2442 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (9), 2442—2446 (1977) [Vol. 50, No. 9

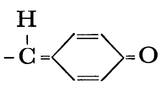
Indirect Chemiluminescence from the Air Oxidation of Ketones and Carboxylic Acids in Alkaline Aprotic Solvents Containing 9,10-Diphenylanthracene and 9,10-Dibromoanthracene

Isao Kamiya and Takashi Sugimoto

Department of Chemistry, College of General Education, Nagoya University, Chikusa-ku, Nagoya 464

(Received March 15, 1977)

A number of ketones and carboxylic acids have been examined for direct and indirect chemiluminescence with 9,10-diphenylanthracene and 9,10-dibromoanthracene by air oxidation. From the finding that the efficiency of the chemiluminescence was dramatically influenced by the class of the C–H bond adjacent to the carbonyl group, it was concluded that the molecules with a –COCH– group surely give an excited product during air oxidation in alkaline aprotic solvents. The reaction scheme was consistent with the evidence that most simple carboxylic acids exhibited no chemiluminescence, probably because the C–H bond adjacent to the carboxyl group is no more acidic, but keto acids exhibited emission. In several compounds, however, the chemiluminescent reaction was retarded by other functional groups.

In the previous studies of the chemiluminescence from the air oxidation of 3,5-dihalogeno-4-hydroxyphenylpyruvic acid[1)] and succinylfluorescein[2)] in alkaline aprotic solvents, a mechanism involving dioxetane intermediate was proposed for the luminescent reactions, and the reaction pathway leading to the dioxetanes which will be formed by the oxygenation of the anion of these compounds, formed by the loss of a proton from the carbon adjacent to the carbonyl or  group, was discussed as a possible mechanism for the generation of the excited products.

These results suggest that other simple molecules with a –COCH– group should also follow the same reaction pathways, involving a dioxetane, to yield a product in an excited state. In order to test this hypothesis, we carried out a preliminary study to investigate the chemiluminescent reaction of several carbonyl compounds by means of the indirect chemiluminescence technique with 9,10-diphenylanthracene(DPA) and 9,10-dibromoanthracene(DBA); we found that excited acetone and benzoic acid, mainly in the triplet state, were generated by air oxidation of 3-methyl-2-butanone and benzoin respectively in dimethyl sulfoxide(DMSO) or *N*,*N*-dimethylformamide(DMF) containing potassium *t*-butoxide (*t*-BuOK) as the base.[3)]

In the present study, we have examined a number of simple ketones and carboxylic acids for the chemiluminescence from the air oxidation under the same experimental condition in order to test the validity of, and to broaden the scope of this interesting reaction mechanism.

Results and Discussion

The indirect chemiluminescence was observed upon adding a *t*-BuOK solution in *t*-BuOH to an aerated solution of ketones in DMSO or DMF containing DPA or DBA. However, no direct chemiluminescence could be detected on an appreciable scale except with some aromatic ketones (see below). The intensity of the indirect chemiluminescence with DBA was markedly higher than with DPA, in spite of the much higher fluorescence efficiency of the latter. From these findings, we concluded that the excited species, predominantly in the triplet rather than the singlet state, were produced during the air oxidation of the ketones, because DBA is more capable of converting the energy of excited triplet species into singlet energy than is DPA because of the increased spin-orbit coupling and mixing of singlet and triplet states by the heavy-atom effect.[4)]

The features of the chemiluminescent reaction were affected by the experimental conditions— *i.e.* the temperature, solvents, and the concentrations of the ketones,

Table 1. Relative intensities (i_M) and 1/4-lifetimes ($t_{1/4}$) of the indirect chemiluminescence of aliphatic ketones with DBA in a DMSO-*t*-BuOK system at 313 K, and the colors of the spent reaction solutions[a)]

