

in 100 mL of anhydrous ether under a nitrogen atmosphere. The solution was cooled in an ice bath during the addition, and cooling was continued while the solution was stirred for 2.5 h after the addition. To this was added carefully 9.75 mL of water, and the solution was then allowed to warm to room temperature. The solids were removed by filtration and washed well with ether. The combined ether solutions were dried. Distillation yielded 3.08 g (76%) of **16**: bp 163–164 °C (1.5 mm); NMR (CDCl₃) τ 2.7 (m, 9 H, aromatics) 4.27 (d, J = 1.2 Hz, 1 H, vinylic), 4.80 (d, J = 1.2 Hz, 1 H, vinylic), 5.64 (s, 2 H, methylenes), 8.20 (s, 1 H, OH); λ_{\max} (hexane) 257 nm (ϵ 9080).

Anal. Calcd for C₁₅H₁₄O: C, 85.68; H, 6.71. Found: C, 85.57; H, 6.71.

Preparative Irradiation of 1-[2-(Hydroxymethyl)phenyl]-1-phenylethene (16). A solution of 0.500 g (0.00238 mol) of **16** in 284 mL of benzene was irradiated for 2.75 h. The solvent was removed in vacuo, and the residue was chromatographed on silica gel with 3% ether in hexane as eluant to give 0.09 g (18%) of **9**. This sample of **9** had IR and NMR spectra identical with those of authentic **9**. Furthermore, this sample gave a 2,4-dinitrophenylhydrazone derivative which had the same melting point as an authentic sample and which gave an un-depressed mixture melting point.

An analytical photolysis of 10 mL of 5×10^{-3} M **16** in hexane showed, by GC analysis (190 °C) using benzophenone as an internal standard, that 21% of **16** had reacted to produce a 30% yield of **9** after 10 min of irradiation. An analytical photolysis of 5×10^{-3} M **16** and 7×10^{-2} M xanthone as photosensitizer showed 36% of **16** had reacted to produce a 42% yield of **9** after 10 min of irradiation through Pyrex.

1-[2-(Hydroxydeuteriomethyl)phenyl]-1-phenylethene (18). A solution of 1.77 g (0.0074 mol) of **15** in 50 mL of anhydrous ether was added dropwise over a period of 40 min to a slurry of 0.600 g (0.014 mol) of LiAlD₄ in 50 mL of anhydrous ether. The addition was conducted under a nitrogen atmosphere with cooling in an ice bath, and cooling was continued while the solution was stirred for an additional 1.25 h. Then 2.4 mL of water was carefully added, and the mixture was stirred for 50 min as it was allowed to warm to room temperature. The solids were removed by filtration and washed well with ether. The combined ether solutions were dried. Distillation gave 1.05 g (59%) of **18**: bp 191–195 °C (1.65 mm); NMR (CDCl₃) τ 2.75 (m, 9 H, aromatics), 4.24 (d, J = 1.2 Hz, 1 H, vinylic), 4.80 (d, J = 1.2 Hz, vinylic), 8.44 (br s, 1 H, OH).

Preparative Irradiation of 1-[2-(Hydroxydeuterio-methyl)phenyl]-1-phenylethene (18). A solution of 0.803 g (0.00378 mol) of **18** in 290 mL of benzene was irradiated for 2.75 h. The solvent was removed in vacuo, and the residue was chromatographed on silica gel to give 0.18 g (22%) of **19**: NMR

(CDCl₃) τ 2.1–3.1 (m, 9 H, aromatics), 4.84 (t, J = 7.2 Hz, 1 H, methine), 8.44 (br d, J = 7.2 Hz, 2 H, CH₂D).

The effect of the deuteriums on the efficiency of the reaction was determined in the following manner. Equimolar solutions (10 mL, 0.0100 M) of **16** and **18** were irradiated in parallel in the "merry-go-round" apparatus for 30 min. GC analysis (200 °C), using benzophenone as internal standard, showed that **16** had produced 1.3 mg of **9**, and **18** had produced 0.3 mg of **19** (Φ_H/Φ_D = 4).

