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PHOTOCHEMICAL REACTIONS OF AROMATIC ESTERS—I

PHOTOCHEMICAL SYNTHESIS OF NEW OXETANES FROM AROMATIC ESTERS WITH 1,1-DIPHENYLETHYLENE

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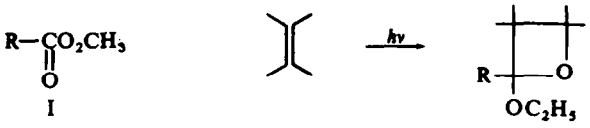
Abstract—Irradiation of dimethyl terephthalate IIIa with 1,1-diphenylethylene IV afforded an oxetane Va as a sole adduct. The structure of the oxetane was established on the basis of its spectroscopic properties. Similar irradiation of *p*- or *o*-cyanobenzoate with IV gave a corresponding oxetane Vb or Vc, respectively. Trimethyl trimesate VII could also add to IV photochemically to form an oxetane VIII. On the other hand, irradiation of dimethyl phthalate IIId with IV could not give an oxetane Vd but an olefin VI which was considered to be produced through the elimination of a formaldehyde molecule from an unstable intermediate oxetane Vd. A reactive species of the photocycloaddition was suggested to be an n–π^* triplet state of the aromatic ester from the evidences of the phosphorescence emissions of the esters and the direction of the addition.

As is well known, a wide variety of aldehydes or ketones undergo photocycloaddition with olefins to form various oxetanes.[1] No attempt, however, has been made as yet to prepare new oxetanes from carboxylate esters. Recently, we succeeded in the synthesis of the oxetanes II by the photocycloaddition of ethyl cyanoformate Ia or diethyl oxalate Ib to various olefins and also clarified that the electron-withdrawing cyano or carbethoxyl substituent is necessary for the successful formation of the oxetanes.[2,3]



I II

a: R = CN; b: R = $CO_2C_2H_5$

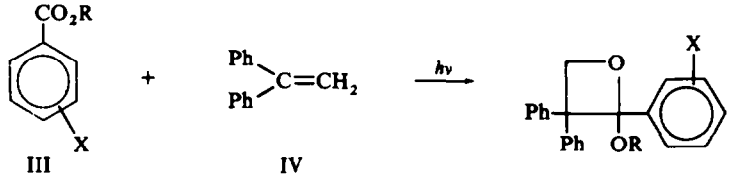
These investigations have been extended to the synthesis of new oxetanes from aromatic esters having an electron-withdrawing substituent. In this paper, we wish to report the photocycloaddition of mono- or di-substitued benzoates by cyano or carbalkoxyl group to 1,1-diphenylethylene.

RESULTS AND DISCUSSION

The results with aliphatic carboxylate esters indicate that aromatic diesters or cyanobenzoates III will add to 1,1-diphenylethylene IV leading to the formation of oxetanes V.

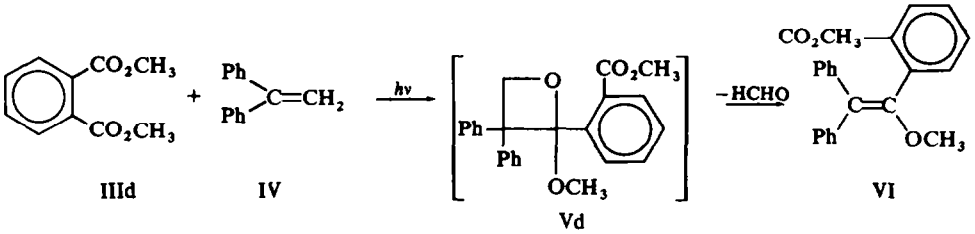
Irradiation of dimethyl terephthalate IIIa and IV in benzene through a pyrex filter gave an oxetane Va (62%) as a sole adduct. The structure of Va was elucidated on the

basis of its spectroscopic properties. Namely, the IR spectrum showed the presence of an ester group (1735 cm^{-1}), a trimethylene oxide ring (975 cm^{-1}), and mono-substituted aromatic ring (775 and 700 cm^{-1}). The NMR spectrum showed the aromatic hydrogens at 2–3 τ (14H), the trimethylene oxide ring hydrogens as an AB quartet at 4·70 and 4·83 τ (2H), the carbomethoxyl hydrogens as a singlet at 6·15 τ (3H), and the methoxyl hydrogens as a singlet at 6·89 τ(3H). Similar irradiation of a solution



a: X = *p*-CO_2CH_3, R = CH_3; b: X = *p*-CN, R = C_2H_5;
c: X = *o*-CN, R = CH_3; d: X = *o*-CO_2CH_3, R = CH_3

