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# Catalytic photocarboxylation of 1,1-diphenylethylene with *N*,*N*,*N*′,*N*′-tetramethylbenzidine and carbon dioxide

Yoshikatsu Ito*

*Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Kyoto 615-8510, Japan*

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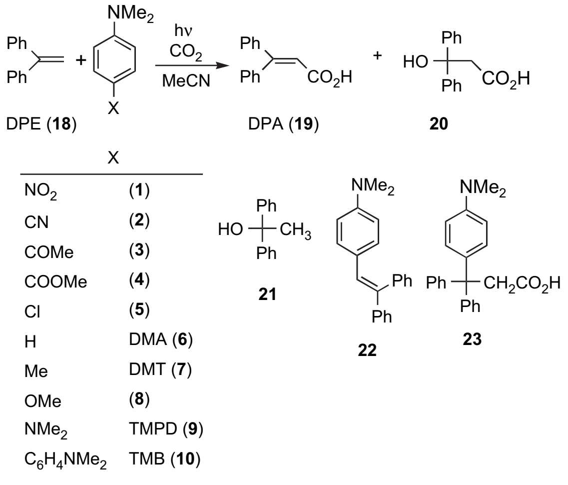
**Abstract**—Photocarboxylation of 1,1-diphenylethylene with *N*,*N*,*N*′,*N*′-tetramethylbenzidine (TMB) in MeCN under bubbling of $CO_2$ proceeded with high catalytic efficiency, giving 3,3-diphenylacrylic acid (DPA) and 3-hydroxy-3,3-diphenylpropionic acid (**20**). The turnover number (TON=(DPA+**20**)/TMB) reached 17. Similarly, 1-phenyl-1-cyclohexene yielded *cis*-2-acetamido-2-phenylcyclohexanecarboxylic acid with TON 5.9. As compared with related *N*,*N*-dimethylaniline derivatives, TMB is more resistant to photodecomposition, has the much larger absorbance in the $S_0 \rightarrow S_1$ transition, and has the lower quenching efficiency by $CO_2$. Probably these factors are partly responsible for the high TON observed for TMB.

## 1. Introduction

A variety of methods were performed toward photofixation of carbon dioxide into organic compounds (photocarboxylation):[1] for example, (a) metalloporphyrins[2] and other organometallic or metal complexes,[3] which cause insertion, cycloaddition, or carboxylation, (b) particular semiconductors and polymers, which usually fix $CO_2$ through reduction to $CO_2^{\bullet-}$,[4] (c) photocatalysts or photosensitizers that are conjugated with enzyme-catalyzed reactions,[5] and (d) trapping by reactive species such as 1,3-dipolar species,[6] carbenes,[7] and radical anions.[8] Among these, catalytic reactions seem to be most attractive to realize the practical photofixation. Indeed, high turnover numbers (TONs) were reported for the malic acid formation (TON 1074)[5c] and the malonic acid derivative formation (TON 93),[2a] although their reaction systems are complex. Traditional organic photochemistry might not look very promising in this field.[6–8] Irradiation of unsaturated hydrocarbon–amine systems, where the amine is used as electron donor or sensitizer, can efficiently generate radical anions from the former, but unfortunately the molar ratio between the carboxylated product versus the amine is very low (<0.1) in most cases.[8] Radical anions, which have enough nucleophilicity to attack $CO_2$, form a stable bond to $CO_2$, and end up with final products with high reaction selectivity, are necessary.[8g,9]

Nearly two decades ago we reported that 1,1-diphenylethylene (DPE, **18**) underwent photolysis in MeCN in the presence of *N*,*N*-dimethyl-*p*-toluidine (DMT, **7**) and $CO_2$ to yield 3,3-diphenylacrylic acid (DPA, **19**) with the DPA/DMT ratio of 0.16.[8e] Inspection of the reported papers[8] has suggested that the radical anion of DPE appears to satisfy most the aforementioned requisite. To develop a new useful $CO_2$ photofixation system, therefore, the author resumed this investigation by using a series of *para*-substituted *N*,*N*-dimethylanilines (DMAs) as sensitizer (Eq. 1). The *para*-substitution precludes the known *para*-coupling, which consumes DMA.[8e] Here *N*,*N*,*N*′,*N*′-tetramethylbenzidine (TMB, **10**) is demonstrated to be a respectable photocatalyst.



| X | |
|---|---|
| $NO_2$ | (**1**) |
| CN | (**2**) |
| COMe | (**3**) |
| COOMe | (**4**) |
| Cl | (**5**) |
| H | DMA (**6**) |
| Me | DMT (**7**) |
| OMe | (**8**) |
| $NMe_2$ | TMPD (**9**) |
| $C_6H_4NMe_2$ | TMB (**10**) |

(1)

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*Keywords*: *N*,*N*,*N*′,*N*′-Tetramethylbenzidine; Carbon dioxide; Catalytic photocarboxylation; High turnover number.