Quantum Yields. Quantum yields were measured with an apparatus similar to the "Wisconsin Black Box"²⁵ by using potassium ferrioxalate actinometry.²⁶

For direct quantum yields, 2 cm each of 2 M NiSO₄ in 5% H₂SO₄, 0.38 M CoSO₄ in 5% H₂SO₄, and 1.9×10^{-4} M BiCl₃ in 10% HCl were used as filter solutions to isolate a window from 260–300 nm. Conversions were less than 15% for three runs using ca. 0.0015 M **16** in hexane, and the average quantum yield was 0.085 ± 0.006 .

For the sensitized quantum yield, 2 cm each of the Ni and Co filter solutions described above and 2 cm of 0.02 M SnCl₂ in 40% HCl were used to isolate a window from 300–350 nm. A solution containing approximately 0.05 M xanthone and 0.003 M **16** in benzene was irradiated for a period of time so that conversions were less than 15%. For two runs the average quantum yield was 0.027 ± 0.001 .

An analytical photolysis of 3.85×10^{-2} M **9** in benzene showed no detectable **16** by GC analysis (SE-30 column at 185 °C) after irradiation for 2 h (30% of **9** had disappeared), showing that *o*-xylylene **17** does not produce **16**.

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Registry No. **3a**, 947-77-3; **3b**, 71264-79-4; **3c**, 71264-80-7; **5a** isomer 1, 71264-81-8; **5a** isomer 2, 71301-40-1; **5b**, 71264-82-9; **5c**, 71264-83-0; **6a**, 61608-91-1; **6b**, 739-45-7; **7a**, 61608-94-4; **7b**, 6624-03-9; **8**, 61608-89-7; **9**, 61608-90-0; **9-DNP**, 71264-84-1; **10**, 61608-92-2; **14**, 17582-84-2; **15**, 71264-85-2; **16**, 71264-86-3; **18**, 71264-87-4; **19**, 71264-88-5; bromobenzene, 108-86-1; methyl iodide, 74-88-4; methyl 2-(phenylmethyl)benzoate, 6962-60-3; α -phenyl-*o*-toluic acid, 612-35-1; 2-(*o*-benzylphenyl)propanol, 71264-89-6; 9,9-dimethyl-9,10-dihydroanthracene, 42332-94-5.

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Thermal and Photochemical Reactions of Sodium Salts of β -Phosphono Tosylhydrazones

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Thermal and photochemical reactions of sodium salts of β -phosphono tosylhydrazones have been investigated. When the sodium salt of dimethyl α -acetylmethylphosphonate tosylhydrazone is heated, the dimethoxyphosphonyl anion, though a relatively strong base, was eliminated. On the other hand, ultraviolet irradiation of the sodium salts of β -phosphono tosylhydrazones leads to dimethoxyphosphonyl-substituted olefins, presumably via the carbene intermediate. Some of the products result from a previously unreported phosphonyl group migration to a carbene.

The migration of phosphonyl groups to electron-deficient centers has been intensively investigated for carbonium ion,^{1–3} oxygen,⁴ and nitrogen.⁵ In the migration

to the carbonium ion center the preference order was Ph > PO(OR)₂ > H > R, while in the case of the oxygen center

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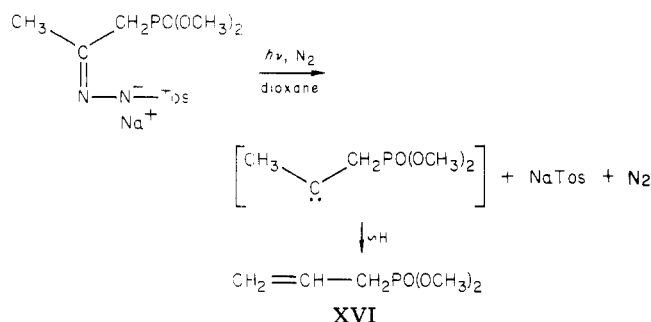
cleophilic attack of the sulfinate ion on the methyl phosphonate.

To establish the fate of the three-carbon skeleton, we passed the gaseous products through a solution of bromine in methylene chloride. The only bromine-containing organic materials were 1,2-dibromopropane and 1,2,2,3-tetrabromopropane.¹⁷ Therefore, the reaction may be summarized as in Scheme I.