Compound	i_M[b)]	$t_{1/4}$(s)	Colors of spent reaction solns
$CH_3COCH(CH_3)_2$ (**1**)[c)]	1.0	40	colorless
$CH_3COCH(CH_3)$-CH_2CH_3 (**2**)	1.2	40	colorless
CH_3COCH_2CH-$(CH_3)_2$ (**6**)	0.3	20	reddish brown
$CH_3COCH_2CH_2$-$CH(CH_3)_2$ (**7**)	0.2	15	reddish brown
$CH_3COCH_2CH_3$ (**8**)	0.5	10	dark red
$CH_3COC(CH_3)_3$ (**12**)	0.0	—	light brown
$CH_3COCH(OH)$-CH_3 (**5**)	0.0	—	yellowish brown
$(CH_3)_2CHCOCH(CH_3)_2$	0.2	20	colorless
$CH_3CH_2CH_2COCH_2$-CH_2CH_3	0.1	15	brown
$CH_3CH_2CH_2COCH$-$(CH_3)_2$	0.0	—	colorless
$CH_3CH_2COCH_2CH_3$	0.1	15	light reddish brown
$CH_3(CH_2)_{20}CO(CH_2)_{20}$-$CH_3$	0.0	—	colorless
CH_3COCH_3	0.0	—	dark orange

a) The intensity of the emission peak from **1** was defined as 1.0. b) The ratios of the (total) light emission were given approximately by $i_M \cdot t_{1/4}$. c) The quantum yield for the indirect chemiluminescence of **1** at an infinite concentration of DBA was estimated to be 2.1×10^{-7} einstein mol^{-1} (the details of the measurement will be reported in the next paper).

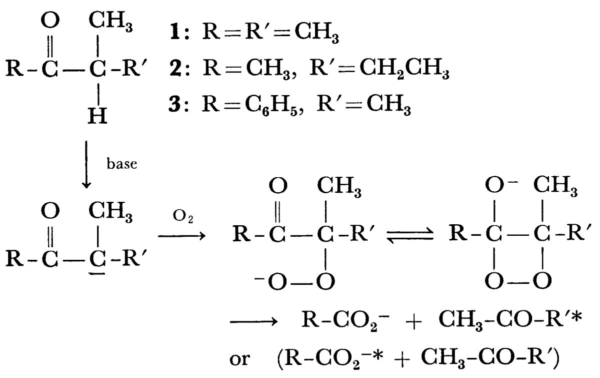
Table 2. The values of i_M and $t_{1/4}$ of the indirect chemiluminescence of aromatic ketones with DBA in a DMSO-*t*-BuOK system at 313 K, and the colors of the spent reaction solutions

Compound	i_M[a]	$t_{1/4}$(s)	Colors of spent reaction solns
$C_6H_5COCH(CH_3)_2$ **(3)**[b]	200	20	colorless
$C_6H_5COCH(OH)$-C_6H_5 **(4)**	25	5	colorless
$C_6H_5CO(CH_2)_2CH_3$ **(10)**	15	12	brown
$C_6H_5CO(CH_2)_4CH_3$ **(11)**	15	12	orange
$C_6H_5COCH_2CH_3$ **(9)**	7	10	dark orange
$C_6H_5COCH_3$	1.0	10	brown
$C_6H_5CH_2COCH_2C_6H_5$	0.5	10	brown
$C_6H_5COCH_2C_6H_5$	0.0	—	yellow
$C_6H_5COCH_2COC_6H_5$	0.0	—	colorless
$(C_6H_5)_2CHCOCH_3$	0.0	—	colorless

a) The values of i_M were also estimated by comparison with the i_M value from **1**, which was defined as 1.0. b) The quantum yield for the indirect chemiluminescence of **3** at an infinite concentration of DBA was estimated to be 2.6×10^{-5} einstein mol^{-1}.

t-BuOK, and the fluorescers, and also, more essentially, by the chemical structure of the ketones. In general, the intensity was much higher with aromatic ketones than with aliphatic ketones. The relative intensities of the emission peaks (i_M) and the times for the decay of intensities to one fourth of the maxima ($t_{1/4}$), as measured in a DMSO solution with equal concentrations of ketones, *t*-BuOK, and DBA at 313 K, are listed in Tables 1 and 2 for aliphatic and aromatic ketones respectively, together with the colors of the spent reaction solutions. The results in the tables clearly show that the efficiency of the emission is dramatically influenced by the class of the C–H bond adjacent to the carbonyl group, as was expected.