* Tel./fax: +81 75 383 2718; e-mail: yito@sbchem.kyoto-u.ac.jp

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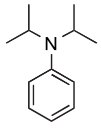
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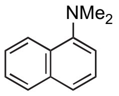
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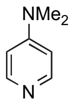
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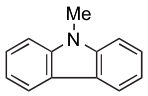
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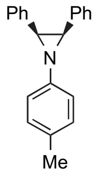
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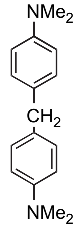
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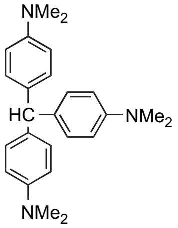

**17**

## 2. Results and discussion

### 2.1. Photocarboxylation of DPE

Neither the DMA derivatives having an electron-withdrawing *para*-substituent **1–4** and **13** nor the DMA analogs **14** and **15** photocarboxylated DPE upon photolysis in DMSO-$d_6$. As shown in Table 1, however, the DMA derivatives without a strong electron-withdrawing group **5–12** gave DPA (DPA/amine>0.06), although the main product in the case of **5** was **22** formed via a triplet phenyl cation,[10] and the major reaction by DMA (**6**) in MeCN was *para*-coupling to give **23**, thereby consuming DMA.[8e] The reaction by *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD, **9**) was considerably solvent dependent. In fact, as seen from the results for **5–9** (runs 1–11), the DPA formation is always more efficient in DMSO or DMF than in MeCN. For TMB (**10**), however, MeCN was a better solvent than DMF. The yield of DPA in MeCN (71%, run 13) overwhelms others. The finding that DPA/amine=1.5 is surprising, because the corresponding ratios were <0.1 in the earlier cognate photocarboxylation.[8]

The very encouraging result found by TMB led the author to vary the molar ratio between DPE and TMB with the intention of raising the DPA/amine ratio. Since considerable production of 3-hydroxy-3,3-diphenylpropionic acid (**20**) and 1,1-diphenylethanol (**21**) was observed, their yields were also determined and the ratio (DPA+**20**)/TMB was calculated. This ratio may be called the turnover number (TON) for the photocarboxylation. As summarized in Table 2, higher TONs were obtained by decreasing the concentration of TMB relative to DPE. Notably, at DPE/TMB=48 ([TMB]=4.6 mM, [DPE]=0.22 M), the TON reached 17 (run 5). The major products DPA and **20** could be easily isolated, as described in Section 4. The quantum yield for the formation of DPA under the conditions of run 5 was estimated to be 0.018 at 313-nm irradiation.[11] This is as good as those for the previous high TON reactions ($\Phi$ 0.017[2a] and 0.019[5c]).

### 2.2. Possible pathways for photocarboxylation of DPE by TMB

Possible reaction pathways are described in Scheme 1. The previously proposed mechanism[8e] was slightly modified. First the photoinduced electron transfer occurs from the TMB excited state. Since the reduction potentials of DPE (about −2.3 V[12]) and $CO_2$ (about −2.2 V[13]) are comparable, both DPE$^{\bullet-}$ and $CO_2^{\bullet-}$ can be generated, leading to formation of the distonic radical anion A according to step a or step b, respectively. Similar electron transfer paths have already been demonstrated to occur, e.g., see Ref. 8b for step a and Refs. 3a and 4b for step b. After regeneration of TMB by back-electron transfer, the resulting zwitterion B will be transformed to DPA or, in the presence of impurity water, to the hydration product **20**. Because DPA was slowly converted to **20** under similar photolysis conditions, a part of