Elimination of functional groups such as acetate, hydroxide, and benzoate from the α position of tosylhydrazones has been reported.¹⁸ An analogous role is served here by the relatively strong base dimethyl phosphite anion in an unusual fashion.¹⁹ Thus the primary, but unisolated, elimination product VII is assumed by analogy to a reported isolated one.²⁰ The acetone tosylhydrazone XI may be regarded as the reduction product of VII. This intermediate decomposes (either homolytically or heterolytically) to give the hydrocarbon products propene and allene. The formation of allene rather than of methylacetylene can be rationalized on the basis of the preferred abstraction of a hydrogen atom (or proton) from an allylic rather than vinylic position.

Since in the thermal reaction elimination of the phosphonyl group occurred, we turned to the photochemical decomposition.

B. Photochemical Reactions. The irradiation of the sodium salt of I gave a mixture of phosphorus compounds from which dimethyl allylphosphonate (XVI)²¹ was isolated

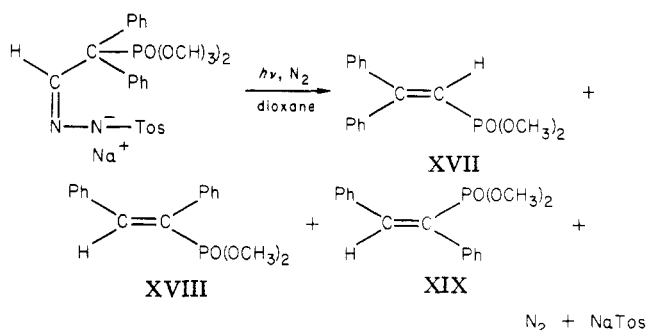


in 70% yield. The formation of XVI can be rationalized in the manner shown, indicating the preference of hydrogen atom migration to the carbene.

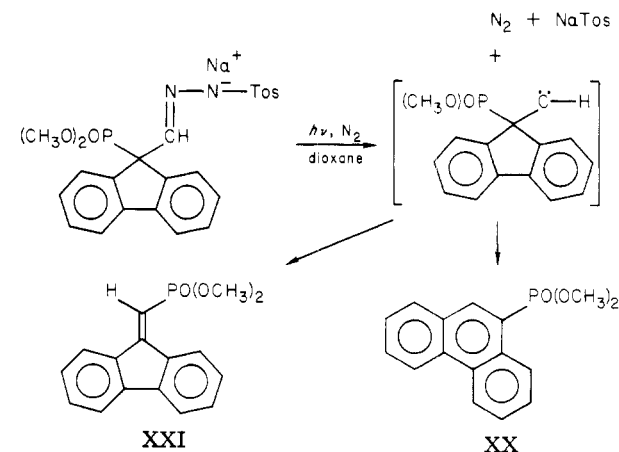
Dimethyl α -formylbenzohydrilphosphonate tosylhydrazone (II) was chosen next because it has no hydrogens α to the phosphonyl group. Irradiation of the sodium salt of II gave three compounds identified as dimethyl β,β -diphenylvinylphosphonate (XVII, 25%) and dimethyl *cis*-stilbenephosphonate (XVIII) and dimethyl *trans*-stilbenephosphonate (XIX)²² (together 75%).

Compound XVII is the product of phosphonyl group migration, while compounds XVIII and XIX are the result of phenyl migrations. Thus the migration preference of the phenyl over phosphonyl group, taking into account the statistical preference of phenyl migration, is 3:2. This preference is intermediate to that for carbon and oxygen electron-deficient centers.

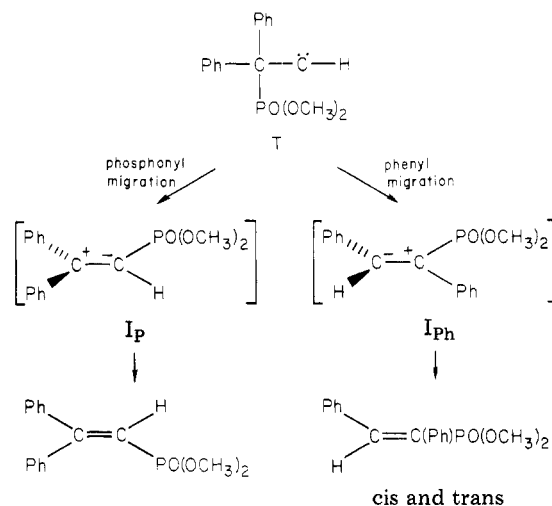
For dimethyl α -formyl-9-fluorenylphosphonate tosylhydrazone (III) phenyl migration should be restricted.



