Photorearrangement of N-Chlorophosphoramidates

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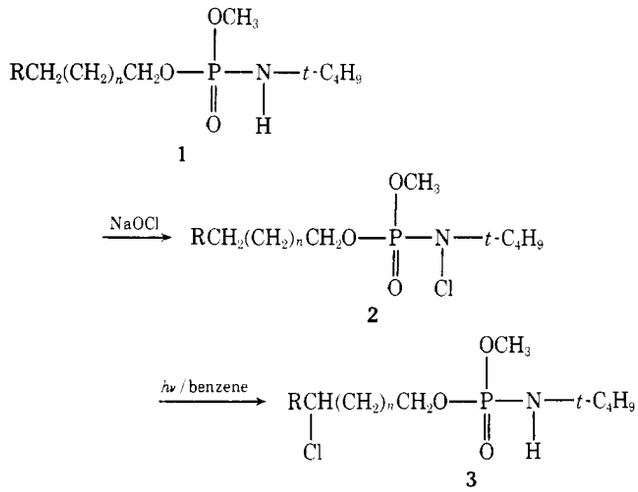
The photodecomposition of alkyl methyl *N*-chloro-*N*-*tert*-butylphosphoramidates in benzene with or without scavenger was attempted with a view to ascertaining the ability of hydrogen abstraction by phosphoramidate radical. In the photodecomposition of *N*-chlorophosphoramidates in benzene, the rearrangement products, *O*-monochloroalkyl isomers, were obtained in high yield but their isomer compositions were almost the same as those of photochlorination products of original phosphoramidates. On the other hand, in the reactions with scavengers of chlorine atoms or hydrogen chloride, such as dichloroethylene or 2,4,6-trimethylpyridine, the fairly selective rearrangements were observed. The major product was the 3-chloralkyl derivative in the phosphoramidates having *O*-butyl or *O*-pentyl group. The regioselective rearrangements observed in this investigation clearly suggest the intramolecular hydrogen abstraction by phosphoramidate radicals via the seven-membered-ring transition state.

Addition to the double bonds and hydrogen abstraction from alkyl chains are the main possible reactions of nitrogen radicals derived from *N*-halo compounds.[1,2]

Until now, rearrangements via intramolecular hydrogen transfer by nitrogen radicals have been investigated on many *N*-halo compounds such as *N*-halo amines,[3-5] *N*-haloamides,[6-11] *N*-halosulfonamides,[13-17] and others.[17]

N,N-Dihalophosphoramidates, a relatively new class of pseudohalogens, have recently been reported to add to olefins and dienes by Zwierzak et al.[18-24] However, it has not yet been determined whether the phosphoramidate radical is capable of abstracting hydrogen atoms from alkyl chains.

To verify the ability of the phosphoramidate radical to abstract hydrogen, photodecomposition of alkyl methyl *N*-chloro-*N*-tert-butylphosphoramidates was attempted.



Reaction products halogenated in the *O*-alkyl chain were obtained in high yield from the above rearrangement which were fairly selective under the proper conditions to eliminate or control the hydrogen atom abstraction by the chlorine atom. The major rearrangement product was the 3-chloroalkyl derivative thought to be derived from intramolecular 1,6-hydrogen transfer of phosphoramidate radicals except in the case of methyl propyl *N*-chloro-*N*-*tert*-butylphosphoramidate (**2a**), in which the 3 position is substituted exclusively by primary hydrogens.

Among the rearrangement products, the 2- and 3-chloroalkyl derivatives are intermediates for the synthesis of cyclophosphorine derivatives such as 1,3,2-oxazaphospholidines[25-28] and 1,3,2-oxazaphosphorines.[25,27] From the standpoint of synthetic interest, the reaction was investigated in detail.

Results and Discussion

Alkyl methyl *N*-chloro-*N*-*tert*-butylphosphoramidates (**2a,** R = H, n = 1; **2b,** R = CH_3, n = 1; **2c,** R = C_2H_5, n = 1) were prepared by the chlorination of the corresponding phosphoramidates (**1a–c**) with chlorine in a buffered solution.

Their photodecomposition was carried out in benzene using a high-pressure mercury arc lamp and the rearrangement products were analyzed by GLC. In the gas chromatogram of **3a,** three peaks were observed. The first and the last peak were identified as **1a** and propyl methyl 3-chloro-*N*-tert-butylphosphoramidate, respectively, by comparing their retention times with those of authentic compounds. The main component (the second peak) was separated by preparative GLC and identified by ^{1}H NMR as propyl methyl 2-chloro-*N*-*tert*-butylphosphoramidate.