**Table 1**. Photocarboxylation of 1,1-diphenylethylene (DPE) with *N*,*N*-dimethylaniline derivatives **5–12**[a]

| Run | Amine | Solvent | Products, %[b] | | Recovery, % | | DPA/amine |
|---|---|---|---|---|---|---|---|
| | | | DPA | Others | DPE | Amine | |
| 1 | **5** | DMSO | 10 | **22**, 18 | 70 | 72 | 0.098 |
| 2 | | MeCN | 6 | **22**, 16 | 75 | 70 | 0.063 |
| 3 | DMA (**6**) | DMSO-$d_6$ | 21 | **23**, Trace | 24 | 53 | 0.21 |
| 4 | | MeCN | 12 | **23**, 40 | 45 | 53 | 0.12 (0.005[c]) |
| 5 | DMT (**7**) | DMSO-$d_6$ | 26 | — | 39 | 81 | 0.27 |
| 6 | | MeCN | 17 | — | 75 | 93 | 0.17 (0.16[c]) |
| 7 | **8** | DMSO-$d_6$ | 25 | — | 63 | 100 | 0.25 |
| 8 | | MeCN | 9 | — | 69 | 92 | 0.093 |
| 9 | TMPD (**9**) | DMSO-$d_6$ | 28 | — | 69 | 91 | 0.28 |
| 10 | | DMF-$d_7$ | 9 | — | 88 | 100 | 0.081 |
| 11 | | MeCN | ~0 | — | 100 | 95 | ~0 |
| 12 | TMB (**10**) | DMF-$d_7$ | 43 | — | 24 | 90 | 0.94 |
| 13 | | MeCN | 71 | **20**, 8; **21**, 1[d] | 9 | 80 | 1.5 |
| 14 | **11** | DMSO-$d_6$ | 7 | — | 30 | 98 | 0.073 |
| 15 | **12** | DMSO-$d_6$ | 9 | — | 15 | 98 | 0.084 |

[a] A solution containing 0.13 M of amine (except TMB) and 0.13 M of DPE was irradiated under bubbling $CO_2$ with a 400-W high pressure mercury lamp (Pyrex filter, >290 nm) for 10 h. In the case of TMB, a solution containing (a) 0.065 M of TMB and 0.13 M of DPE in DMF-$d_7$ or (b) 0.018 M of TMB and 0.037 M of DPE in MeCN was irradiated. Product yields and recoveries were estimated by NMR and HPLC analyses of the photolysates.

[b] Yields are based on the initially used DPE.

[c] The isolation yield of DPA[8e] was used to calculate the ratio.

[d] Benzophenone (0.6% yield).

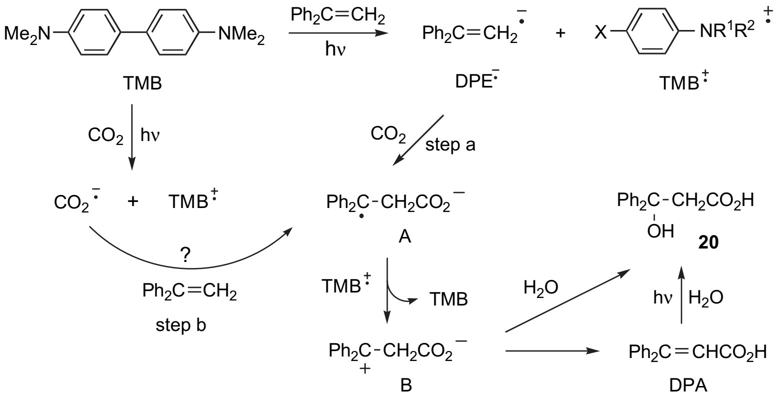
**Table 2**. Photocarboxylation of 1,1-diphenylethylene (DPE) with *N*,*N*,*N*′,*N*′-tetramethylbenzidine (TMB) in MeCN

| Run | [TMB], mM | [DPE], M | DPE/TMB | Carboxylated products, %[a] | | Noncarboxylated products, %[a] | | Recovery, % | | (DPA+**20**)/TMB[b] |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | DPA | **20** | **21** | Others | DPE | TMB | |
| 1 | 18 | 0.037 | 2 | 71 | 8 | 1 | [c] | 9 | 80 | 1.6 |
| 2 | 18 | 0.11 | 6 | 47 | 4 | 0 | [c] | 38 | 77 | 3.1 |
| 3 | 9.0 | 0.11 | 12 | 44 | 6 | 2 | [c] | 35 | 54 | 6.0 |
| 4 | 4.6 | 0.11 | 24 | 34 | 13 | 9 | [c] | 33 | 34 | 11 |
| 5 | 4.6 | 0.22 | 48 | 22 | 14 | 10 | [c] | 48 | 20 | 17 |
| 6 | **16**, 4.6 | 0.11 | 24 | 10 | 8 | 3 | [c] | 51 | **16**, 3 | 4.5 |
| 7 | **17**, 4.6 | 0.11 | 24 | 12 | 5 | 2 | [c] | 66 | **17**, 0 | 4.1 |

[a] Yields are based on the initially used DPE.

[b] The molar ratio between the carboxylated products (DPA+**20**) versus the initially used TMB (or **16** or **17**).

[c] A trace amount of benzophenone was formed (0.3–1% yield).



**Scheme 1**. Possible mechanism.

**20** produced may be a secondary photoproduct of DPA. DPE was irradiated in the presence of added water (2 M) under the conditions similar to run 5 of Table 2. The conversion of DPE was complete (recoveries of DPE∼0% and TMB 26%), but most of the product was **21** (90% yield). Only a small amount of **20** (5% yield) and a trace of DPA were obtained (TON 2.5).

