Photosensitized Polar Addition of Acetic Acid to 4-Homoadamantene: The Behavior of the 4-Homoadamantyl Cation*

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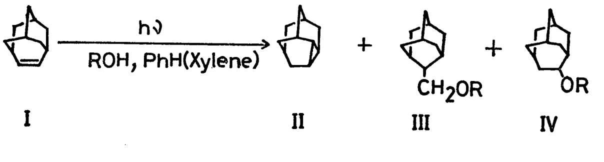
The photosensitized polar addition of acetic acid to 4-homoadamantene (I) gave 2,4-dehydrohomoadamantene (II), 2-adamantylmethyl acetate (IIIa), and 4-homoadamantyl acetate (IVa). The same treatment of I in pivalic acid gave analogous products, II, 2-adamantylmethyl pivalate (IIIb), and 4-homoadamantyl pivalate (IVb). It was shown that II and III were derived from the 4-homoadamantyl cation (V). On the other hand, the diazotization of 4-homoadamantylamine (XV) in the presence of acetic acid gave I, II, and IVa, whereas it has been reported that a buffered acetolysis of 4-homoadamantyl tosylate (XIV) gave I and IVa, but not II. The formation of II may be explained by assuming a different energy state of V of different origin; it proves a vibrationally excited nature of V generated in the photosensitized polar addition reaction.

The photochemical incorporation of protic solvents into 6- and 7-membered cycloalkenes in the presence of BTX (aromatic hydrocarbon sensitizer) has been extensively investigated.[1] We ourselves have reported that the chemically reactive species in the reaction of photosensitized polar addition to *cis*-cyclooctene was *trans*-cyclooctane[2] and that a carbocation was the intermediate in the photosensitized polar addition to bicyclo[3.3.1]non-2-ene system, a bridged cyclooctene, since a novel intramolecular hydride shift was observed.[3]

On the other hand, the behavior of carbocations of cage compounds has attracted considerable attention in the field of carbocation chemistry.[4] The behavior of the 4-homoadamantyl cation (V) has been studied in three different ways—solvolysis of 4-homoadamantyl tosylate (XIV),[5,6] the treatment of 4-homoadamantene (I) with Lewis acid,[7] and the treatment of I or 4-homoadamantanol (VIII) with concentrated sulfuric acid in the presence of pentane.[8] In this paper, we wish to report on the behavior of V, which is generated by the photosensitized polar addition of acetic acid to I[9] and by diazotization of 4-homoadamantylamine (XV).

Results and Discussion

A solution of I in acetic acid containing benzene or xylene as a sensitizer was irradiated in a quartz vessel by means of a medium-pressure mercury arc; three products were detected by glc analysis: 2,4-dehydrohomoadamantane(II), 2-adamantylmethyl acetate (IIIa), and 4-homoadamantyl acetate (IVa).[10] A similar reaction of I in pivalic acid gave II, 2-adamantylmethyl pivalate (IIIb), and 4-homoadamantyl pivalate (IVb). The results are summarized in Table 1.



Formula 1.

Table 1. Irradiation of I in protic solvents[a)]

	R	Conversion[b)] (%)	Products ratio[b)]		
			II(%)	III(%)	IV(%)
a	Ac	62	40	8	52
b	*t*-BuCO	46	63	9	28

a) Irradiated at room temperature for 7 day.
b) Determined by glc (PEG 20 M, 160 °C).

The structures of the products were confirmed by comparison with the corresponding authentic samples. No product other than II, III, and IV was detected by glc or NMR analyses. The ratio of II in the reaction with pivalic acid was larger than that in the reaction with acetic acid, probably because of the bulkiness of pivalic acid.