In the gas chromatogram of **3b,** four peaks were found. The first and the last peak were identified as **1b** and butyl methyl 4-chloro-*N*-*tert*-butylphosphoramidate, respectively, comparing their retention times with those of the authentic compounds. The third peak (major component) and the second peak were separated by preparative GLC and identified as the 3- and 2-chlorobutyl isomers, respectively. Five peaks in the GLC of **3c** were identified as **1c** and pentyl methyl 2-, 3-, 4-, and 5-chloro-*N*-*tert*-butylphosphoramidate, respectively, in order of increasing retention time in accordance with reported results on various chlorinated aliphatic compounds.[29-32] The isomer composition of the rearrangement and photochlorination products are summarized in Table I.

As shown in Table I, no marked differences are observed between the isomer composition of the rearrangement products and the free-radical chlorination products. Whether phosphoramidate radicals are involved in these reactions could not be ascertained.

However, these results may be explained if it is assumed that phosphoramidate radicals cannot compete with chlorine atoms in hydrogen abstraction because the latter are far more reactive.

To substantiate the above assumption, photodecomposition of *N*-chlorophosphoramidate (**2a–c**) was conducted in the presence of dichloroethylene, which is known to be a potential chlorine atom trap.[33,34]

As shown in Table II, considerable changes in the isomer composition of the rearrangement products are observed when over 5 mol of dichloroethylene are added to 1 mol of *N*-chlorophosphoramidates.

Furthermore, **2a, 2b,** and **2c** were photodecomposed in the presence of 2,4,6-trimethylpyridine (TMP), reported by Johnson and Greene[11,12] to be an effective scavenger of hydrogen chloride generated in the chlorine atom chain reaction.

Table I. Photodecomposition (A) of Alkyl Methyl *N*-Chloro-*N*-*tert*-butylphosphoramidates (2a, 2b, 2c) and Photochlorination (B) of Alkyl Methyl *N*-*tert*-Butylphosphoramidates (1a, 1b, 1c) in Benzene

Sample	Reaction type	Concn, mol	Reaction time, h	Recovery, %	Chlorine content, % (calcd)	Isomer composition, %[a,b] 1-	2-	3-	4-	5-
2a	A	0.05	1.0	93	11.7 (14.5)	0	86	14		
1a	B	0.2	0.2		7.1 (14.5)	0	85	15		
2b	A	0.1	3.0	98	11.4 (13.8)	0	19	72	9	
1b	B	0.1	0.1		3.5 (13.8)	0	22	70	8	
2c	A	0.08	3.0	95	11.9 (13.0)	0	10	38	47	5
1c	B	0.1	0.1		3.0 (13.0)	0	6	38	53	3

[a] Analyzed by GLC, 20% Carbowax 1000 on Celite 545, 1 m, at 165 °C for **3a, 3b;** 30% Carbowax 20M on Celite 545, 2 m, at 185 °C for **3c.** [b] 10–20% of unsubstituted phosphoramidate (**1a, 1b, 1c**) was detected in the rearrangement products.

Table II. Photodecomposition of Alkyl Methyl *N*-Chloro-*N*-*tert*-butylphosphoramidates in Benzene in the Presence of Dichloroethylene (DCE)[a]

N-Chloro compd	Mole ratio DCE[b]/2	Reaction time, h	Recovery,[c] %	Chlorine content,[c] % (calcd)	Isomer composition, %[d,e] 1-	2-	3-	4-	5-
2a	5	1.5	102	14.6 (14.5)	0	72	28		
2b	5	2.0	98	14.0 (13.8)	0	13	74	13	
2c	2	2.5	99	13.7 (13.8)	0	16	38	38	8
2c	5	3.0	102	13.5 (13.8)	0	17	54	21	8
2c	10	5.0	103	13.7 (13.8)	0	16	55	21	8

[a] Concentration, 0.1 mol, 15 ± 2 °C under nitrogen. [b] *cis*-Dichloroethylene. [c] The crude products contained small amounts of chlorine-containing compounds derived from dichloroethylene. [d] Analyzed by GLC; see Table I. [e] 10–15% of unsubstituted phosphoramidate (**1a–c**) was found in the products.