## 2.3. Reflection on the merit of TMB

Why TMB is a better photocarboxylation catalyst than other DMA derivatives? The answer will allow us to design even better photocatalysts. Since the TMB molecule consists of two DMA moieties, bis[4-(dimethylamino)phenyl]methane (**16**) and leucocrystal violet (**17**) were tested. Their TONs, however, were much lower than that of TMB: compare runs 6 and 7 with run 4 in Table 2. Furthermore, **16** and **17** are more photolabile than TMB: their recoveries were 3, 0, and 34%, respectively. Next, some photophysical properties of TMB were examined.

The absorption spectra of DMT, TMPD, TMB, DPE, and DPA are shown in Figure 1A. Evidently, TMB ($\lambda_{max}$ 310 nm, $\varepsilon$ 42,000 $M^{-1}$ $cm^{-1}$) absorbs the Pyrex-filtered light (>290 nm) much more effectively than DMT or TMPD. While the absorbance of DPE is very weak at >290 nm, that of DPA is substantial at this region. Hence, in view of a considerable inner filter effect by DPA, TMB will be a much better sensitizer than DMT or TMPD.

The occurrence of photoinduced electron transfer from an amine sensitizer requires that its excited-state oxidation potential $E^*_{ox}$ is sufficiently more negative than the reduction potential of DPE or $CO_2$. All the sensitizers in Table 3 appear to meet this requirement and therefore the difference in $E^*_{ox}$ is probably not the reason for the observed advantage of TMB. The oxidation of A into B with the concomitant back-electron transfer to regenerate TMB (Scheme 1) is also a crucial step. TMB is not energetically advantageous in this step when compared with DMA and DMT, because $E_{ox}$ of TMB is slightly lower (∼0.1 V) than that of DMA or DMT (Table 3). However, the high TON found for TMB suggests that this step is pretty efficient in the case of TMB, although the reason is unclear.

The fluorescence measurement for DMT, TMPD, and TMB (Fig. 1B) shows that under these conditions, the TMB singlet is quenched more by DPE rather than by $CO_2$, whereas the reverse is the case for the TMPD singlet and that the degree of quenching of the DMT singlet by DPE and $CO_2$ is approximately equal.[†] As already seen in Table 1, the efficiency for DPA formation in MeCN is TMB>DMT>TMPD. This correlation between the fluorescence quenching and the DPA

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[†] The fluorescence quenching constant $k_q\tau_s$ by $CO_2$ or DPE was estimated from Figure 1B for each of DMT, TMPD, and TMB. The values were 3.7, 6.7, 6.7 $M^{-1}$ ($CO_2$) or 61, 51, 180 $M^{-1}$ (DPE), respectively. Since the singlet lifetime $\tau_s$ for DMA, TMPD, and TMB in MeCN is 3.8,[15] 1.3,[16] and 10 ns,[17] respectively, the quenching rate $k_q$ by $CO_2$ or DPE was calculated as $9.7\times10^8$, $5.2\times10^9$, $6.7\times10^8$ $M^{-1}$ $s^{-1}$ ($CO_2$) or $1.6\times10^{10}$, $3.9\times10^{10}$, $1.8\times10^{10}$ $M^{-1}$ $s^{-1}$ (DPE), respectively. Thus, $k_q$ by DPE appears to be nearly diffusion controlled ($k_{diff}$=$1.9\times10^{10}$ $M^{-1}$ $s^{-1}$ in MeCN at 25 °C[14a]) regardless of the amine, whereas $k_q$ by $CO_2$ decreases in the order TMPD>DMT>TMB.