The following observations confirm that the presence of a proton source is indispensable for the isomerization of I into II. (a) When the irradiation of I in an xylene or benzene solution was effected without a proton source—*i.e.*, acetic acid or pivalic acid, no isomerization of I into II was observed. (b) The irradiation of I in xylene containing a small amount of methanesulfonic acid as a proton source did induce the isomerization of I into II. (c) When I was irradiated in AcOD containing xylene, the resulting II contained one deuterium (41% d_1 by mass spectroscopic analysis). The above observations, as well as the diazotization of XV (*vide infra*), prove that II is produced *via* 4-homoadamantyl cation (V).

In order to ascertain that III was produced from V by rearrangement, the photochemical reaction was effected in AcOD. The resulting deuterated compound (III-d_1) was reduced by lithium aluminum hydride to give deuterated 2-adamantylmethanol (IX-d_1). The mass spectra of IX-d_1 and an authentic

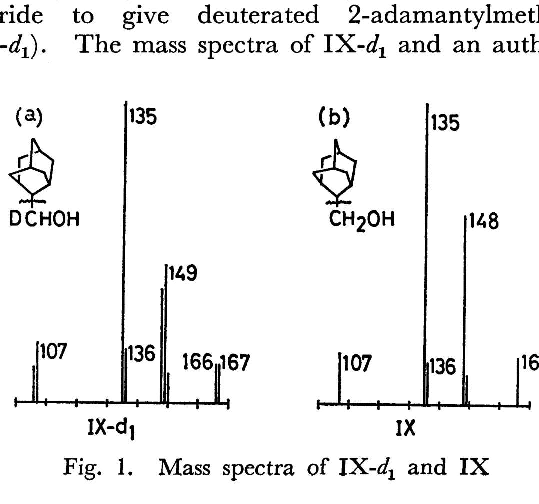
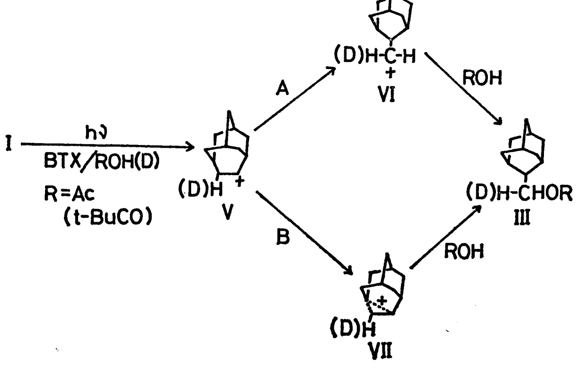


Fig. 1. Mass spectra of IX-d_1 and IX

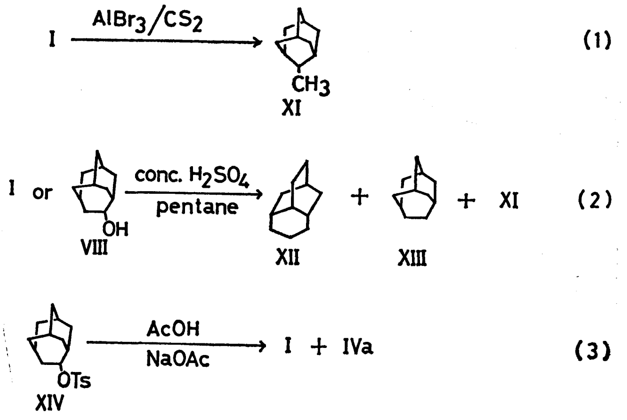
2-adamantylmethanol (IX) are depicted in Fig. 1.

As is shown in Fig. 1a, IX-d_1 contains one deuterium (49% d_1). The base peak at *m/e* 135 in Fig. 1b is characteristic of the adamantyl skeleton. The fact that the intensity of the peak at *m/e* 136 in Fig. 1a is almost the same as that in Fig. 1b implies that deuterium is not located on the adamantyl skeleton, but on the α-carbon atom. These results shows that V must rearrange into the 2-adamantylmethyl cation (VI) through a simple Wagner-Meerwein rearrangement (Path A) or into a non-classical cation (VII) (Path B), which subsequently gives III due to the nucleophilic trapping of the solvent (Scheme 1). In our experiments it is still not clear which pathway (A or B) the rearrangement proceeds through, although we feel that Path B is more likely because a simple primary carbocation appears to be energetically inaccessible under usual reaction conditions.[7,11,18b)]



Scheme 1.

