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Photochemical Type I and II Elimination Reactions of Dialkyl (Trichloromethyl)phosphonates

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Irradiation of diisobutyl, dipropyl, and diethyl (trichloromethyl)phosphonates in MeCN gave corresponding monoesters and olefins *via* photochemical type II elimination. In addition, products *via* type I elimination were obtained from diisobutyl (trichloromethyl)phosphonate and its dimethyl ester.

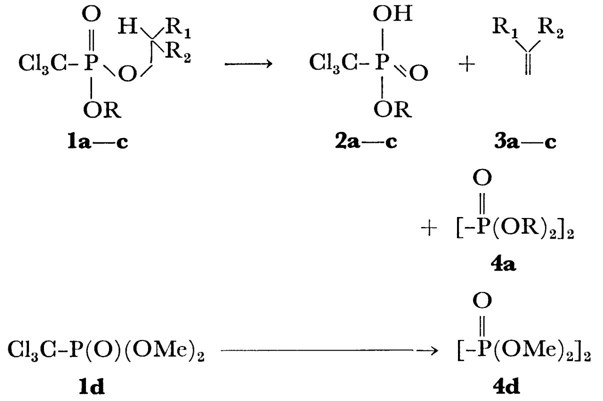
In the previous paper, we briefly reported[1)] that electron-withdrawing group attached on phosphorus atom of phosphonates compete with a double-bonded oxygen atom to attract electron, resulting in a stiffer P=O double bond and a higher frequence absorption and thus diisobutyl (trichloromethyl)phosphonate (**1a**) having a strongly electron-withdrawing group on phosphorus atom, photochemically decomposed by type II elimination to give the corresponding monoester and isobutylene.

In this paper, we wish to report further investigations on the photochemical elimination of dialkyl (trichloromethyl)phosphonates (**1a**, **1b**, and **1c**) in hope of exploring the exact nature of this reaction.

Results and Discussion

A solution of the phosphonates[2)] (**1a**—**d**: 4.2 mmol: 24.7 mmol/l) in acetonitrile (170 ml) was flushed with nitrogen before and during irradiation to prevent photooxidation of the starting material and/or the product(s). During irradiation with a low-pressure mercury lamp (30 w; immersion type) the photo-reaction was monitored with GLC as the decrease of **1** (see Table 1). The generated monoester (**2a**—**c**) and/or tetraalkyl hypophosphate (**4a** and **4d**) were isolated from the each resulting mixture by preparative TLC after evaporation. The R_f values of them were *ca.* 0.1 for **2a**—**c** and *ca.* 0.3—0.4 for **4a** and **4d**, respectively. The results and spectral data for the products, **2**, are shown in Tables 1 and 2, respectively.

Structure of **2a** had been reported in the previous paper[1)] as a monoester of **1a** on the basis of its spectral properties. Both **2b** and **2c** showed very similar spectral properties to those of **2a**, respectively. Furthermore, the structures were confirmed by comparing IR spectra with the authentic samples prepared according to the methods and analogous ones of Kamai and Kharasova[3)] from thermal reactions of the parent phosphonic acid **5**[4)] and the corresponding diesters (**1a**—**c**). (See Table 3). Thus, we conclude that **2b** and **2c** are the corresponding monoesters of **1b** and **1c**.



$$\underset{\mathbf{5}}{\mathrm{Cl_3CP(O)(OH)_2}} + \underset{\mathbf{1a—c}}{\mathrm{Cl_3CP(O)(OR)_2}} \xrightarrow[\text{over night}]{110\,^{\circ}\mathrm{C}} \underset{\mathbf{2a—c}}{\mathrm{Cl_3CP(O)(OH)(OR)}}$$

Obviously, the olefins and the monoesters are produced *via* the photochemical type II cleavage of **1**. Norrish type II reaction of carbonyl compounds having γ-hydrogen was now well documented,[5,6)] however, that of phosphoryl compounds has been reported only in our preceding paper.[1)] The present results reveal this type of reaction to be general in the (trichloromethyl)phosphonates.

In contrast, a product (**4d**) from photo-reaction of **1d** which can not give Norrish type II hydrogen abstraction by phosphoryl group, showed its molecular

Table 1. Photo-elimination of the phosphonates (**1a**—**e**)

1	R	R_1	R_2	Conv. %[a)]	Time h	Yields/% **2**[b)]	Yields/% **3**[c)]	Yields/% **4**[b)]	Rel. ratio of Type II
a	*i*-Bu	Me	Me	28	2	7.2	15	60.7	0.83
b	*n*-Pr	Me	H	35	2	8.1	23.9	n.d.	0.66
c	Et	H	H	23	2	16.4	54.3	n.d.	1.00
d	Me	—	—	32	2	n.d.[e)]	n.d.	92.5	
e	*n*-Bu	Et	H	18[d)]	2	—	25.3[a)]	n.d.	0.70

a) Determined by GLC. b) Isolated yield. c) Determined by GLC as dibromide. d) Irrad. externally in a quartz cell. e) Not detected.