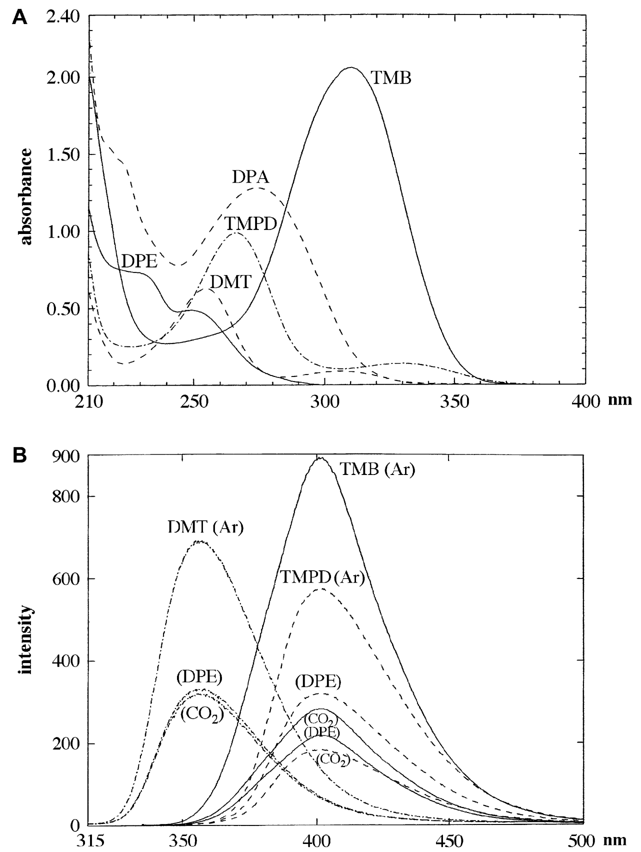


**Figure 1**. (A) Absorption spectra for DMT, TMPD, TMB, DPE, and DPA in MeCN: [amine]=$5.0\times10^{-5}$ M. (B) Fluorescence spectra of DMT (dotted broken line, $\lambda_{ex}$=305 nm), TMPD (broken line, $\lambda_{ex}$=330 nm), and TMB (solid line, $\lambda_{ex}$=330 nm) in MeCN: [amine]=$6–11\times10^{-5}$ M. The fluorescence measurements were conducted under three different conditions: (a) in argon-saturated MeCN, (b) in $CO_2$-saturated MeCN ([$CO_2$]~0.32 M[1a]), and (c) in argon-saturated MeCN in the presence of DPE (0.017 M).

**Table 3**. Electron-donor properties of the sensitizers in MeCN[a]

| Sensitizer | $E_{ox}$ versus SCE[b] | $E_{00}$ | $E^*_{ox}$ versus SCE[b] | Sensitizer | $E_{ox}$ versus SCE | $E_{00}$ | $E^*_{ox}$ versus SCE[b] |
|---|---|---|---|---|---|---|---|
| DMA | 0.53 V | 3.89 V | −3.36 V | TMPD | 0.32 V | 3.41 V | −3.09 V |
| DMT | 0.50 | 3.77 | −3.27 | TMB | 0.43 | 3.60 | −3.17 |

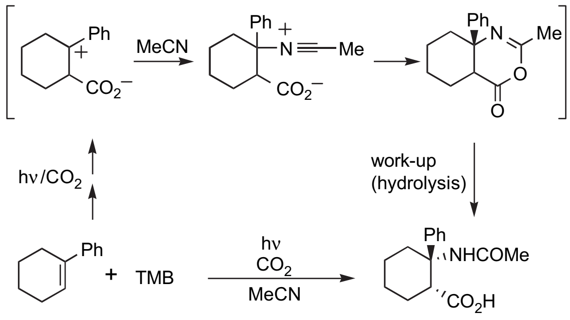
[a] The properties for DMA, TMPD, and TMB were derived from Ref. 14. The $E_{ox}$ value for DMT was assumed from Ref. 12.

[b] The excited-state oxidation potential $E^*_{ox}=E_{ox}-E_{00}$, where $E_{ox}$ is the oxidation potential and $E_{00}$ is the excited singlet state energy.

formation may be taken to indicate that DPA is formed via the route involving step a, rather than step b (see Scheme 1).

## 2.4. Photocarboxylation of 1-phenyl-1-cyclohexene

Photocarboxylation of α-methylstyrene by TMB was not efficient, similar to that by DMT.[8e] *trans*-Stilbene was not photocarboxylated by TMB, neither by DMA.[8e] Biphenyl was photocarboxylated to give 4-phenylbenzoic acid cleanly but only in a low efficiency (by TMB, 2.7% yield, TON 0.16; by DMA, 3.5% yield,[8e] TON 0.03). On the other hand, 1-phenyl-1-cyclohexene (**24**) yielded *cis*-2-acetamido-2-phenylcyclohexanecarboxylic acid (**25**) with reasonable efficiency (Eq. 2): 25% yield, TON (=**25**/TMB) 5.9. Other carboxylated products were also formed (see Section 4). The major product **25** could be isolated simply by recrystallization of the photolysate. Incorporation of MeCN in the product structure presumably proceeded through the Ritter-like reaction,[18] giving a heterocyclic intermediate, which was then hydrolyzed during the work-up (Eq. 2).