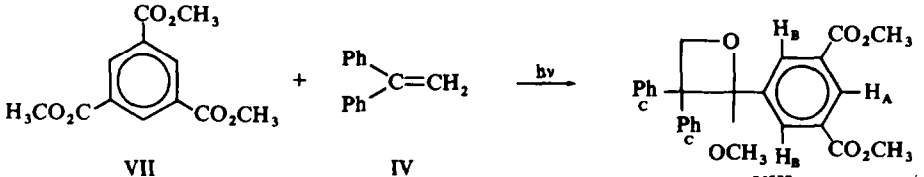
of ethyl *p*-cyanobenzoate IIIb and IV in benzene led to the formation of a sole oxetane Vb in 57% yield. The IR spectrum of the oxetane Vb showed bands at 2240 (—CN) and 970 cm^{-1} (oxetane ring), but there was no characteristic band assigned to a carbonyl group. The NMR spectrum of Vb consisted of four regions of resonance corresponding to phenyl (τ 2·70, 2·84, 3·18, 14H), oxetane ring (AB quartet, τ 4·85, 4·92, 2H), methylene (τ 6·36–7·14, m, 2H), and methyl protons (τ 8·95, t, 3H). The photochemical reaction of methyl *o*-cyanobenzoate IIIc with IV also afforded a corresponding oxetane Vc in 80% yield. Its structure was established by the same analytical techniques as employed above. Interestingly, the product obtained was not an oxetane Vd but an olefin VI, when similar irradiation of a solution of dimethyl phthalate IIId and IV in benzene was undertaken. The IR spectrum of VI showed the presence of an enol ether (1640 cm^{-1}). The NMR spectrum showed the aromatic hydrogens at 2·40–3·14 τ (14H), the carbomethoxyl hydrogens as a singlet at 6·28 τ(3H), and the methoxyl hydrogens as a singlet at 6·59 τ(3H), but there was no band assigned to the trimethylene oxide ring hydrogens. As reported on the formation of a stilbene derivative from the photocycloaddition of benzaldehyde to *trans*-anethole,[4] the present olefin may be also produced through the elimination of a formaldehyde molecule from an intermediate oxetane Vd which is considered to be unstable due to the presence of a bulky *o*-carbomethoxyl group in the aromatic ring.



On the other hand, when a solution of methyl benzoate and IV in benzene was irradiated under the similar conditions as described above, any oxetane, however,

was not detected. These results are compatible with the case of aliphatic esters.[2,3,5,*] This fact obviously demonstrates that an electron-withdrawing substituent such as a cyano or a carbalkoxyl group in a carboxylate ester is essential for the successful synthesis of oxetanes by the photocycloaddition of a carboxylate ester to olefins.

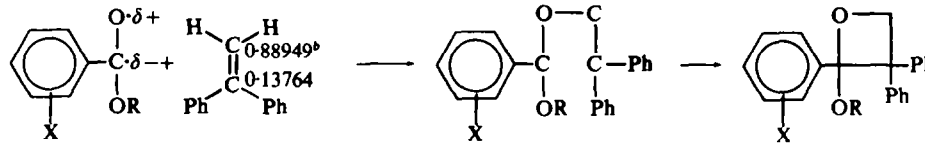
Furthermore, from this conclusion, a photocycloaddition of aromatic triesters to 1,1-diphenylethylene might be expected to give a corresponding oxetane or a similar olefin as VI derived from an intermediate oxetane. Trimethyl trimesate VII did indeed add to IV in dioxan solution under irradiation leading to the formation of a sole oxetane VIII.



VII IV VIII

The IR spectrum of the oxetane VIII exhibited bands at 1735 (—CO_2CH_3) and 970 cm^{-1} (oxetane ring). The NMR spectrum of VIII had three regions of signals corresponding to Ph, trimethylene oxide ring, and Me protons. The Ph protons A, B, and C appeared at 1·80, 1·93, 2·76 and 3·14 τ, respectively. The two trimethylene oxide ring protons appeared as a singlet at 4·77 τ. The carbomethoxyl and OMe protons showed the peak as a singlet at 6·15 and 6·92 τ, respectively.

