state of the anhydride. When **1**. X = H is irradiated in benzene with the solvent absorbing >95% of the light, sensitization does occur since the rate of formation of **3** is undiminished. The anhydrides **1**. X = NMe_2 and NO_2 react similarly, as shown in Table 1.



1. X = H

$$+ \; h\nu \longrightarrow Ph_2C = NPh + CO_2 + CO \qquad (1)$$

3

TABLE 1. CORRELATION OF POSITION OF EXCITATION AND REACTION PATH FOR ANHYDRIDES

Compound	Lowest energy chromophore		Reaction *via*		Quantum yield[a]
	N_3	C_4	eq. 1	eq. 2	
1. X = H	+		100		0·4[b]
NMe_2	+		100		0·1[b]
NO_2	+		100		0·2[b]
2. X = H		+		100	0·2[c]
OMe	+	+?	29	71	0·1[c]
NMe_2	+		100		0·03[c]
NO_2	+				Slow

[a] Quantum yield for disappearance of anhydride calculated from the rate of appearance of anil and/or bifluorene as shown by the visible spectrum.

[b] In EtOH.

[c] In C_6H_6.

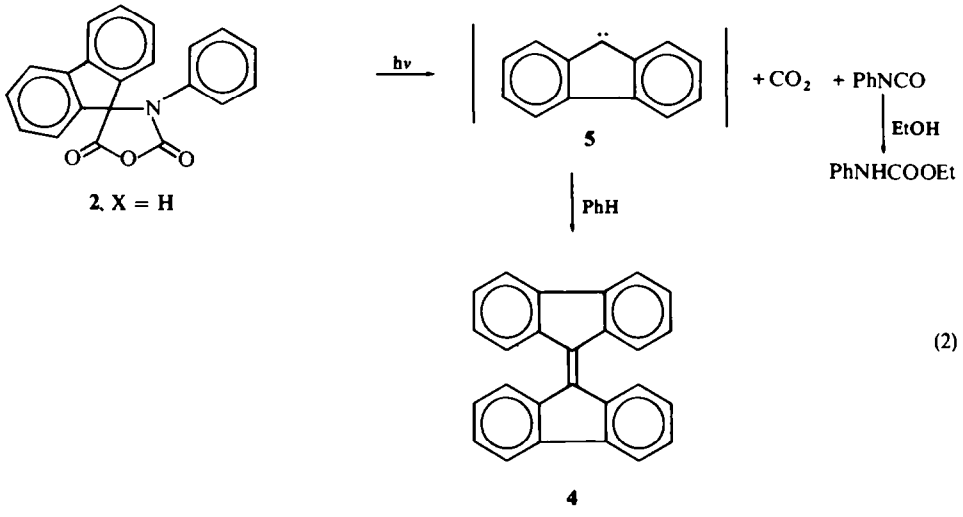
Surprisingly, irradiation of the fluorenylidine anhydride **2**, X = H with 254 mμ light in a variety of solvents gave *no* anil and only faintly colored solutions. After irradiation of **2**. X = H in EtOH, phenylurethane was isolated, while from undegassed benzene solution fluorenone was obtained. In degassed benzene, however, the anhydride afforded deep orange solutions from which Δ-9,9′-bifluorene **4**, but no imine, could be isolated by TLC (eq. 2).‡

* The anil products were identified by their visible spectra and by isolation and comparison with authentic compounds. (See Experimental).

† Imine formation is not observed in halogenated solvents such as methylene chloride.

‡ This compound was identified spectroscopically and by isolation and comparison with authentic Δ-9,9′-bifluorene.

A plausible explanation is that this anhydride cleaves in a different manner to give fluorene-9-carbene (**5**), phenylisocyanate and CO_2. The carbene **5** is known to dimerize in degassed benzene,[4a] oxididize to fluorenone in undegassed benzene,[4b] and react with other solvents. The phenylisocyanate reacts in EtOH to give phenylurethane.