Table III. Photodecomposition of Alkyl Methyl *N*-Chloro-*N*-*tert*-butylphosphoramidates in Benzene in the Presence of 2,4,6-Trimethylpyridine (TMP)[a,b]

N-Chloro compd	Concn, mol	Reaction time, h	Recovery, %	Chlorine content, % (calcd)	Isomer composition, %[c,d] 1-	2-	3-	4-	5-
2a	0.10	4.5	85	9.6 (14.5)	0	73	27		
2b	0.19	2.5	60	13.2 (13.8)	0	16	77	7	
2c	0.10	2.5	86	12.9 (13.1)	0	20	64	16	0

[a] Photolysis at 20 ± 2 °C under nitrogen. [b] Mole ratio, TMP:*N*-chloro compound 2:1. [c] Analyzed by GLC; see Table I. [d] 5–10% (**2b, 2c**) and 40% (**2a**) of unsubstituted phosphoramidate was found in the crude products.

In the rearrangement of **2a,** the active chlorine persisted for a long period and relatively large amounts of TMP hydrochloride were isolated from the reaction, while the photodecomposition of **2b** and **2c** proceeded rapidly. The crude rearrangement products were analyzed by GLC and ^{1}H NMR. The results of GLC analyses are shown in Table III.

In the NMR of the crude rearrangement product (**3a**), a doublet at δ 1.52, assigned to the terminal methyl protons of the 2-chloropropyl isomer, and a quintet at δ 2.10, assigned to the center methylene protons of the 3-chloropropyl isomer, were observed in a ratio of 3:1, along with the other expected signals.

In the NMR of **3b,** a doublet at δ 1.55 (2.5 H based on *tert*-butyl protons), multiplets centered at δ 2.0 (2.0 H) and 4.2 (2.9 H), and small triplets at δ 1.07 (0.35 H) and 0.93 (0.3 H) were observed together with the signals of *tert*-butyl protons (δ 1.28, s, 9 H) and *O*-methyl protons (δ 3.70, d, 3 H). The signals at δ 1.55 and 1.07 were assigned to the terminal methyl protons of the 3- and 2-chlorobutyl isomers, respectively. The triplet at δ 0.93 may be assigned to the terminal methyl protons of the 4-chlorobutyl isomer and unsubstituted phosphoramidate (**1b**), though the content of the former is small.

Also, in the NMR of **3c,** a doublet at δ 1.52, assigned to the terminal methyl protons of the 4-chloropentyl derivative, was small (0.5 H) and a large triplet (δ 1.04, 1.8 H), assigned to the terminal methyl protons of the 3-chloropentyl derivative, was observed.

Although a few small unidentified peaks were found in some gas chromatograms of the rearrangement products, besides the identified main peaks, no indication of substitution of the chlorine atom on an *O*-methyl or *tert*-butyl group was found in the NMR spectra.

The isomer composition estimated by NMR analyses showed good agreement with GLC results. Striking differences in isomer composition were noted between rearrangements in the presence or absence of DCE or TMP.

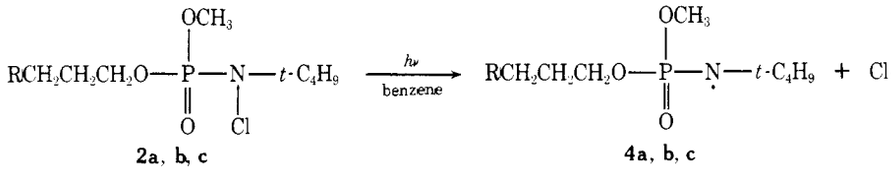
In addition, it was found that in rearrangements with scavengers, substitution at the 3 position of the *O*-alkyl chain was most preferred in **2b** and **2c.** Even in **2a** in which the 3 position contains only primary hydrogens, the content of the 3-chloropropyl isomer increased considerably.

Based on the above results, a reaction pathway is proposed in Scheme I.

In the rearrangements without scavengers, a chlorine atom chain reaction may be the main process due to the higher rate of hydrogen atom abstraction by chlorine atoms. However, in the rearrangements with scavengers, the influence of chlorine atoms is suppressed and phosphoramidate radicals are by far the most important hydrogen atom abstracting agents.