**24** **25**

24 : 1

major product
25 % yield (TON 5.9)

(2)

## 3. Conclusion

Photocarboxylation via traditional organic photochemistry might not look very promising.[6–8] The present author now found the highly catalytic photocarboxylation of DPE by using TMB as sensitizer, yielding DPA and **20**. The turnover number (TON=(DPA+**20**)/TMB) reached 17. The formation of **25** is an interesting type of photocarboxylation reaction. As compared with related DMAs, TMB is more resistant to photodecomposition, has the much larger absorbance in the $S_0\rightarrow S_1$ ($E_{00}$) transition, and has the lower quenching efficiency by $CO_2$. Probably these factors are partly responsible for the observed high TON. It is assumed that the regeneration of TMB through possibly the back-electron transfer from the radical anion A occurs pretty efficiently. Analogous highly catalytic photocarboxylation models are likely to be devised by appropriate choices of substrate and catalyst.

## 4. Experimental

### 4.1. Instruments and materials

$^1H$ and $^{13}C$ NMR spectra were measured on a JEOL EX-270J, AL-300, or JUM-A400 spectrometer. Measurements of 2D NMR were carried out with JEOL JUM-A400. Mass, IR, and absorption spectra were recorded on JEOL JMS-HX 110A, SHIMADZU FTIR-8400, and SHIMADZU UV-2400PC spectrometers, respectively. Fluorescence spectra were gathered with a SHIMADZU RF-5300PC spectrometer and excited near the absorption maximum. HPLC analyses were performed with a JASCO PU-980 pump and a SHIMADZU SPD-6AV detector (fixed at 254 nm) by using a Cosmosil $5C_{18}$-AR column (4.6 mm i.d.×150 mm) and were eluted with a mixture of MeOH–acetate buffer (20 mM, pH 3.6) or a mixture of MeOH–$H_2O$.

Most of the materials employed here were purchased from the company. 4-Chloro-*N*,*N*-dimethylaniline (**5**) and

*N*,*N*-dimethyl-*p*-anisidine (**8**) were prepared by literature methods.[19] *trans*-2,3-Diphenyl-1-*p*-tolylaziridine (**15**) was available from our previous work.[20]

### 4.2. Photocarboxylation (general)

The photocarboxylation experiments (Tables 1 and 2) were conducted as follows. An equimolar mixture containing 0.13 M of *N*,*N*-dimethylanilines (DMAs) or analogs **1–15** (except TMB) and 0.13 M of DPE in suitable solvent was placed in a Pyrex (or NMR) tube and was irradiated externally, under bubbling $CO_2$, with a 400-W high pressure mercury lamp (Pyrex filter, >290 nm) for 10 h. During the irradiation, the solution was maintained at either 20 °C (for DMSO-$d_6$ or DMSO solvent) or 10 °C (for MeCN or DMF-$d_7$ solvent) with thermostated circulating water. In the case of TMB (**10**), a 1:2 mol/mol mixture containing (a) 0.065 M of TMB and 0.13 M of DPE in DMF-$d_7$ or (b) 0.018 M of TMB and 0.037 M of DPE in MeCN was irradiated. TMB is insoluble in DMSO.

Product yields and recoveries were estimated by NMR and HPLC analyses of the photolysates. In several experiments (runs 3–6, 12, and 13 (=run 1 in Table 2) in Table 1), a small $^1$H NMR peak at around $\delta$ 8.5, which is probably ascribed to the aldehyde proton of Ar–N(C*H*O)$CH_3$, was visible in the spectra. Also, in all the experiments in Table 2 (run 13 in Table 1=run 1 in Table 2), formation of a trace amount of benzophenone was observed (0.3–1% yield from HPLC), probably due to photooxidation of DPE with the residual oxygen in $CO_2$ gas. However, the production of **20**, **21**, and benzophenone was examined only for the experiments using TMB (Table 2).

The photocarboxylation by TMB progressed rapidly at first (irradiation time<2 h), but almost stopped after 10 h of irradiation. This is probably due to an inner filter effect by DPA as well as to the decomposition of TMB. The product ratio between DPA and **20** did not change significantly with the irradiation time.

As an illustrative example of photocarboxylation, the experimental procedure for run 5 in Table 2 is described below. In addition, the photocarboxylation experiment of 1-phenyl-1-cyclohexene (**24**) is described.