3-Methyl-2-butanone(**1**) and 3-methyl-2-pentanone (**2**), which possess a tertiary C–H bond, exhibited the most intensive chemiluminescence among all the aliphatic ketones examined. Among the aromatic ketones, isopropyl phenyl ketone(**3**) exhibited the most intensive emission; it could be easily observed even by the naked eye in a dark place. These ketones, **1**, **2**, and **3**, absorbed equimolar amounts of oxygen and yielded acetone, 2-butanone, and both acetone and benzoic acid respectively, as the main products. Thus, the chemiluminescent reaction of these ketones can be explained reasonably by the following mechanism:

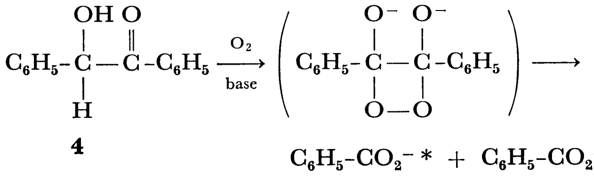


1: $R=R'=CH_3$
2: $R=CH_3$, $R'=CH_2CH_3$
3: $R=C_6H_5$, $R'=CH_3$

$$\longrightarrow R\text{-}CO_2^- + CH_3\text{-}CO\text{-}R'^*$$
$$\text{or}\quad (R\text{-}CO_2^{-*} + CH_3\text{-}CO\text{-}R')$$

A similar reaction mechanism has been proposed for the decomposition of α-hydroperoxy ketones, which are known to be intermediates in the autoxidation of the parent ketones.[5)]

Benzoin(**4**), whose emission was fairly intensive but rapidly decayed, yielded benzoic acid as the main product in a 59% yield (based on the two moles of the acid). This result implies that excited triplet benzoic acid is generated by the oxidation of benzoin, presumably *via* a dioxetane intermediate:

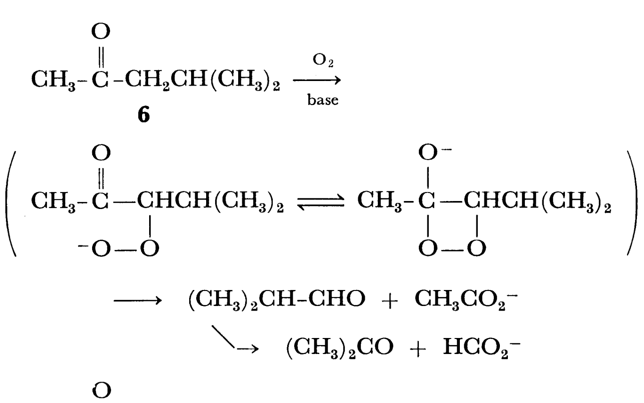


4

$$C_6H_5\text{-}CO_2^-{}^* + C_6H_5\text{-}CO_2^-$$

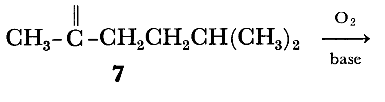
Acetoin(**5**), though it absorbed equimolar oxygen upon oxidation, showed no appreciable indirect chemiluminescence with DBA or DPA. This is probably because a large amount of energy, greater than the sum of the reaction enthalpy and activation energy, would be required to excite the acetic acid produced. Therefore, it is more reasonable to assert that excited triplet acetone and 2-butanone, rather than excited triplet acetic acid, are generated in the air oxidation of **1** and **2** respectively. However, it is difficult to decide which, acetone or benzoic acid, is the excited species in the case of **3**.

