

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

Nobutaka SUZUKI, Teruyuki KAWAI, Susumu INOUE,
Naoki SANO, and Yasuji IZAWA*

Chemistry Department, Faculty of Engineering, Mie University, Tsu 514

(Received December 7, 1979)

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 reported¹⁾ 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 frequency 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.

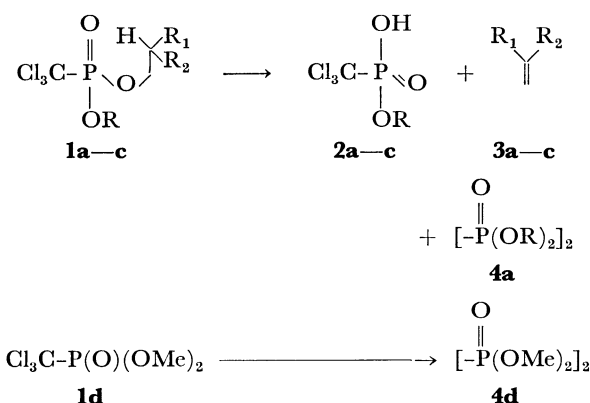
In this paper, we wish to report further investigations on the photochemical elimination of dialkyl (trichloromethyl)phosphonates (**1a**, **1b**, and **1c**) in hope of exploring the exact nature of this reaction.

Results and Discussion

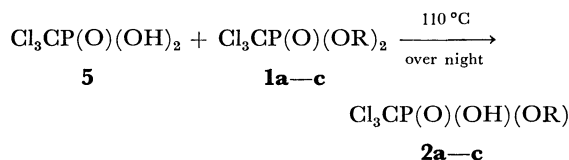
A solution of the phosphonates²⁾ (**1a—d**: 4.2 mmol: 24.7 mmol/l) in acetonitrile (170 ml) was flushed with nitrogen before and during irradiation to prevent photo-oxidation of the starting material and/or the product(s). During irradiation with a low-pressure mercury lamp (30 w; immersion type) the 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 paper¹⁾ 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 Kharasova³⁾ 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**.



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/%			Rel. ratio of Type II
						2 ^{b)}	3 ^{c)}	4 ^{b)}	
a	<i>i</i> -Bu	Me	Me	28	2	7.2	15	60.7	0.83
b	<i>n</i> -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	<i>n</i> -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 (<i>m/z</i>)	198.8877; ³⁵ Cl ₃ CP(OH) ₃ ⁺ (calcd 198.889) 137.0373; P(O)(OH)(OC ₄ H ₉) ⁺ 137.037 ^{a)} (calcd 137.036)	198.8880 (calcd 198.889) 123.0223; P(O)(OH)(OC ₃ H ₇) ⁺ (calcd 123.021)	198.8880 (calcd 198.889) 109.0080; P(O)(OH)(OC ₂ H 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)

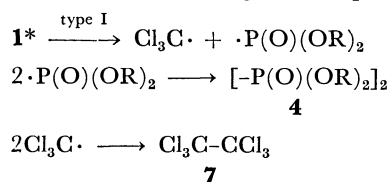
a) Mass number of the photoproduct, see Ref. 1. b) On Silica gel PF₂₅₄-gipshaltig (Merck; thickness 2.2 mm; hexane-acetone, 5:1).

TABLE 3. PREPARATION OF THE MONOESTERS (2a—c)

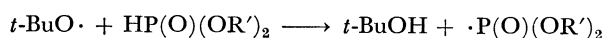
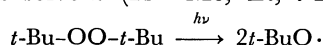
	R	5	1a—c	Yield/% ^{a)}	Cryst. ^{b)} color and form	Mp
a	<i>i</i> -Bu	100 mg	600.5 mg	92 mg (71.7%)	C—L	>250 °C
b	<i>n</i> -Pr	105	316	90 (70.8%)	C—CP	>300 °C
c	Et	115.7	318.6	80 (60.7%)	C—CP	228—229 °C

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 sample⁷⁾ prepared by the esterification of anhydrous hypophosphoric acid⁸⁾ (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



et al. observed the dialkoxyphosphinyl radicals, $\cdot\text{P}(\text{O})(\text{OR})_2$, 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,



product of hydrogen abstraction by the $\cdot\text{P}(\text{O})(\text{OR})_2$ radical, H—P(O)(OR)₂ was not detected in the present reactions. Thus, $\cdot\text{P}(\text{O})(\text{OR})_2$ 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, $\cdot\text{CCl}_3$.

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 eluted, 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 occurred, while competitive type I and II eliminations occurred 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 ketones^{6b)} the reactivity of phosphoryl compounds is significantly different from that of ketones or alkanals.