Irradiation of the sodium salt of III gave two compounds identified as dimethyl 9-phenanthrenylphosphonate (XX, 57%) and 1-(dimethoxyphosphonyl)-1-methylenedibenzocyclopentadiene (XXI, 43%). When a correction is made for the statistical preference for aryl migration, the ratio of 3:2 for $\text{PO}(\text{OCH}_3)_2\text{Ph}$ is obtained.



Zwitterions are suggested as intermediates for the migration of phosphonyl and phenyl groups to a carbene center. Thus the stabilization of the positive charge formed on the migration origin (according to Warren⁸) together with the stabilization of the negative charge formed on the migration terminus should be examined for the two intermediates I_Ph and I_P .



Consequently, a large difference in the migratory aptitudes of phosphonyl and phenyl groups might be expected, since according to the above stabilization mechanism I_P is more stable than I_Ph . This, however, is not observed. It seems that the stabilization of the positive charge on the migrating group in the two different transition states leading to these intermediates should also be considered. The migrating phenyl group stabilizes the

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Table I. Analytical Data for the Products Obtained in the Thermal Reaction of the Sodium Salt of I

compd	yield, %	mp (lit), °C	MS, <i>m/e</i>	NMR, δ^a
VIII	5.9	43 (45)	246 (M ⁺)	2.28 (s), 7.14 (AB, $J_{AB} = 8$ Hz)
IX	3.0	76 (77)	278 (M ⁺)	2.30 (s), 2.34 (s), 7.15 (m)
X	7.4	87 (87)	170 (M ⁺)	2.24 (s), 3.04 (s), 7.57 (AB, $J_{AB} = 9$ Hz)
XI	11.8	149 (150)	226 (M ⁺)	1.75 (s), 1.90 (s), 2.21 (s), 7.56 (AB, $J_{AB} = 8$ Hz), 7.74 (s)
XIV	8.7			2.76 (s), 7.89 (AB, $J_{AB} = 8$ Hz)

^a D₂O was used for compound XIV.

positive charge on itself better than the phosphonyl group, and this is probably what counteracts the effect of the greater stability of intermediate I_p. The photochemically generated carbenes are high-energy species. Hence the transition states should be carbene-like rather than olefin-like, and selectivity in the formation of *cis* and *trans* isomers should not be found. The equal amounts of the *cis*- and *trans*-stilbenephosphonates observed in this reaction support this mechanism.

For the fluorene system, phenyl migration is restricted. The migrating phenyl is bonded in its ortho position, and its rotation, required for migration, is constrained. Thus the activation energy for phenyl migration in this case is higher, and phosphonyl group migration dominates.

Experimental Section

Melting points were determined with a Fisher-Johns apparatus and are not corrected. NMR spectra were determined in solution in CDCl₃ (except where otherwise stated) with a Varian HA-100 spectrometer using Me₄Si as internal (or external) reference (δ scale, J in Hz). Mass spectra were obtained by direct insertion into the ion source of an Hitachi Perkin-Elmer instrument. C, H, N, P, and S analyses were done at the Department of Chemistry, The Hebrew University, Jerusalem, Israel. All the yields were calculated from the starting material.

Dimethyl α -Acetylmethylphosphonate Tosylhydrazone (I). A 1.66-g (0.01 mol) sample of dimethyl α -acetylmethylphosphonate [92–94 °C (2 mmHg)]⁶ was added to a solution of 1.86 g (0.01 mol) of *p*-toluenesulfonyl hydrazide (Fluka) in 15 mL of glacial acetic acid at 80 °C. The mixture was stirred for 15 min, and after it was cooled water was added. The precipitate thus obtained was collected and recrystallized from methanol to give 3.1 g (89%) of product: mp 180–182 °C; NMR δ 1.91 (s), 2.42 (s), 2.85 ($J_{PH} = 23$ Hz), 3.60 ($J_{PH} = 11$ Hz), 7.56 (AB, $J_{AB} = 8$ Hz), 7.70 (s). Anal. Calcd for C₁₂H₁₉N₂O₅PS: C, 43.10; H, 5.72; N, 8.37; P, 9.26; S, 9.59. Found: C, 42.82; H, 5.68; N, 8.25; P, 9.22; S, 9.62.