4-Methyl-2-pentanone(**6**), 5-methyl-2-hexanone(**7**), and 2-butanone(**8**), whose C–H bond adjacent to the carbonyl group is not tertiary but secondary, showed a much weaker emission than **1** and **2**. Similarly, ethyl phenyl ketone(**9**), phenyl propyl ketone(**10**), and pentyl phenyl ketone(**11**) exhibited a medium indirect chemiluminescence emission. In the system of **6** and **7**, where the molar ratios of absorbed oxygen to the ketones were about 2 : 1 and 3 : 1 respectively, acetone was formed, though in low yields. The difference in the amounts of absorbed oxygen and the formation of acetone can be best explained by the following consecutive reaction mechanism, in which the aldehydes formed by the initial oxidation undergo a sequential oxidation reaction to give acetone:



6

$$\longrightarrow (CH_3)_2CH\text{-}CHO + CH_3CO_2^-$$
$$\searrow (CH_3)_2CO + HCO_2^-$$



7

$$CH_3CO_2^- + 2HCO_2^- + (CH_3)_2CO$$

However, no aldehydes could be detected in the spent reaction solutions of these ketones, probably because they were quickly consumed by sequential oxidation or by other concurrently proceeding reactions, such as addition and polymerization. In fact, the spent reaction solutions were colored probably because of the concurrent reactions (see Tables 1 and 2). The aromatic ketones, **9**, **10**, and **11**, reacted similarly and gave benzoic acid in yields of 38, 57, and 23% respectively. Thus it may be reasonable to decide that excited triplet benzoic acid is generated from **9**, **10**, and **11** in the same way as it is from benzoin. However, we cannot exclude the possibility that aldehydes in the excited state are generated from **8**.[b)]

Such ketones as 3,3-dimethyl-2-butanone(**12**), acetone, and acetophenone, whose C–H bond adjacent to the carbonyl group is primary, exhibited little or very feeble emission.

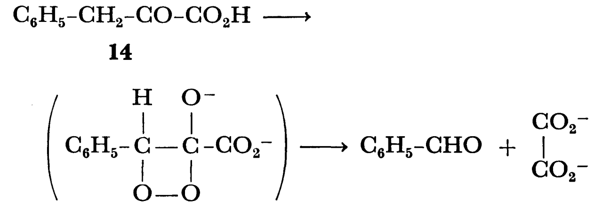
We also examined the chemiluminescent reaction of carboxylic acids. With simple carboxylic acids, such as acetic acid, propionic acid, isobutyric acid, phenyl acetic acid, diphenylacetic acid, and α(and β)-naphthylacetic acids, neither direct nor indirect chemiluminescence could be detected. However, β-benzoylpropionic acid(**13**) and β-phenylpyruvic acid(**14**), which possess a carbonyl group in addition to a carboxyl group, exhibited indirect chemiluminescence with the emission characteristics shown in Table 3. The results obtained from these keto acids also support our reaction scheme for the luminescent reaction shown above.

TABLE 3. THE VALUES OF i_M AND $t_{1/4}$ OF THE INDIRECT CHEMILUMINESCENCE OF CARBOXYLIC ACIDS WITH DBA IN A DMSO-t-BuOK SYSTEM AT 313 K, AND THE COLORS OF THE SPENT REACTION SOLUTIONS

Compound		i_M[a)]	$t_{1/4}$(s)	Colors of spent reaction solns
$C_6H_5COCH_2CH_2$-COOH	(**13**)	1.0	40	dark orange
$C_6H_5CH_2COCOOH$	(**14**)	2.5	60	dark brown

a) The values were estimated by comparison with the i_M value from **1**, which was defined as 1.0.

β-Phenylpyruvic acid(**14**) exhibited a direct chemiluminescence whose spectral distribution was similar to that of the fluorescence spectrum of benzaldehyde. This implies that both excited singlet and triplet benzaldehydes are produced, presumably *via* a dioxetane intermediate:

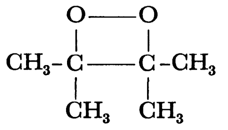


$$C_6H_5\text{-}CH_2\text{-}CO\text{-}CO_2H \longrightarrow$$

14

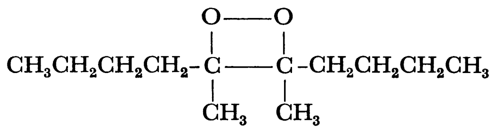
$$\left(C_6H_5\text{-}\underset{|}{\overset{H}{C}}-\underset{|}{\overset{O^-}{C}}\text{-}CO_2^-\right)_{O-O} \longrightarrow C_6H_5\text{-}CHO + \begin{matrix}CO_2^-\\|\\CO_2^-\end{matrix}$$