2, X = H

5

4

(2)

In sharp contrast to the above result, the anhydride **2**, X = NMe_2 gave, on irradiation in degassed benzene, only imine and no Δ-9,9′-bifluorene, as shown by TLC. Intermediate behavior was exhibited by the anhydride **2**, X = OMe, which gives, in degassed benzene, both imine and bifluorene (Table 1). The product distribution in benzene was the same when 313 mμ light was used (direct absorption) as when 254 mμ light was used (singlet sensitization). The anhydride **2**, X = NO_2 reacted only very slowly, and no products could be identified.

The dichotomy of mechanism, *i.e.* the formation of imine in some cases and of bifluorene in others, appears to be related to the presence of two chromophores separated by a saturated center. The position of excitation, or that portion of the molecule with the lowest excitation energy, rather than the initially absorbing chromophore, appears to control the cleavage pathway. In the unsubstituted anhydride **1**, X = H, the lowest energy portion of the molecule is clearly the anilide system, not the Ph groups attached to the saturated carbon of the anhydride ring. Addition of the substituent X = NMe_2 or NO_2 does not change the situation, as is shown by the shift of the leading edge of the long wavelength band* from 275 to 335 and 330 mμ, respectively (Fig. 1). In **2**, X = H, however, the excitation must reside in the fluorenylidine group as is shown by the shift of the leading edge of the long wavelength band from 275 mμ to 300 mμ (Fig. 2). There is no apparent further shift in the long wavelength band edge on substitution of X = OMe, even though it must lower the transition energy of the anilide system. In **2**, X = NMe_2, the shift in the long wavelength

* Since the fluorescence of the anhydrides could not be detected the position of the 0–0 band was taken to be the leading edge of the longest wavelength peak.

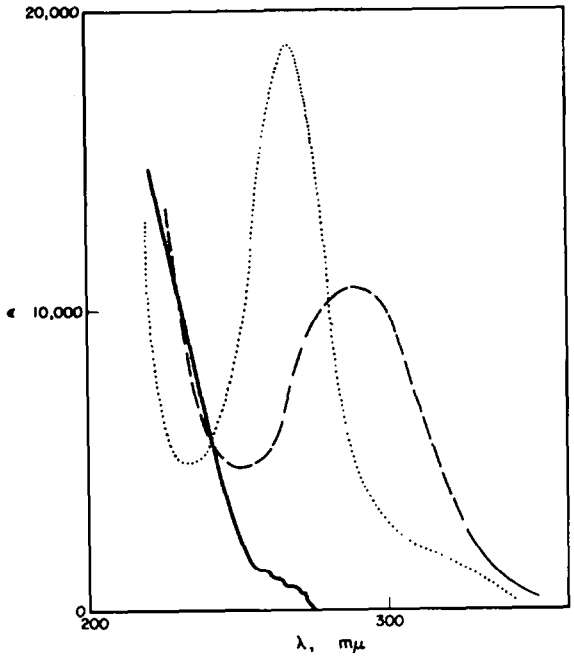


FIG 1. UV spectra in EtOH of 1. X = H——. X = NMe_2 ····· and X = NO_2- - - - -.

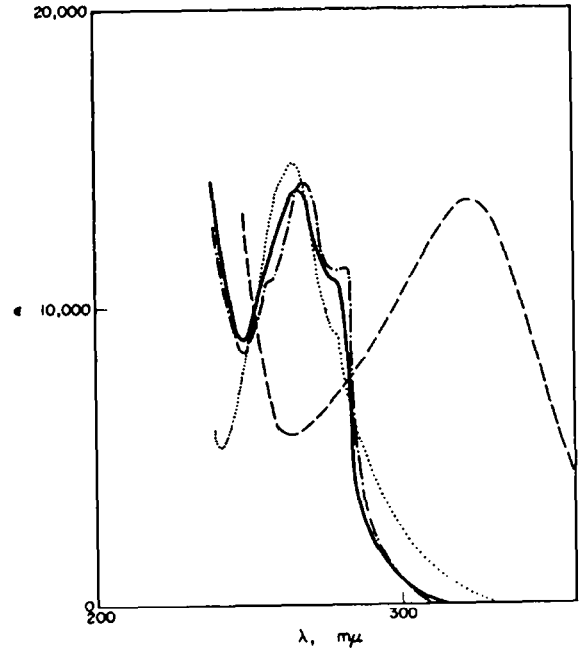


FIG 2. UV spectra in EtOH of 2. X = H ———. X = OMe-·-·-. X = NMe_2 ····· and X = NO_2- - - - -.