Table 2. Spectral data for the generated and synthetic monoesters (**2a**—**c**)

	2a	**2b**	**2c**
MS (m/z)	198.8877; $^{35}Cl_3CP(OH)_3^+$ 198.889[a] (calcd 198.889) 137.0373; $P(O)(OH)(OC_4H_9)^+$ 137.037[a] (calcd 137.036)	198.8880 (calcd 198.889) 123.0223; $P(O)(OH)(OC_3H_7)^+$ (calcd 123.021)	198.8880 (calcd 198.889) 109.0080; $P(O)(OH)(OC_2H_5)^+$ (calcd 109.006)
IR (cm^{-1})	1640, 1110 (P-OH) 1245 (P=O) 1040 (P-O-C) 760 (P-C) 550 (C-Cl)	1635, 1110 1250 1010 760 550	1630, 1085 1245 1040 755 545
NMR (δ ppm)	identical with the appropriate starting material (**1a**—**c**) except the following signals. 2.25 (1H, s) 1.30 (1H, br.s)	2.19 (1H, s) 1.30 (1H, br.s)	2.30 (1H, s) 1.30 (1H, br.s)

a) Mass number of the photoproduct, see Ref. 1. b) On Silica gel PF_{254}-gipshaltig (Merck; thickness 2.2 mm; hexane-acetone, 5:1).

Table 3. Preparation of the monoesters (**2a**—**c**)

	R	**5**	**1a**—**c**	Yield/%[a]	Cryst.[b] color and form	Mp
a	*i*-Bu	100 mg	600.5 mg	92 mg (71.7%)	C-L	>250 °C
b	*n*-Pr	105	316	90 (70.8%)	C-CP	>300 °C
c	Et	115.7	318.6	80 (60.7%)	C-CP	228—229 °C

a) Based on **5**. b) C: colorless; L: leaflets; CP: crystalline powder.

peak at m/z 218 in MS. IR spectrum showed the presence of P=O bond and the absence of P–C and C–Cl bonds, and is identical with that of the authentic sample[7] prepared by the esterification of anhydrous hypophosphoric acid[8] (**6**) with diazomethane in ether. The NMR spectrum showed the presence of methyl protons which exhibited upfield shift by δ 0.32 ppm than that of **1d** and was very similar to that of $HP(O)(OMe)_2$ except P–H signal, and the Beilstein test was negative (Table 3). These data supported the structure, **4d**, which seems to be derived from the type I photo-elimination of **1d** as shown below. Photolysis of **1a** gave also an analogous compound, **4a**. Davies

$$1^* \xrightarrow{\text{type I}} Cl_3C\cdot + \cdot P(O)(OR)_2$$

$$2\cdot P(O)(OR)_2 \longrightarrow \underset{\textbf{4}}{[-P(O)(OR)_2]_2}$$

$$2Cl_3C\cdot \longrightarrow \underset{\textbf{7}}{Cl_3C\text{-}CCl_3}$$

et al. observed the dialkoxyphosphinyl radicals, $\cdot P(O)(OR)_2$, by ESR spectra in photolysis of di-*t*-butyl peroxide in the presence of a dialkyl phosphonate, in the peroxide as solvent (R′=Me, Et, *i*-Pr, or *n*-Bu):[9] However,

$$t\text{-Bu-OO-}t\text{-Bu} \xrightarrow{h\nu} 2t\text{-BuO}\cdot$$

$$t\text{-BuO}\cdot + HP(O)(OR')_2 \longrightarrow t\text{-BuOH} + \cdot P(O)(OR')_2$$

product of hydrogen abstraction by the $\cdot P(O)(OR)_2$ radical, $H\text{–}P(O)(OR)_2$ was not detected in the present reactions. Thus, $\cdot P(O)(OR)_2$ radical would recombine with another one to afford **4**. On the other hand, hexachloroethane (**7**) was detected by GLC, which is supposed to be a coupling product of the partner radical, $\cdot CCl_3$.

The type **4** compounds, somehow, could not be detected in the photolyses of **1b** and **1c**.

The nitrogen streams bubbled through the each reaction mixture during irradiation were introduced into a bromine solution in carbon tetrachloride in order to trap the generated olefins, **3a**—**c**, and the resulting olefin dibromides (**8a**—**c**) were determined by GLC. For **1a** and **1e**, the olefin (**3a** and **3e**) in the reaction mixtures were also determined directly by GLC (Table 1).