Cilento *et al.* have proposed the same reaction mechanism for the oxidation of the phenylthio ester of 3-indoleacetic acid.[7)] β-(p-Hydroxyphenyl)pyruvic acid (**15**) also exhibited both direct and indirect chemiluminescence. It should be noted here that the intensity of the indirect chemiluminescence of **15** with DPA was higher than that with DBA, while the total intensity of the emissions was lower compared to the case of **14**. Ethyl p-hydroxyphenyl ketone(**16**) also exhibited both direct and indirect chemiluminescence with emission features similar to those from **15**. The relative intensities of the direct and the indirect chemiluminescence with DPA and DBA are listed in Table 4. These results indicate that the substitution of a hydroxyl group at the 4 position of the benzene ring in aromatic ketones increases the yield of the excited singlet product, but causes a reduction in the total yield of excited products. An analogous substitution effect was observed in the cleavege of dioxetanes. Turro and coworkers reported that tetramethyl-1,2-dioxetane(**17**) gave excited triplet acetone in high yields and a little amount of excited singlet acetone.[8)] On the other hand, it has been shown that relatively low and nearly equal yields of excited singlet and triplet 2-hexanone were formed upon the cleavage of 3,4-dibutyl-3,4-dimethyl-1,2-dioxetane(**18**).[18)]



$$CH_3\text{-}\underset{CH_3}{\overset{O}{C}}-\underset{CH_3}{\overset{O}{C}}\text{-}CH_3$$

17



$$CH_3CH_2CH_2CH_2\text{-}\underset{CH_3}{\overset{O}{C}}-\underset{CH_3}{\overset{O}{C}}\text{-}CH_2CH_2CH_2CH_3$$

18

Ethyl o-hydroxyphenyl ketone(**19**) exhibited neither direct nor indirect chemiluminescence, probably because the reaction route is entirely altered by the substituent.

TABLE 4. RELATIVE INTENSITIES[a)] OF THE DIRECT AND INDIRECT CHEMILUMINESCENCE IN THE SYSTEMS OF **14**, **15**, AND **16**

Compound		Direct CL	Indirect CL DPA	Indirect CL DBA	Colors of spent reaction solns
$C_6H_5CH_2COCOOH$	(**14**)	1.0	1.2	2.5	dark brown
p-$HOC_6H_4CH_2COCOOH$	(**15**)	0.3	0.6	0.3	light yellow
$C_6H_5COCH_2CH_3$	(**9**)	0.0	0.5	7	dark orange
p-$HOC_6H_4COCH_2CH_3$	(**16**)	0.4	0.6	0.4	colorless
o-$HOC_6H_4COCH_2CH_3$	(**19**)	0.0	0.0	0.0	bright yellow

a) These values were also estimated by comparison with the i_M value from **1**, which was defined as 1.0.

Table 5. The emission features (i_M and $t_{1/4}$) of the indirect chemiluminescence with DBA of the *p*-substituted isopropyl phenyl ketones, and the colors of the spent reaction solutions

Substituent (and compound)		i_M[a)]	$t_{1/4}$(s)	Colors of spent reaction solns
p-CH_3	(**20**)	180	20	colorless
p-OCH_3	(**21**)	50	20	colorless
p-Cl	(**22**)	50	15	light yellow
p-Br	(**23**)	20	18	yellowish brown
p-F	(**24**)	0	—	colorless
p-SCH_3	(**25**)	0	—	colorless

a) The values were also estimated by comparison with the i_M value from **1**, defined as 1.0.