band edge to 320 mμ indicates that excitation again resides in the anilide moiety.* For those compounds where excitation resides in the anilide system, reaction occurs as in eq. 1. For the compound **2**, X = H, where the excitation resides in the aromatic substituent attached to the C_4 portion of the anhydride ring, reaction occurs as in eq. 2. For the anhydride **2**, X = OMe, where excitation might well be divided between the two chromophores, both modes of reaction occur. These results are summarized in Table 1.

Keller and Dolby,[5] *inter alia*, have reported emission as occurring from the lowest energy chromophore in an excited molecule. The photoreactions of these anhydrides appear to be the first examples where the course of reaction is controlled by the position in the reacting molecule where the electronic excitation ultimately resides.

EXPERIMENTAL

Synthesis and properties of imines

In a typical preparation, 1·00 g (5·6 mmoles) of fluorenone 1·00 g of N,N-dimethyl-*p*-phenylenediamine and 0·05 g of *p*-TsOH in 10 ml of xylene was heated to reflux for 24 hr under N_2. Water was removed with an azeotropic separator. The solvent was evaporated and the residue chromatographed on Florisil with hexane and $CHCl_3$. The appropriate fractions were combined, the solvent evaporated, and the residue recrystallized from EtOH to give 1·17 g (71%) of the anil as dark red plates, m.p. 112–113°.

This compound as well as the other imines synthesized showed a strong C=N band in the IR (Nujol® mull) near 1600 cm^{-1}, and analyzed within 0·3% for C, H and N. The yields, m.ps and spectral properties of the imines prepared are given in Table 2.

TABLE 2. SYNTHESIS AND PROPERTIES OF IMINES, $X_2C = NY$

X	Y	Yield %	m.p.	λ_{max}^{a} mμ	ε^{a}
Ph	Ph	92	114–115[b]	332	2.590
Ph	*p*-$Me_2NC_6H_4$	45	87–89[c]	384	7.330
Ph	*p*-$O_2NC_6H_4$	21	158–160	313	13.100
Fluorenylidine	Ph	61	88–90[d]	382	1.750
Fluorenylidine	*p*-$MeOC_6H_4$	72	136–137[e]	411	2.600
Fluorenylidine	*p*-$Me_2NC_6H_4$	71	112–113	477	4.460
Fluorenylidine	*p*-$O_2NC_6H_4$	80	254–257	312	7.500

[a] In EtOH. [b] Reported[6] 117. [c] Reported[7] 86–87.
[d] Reported[8] 88–89. [e] Reported[9] 135–136.

Synthesis of anhydrides

3,4,4-*Triphenyloxazolidine*-2,5-*dione* **1**, X = H. In a flask with a stirrer, dry ice condenser and gas inlet tube was dissolved 4·20 g (13·9 mmoles) of α-anilino-α,α-diphenylacetic acid[10] in 100 ml of toluene. About 20 ml of $COCl_2$ was added with stirring at 55° to the solution over the course of four hr. The mixture was heated two hr more and then 14 hr without the dry ice condenser. The mixture was filtered to remove amine hydrochloride, the solvent evaporated and the residue recrystallized from benzene-hexane to give 2·70 g (59%) of **1**, X = H, m.p. 128–129°. (Calcd for $C_{21}H_{14}NO_3$: C, 76·70; H, 4·59; N, 4·25. Found: C, 76·74; H, 4·52; N, 4·20%). This and the other anhydrides synthesized showed carbonyl absorption at 1838–1850 and 1770–1780 cm^{-1} and singly bonded carbon–oxygen bands at 1340–1367, 1245–1255 and 952–977 cm^{-1} in the IR (Nujol mull). All compounds showed the parent peak plus a strong peak for the loss of C_2O_3 in the MS.