The each yield of the corresponding **2** and **3** should be equal, if these compounds might be produced only *via* a type II reaction. However, the yields of **2** were lower than those of **3**. The lower yields may be explained by the difficulties on the determination of **2**. Thus, the monoesters (**2**) are very hygroscopic, hard to be eluated, and apt to be hydrolysed. In fact, when chromatographed on the silica-gel TLC, only 52% of the authentic sample of **2a** was recovered on elution. Thus, the yields of **3** were used to evaluate the type II elimination efficiency. For butyl derivative, **1e**, having secondary hydrogen as likely as **1b**, gave also **3** as much as from **1b**. This might suggest that the yield of **3b** reflected the true value of type II elimination.

As shown in Table 1, for **1b** and **1c** type II elimination exclusively occured, while competitive type I and II eliminations occured for **1a**. The competitive α-cleavage and γ-hydrogen abstraction of the phosphonates resemble to those of alkyl phenyl ketones[5c] or alkanals.5d) However, the relative rates of γ-hydrogen abstraction calculated from the yields of olefins slightly change as the γ-C–H bond strength, *i.e.*, 0.83, 0.66, and 1.00 for **1a**, **1b**, and **1c**. Comparing with those of phenyl alkyl ketones6b) the reactivity of phosphoryl compounds is significantly different from that of ketones or alkanals.

Data of Turro and Weiss5b) clearly demonstrate that the abstraction of the γ-hydrogen by alkyl ketones is most favorable when the hydrogen is directed toward the half-filled n orbital of the n-π^* excited carbonyl, that is, with on the hydrogen lying on the plane of the carbonyl group. The substituents at the γ-carbon atom may not affect sterically on the H-abstraction reaction rates. Therefore, reaction rates for the γ-hydrogen abstraction by an excited carbonyl group generally decrease in the order; tertiary>secondary>primary C–H bonds.

In contrast, for the type II elimination of dialkyl (trichloromethyl)phosphonates (**1**) a steric hindrance may play an important role in the reactivities. Thus, location of the γ-hydrogen near the phosphoryl oxygen atom seems to be sterically hindered by the bulky CCl_3 group. Examination of Dreiding models suggests that the co-planarity of the γ-hydrogen and O=P–C of the n-π^* excited states of phosphoryl group are sterically inhibited in the order; tert>sec≥prim C–H bonds, which probably reflect to the rates of type II elimination. In conclusion the efficiency of the present type II eliminations may be explained by both of the steric and the radical-stabilizing effects.

There were not great differences between the rates of the disappearnace of the starting materials (**1**). For the present reactions, it seems apparently that the type I elimination increases as the type II elimination decreases, which corresponds to that of carbonyl compound having been reported.5b) Correlationship between the selectivity of the competitive α-cleavage and γ-hydrogen abstraction and their structure may be explained also by the steric hindrance mentioned above.

Experimental

All mp and bp were uncorrected. Following spectrometers were used for spectral measurements: IR: JASCO IR-G; UV: Shimadzu UV-200; NMR: JEOL JNM-MH-100 (100 MHz); MS: JEOL JMS-D-100; high MS were measured by JEOL Co. The spectral data are presented as follows: IR: in cm^{-1}; UV: in nm (ε given in parentheses); NMR: δ in ppm from int. TMS and J in Hz (accuracy ± 0.3 Hz); and MS in m/z. GLC were carried out by Yanagimoto Yanaco G-80FP and G-1800F.

Materials. Dialkyl (trichloromethyl)phosphonates (**1a**—**e**) were prepared according to the literatures: **1a**: Colorless liquid, bp 72—74.5 °C/10^{-4} mmHg (lit, bp 109—110 °C/1 mmHg,1) 144—145 °C/9 mmHg2)) $\nu_{\max}^{\text{neat}}$ 1280 (P=O), 1020 (P–O–C), 765 (P–C), 545 (C–Cl); $\lambda_{\max}^{\text{MeCN}}$ 256.5 (15.4), 300 (2.97); ($\varepsilon_{254}^{\text{MeCN}}$ 14.9). **1b**: Colorless liquid, bp 59—61 °C/10^{-4} mmHg (lit,2) bp 144—145 °C/12 mmHg), $\nu_{\max}^{\text{neat}}$ 1275 (P=O), 1018 (P–O–C), 770 (P–C), 550 (C–Cl); ($\varepsilon_{254}^{\text{MeCN}}$ 1.32). **1c**: Colorless liquid, bp 51—55 °C/5×10^{-3} mmHg (lit,2) bp 122—123 °C/12 mmHg), $\nu_{\max}^{\text{neat}}$ 1275 (P=C), 1018 (P–O–C), 765 (P–C), 550 (C–Cl); ($\varepsilon_{254}^{\text{MeCN}}$ 0.39). **1d**: colorless liquid, bp 52.5—54 °C/1.6×10^{-3} mmHg (lit,2) bp 120—126 °C/12—13 mmHg; $\nu_{\max}^{\text{neat}}$ 1282 (P=O), 1185, 1020 (P–O–C), 763 (P–C), 550 (C–Cl); ($\varepsilon_{254}^{\text{MeCN}}$ 0.20). **1e**: Colorless liquid, bp 86—89 °C/4×10^{-3} mmHg (lit,2) bp 145 °C/7 mmHg); $\nu_{\max}^{\text{neat}}$ 1280 (P=O), 1028 (P–O–C), 768 (P–C), 552 (C–Cl); ($\varepsilon_{254}^{\text{MeCN}}$ 0.48).