In Table 5, the relative intensities of the indirect chemiluminescence of several substituted isopropyl phenyl ketones with DBA are listed. We can find that the emission efficiencies of the *p*-methyl(**20**), *p*-methoxy (**21**), *p*-chloro(**22**), and *p*-bromo derivatives(**23**) decrease in this order. The *p*-fluoro(**24**) and *p*-methylthio derivatives(**25**) exhibited little emission.

Summarizing the results of the present study, we conclude that excited products are surely generated *via* dioxetane intermediates in the air oxidation of those molecules with a -COCH- group in alkaline aprotic solvents and that the dioxetanes are formed by the oxygenation of the anion formed by the loss of the proton from the carbon atom adjacent to the carbonyl group. However, it should be kept in mind that the luminescent reaction is debased by the competitive and sequential processes brought about by other functional groups.

Recently, we have found that several aldehydes with a -CHCHO group exhibited similar indirect chemiluminescence with DPA and DBA under comparable experimental conditions.[10)]

Experimental

The commercially available ketones (except the substituted isopropyl phenyl ketones), carboxylic acids, and fluorescers, DPA and DBA (Nihon Kasei, extra pure grade) were used without further purification. The substituted isopropyl phenyl ketones(**21**, **22**, **23**, **24**, and **25**) were synthesized by Friedel-Crafts condensation of the appropriately substituted benzene with isobutyric anhydride in carbon disulphide under reflux, using aluminum chloride as the catalyst. The products were purified by fractional distillation under reduced pressure (except for **25**, which was purified by recrystallization from hexane and melted at 42—43 °C): **20**, bp 132.5—133.5 °C/27 mmHg; **21**, bp 116—117 °C/2 mmHg; **22**, bp 89—92 °C/3 mmHg; **23**, bp 85—87 °C/3 mmHg; **24**, bp 49.5—50 °C/3 mmHg. The structures of these compounds were confirmed by means of their ^1H NMR spectra.

The concentrations of the solution of the ketones or carboxylic acids in DMSO (*A*), the solution of *t*-BuOK in *t*-BuOH (*B*), and the solution of DPA or DBA in DMSO (*C*) were usually 3.0×10^{-4}, 3.3×10^{-2}, and 1.0×10^{-3} mol l^{-1} respectively.

A mixed solution composed of 1 ml of *A* and 1 ml of *C* was placed in a quartz cell, which was kept at 313 K by means of a thermostatically controlled cell holder. The intensity of the indirect chemiluminescence at 430 nm (the peak of the spectral distribution) was measured immediately after adding 0.2 ml of *B* into the mixed solution on a Hitachi MPF-2A type fluorescence spectrophotometer, with the exciting source off.

The reaction products, acetone, 2-butanone, benzoic acid, and the *p*-substituted benzoic acids, were detected as follows:

General Procedures for the Isolation of Benzoic Acid and Its p-*Substituted Derivatives.* A solution of *t*-BuOK (2.3 g) in DMF (70 ml) was saturated with oxygen by stirring vigorously under the gas. A solution of isopropyl phenyl ketone (1.50 g) in DMF (30 ml) was then added to the solution through a dropping funnel, and the mixture was stirred under oxygen at 17—18 °C for 15 min, during which period 280 ml of oxygen was absorbed. After being diluted with water (100 ml), the solution was evaporated to dryness under reduced pressure. The residue, dissolved in water (20 ml) and acidified with hydrochloric acid, gave benzoic acid (1.13 g, 92%); mp 122—123 °C (recrystallized from water).

In a similar way, benzoic acid was isolated from the oxidation solution of the following compounds (the yield of the acid is shown in parentheses); benzoin (59%); phenyl propyl ketone (38%); pentyl phenyl ketone (57%); ethyl phenyl ketone (23%); *β*-benzoylpropionic acid (50%).

The substituted isopropyl phenyl ketones (**20**, **21**, **22**, **23**, **24**, and **25**) were similarly oxidized and gave, respectively, the following *p*-substituted benzoic acids, which were all recrystallized from water and identified by means of their melting points: *p*-methylbenzoic acid (80%, mp 182—183 °C), *p*-methoxybenzoic acid (68%, mp 183.5—185 °C), *p*-chlorobenzoic acid (90%, mp 241—242 °C), *p*-bromobenzoic acid (40%, mp 255—256 °C), *p*-fluorobenzoic acid (50%, mp 184.5—186 °C), and *p*-(methylthio)benzoic acid (90%, mp 193.5—194 °C).