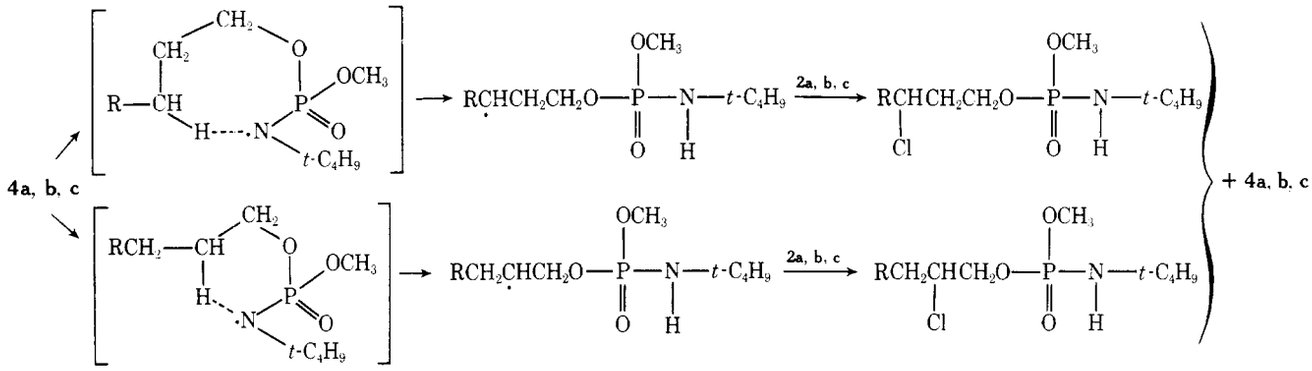
The observed remarkable selectivity at the 3 position seems to be clear evidence of intramolecular hydrogen abstraction by phosphoramidate radicals. If the reaction were intermolecular, the electrophilic nitrogen radicals would allow the

Scheme I. Proposed Pathway of Photodecomposition of *N*-Chloro-*N*-*tert*-butylphosphoramidates



2a, b, c 4a, b, c

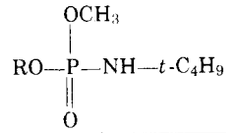
1. Intramolecular hydrogen abstraction by phosphoramidate radical



a, R = H; b, R = CH_3; c, R = C_2H_5

2. Intermolecular hydrogen abstraction by phosphoramidate radical
3. Hydrogen abstraction by chlorine atom

Table IV. Analytical and Physical Data of Alkyl Methyl *N*-*tert*-Butylphosphoramidates[a]



Compd	R	Yield, %	Bp, °C (mm)	IR (neat), cm^{-1}	NMR (CCl_4), δ
1a	n-C_3H_7	78	90–92 (0.5)	3220, 2980, 1245, 1200, 1050, 1005	0.98 (t, 3 H), 1.20 (s, 9 H), 1.64 (sextet, 2.1 H), 3.59 (d, 3 H), 3.85 (q, 2 H), 4.75 (d, 0.9 H)
1b	n-C_4H_9	54	124–125 (2.0)	3220, 2980, 1245, 1205, 1030–1060, 985	0.96 (t, 3 H), 1.19 (s, 9 H), 1.30–1.78 (m, 4 H), 3.58 (d, 3 H), 3.90 (q, 2 H), 4.78 (d, 1 H)
1c	n-C_5H_{11}	73	101–102 (0.5)	3220, 2980, 1250, 1205, 1030–1065, 1000	0.92 (t, 3 H), 1.19 (s, 9 H), 1.34 (m, 4 H), 1.60 (m, 2 H), 3.59 (d, 3 H), 3.88 (q, 2 H), 4.76 (d, 1 H)

[a] Satisfactory analytical data (±0.3% for C, H, N) were obtained for all compounds.

preferential substitution of the secondary hydrogens farthest from the electron-attracting substituent.[2,36] However, in intramolecular hydrogen abstraction by nitrogen radicals, such as amminium,[3,35] amydyl,[8-11] and sulfonamide radicals,[13-17] a six-membered-ring transition state is known to be far more preferable to a seven-membered ring. The distinct preference of the latter to the former observed in this investigation is extraordinary and suggests significant differences in the transition states due to the –O–P–N– bond in the phosphoramidate radicals.

Experimental Section[37]

Alkyl Methyl *N*-*tert*-Butylphosphoramidate (1a–c). Alkyl methyl *N*-*tert*-butylphosphoramidates were prepared by the reaction of alkylmethyl phosphite[38] and *tert*-butylamine according to the procedure of Todd.[39] They were purified by distillation at reduced pressure; purity of all compounds was checked by GLC and ^1H NMR (Table IV).