### 4.3. Photocarboxylation of 1,1-diphenylethylene (DPE, 18) with *N*,*N*,*N*′,*N*′-tetramethylbenzidine (TMB, 10)

A solution containing 7.8 mg (0.032 mmol) of TMB and 275 mg (1.52 mmol) of DPE in MeCN (7 mL) was placed in a Pyrex tube. The solution was irradiated for 10 h under bubbling of $CO_2$ at 2 °C. Only in this run, the photolysis was carried out at 2 °C rather than at 10 °C, expecting that the dissolved $CO_2$ in MeCN increases a little.[21] The photolysate was divided into two equal parts. One part was analyzed by HPLC after addition of biphenyl (7.8 mg) as an internal standard. Another part was rotary-evaporated at 40 °C and was analyzed by $^1$H NMR. The yields and recoveries of DPA, DPE, TMB, and $Ph_2CO$ were determined from the HPLC data and the yields of **20** and **21** were estimated from the $^1$H NMR data. The results are listed in Table 2 (run 5). Next, both parts were combined, the solvent was removed by rotary evaporation at 40 °C, and subsequently the residue was redissolved in $CHCl_3$ (8 mL). A white solid appeared in a little while. After the solution was left overnight at room temperature, the precipitated solid was collected by filtration to afford 42 mg of pure 3-hydroxy-3,3-diphenylpropionic acid (**20**). Then, the filtrate was subjected to preparative TLC on silica gel ($CHCl_3$–MeOH 30:1 v/v). From the lowest band just above the original sample band, 16 mg of additional **20** was obtained as a pale brown solid: total yield of **20**, 58 mg (16%). From the second lowest band, 78 mg (23% yield) of pure 3,3-diphenylacrylic acid (DPA, **19**) was obtained as a pale brown solid. From the third lowest band, 23 mg (8%) of nearly pure 1,1-diphenylethanol (**21**) was obtained as a pale greenish brown solid. All the upper bands were discarded since they should contain mainly DPE, biphenyl, and small amounts of TMB and benzophenone.

DPA (**19**): colorless prisms, mp 162–164 °C (from 2:1 benzene/hexane) (lit.[22] mp 156–157.5 °C); $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 7.4–7.15 (10H, m), 6.32 (1H, s); $^{13}$C NMR (67.7 MHz, $CDCl_3$) $\delta$ 170.37, 158.87, 140.70, 138.29, 129.66, 129.17, 128.44, 128.39, 128.32, 127.86, 116.26; IR (KBr) 3200–2500 (br), 1700 (s), 1613 (m), 1284 (m), 1216 (m), 774 (m), 696 (m) $cm^{-1}$; UV (MeCN, Fig. 1) $\lambda$ 274 ($\varepsilon$ 26,000) nm; MS (EI$^+$) *m/z* 224 ($M^+$, 100), 223 (77), 207 (17), 179 (61), 178 (78); HRMS (EI$^+$) calcd for $C_{15}H_{12}O_2$ 224.0837, found 224.0837.

**20**: White crystals, mp 232–233 °C (from MeCN) (lit.[23] mp 217 °C); $^1$H NMR (270 MHz, DMSO-$d_6$) $\delta$ 12.38 (1H, br s), 7.47–7.43 (4H, m), 7.29–7.23 (4H, m), 7.18–7.12 (2H, m), 5.78 (1H, br s), 3.28 (2H, s); $^{13}$C NMR (67.7 MHz, DMSO-$d_6$) $\delta$ 172.87, 147.13, 127.72, 126.25, 125.35, 75.46, 45.10; IR (KBr) 3477 (s), 3300–2500 (br), 1691 (s), 1442 (s), 1371 (m), 1232 (s), 1062 (m), 1022 (m), 925 (m), 753 (m), 694 (s) $cm^{-1}$; MS (EI$^+$) *m/z* 242 ($M^+$, 3), 224 (11), 183 (86), 182 (70), 180 (59), 165 (29), 105 (100), 77 (15); HRMS (EI$^+$) calcd for $C_{15}H_{12}O_2$ (=$M^+-H_2O$) 224.0837, found 224.0838; HRMS (FAB$^-$) calcd for $C_{15}H_{13}O_3$ (=$[M-H]^-$) 241.0865, found 241.0871.

For the quantum yield measurement, the light that was isolated from a 400-W high pressure mercury lamp with a $K_2CO_3$ (0.67%)–$K_2CrO_4$ (0.067%) filter solution (mainly 313 nm) was employed and the reaction was stopped at a small conversion (the DPA yield<1.3 %). Photocyclization of 2,4,6-triisopropylbenzophenone into its benzocyclobutenol in MeCN under argon ($\Phi_{313}$=0.67) was used as actinometry.[11] Although each sample was irradiated separately without using a merry-go-round apparatus, two runs for the quantum yield measurement agreed within ±2%.