General Procedures for the Detection of Acetone and Other Ketones. A solution of *t*-BuOK (2.5 g) in DMF (100 ml) was saturated with oxygen as above. After adding 3-methyl-2-butanone (0.74 g), the solution was stirred under oxygen at 23 °C for 30 min, during which period 220 ml of oxygen was absorbed. To the solution, 1 M HCl (20 ml) and then 2,4-dinitrophenylhydrazine (1.0 g) in methanol (300 ml) were added. The solution was stirred at 25 °C for 30 min and then under reflux for 20 min. Evaporation to dryness under reduced pressure and trituration with water (30 ml) gave a yellow solid. The crystallization of the solid from methanol gave yellow needles (1.15 g) of acetone 2,4-dinitrophenylhydrazone, identified with an authentic sample by a mixed mp (125—126 °C) and by TLC developed by a mixture of benzene (15 v/v) and ethyl acetate (5 v/v) on a Merck pre-coated silica gel 60 F_{254} plate.

In a similar way, we detected acetone from an oxidation solution of **3**, **6**, and **7** and 2-butanone from **2**, both as the 2,4-dinitrophenylhydrazones; they were identified by means of TLC as above.

References

1) G. Cilento, M. Nakano, H. Fukuyama, K. Suwa, and I. Kamiya, *Biochem. Biophys. Res. Commun.*, **58**, 296 (1974).

2) I. Kamiya and K. Aoki, *Bull. Chem. Soc. Jpn.*, **47**, 1744 (1974).

3) I. Kamiya and T. Sugimoto, *Chem. Lett.*, **1976**, 33.

4) V. A. Belyakov and R. F. Vassilév, *Photochem. Photobiol.*, **11**, 179 (1970); T. Wilson and A. P. Schaap, *J. Am. Chem. Soc.*, **93**, 4126 (1971); N. J. Turro, P. Lechtken, G. Schuster, J. Orell, H. -C. Steinmetzer, and W. Adam, *ibid.*, **96**, 1627 (1974); M. J. S. Dewar and S. Kirschner, *ibid.*, **96**,

7578 (1974); W. Adam, G. A. Simpson, and F. Yany, *J. Phys. Chem.*, **78**, 2559 (1974); I. Simo and J. Stauff, *Chem. Phys. Lett.*, **34**, 326 (1975); G. B. Schuster, N. J. Turro, H.-C. Steinmetzer, A. P. Schaap, G. Faler, W. Adam, and J. C. Liu, *J. Am. Chem. Soc.*, **97**, 7110 (1975); W. Adam, N. Duran, and G. A. Simpson, *ibid.*, **97**, 5464 (1975); M. A. Umbreit and E. H. White, *J. Org. Chem.*, **41**, 479 (1976); T. Wilson, D. E. Golan, M. S. Harris, and A. L. Baumstark, *J. Am. Chem. Soc.*, **98**, 1086 (1976).

5) W. H. Richardson, V. H. Hodge, D. L. Stiggall, M. B. Yelvington, and F. C. Montgomery, *J. Am. Chem. Soc.*, **96**, 6652 (1974).

6) The 2-butanone produced in the **2** system was not further oxidized under the experimental conditions employed, and the spent reaction solution of **2** was almost colorless.

7) N. Durán, K. Zinner, R. C. de Baptisa, C. C. C. Vidigal, and G. Cilento, *Photochem. Photobiol.*, **24**, 383 (1976).

8) N. J. Turro and P. Lechtken, *J. Am. Chem. Soc.*, **94**, 2886, (1972).

9) T. R. Darling and C. S. Foote, *J. Am. Chem. Soc.*, **96**, 1625, (1974).

10) K. Aoki and I. Kamiya, unpublished results.