Alkyl Methyl *N*-Chloro-*N*-*tert*-butylphosphoramidates (2a–c). To a mixture of *n*-pentyl methyl *N*-*tert*-butylphosphoramidate (**1c**, 4.7 g, 0.021 mol), sodium acetate (18 g), glacial acetic acid (1.8 g), and water (40 ml), chlorine gas was introduced with stirring and cooling (10–15 °C) until the solution had a yellow color. After the reaction, excess chlorine was expelled by nitrogen and the yellow, oily product was multiply extracted with dichloromethane. The extracts were combined, washed with water, and dried over magnesium sulfate. The solvent was removed in vacuo to leave an almost colorless liquid (**2c**, 5.87 g, 86%). Active chlorine, 13.0% (calcd, 13.1%).

Similarly, *n*-butyl methyl *N*-chloro-*N*-*tert*-butylphosphoramidate (**2b**, active chlorine, 13.6%) and *n*-propyl methyl *N*-chloro-*N*-*tert*-butylphosphoramidate (**2a**, active chlorine, 14.2%) were obtained in ca. 90% yields.

Photodecomposition of *N*-Chlorophosphoramidates (2a–c) in Benzene. *N*-Chlorophosphoramidate (0.018 mol) was dissolved in 180 ml of benzene and nitrogen was slowly bubbled through the solution for 20 min before irradiation. The solution was irradiated with a high-pressure mercury arc lamp at 20 ± 2 °C under nitrogen until the active chlorine content became negligible. After irradiation, the solvent was removed under reduced pressure; the crude rearrangement product (**3a–c**) was obtained as a viscous, orange oil. The rearrangement products were analyzed by GLC (Table I) and some of the isomers were isolated in pure form by preparative GLC.

Propyl Methyl 2-Chloro-*N*-*tert*-butylphosphoramidate. ^{1}H NMR (CCl_4) δ 1.21 (s, 9 H), 1.53 (d, 3 H), 3.64 (d, 3 H), 3.86–4.23 (complex overlapped multiplets, 3 H), 4.60 (d, 0.9 H).

Anal. Calcd for $C_8H_{19}ClNO_3P$: C, 39.43; H, 7.88; N, 5.75; Cl, 14.55. Found: C, 39.30; H, 8.08; N, 5.61; Cl, 14.30.

Butyl Methyl 2-Chloro-*N*-*tert*-butylphosphoramidate. ^{1}H NMR (CCl_4) δ 1.08 (t, 2.5 H), 1.24 (s, 9 H), 1.65–2.05 (m, 2 H), 3.65 (d, 3 H), 3.90–4.18 (m, 3 H), 4.35 (bs, 1 H).

Anal. Calcd for $C_9H_{21}ClNO_3P$: C, 41.95; H, 8.21; N, 5.44; Cl, 13.76. Found: C, 42.02, H, 8.29; N, 5.48.

Butyl Methyl 3-Chloro-*N*-*tert*-butylphosphoramidate. ^{1}H NMR (CCl_4) δ 1.21 (s, 9 H), 1.55 (d, 3 H), 2.00 (m, 2 H), 3.61 (d, 3 H), 3.90–4.25 (m, 3 H), 4.58 (bs, 1 H).

Anal. Found: C, 41.94; H, 8.45; N, 5.51.

Pentyl Methyl 2-Chloro-*N*-*tert*-butylphosphoramidate. ^{1}H NMR (CCl_4) δ 0.97 (t, 2.7 H), 1.23 (s, 9 H), 1.40–1.90 (m. 4.2 H), 3.62 (d, 3 H), 3.82–4.25 (m, 3.8 H).

Anal. Calcd for $C_{10}H_{23}ClNO_3P$: C, 44.20; H, 8.53; N, 5.15; Cl, 13.09. Found: C, 43.65; H, 8.60; N, 5.30.

Pentyl Methyl 3-Chloro-*N*-*tert*-butylphosphoramidate. ^{1}H NMR (CCl_4) δ 1.07 (t, 2.5 H), 1.22 (s, 9 H), 1.50–2.15 (m, 4.1 H), 3.60 (d, 3.2 H), 3.80–4.20 (m, 3.2 H), 4.70 (bs, 0.5 H).

Anal. Found: C, 44.23; H, 8.51; N, 5.38.

Pentyl Methyl 4-Chloro-*N*-*tert*-butylphosphoramidate. ^{1}H NMR (CCl_4) δ 1.21 (s, 9 H), 1.50 (d, 3 H), 1.60–2.00 (m, 4.2 H), 3.58 (d, 2.7 H), 3.80–4.20 (m, 3.3 H), 4.45 (bs, 0.5 H), and small signals supposed due to the impurities (δ 1.0 and 2.07).