* Models show the N-phenyl group of **1** is twisted out of the plane of the anhydride ring. In **2**, the two rings are coplanar. The resultant increased conjugation of the anilide nitrogen with a p-nitro group in **2**, X = NO_2 over that in **1**, X = NO_2 explains the much greater bathochromic shift of the former.

3-[p-(*Dimethylamino)phenyl*]-4,4-*diphenyloxazolidine*-2,5-*dione* **1**, X = NMe_2. To 4·92 g (20 mmoles) of α-chloro-α,α-diphenylacetic acid[11] in 100 ml of C_6H_6 was added 5·44 g (40 mmoles) of N,N-dimethylphenylenediamine. The mixture was kept at 50° for 14 hr, filtered and the precipitate washed with 150 ml of MeOH to leave 4·10 g (52%) of α-[(*p*-dimethylamino)anilino]-α,α-diphenylacetic acid. m.p. 120–122°.

To 1·00 g (2·9 mmoles) of the above acid in 50 ml of toluene was added with stirring at 50° ~5g of $COCl_2$. The mixture was kept at 60° under a dry ice condenser for four hr and then at 60° overnight without condenser. Filtration and recrystallization of the precipitate from a small amount of MeOH and water gave 430 mg (40%) of **1**. X = NMe_2. m.p 184–185°. (Calcd. for $C_{23}H_{20}N_2O_3$: C. 74·19; H. 5·41; N. 7·52. Found: C. 73·97; H. 5·25; N. 7·84%).

3'-[*Phenyl*]*spiro*-[*fluorene*-9,4'-*oxazolidine*]-2',5'-*dione* **2**. X = H. A solution of 22·4 g (100 mmoles) of methyl fluorene-9-carboxylate and 16·0 g (100 mmoles) of Br_2 in 600 ml CCl_4 was irradiated in Pyrex test tubes until most of the Br_2 color was gone. The solutions were combined, most of the solvent removed, and hexane added to precipitate 26·2 g (87%) of methyl 9-bromofluorene-9-carboxylate. m.p. 110–111°. (Calcd. for $C_{15}H_{11}BrO_2$: C. 59·43; H. 3·66; Br. 26·37. Found: C. 60·00; H. 3·57; Br. 26·23%).

To 2·00 g (6·7 mmoles) of the above ester in 20 ml of C_6H_6 was added 2·30 g (25 mmoles) of aniline. The mixture was heated 20 min on a steam bath and then filtered. The solvent was evaporated and the residue recrystallized from C_6H_6-MeOH to give 1·80 g (86%) of methyl 9-anilinofluorene-9-carboxylate, m.p. 164–164°. An analytical sample, m.p. 167–168°, was prepared by recrystallization from MeOH. Calcd. for $C_{21}H_{17}NO_2$; C. 79·98; H. 5·43; N. 4·44. Found: C. 80·11; H. 5·36; N. 4·49%).

To 1·26 g (4 mmoles) of the above amino acid ester in 25 ml of toluene was added 5 ml of $COCl_2$. The solution was heated four hr under a dry ice condenser and then 16 hr without condenser, and filtered to remove traces of aminoacid hydrochloride. Solvent was evaporated to leave white, crystalline material. This was heated under N_2 to 160° for 15 min. Vigorous gas evolution occurred. The product was recrystallized from benzene-hexane to give 0·45 g (34%) of **2**, X = H. m.p. 263–265° (decomp. with gas evolution and turning yellow). (Calcd. for $C_{21}H_{13}NO_3$: C. 77·05; H. 4·00; N. 4·28. Found: C. 77·03; H. 3·93; N. 4·23%).