Data of Turro and Weiss^{5b)} 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 $n\text{-}\pi^*$ 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 $\text{O}=\text{P}-\text{C}$ of the $n\text{-}\pi^*$ excited states of phosphoryl group are sterically inhibited in the order; *tert* > *sec* $\geq$ *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 disappearance 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)} Correlation 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⁾ $\nu_{\text{max}}^{\text{neat}}$ 1280 (P=O), 1020 (P—O—C), 765 (P—C), 545 (C—Cl); $\lambda_{\text{max}}^{\text{MeCN}}$ 256.5 (15.4), 300 (2.97); ($\epsilon_{254}^{\text{MeCN}}$ 14.9). **1b**: Colorless liquid, bp 59—61 °C/10⁻⁴ mmHg (lit,²⁾ bp 144—145 °C/12 mmHg, $\nu_{\text{max}}^{\text{neat}}$ 1275 (P=O), 1018 (P—O—C), 770 (P—C), 550 (C—Cl); ($\epsilon_{254}^{\text{MeCN}}$ 1.32). **1c**: Colorless liquid, bp 51—55 °C/5 $\times$ 10⁻³ mmHg (lit,²⁾ bp 122—123 °C/12 mmHg, $\nu_{\text{max}}^{\text{neat}}$ 1275 (P=O), 1018 (P—O—C), 765 (P—C), 550 (C—Cl); ($\epsilon_{254}^{\text{MeCN}}$ 0.39). **1d**: colorless liquid,

bp 52.5—54 °C/1.6 $\times$ 10⁻³ mmHg (lit,²⁾ bp 120—126 °C/12—13 mmHg; $\nu_{\text{max}}^{\text{neat}}$ 1282 (P=O), 1185, 1020 (P—O—C), 763 (P—C), 550 (C—Cl); ($\epsilon_{254}^{\text{MeCN}}$ 0.20). **1e**: Colorless liquid, bp 86—89 °C/4 $\times$ 10⁻³ mmHg (lit,²⁾ bp 145 °C/7 mmHg; $\nu_{\text{max}}^{\text{neat}}$ 1280 (P=O), 1028 (P—O—C), 768 (P—C), 552 (C—Cl); ($\epsilon_{254}^{\text{MeCN}}$ 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 $\times$ 10⁻⁴ mmHg (lit,⁷⁾ bp 85—87 °C/10⁻⁴ mmHg, m/z 218 (M^+) $\nu_{\text{max}}^{\text{neat}}$ 1460, 1260, 1180, 1020, 850, 825. Tetraisobutyl hypophosphate (**4a**) was prepared by the analogous 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 $\text{C}_{16}\text{H}_{36}\text{O}_6\text{P}_2$: 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. Photo-reaction 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].

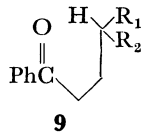
The photoproducts were separated by preparative TLC [Silica gel PF₂₅₄-gipshaltig (Merck); 20 $\times$ 20 cm, thickness, 2.2 mm; 4-plates, hexane—acetone, 5:1], and the fractions were eluted with acetone. The results and spectral data of the products are summarized in Tables 1, 2, and 3.

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 occurring olefins as olefin dibromides (**8**). These solutions were analyzed by GLC with the same column as above, [column 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.

The authors are grateful to JEOL Co. for the measurements of high mass spectra.

References

- 1) Previous paper in this series: Y. Ogata, Y. Izawa, and T. Ukigai, *Bull. Chem. Soc., Jpn.*, **46**, 1009 (1973), and references cited therein.
- 2) G. Kamai, and L. P. Egorova, *Zh. Obshch. Khim.*, **16**, 1521 (1946); *Chem. Abstr.*, **41**, 5439i (1947).
- 3) G. Kamai and F. M. Kharasova, *Zh. Obshch. Khim.*, **27**, 953 (1957); *Chem. Abstr.*, **52**, 3666a (1958).
- 4) A. Ya. Yakubovich and V. A. Ginsgurg, *Dokl. Akad. Nauk, SSSR*, **82**, 273 (1952); *Chem. Abstr.*, **47**, 2685 (1953); for IR: C. J. Pouchert, "The Aldrich Library of IR Spectra," Aldrich Chem. Co., Milwaukee, Wisconsin (1970), p. 410.
- 5) For examples: (a) J. A. Barltrop and J. D. Coyle, *Tetrahedron Lett.*, **1968**, 3235; (b) N. J. Turro and D. S. Weiss, *J. Am. Chem. Soc.*, **90**, 2185 (1968); (c) F. D. Lewis, R. W. Johnson, and D. E. Johnson, *ibid.*, **96**, 6090 (1974); (d) J. C. Dalton, M. W. Geiger, and J. J. Snyder, *ibid.*, **98**, 398 (1976).
- 6) (a) P. J. Wagner, *Tetrahedron Lett.*, **1968**, 5385; (b) *Acc. Chem. Res.*, **4**, 168 (1971): Photochemical abstraction of γ -hydrogen of phenyl alkyl ketones:



	R ₁	R ₂	Φ_{11}	$10^{-8} k_r (s^{-1})$
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.

- 7) M. Baudler, *Z. Anorg. Allg. Chem.*, **288**, 171 (1956).
- 8) M. Baudler, *Z. Anorg. Allg. Chem.*, **279**, 115 (1955); E. Leininger and T. Chylski, *Inorg. Synth.*, **4**, 68 (1962).
- 9) A. G. Davies, D. Griller, and B. P. Roberts, *J. Am. Chem. Soc.*, **94**, 1782 (1972).
- 10) H. J. Lucas and R. T. Dillon, *J. Am. Chem. Soc.*, **50**, 1461 (1928).
- 11) M. S. Kharasch, W. Hered, and F. R. Mayo, *J. Org. Chem.*, **6**, 818 (1941).