(Trichloromethyl)phosphonic acid (**5**) was prepared according to the literature; mp 158.5—161.5 °C (lit,4) mp 163.2 °C).

Alkyl (trichloromethyl)phosphonates (**2a**—**c**) were prepared by analogous method of the literature3) by thermal reactions (110 °C for 12 h in sealed tube) of the phosphonic acid (**5**) (1 equiv.) and the corresponding diester (**1a**—**c**, respectively; 2—3 equiv.). The results and spectral data of the products are summarized in Tables 2 and 3.

Tetramethyl hypophosphate (**4d**) was prepared by the method of the lit,7) from the esterification of hypophosphoric acid (**7**)8) with diazomethane in ether: Colorless liquid, bp 80 °C/2×10^{-4} mmHg (lit,7) bp 85—87 °C/10^{-4} mmHg), m/z 218 (M^+) $\nu_{\max}^{\text{neat}}$ 1460, 1260, 1180, 1020, 850, 825. Tetraisobutyl hypophosphate (**4a**) was prepared by the analogus method as above; colorless liquid, bp 92—94 °C/10^{-4} mmHg; m/z (M^+) 386; (Found: C, 49.42; H, 9.16%. Calcd for $C_{16}H_{36}O_6P_2$: C, 49.734; H, 9.391%).

Isobutylene (**3a**) was prepared with the general procedure dehydrating *t*-BuOH with anhydrous oxalic acid: Colorless liquid, δ (CCl_4) 1.70 (s, 6H), 4.62 (s, 2H). 1-Butene (**3e**) was prepared by the method of lit.,10) reacting alkyl bromide with Grignard reagent (MeMgI): Colorless liquid, δ (CCl_4) 0.99 (t, 3H, J=7.0), 2.05 (m, 2H), 4.93 (m, 2H), 5.80 (m, 1H). 1,2-Dibromo-2-methylpropane (**8a**) was synthesized according to the lit,11) Colorless liquid, bp 41—42.5 °C/17 mmHg (lit,11) bp 165.6—166 °C). Propylene dibromide (**8b**) and ethylene dibromide (**8c**) were purchased from Tokyo Kasei Chem. Co.

Acetonitrile was dried over P_2O_5 and distilled from K_2CO_3 before use.

*Irradiation of Dialkyl (Trichloromethyl)phosphonates (**1a**—**d**):* Solution of the phosphonate (**1**) (4.2 mmol: 42.7 mM) in MeCN (170 ml) were irradiated directly with a low-pressure mercury lamp (Eikosha PIL-30; 30 w) in an immersion apparatus for 2—5 h at 20 °C. Nitrogen was bubbled through the solution before and during irradiation. Photoreaction was monitored by GLC as the decrease of the starting material (**1**) [10% SE-GE-31 on Diasolid L (60—80 mesh) in a stainless steel column 2.25 m, ϕ 2.5 mm; column temp, 180 °C; inj. temp, 250 °C; carrier gas (N_2); 50 ml/min; internal standard method].

The photoproducts were separated by preparative TLC [Silica gel PF_{254}-gipshaltig (Merck); 20×20 cm, thickness, 2.2 mm; 4-plates, hexane–acetone, 5:1], and the fractions were eluted with acetone. The results and spectral data of the products are summarized in Tables 1, 2, and 3.

The nitrogen streams bubbling through the solution during irradiation were introduced into bromine (0.5 g) solution of CCl_4 (20 ml) to trap the occuring olefins as olefin dibromides (**8**). These solutions were analyzed by GLC with the same column as above, [columm temp, 100 °C; inj. temp., 250 °C; carrier (N_2), 30 ml/min] and the olefin dibromides (**8a**—**c**) were assigned comparing the retention time in GLC with the corresponding authentic samples and the quantities were determined by the internal standard method.

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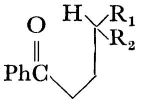

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	R_1	R_2	Φ_{II}	$10^{-8} k_r (s^{-1})$
9a	Me	Me	0.25	4.8
b	Me	H	0.33	1.3
c	H	H	0.36	0.08

0.1 M ketone in benzene, 313 nm irradiation.

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