Photochlorination of Alkyl Methyl *N*-*tert*-Butylphosphoramidates (1a–c) with Chlorine. 1b (**1a, 1c**) (0.016 mol) was dissolved in 160 ml of benzene and chlorine gas was introduced to the solution for 6 min at 20 °C under irradiation by a tungsten lamp. The crude chlorination products were analyzed by GLC. Results are summarized in Table I.

Photodecomposition of *N*-Chlorophosphoramidates (2a–c) in the Presence of Dichloroethylene. 2b (0.015 mol) and 0.03–0.15 mol of *cis*-dichloroethylene were dissolved in 150 ml of benzene and the solution was irradiated under nitrogen as described above. **2a** and **2c** were also photodecomposed and the results of analyses of the crude reaction products by GLC are summarized in Table II. The major component in **3c** was separated by GLC and characterized as pentyl methyl 3-chloro-*N*-*tert*-butylphosphoramidate, a colorless, viscous liquid, Cl, 13.3 (calcd, 13.1): IR (neat) 3240, 1250, 1200, 1070, 1025 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.08 (t, 3 H), 1.24 (s, 9 H), 1.50–2.20 (m, 4 H), 3.60 (d, 3 H), 4.10 (multiplets, 4 H).

Photodecomposition of *N*-Chlorophosphoramidates in the Presence of 2,4,6-Trimethylpyridine (TMP). 2b (4.84 g, 0.019 mol) and TMP (4.56 g, 0.038 mol) was dissolved in 100 ml of benzene and solution was irradiated under nitrogen at 20 ± 2 °C until the active chlorine content was negligible. After irradiation, benzene was removed in vacuo and ether was added to the residue. Insoluble TMP hydrochloride (0.24 g) was filtered off and the filtrate was washed with dilute hydrochloric acid and water successively. The ether solution was dried over anhydrous magnesium sulfate and the solvent was removed, leaving a red, viscous liquid (**3b**, 2.92 g), Cl, 13.2. ^{1}H NMR ($CDCl_3$) δ 0.93 (t, 0.3 H), 1.07 (t, 0.35 H), 1.28 (s, 9 H), 1.55 (d, 2.5 H), 1.8–2.3 (m, 2 H), 3.70 (d, 3 H), 4.2 (m, 2.9 H).

In a similar procedure, **2c** (5.22 g, 0.017 mol) afforded 4.50 g of **3c** and TMP hydrochloride (0.18 g), Cl, 12.9. ^{1}H NMR ($CDCl_3$) δ 0.92 (t, 0.3 H), 1.04 (t, 1.8 H), 1.26 (s, 9 H), 1.52 (d, 0.5 H), 1.55–2.30 (complex multiplets, 4.1 H), 3.68 (d, 3 H), 3.83–4.38 (m, 3.1 H). Also, **3a** (3.30 g, Cl, 9.6) and TMP hydrochloride (0.60 g) were obtained from the reaction of **2a** (3.90 g, 0.016 mol). ^{1}H NMR (CCl_4) δ 0.97 (t, 1.2 H), 1.22 (s, 9 H), 1.52 (d, 1.2 H), 1.63 (sextet?, 0.8 H), 2.10 (quintet 0.4 H), 3.53–3.68 (complex signals, 3.4 H), 3.74–4.20 (complex signals, 2.8 H), 4.50 (bs, 1 H).

Authentic Compounds. Propyl Methyl 3-Chloro-*N*-*tert*-butylphosphoramidate. 3-Chloropropyl methyl phosphite was synthesized by the reaction of dimethyl phosphite (27.5 g, 0.25 mol) and 3-chloropropanol (23.6 g, 0.25 mol) at 115–130 °C for 4 h. The crude product was purified by vacuum distillation: bp 88–89 °C (1.0 mm); yield 11.7 g; Cl, 20.4 (calcd, 20.5). 3-Chloropropyl methyl phosphite (6.85 g, 0.04 mol) was dissolved in 50 ml of CCl_4 and a CCl_4 solution of *tert*-butylamine (8.0 g/25 ml) was added dropwise with stirring and cooling. The crude reaction product (6.95 g) was distilled at reduced pressure and the pure compound (4.23 g, 42%) was obtained as a colorless liquid: bp 105–107 °C (0.17 mm); IR (neat) 3240 m, 2970 s, 1482 w, 1440 m, 1398 m, 1370 m, 1310 w, 1245 s, 1200 s, 1050 s, 1025 s, 970 s, 880 w, 793 m, 655 cm^{-1} w; ^{1}H NMR (CCl_4) δ 1.22 (s, 9 H), 2.10 (quintet 2 H), 3.55–3.70 (d + t?, 5 H), 4.03 (d + t?, 2 H), 4.65 (d, 1 H).