Dimethyl α -Formylbenzohydrylphosphonate Tosylhydrazone (II). β,β -Diphenylepoxyethylphosphonate¹ was purified by chromatography on silica gel with acetone (6–40%) in petroleum ether as eluent. To the epoxyphosphonate (5.2 g) in 50 mL of dry benzene was added 0.035 mol of BF₃·Et₂O. The mixture was refluxed for 5 min. The cold benzene solution was washed with water (3 × 50 mL), and the aqueous layers were combined and washed with ether (50 mL). The organic layers were dried (Na₂SO₄), and the solvents were evaporated under reduced pressure. The aldehyde (5.02 g, 96.5%) was used without further purification: NMR δ 3.86 ($J_{PH} = 11$ Hz), 7.31 (aromatic), 7.32 (aromatic), 9.78 ($J_{PH} = 5$ Hz).

To a solution of 3.2 g (0.017 mol) of *p*-toluenesulfonyl hydrazide in 20 mL of glacial acetic acid at 80 °C was added 5.02 g of the above aldehyde (0.017 mol). After 15 min at 80 °C the solution was cooled, and white crystalline solid appeared. Water was added (50 mL), and the mixture was kept overnight in a freezer. Filtration followed by recrystallization from methanol gave 4.25 g (51%) of product: mp 214–215 °C; NMR δ 2.44 (s), 3.56 ($J_{PH} = 11$ Hz), 7.15 (s), 7.31 (aromatic), 7.40 (AB, $J_{AB} = 8$ Hz). Anal. Calcd for C₂₃H₂₅N₂O₅PS: C, 58.47; H, 5.33; N, 5.93; P, 6.56; S, 6.79. Found: C, 58.90; H, 5.38; N, 5.90; P, 6.80; S, 6.97.

Dimethyl α -Formyl-9-fluorenylphosphonate Tosylhydrazone (III). Dimethyl β,β -(2,2'-biphenyl)epoxyethylphosphonate (IV) was prepared by the dropwise addition of 7 g (0.044 mol) of dimethyl chloromethylphosphonate [64–66 °C (0.6 mmHg)]⁷ and 8 g (0.042 mol) of fluorenone in 10 mL of dry

benzene to 2.3 g of NaH (50% in mineral oil) in 15 mL of benzene containing 3 drops of absolute ethanol. A viscous suspension was obtained after 48 h of vigorous stirring. The mixture was filtered with suction, the solid was carefully washed with ether (3 × 20 mL), and the filtrate was evaporated under reduced pressure to give a yellow viscous residue. Chromatography on 600 g of silica gel with 10% acetone in petroleum ether as the eluent gave 3.1 g (24.4%) of colorless crystals (by evaporation of the acetone from the epoxide fractions): mp 85 °C; NMR δ 3.62 ($J_{PH} = 11$ Hz), 3.77 ($J_{PH} = 26$ Hz), 3.90 ($J_{PH} = 11$ Hz), 7.28 (m), 7.65 (m), 8.10 (m). Anal. Calcd for C₁₆H₁₅O₄P: C, 63.58; H, 5.00; P, 10.51. Found: C, 63.65; H, 5.08; P, 10.51.

The rearrangement of the epoxide to dimethyl α -formyl-9-fluorenylphosphonate (VI) was carried out as described above. The yield was 3.01 g (97%) of aldehyde which was used without further purification: NMR δ 3.52 ($J_{PH} = 11$ Hz), 7.45 (m), 7.84 (m), 9.54 ($J_{PH} = 5$ Hz).