The evidence described below suggests that the n–π^* triplet state of the ester group is a reactive species in the photochemical formation of the oxetanes. First, the phosphorescence emissions of the present aromatic esters at 77°K in EP glass was observed. The position of 0—0 bands of dimethyl terephthalate IIIa and ethyl p-cyanobenzoate IIIb are at 392 mμ (73·5 Kcal/mole) and 398 mμ (72·0 Kcal/mole), respectively. These triplet states may be n–π^* in nature, although from the long half-life time of 1·8–2·0 sec the possibility cannot be ruled out that these triplet states may be π–π^* in nature. Second, the direction of the cycloaddition furthermore supports that the reaction would proceed through the electrophilic attack of the electron deficient O atom of the n–π^* triplet state on a C atom having a large free valence of an olefin to form a more stable diradical intermediate IX which subsequently leads to the oxetane III.



n–π^* triplet IV IX III

The electrophilic attack of the electron deficient O atom to an olefin is also suggested from the photo-oxidation of iso-propyl alcohol with the aromatic ester III. Irradiation of a solution of iso-propyl alcohol and an ester III afforded acetone and hydrogen.†

* Despite the success of the formation of the oxetane IIa and IIb from ethyl cyanoformate or diethyl oxalate, ethyl acetate gives no oxetane.

† Acetone was confirmed by gas chromatography using a 1·5 m polyethylene glycol 20M column and derived to 2,4-dinitrophenylhydrazone. Hydrogen was identified by gas chromatography using a 1·0 m activated carbon column.

On the other hand, the photo-oxidation of iso-propyl alcohol with methyl benzoate which gave no oxetane did not occur. From these results, it is obvious that an electron-withdrawing substituent has an influence on the nature of the low-lying triplet state of atomatic esters. Namely, the low-lying triplet state of the aromatic ester III would be more n–π^* in nature.

More detailed studies on this interesting photo-reduction of an aromatic ester are in progress.

EXPERIMENTAL

All m.ps are uncorrected. IR spectra were recorded on a Shimazu IR spectrophotometer IR-27C. NMR spectra were determined with 5–6% soln in CCl_4 or $CDCl_3$ with TMS as an internal standard, on a Japan Electron Optics JNM-3H-60 spectrometer. The mol wts were determined with a Mechrolab vapor pressure osmometer model 302 at 25 or 37°C using benzene as a solvent.

Materials. 1,1-Diphenylethylene was prepared by the method of Allen and Converse.[7] Ethyl *p*-cyanobenzoate was prepared from ethyl *p*-aminobenzoate by the Sandmeyer reaction according to the procedure of Rupe and Majewski.[8] Other aromatic esters were commercial grade chemicals and were purified by the usual method before use.

Oxetane Va *from dimethyl terephthalate* IIIa. Dimethyl terephthalate (3·8 g, 0·02 mole) and 1,1-diphenylethylene (10·8 g, 0·06 mole) were dissolved in 135 ml benzene. The soln was flushed with N_2 for 30 min and irradiated externally through a pyrex filter using a 500 W high-pressure mercury lamp for 60 hr. After removal of the solvent *in vacuo*, the unreacted ester (3·3 g) was recovered by filtration and the unreacted olefin was distilled off from the filtrate. The brown residual oil was dissolved in benzene and poured onto a 2·0 × 30 cm column prepared with 25 g of 200 mesh silica gel. Benzene–pet. ether elution (1:1) gave an oxetane Va which was recrystallized from EtOH (0·6 g, 62% based on the reacted ester, white needles, m.p. 116–118°). The IR spectrum showed characteristic bands at 3000, 1735, 1620, 1500, 975, 775, and 700 cm^{-1}. The NMR spectrum (CCl_4) showed aromatic protons (τ 2·0–3·0, 14H), methylene protons (AB pattern, τ_A 4·70, τ_B 4·83, J_{AB} ~6 c/s), carbomethoxyl protons (τ 6·15, 3H, s), and OMe protons (τ 6·89, 3H, s). (Found: C, 76·95; H, 6·19; M. wt. 361; $C_{24}H_{22}O_4$ requires: C, 76·98; H, 5·92%; M.wt. 374).

Oxetane Vb *from ethyl p-cyanobenzoate* IIIb. A soln of ethyl *p*-cyanobenzoate (4·0 g, 0·032 mole) and IV (12·4 g, 0·096 mole) in 100 ml benzene was irradiated externally through a pyrex filter with a 500 W high-pressure mercury lamp for 150 hr. After the removal of the solvent under reduced press, the unreacted ester and olefin were recovered by distillation under reduced press. The conversion of the ester was estimated as about 43%. The residual oil (4·7 g) was dissolved in pet. ether–benzene (1:1) and poured onto a 3·0 × 36 cm column prepared with 86 g of 200 mesh silica gel. Benzene–pet. ether elution (2:3) gave an oxetane Vb which was recrystallized from pet. ether (2·2 g, 57% based on the reacted ester, white plates, m.p. 87·5–88·5°). The IR spectrum (KBr) showed bands at 3060, 3030, 2980, 2900, 2250, 1615, 1495, 970, 775 and 700 cm^{-1}. The NMR spectrum (CCl_4) showed aromatic protons (τ 2·70–3·18, 14H), trimethylene oxide ring protons (AB pattern, τ_A 4·85, τ_B 4·92, J_{AB} ~5 c/s), methylene protons (τ 6·36–7·14, 2H, m), and Me protons (τ8·95, 3H, t). (Found: N, 4·02; M. wt. 356; $C_{24}H_{21}NO_2$ requires: N, 3·94%; M.wt. 355).