Anal. Calcd for $C_8H_{19}ClNO_3P$: C, 39.43; H, 7.88; N, 5.75; Cl, 14.55. Found: C, 39.27; H, 8.15; N, 5.69; Cl, 14.34.

Butyl Methyl 4-Chloro-*N*-*tert*-butylphosphoramidate. 4-Chloro-1-butanol was prepared by the method of Kerner.[40] Transesterification of 4-chloro-1-butanol (7.0 g) and dimethyl phosphite (10 g) was carried out at 110–130 °C and the crude 4-chlorobutyl methyl phosphite was purified by distillation in vacuo, a colorless liquid, 2.8 g, Cl, 18.5 (calcd, 19.0). Butyl methyl 4-chloro-*N*-*tert*-butylphosphoramidate (0.7 g) was obtained by the reaction of phosphite (0.5 g) and *tert*-butylamine (1.2 g) in CCl_4, Cl, 13.5 (calcd, 13.8): IR (neat) (major absorptions) 3220, 2970, 1250, 1200, 1050 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.20 (s, 9 H), 1.83 (m, 4 H), 3.45–3.68 (d + t, 5 H), 3.90 (q, 2 H), 4.50 (bs, 1 H).

Pentyl Methyl 5-Chloro-*N*-*tert*-butylphosphoramidate. The pure compound was obtained by the reaction of 5-chloropentyl methyl phosphite, which was prepared by transesterification of dimethyl phosphite with 5-chloro-1-pentanol, and *tert*-butylamine in the presence of CCl_4, Cl, 12.8 (calcd, 13.1): IR (neat) 3220, 2960, 1250, 1200, 1040 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.21 (s, 9 H), 1.50–1.95 (m, 6 H), 3.50 (t, 2 H), 3.63 (d, 3 H), 3.92 (q, 2 H), 4.38 (d, 1 H).

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Registry No.—**1a,** 61047-44-7; **1b,** 61047-45-8; **1c,** 61047-46-9; **2a,** 61047-47-0; **2b,** 61047-48-1; **2c,** 61047-49-2; **3** (R = CH_3; n = 0), 61047-50-5; **3** (R = C_2H_5; n = 0), 61047-51-6; **3** (R = CH_3; , n = 1), 61047-52-7; **3** (R = C_3H_7; n = 0), 61047-53-8; **3** (R = C_2H_5; n = 1), 61047-54-9; **3** (R = CH_3; n = 2), 61047-55-0; **3** (R = H; n = 1), 61047-56-1; **3** (R = H; n = 2), 61047-57-2; **3** (R = H; n = 3), 61047-58-3; 3-chloropropyl methyl phosphite, 61047-59-4; dimethyl phosphite, 868-85-9; 3-chloropropanol, 627-30-5; *tert*-butylamine, 75-64-9; 4-chloro-1-butanol, 928-51-8; 4-chlorobutyl methyl phosphite, 61047-60-7; 5-chloropentyl methyl phosphite, 61047-61-8; 5-chloro-1-pentanol, 5259-98-3.

References and Notes

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Photochemical Rearrangements of an Unsaturated Nitro Compound. Mechanistic and Exploratory Organic Photochemistry[1,2]

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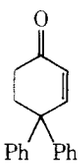
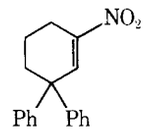
3,3-Diphenyl-1-nitrocyclohexene was synthesized for photochemical study in order to compare nitro n–π^* photochemistry with carbonyl n–π^* reactivity. Both direct and sensitized irradiations in benzene gave rise to *trans*-5,6-diphenyl-1-nitrobicyclo[3.1.0]hexane; the preference for formation of trans product was shown to be kinetic. Additionally, the photolysis afforded 3,3-diphenylcyclohexanone. Quantum efficiencies were determined, and these were found to be quite low compared with the corresponding enone analogue. Thus, for formation of bicyclic nitro compound the unsensitized and sensitized efficiencies were found to be $\phi = 3.05 \times 10^{-4}$ and 4.52×10^{-4} (acetophenone). Evidence favoring triplet multiplicity of the rearranging species is discussed as is the low reaction efficiency. It was observed that irradiation in isopropyl alcohol gave rise to 3,3-diphenylcyclohexanone oxime as the major product with the oxime to bicyclic product ratio increasing with increasing isopropyl alcohol concentration in isopropyl alcohol–benzene mixtures. Finally, *cis*-5,6-diphenyl-1-nitrobicyclo[3.1.0]hexane was independently synthesized by reaction of 2-phenyl-1-nitrocyclopentene with diphenylsulfonium benzylide. This stereoisomer was converted, both in direct and sensitized irradiations, to the trans stereoisomer with a steady state favoring trans isomer over 1000:1.