The above aldehyde was added to a solution of 1.8 g (0.097 mol) of *p*-toluenesulfonyl hydrazide in 10 mL of glacial acetic acid at 80 °C. A precipitate appeared immediately. The precipitate was filtered and recrystallized from methanol to give 4.52 g (94%) of product: mp 249–250 °C; NMR (Me₂SO-*d*₆) δ 2.40 (s), 3.32 ($J_{PH} = 11$ Hz), 7.46 (m), 7.90 (half of AB, $J_{AB} = 6.5$ Hz). Anal. Calcd for C₂₃H₂₃N₂O₅PS: C, 58.72; H, 4.93; N, 5.78; P, 6.58; S, 6.82. Found: C, 58.76; H, 5.03; N, 5.68; P, 6.62; S, 6.92.

Thermal Reaction of the Sodium Salt of I. The diglyme was distilled from LiAlH₄ shortly before use. The nitrogen was carefully dried and was oxygen free. To 17.2 g (0.05 mol) of well-crushed I in 150 mL of diglyme was added 1.2 g of NaH (dry, Fluka) with vigorous stirring. There was a strong evolution of gas, and white precipitate appeared. The mixture was heated, and at 110 °C the solid dissolved to give a pale yellow solution. At 130 °C evolution of gas started and solid appeared. The solution was refluxed for 30 min. All the gaseous products were passed through a solution of 8 g of bromine in 80 mL of CH₂Cl₂. The cold diglyme solution was diluted with 350 mL of water and extracted with methylene chloride (3 × 150 mL). The combined organic layers were washed with water (150 mL) and dried on MgSO₄, and the solvent was distilled off. Separation of the residue (5.4 g) was accomplished by chromatography on silica gel (60–120 mesh) with increasing concentration of acetone in petroleum ether as eluent (10–90%). The different fractions thus obtained were purified by chromatography using 80 g of silica-H/g of mixture and the same eluent. The columns were finally washed with methanol. The yields, melting points, and mass spectral and NMR data appear in Table I.

The bromine solution was washed with 20% NaHSO₃ (2 × 80 mL) and water (80 mL) and dried over CaCl₂. Distillation gave 2.1 g of brown residue. Gas chromatography was used to identify the constituents of the mixture. Comparison with authentic samples¹⁷ as well as examination of different mixtures of the known compound with the residue showed that 1,2-dibromopropane and 1,2,2,3-tetrabromopropane appear to be the only bromine-containing organic compounds in this residue.

Irradiation of the Sodium Salts of I, II, and III. The irradiations were carried out in dioxane. The dioxane was dried over Na for 24 h and distilled from LiAlH₄ [40 °C (100 mmHg)] directly to the irradiation tube. The quartz tube was fitted so that the nitrogen could bubble through the bottom and stir the mixture throughout the irradiation. A reflux condenser was fitted on the top of the tube. The irradiation was carried out in a "merry-go-round" type apparatus with 350-nm Xenon lamps. Strong ventilation was provided to avoid heating and thermal reactions. In all cases the sodium salts were prepared from 0.01 mol of the tosylhydrazone in 150 mL of dioxane by using an excess of NaH. After the evolution of gas was finished, the suspension

was transferred under nitrogen to the irradiation tube and diluted to 500 mL. The nitrogen was bubbled through the mixture for 30 min, and then irradiation took place for 6 h. Filtration followed by evaporation and chromatography on silica-H with 10% acetone in petroleum ether as eluent was the usual workup procedure.

I. In this case 1.35 g of white solid was isolated from the irradiation mixture, 0.5 g of which were identified as starting material. The weight of the residue after evaporation was 1.4 g. Dimethyl allylphosphonate (XVI)²¹ was isolated in 70% yield (1.05 g): NMR δ 2.48 ($J_{PH} = 22$ Hz, $J_{HH} = 7$ Hz), 3.65 ($J_{PH} = 11$ Hz), 5.13 (m), 5.70 (m).

II. In this case 1.14 g of white solid identified as sodium *p*-toluenesulfinate (XIV) was isolated from the irradiation mixture (70%). From the residue after evaporation (3.01 g) 0.544 g (19.7%) of phosphorus-containing organic materials could be isolated: dimethyl β,β -diphenylvinylphosphonate (XVII; 0.134 g, 25% of the above mixture), dimethyl *cis*-stilbenephosphonate (XVIII; 0.207 g, 38%), dimethyl *trans*-stilbenephosphonate (XIX; 0.204 g, 37%). Compound XVII was compared with an authentic sample prepared from the known acid:²³ NMR δ 3.37 ($J_{PH} = 11$

Hz), 6.09 ($J_{PH} = 14$ Hz), 7.20 (m), 7.29 (m); MS *m/e* 288 (M^+).