3'-[p-*methoxyphenyl*]*spiro*[*fluorene*-9,4'-*oxazolidine*]-2',5'-*dione* **2**. X = OMe. To 1·23 g (100 mmoles) of *p*-methoxyaniline in 10 ml of MeCN was added 1·50 g (50 mmoles) of methyl 9-bromofluorene-9-carboxylate in 10 ml of MeCN. The mixture was heated on a steam bath for two hr, and filtered. Addition of water to the filtrate gave brown crystals. These were filtered and recrystallized from C_6H_6-MeOH to give 1·10 g (64%) of product. m.p. 151–161°. An analytical sample, m.p. 159–160°, was prepared by recrystallization from benzene-hexane. (Calcd. for $C_{22}H_{19}NO_3$: C. 76·50; H. 5·55; N. 4·06. Found: C. 76·79; H. 5·82; N. 4·0 %).

To 1·00 g (2·9 mmoles) of the above amino acid ester in 10 ml of toluene was addded ~1 ml of $COCl_2$. The reaction was conducted as for **2**, X = H. The product was recrystallized from acetone-water and then acetone-hexane to give 390 mg (38%) of **2**, X = OMe, m.p. 207–208°. (Calcd. for $C_{22}H_{15}NO_4$: C. 73·94; H. 4·23; N. 3·92. Found: C. 73·87; H. 4·42; N. 3·86%).

3'-[p-(*dimethylamino*)*phenyl*]*spiro*-[*fluorene*-9,4'-*oxazolidine*]-2',5'-*dione* **2**. X = NMe_2. To 18·0 ml of N,N-dimethylphenylenediamine in C_6H_6 was added with stirring 12·1 g (40 mmoles) of methyl 9-bromofluorene-9-carboxylate. The mixture was kept at 50° overnight and then filtered. Most of the solvent was removed and ether added to precipitate the amino acid ester. 12·8 g (89%), m.p. 126–130°. (Calcd. for $C_{23}H_{22}N_2O_2$: C. 77·07; H. 6·19; N. 7·82. Found: C. 77·12; H. 6·29; N. 7·85%).

To a solution of 10·0 g of the above ester and 8 ml of Et_3N in 100 ml of toluene was added ~10 ml of $COCl_2$ in the usual way. The mixture was stirred four hr at room temp. under a dry ice trap, after which it was filtered to remove amine hydrochloride. The solvent, Et_3N and excess $COCl_2$ were evaporated and the residue heated under N_2 to 150° for 10 min. The product was recrystallized twice from acetone to give 4·22 g (41%) of colourless crystals of **1**. X = NMe_2. m.p. 293–294°. (Calcd. for $C_{23}H_{20}N_2O_3$: C. 74·17; H. 5·41; N. 7·52. Found: C. 73·97; H. 5·30; N. 7·59%).

3-(p-*Nitrophenyl*)-4,4-*diphenyloxazolidine*-2,5-*dione* **1**. X = NO_2. To a solution of 200 mg of triphenylazasuccinic anhydride in 3 ml of Ac_2O was added at 0° 0·4 ml of fuming HNO_2 in 1 ml of AcOH and 1 ml Ac_2O. The mixture was allowed to stand overnight, after which the solvent was removed as before to leave crystals, recrystallized from benzene-hexane and then MeOH; giving 110 mg of pale yellow platelets. m.p. 143–144; (Calcd. for $C_{21}H_{14}N_2O_5$: C. 67·37; H. 3·77; N. 7·48. Found: C. 67·56; H. 3·71; N. 7·30%).

3'-(p-*Nitrophenyl*)*spiro fluorene*-9,4'-*oxazolidine*)-2',5'-*dione* **2**. X = NO_2. A solution of the anhydride was nitrated as above. The residue obtained on evaporation of solvent was extracted with boiling MeOH to leave product as white powder. m.p. 254–257° (dec.) (Calcd. for $C_{21}H_{12}N_2O_5$: C. 67·74; H. 3·25; N. 7·52. Found: C. 67·87; H. 3·41; N. 7·39%).

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