Some of our previous studies[3-6] have involved the n–π^* triplet photochemical rearrangement of 4,4-diphenylcyclohexenone (**1**) and substituted derivatives. The evidence favored promotion of a nonbonding (i.e., p_y or n) electron to the antibonding π system with rearrangement involving bonding of a γ aryl group to the β carbon.

Nitroalkenes also have an n–π^* triplet as their lowest electronic excited state, although the literature on the subject is sparse.[7] Thus we were interested in seeing if the photochemistry of a nitro analogue of 4,4-diphenylcyclohexenone (**1**) would prove parallel to that of the ketone. For this study we selected 3,3-diphenyl-1-nitrocyclohexene (**2**).

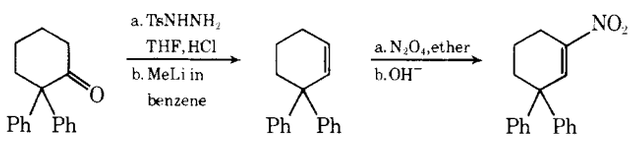


1



2

Synthesis of the Photochemical Reactant. The synthesis utilized 3,3-diphenyl-1-cyclohexene[8] (**4**) which was prepared from 2,2-diphenylcyclohexanone (**3**) using the method of Dauben.[9] Reaction of the diphenylcyclohexene **4** with nitrogen tetroxide in ether followed by hydroxide treatment gave a 19% yield of the desired 3,3-diphenyl-1-nitrocyclohexene (**2**), mp 106–107 °C. Note eq 1.



3 **4** **2**

(1)

Exploratory Photochemistry. Exploratory irradiations were carried out using a 450-W medium-pressure immersion lamp along with either a Pyrex or a circulating sodium metavanadate filter, thus using light above 290 or 330 nm. A slow reaction was observed and could be monitored with analytical GC; two products were observed and these appeared linearly with time.

Preparative isolation employed column chromatography on Florisil. One product proved to be the known 3,3-diphenylcyclohexanone.[10] The major product, **5**, was a solid, mp 127.5–129 °C; at the end of 10 h a 9% yield of this photoproduct was formed. The minor diphenylcyclohexanone product was found in 0.5% yield. Thus, qualitatively, this contrasts with the very facile rearrangement of 4,4-diphenylcyclohexenone (**1**) where a similar conversion is complete in ca. 0.5 h.

Photoproduct Structure Elucidation. The first evidence regarding photoproduct **5** was the appearance of 6.59- and 7.37-μ bands in the infrared suggesting that this was a nitro compound. Substantial further evidence derived from the 270-MHz ^{1}H and 67.9-MHz ^{13}C NMR spectra (Tables I and II). The first point noted was the presence of two unsplit ^{13}C peaks at 79.8 and 53.3 ppm downfield from Me_4Si, indicating the presence of two quaternary carbons. The low field of the former suggested that it bore the nitro group (i.e., a C–NO_2 group present). Additionally, the doublet at 38.6 ppm proved suggestive of a benzylic cyclopropyl group (i.e., CHPh) bearing a hydrogen. Finally, the ^{1}H and ^{13}C NMR spectra both suggested the presence of three methylene groups (i.e., CH_2) and the former suggested that these formed a contiguous chain of three ($-CH_2CH_2CH_2-$); thus these are mutually coupled as indicated in Table II.

With evidence for these structural moieties in hand and with the course of the rearrangement of 4,4-diphenylcyclohexenone[3] in mind, a tentative assignment of **5** as *cis*- or *trans*-5,6-diphenyl-1-nitrobicyclo[3.1.0]hexane was made.

It seemed desirable to have the model compounds *cis*- and *trans*-1,6-diphenylbicyclo[3.1.0]hexane[8] (**8** and **7**, respectively), so these were prepared from the *cis*- and *trans*-5,6-