III. In this case 2.85 g (67%) of the starting material could be isolated from the irradiation mixture. The residue after evaporation (1.7 g, 36%) was chromatographed to give dimethyl 9-phenanthrenylphosphonate (XX; 0.97 g, 53% of the above mixture) which was compared with an authentic sample prepared by esterification of the corresponding acid²⁴ with CH_2N_2 in ether [NMR δ 3.79 ($J_{PH} = 11$ Hz), 7.57 (m), 8.53 (m)] together with 1-(dimethoxyphosphonyl)methylenedibenzocyclopentene (XXI): 0.73 g (43%); NMR δ 3.51 ($J_{PH} = 11$ Hz), 5.19 ($J_{PH} = 30$ Hz), 7.32 (m), 7.79 (m), 8.53 (m); MS *m/e* 286 (M^+).

Registry No. I, 71265-00-4; I sodium salt, 71265-01-5; II, 71265-02-6; II sodium salt, 71265-03-7; III, 71265-04-8; III sodium salt, 71265-05-9; IV, 71265-06-0; VI, 71302-35-7; VIII, 103-19-5; IX, 2943-42-2; X, 3185-99-7; XI, 3900-79-6; XIV, 71161-92-7; XVI, 757-54-0; XVII, 71265-07-1; XVIII, 71265-08-2; XIX, 71265-09-3; XX, 71265-10-6; XXI, 71265-11-7; dimethyl α -acetylmethylphosphonate, 4202-14-6; *p*-toluenesulfonyl hydrazide, 1576-35-8; β,β -diphenylepoxyethylphosphonate, 71265-12-8; dimethyl α -formyldiphenylmethylphosphonate, 22894-34-4; benzophenone, 119-61-9; fluorenone, 486-25-9; dimethyl chloromethylphosphonate, 6346-15-2.

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Ethanolysis of 1-Chloro-2-azaadamantanes¹

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Solvolyses of 1-chloro-2-azaadamantanes (**1b** and **1c**) in ethanolic solution follow first-order kinetics. Reaction proceeds via an S_N1 mechanism. The solvolysis is accelerated by a factor of 10^3 – 10^4 relative to 1-chloroadamantane, due to stabilization of the bridgehead carbonium ion by the lone pair on adjacent nitrogen. Addition of ethanol to the bridgehead cation with subsequent loss of a proton yields 1-ethoxy-2-azaadamantanes (**1j** and **1k**). Results are compared with published data for other ring systems.

Since 1939, considerable attention has been devoted to solvolytic reactions involving bridgehead carbonium ions in bi- and tricyclic ring skeletons. This research has resulted in important contributions to mechanistic organic chemistry. Some excellent reviews are available.^{3,4} In recent years, there has been a surge of activity with such systems modified by substitution of a heteroatom in the ring structure adjacent to the bridgehead.^{5–11} However, only two papers have been concerned with hetero-

adamantanes. The solvolysis rate of 1-bromo-2-oxaadamantane (**1e**) was determined and compared with that of 1-bromoadamantane (**1d**).⁵ The corresponding tosylates **1g** and **1f** have also been solvolyzed.⁷ Although a more extensive study was made of 2-hetero-3-cyano-1-adamantyl tosylates (**2**), the presence of the cyano group complicates comparison with solvolytic data from related compounds.⁷

In the present study, we report on the solvolytic behavior of 1-chloro-2-azaadamantanes (**1b** and **1c**) and explore the possibility of base-promoted elimination in the case of **1b**. Results are compared with literature data for the solvolyses of related adamantane substrates (**1** and **2**), as well as for bicyclo[2.2.2]octyl (**3**),⁹ bicyclo[3.3.1]nonyl (**4**),¹⁰ and homoadamantyl (**5**)¹¹ systems.

Results and Discussion

Chlorides **1b** and **1c** were prepared according to published procedures.^{5,6} In most cases, the ethanolysis reaction was followed by "rapid intermittent titration" of the hydrogen chloride generated in the reaction. Little or no

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