Oxetane Vc *from methyl o-cyanobenzoate* IIIc. A soln of methyl *o*-cyanobenzoate (4·8 g, 0·03 mole) and IV (16·2 g, 0·09 mole) in benzene (100 ml) was placed in a pyrex irradiation vessel and irradiated with a 500 W high-press mercury lamp for 150 hr. After the solvent was removed by distillation under reduced press, the unreacted ester and olefin were recovered by distillation. The residual oil (1·6 g) was dissolved in pet. ether–benzene (1:1) and poured onto a 2·0 × 30 cm column prepared with 28 g of 200 mesh silica gel. The column was eluted with 700 ml pet. ether-benzene (85:15), which upon evaporation gave an oxetane Vc (630 mg, 80%). It was recrystallized from pet. ether to yield white needles, m.p. 106·5–108°; IR (KBr): 3060, 3030, 2940, 2890, 2230, 1598, 970, 710 and 695 cm^{-1}; NMR (CCl_4): aromatic protons (τ 2·33–3·19, 14H, m), trimethylene oxide ring protons (AB pattern, τ_A 4·60, τ_B 4·85, J_{AB} ~5 c/s), and OMe protons (τ 6·81, 3H, s). (Found: C, 80·80; H, 5·90; M.wt. 342; $C_{23}H_{19}NO_2$ requires: C, 80·91; H, 5·61%; M.wt. 341).

Olefin VI *from dimethyl phthalate* IIId. A soln of dimethyl phthalate (3·8 g, 0·02 mole) and IV (10·8 g, 0·06 mole) in 50 ml benzene was placed in a quartz vessel and purged with N_2 for 30 min. Irradiation of the soln was carried out with a 300 W high-press mercury lamp for 50 hr. After the solvent was removed *in vacuo*, the unreacted ester and olefin were recovered by distillation. The conversion of the ester was 11%. The residual oil was dissolved in pet. ether–benzene (1:1) and poured onto a 1·8 × 31 cm column prepared

with 29 g of silica gel. The column was eluted with 800 ml pet. ether–benzene (85:15) to give an olefin VI which was recrystallized from *n*-hexane (250 mg, 35% based on the reacted ester, white needles, m.p. 107–108°). The IR spectrum (KBr) gave absorption bands at 3050, 2870, 1745, 1640, 1605, 1580, 1282, 1265, 1250, 1070, 780, 765 and 700 cm^{-1}. The NMR spectrum (CCl_4) showed aromatic protons (τ 2·40–2·75, 2·80, 3·14, 14H), carbomethoxyl protons (τ 6·28, 3H, s), and OMe protons (τ 6·59, 3H, s). (Found: C, 79·94; H, 5·87; M.wt. 341; $C_{23}H_{20}O_3$ requires: C, 80·21; H, 5·85%; M.wt. 344).

Oxetane VIII *from trimethyl trimesate* VII. A soln of VII (7·5 g, 0·03 mole) and IV (16·2 g, 0·09 mole) in dioxan (100 ml) was irradiated externally through a pyrex filter with a 500 W high-press mercury lamp for 150 hr. After removal of the solvent *in vacuo*, the unreacted ester (5·9 g) was recovered by filtration and the unreacted olefin was distilled from the filtrate. The brown residual oil was dissolved in benzene and poured onto a 3·0 × 43 cm column prepared with 95 g of silica gel. Unreacted ester (0·6 g) was eluted by benzene. Benzene containing 2% ether eluted an oxetane VIII which was recrystallized from ether (430 mg, 24% based on the reacted ester, white needles, m.p. 180–182·5°). The IR spectrum (KBr) showed bands at 1735, 1605, 1500, 1255, 970, 765, 730 and 710 cm^{-1}. The NMR spectrum ($CDCl_3$) showed aromatic protons (τ 1·80, 1·93, 2·76, 3·14, 13H), methylene protons (τ 4·77, 2H, s), carbomethoxyl protons (τ 6·15, 6H, s), and OMe protons (τ 6·92, 3H, s). (Found: C, 72·11; H, 5·62; M.wt. 441; $C_{26}H_{24}O_6$ requires: C, 72·21; H, 5·59%; M.wt. 432).

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