### 4.4. Photocarboxylation of 1-phenyl-1-cyclohexene (24) with *N*,*N*,*N*′,*N*′-tetramethylbenzidine (TMB, 10)

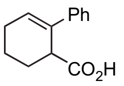
Under bubbling of $CO_2$, a solution containing 9.4 mg (0.039 mmol) of TMB and 151 mg (0.94 mmol) of **24** in MeCN (8 mL) was irradiated as described above at 10 °C for 10 h. From the analysis of the divided photolysates by HPLC and $^1$H NMR as described above, formation of many products was disclosed. The recoveries of **24** and

TMB were 48 and 0%, respectively. After rotary evaporation of the recombined photolysate, the residue was redissolved in 3 mL of $CHCl_3$ and the solution was allowed to stand at room temperature for 5 days. Pale brownish yellow crystals appeared and these were collected by filtration to obtain 49 mg (20%) of *cis*-2-acetamido-2-phenylcyclohexanecarboxylic acid (**25**). Since an HPLC peak corresponding to **25** was not observable directly after the photolysis, **25** must have been formed during the work-up of the photolysate. The assumed heterocyclic intermediate shown in Eq. 2 may be formed via the Ritter-like reaction.[18] The filtrate was separated with preparative TLC on silica gel ($CHCl_3$–MeOH 30:1 v/v), followed by preparative HPLC (Cosmosil $5C_{18}$, 20 mm i.d.×250 mm, MeCN–$H_2O$ 70:30 v/v). This gave 12 mg of additional **25** along with 13 mg (7%) of crude 2-phenylcyclohex-2-enecarboxylic acid (**26**).[24] The total yield of **25** is 61 mg (25%) and thus the TON for **25** (=**25**/TMB) is 5.9. Many other carboxylated products (total 30 mg), including 2-phenylcyclohex-1-enecarboxylic acid (**27**) and *trans*- and *cis*-2-hydroxy-2-phenylcyclohexanecarboxylic acid (**28**), were formed in minor amounts, judging from the $^1H$ NMR, IR, MS, and HPLC data, but these products were not further separated.

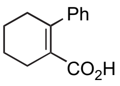
**25**: White plates, mp 245–247 °C (from MeOH–acetone); $^1H$ NMR (400 MHz, $CD_3OD$) $\delta$ 7.44–7.40 (2H, quasi-d,[§] $J\sim7$ Hz), 7.26–7.20 (2H, quasi-t,[§] $J\sim7.5$ Hz), 7.16–7.11 (1H, quasi-t,[§] $J\sim7$ Hz), 3.34–3.31 (1H, m), 2.73–2.68 (2H, m), 2.13–2.02 (1H, m), 1.9–1.83 (1H, m), 1.89 (3H, s), 1.74–1.52 (4H, m) (Fig. 2); $^{13}C$ NMR (100 MHz, $CD_3OD$) $\delta$ 176.01 (CONH), 172.18 (COOH), 146.72, 128.70, 127.52, 127.22, 59.84, 50.15, 28.07, 26.41, 23.57, 22.51, 21.92 (Fig. 2); IR (KBr) 3369 (s), 1711 (s), 1640 (s), 1545 (s), 1374 (m), 1179 (s), 1155 (s), 1125 (s), 769 (m), 697 (m) $cm^{-1}$; MS ($EI^+$) *m/z* 261 ($M^+$, 13), 243 (11), 218 (18), 202 (93), 184 (19), 176 (31), 156 (56), 132 (100), 119 (33), 104 (51), 91 (64), 77 (30), 60 (27); HRMS ($EI^+$) calcd for $C_{15}H_{19}NO_3$ 261.1365, found 261.1367.

The cis configuration of $CO_2H$ and NHCOMe was assigned on the basis of a pronounced NOESY correlation between the methine hydrogen ($H_a$) of $CH_aCO_2H$ ($\delta$ 3.34–3.31) and the *ortho* hydrogen of Ph ($\delta$ 7.44–7.40) (Fig. 3). The $^1H$ NMR signal of $H_a$ appeared as approximately a double doublet (Fig. 2), which is also consistent with the cis structure.[25]

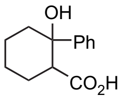
**26**:[24] Colorless solid; $^1H$ NMR (300 MHz, $CD_3OD$) $\delta$ 7.35–7.12 (5H, m), 6.17 (1H, t, $J=3.8$ Hz), 3.68 (1H, br), 2.3–1.7 (6H, m); IR (film) 1700 (s), 758 (s), 697 (s) $cm^{-1}$; MS ($EI^+$) *m/z* 202 ($M^+$, 64), 156 (100), 130 (69), 115 (57), 91 (97), 77 (33); HRMS ($EI^+$) calcd for $C_{13}H_{14}O_2$ 202.0994, found 202.0993.



**26**



**27**



*trans*- and *cis*-**28**

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## Supplementary data

The $^1H$ and $^{13}C$ NMR spectra (Fig. 2) and the NOESY spectrum (Fig. 3) for *cis*-2-acetamido-2-phenylcyclohexanecarboxylic acid (**25**). Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.02.013.

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[§] Each peak is finely split ($J=1$–2 Hz).

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