It has been proposed that a photosensitized polar addition of protic solvents to 6—8 membered cycloalkenes proceeds through the following sequences:[1-3)] (i) the BTX sensitized photo-induced *cis-trans* isomerization of olefins,[12)] (ii) protonation to the strained *trans*-olefins producing cycloalkyl cations, and (iii) nucleophilic trapping by the protic solvents, deprotonation to other olefins (*i.e.*, exocyclic olefins), and the regeneration of the starting olefins. Since I is regarded as a bridged cycloheptane, it is highly probable that the present reaction proceeds through the same sequences.[13)] Consequently, the corresponding cycloalkyl cation is the 4-homoadamantyl cation (V).



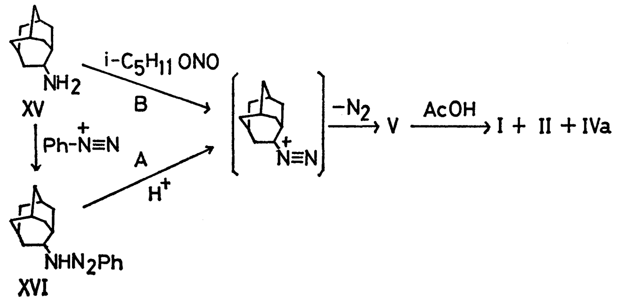
Scheme 2.

As to the behavior of V, there have been several reports, as has been mentioned above. The treatment of I with Lewis acid gave a single product, 2-methyladamantane (XI)[7)] (Scheme 2, Eq. 1), while the reaction of I or 4-homoadamantanol (VIII) with concentrated sulfuric acid in the presence of pentane gave 4-homoisotwistane (XII), homoadamantane (XIII), and XI[8)] (Scheme 2, Eq. 2). Furthermore, the buffered acetolysis of 4-homoadamantyl tosylate (XIV) gave I and IVa[5,6)] (Scheme 2, Eq. 3).

The photochemical reaction and the buffered acetolysis are kinetically controlled,[15)] while the adamantane rearrangement (Scheme 2, Eqs. 1 and 2) is thermodynamically controlled. However, differences were observed in the reaction products between the photochemical reaction and the acetolysis. These differences can be explained by assuming a vibrationally excited nature of V generated in the photosensitized polar addition reaction.[16)] In order to support this assumption, we have examined the diazotization of 4-homoadamantylamine (XV), since it has been suggested that a "hot" ("highly energetic" or "poorly solvated") carbocation is formed from the diazonium ion and that it is different from the "normal carbocation" formed during solvolysis.[17)]

The diazotization of XV was effected in two different ways. A compound, 3-(4-homoadamantyl)-1-phenyltriazene (XVI), was prepared from XV by a conventional method and decomposed with acetic acid (Method A), and isopentyl nitrite was used in the direct diazotization of XV (Method B). The results are summarized in Table 2.

The products, I, II, and IVa, were identical with the respective authentic samples in glc retention time, mass, and IR spectra. Every reaction mixture contained I, II, and IVa, but IIIa could not be detected by glc analysis. On the other hand, as has been mentioned above, it has been reported that no II was



Formula 2.

Table 2. Diazotizations of XV

Method	Sovent	AcOH	Temp.	Time (hr)	Products ratio (%)[a)] I	II	IVa
A	AcOH	excess	room temp.	1	31	20	49
A	PhH	1 eq.	room temp.	12	35	37	28
B	AcOH	excess	room temp.	72	7	14	79
B	PhH	1 eq.	reflux	12	26	39	35

a) Determined by glc (PEG 20 M, 160 °C).

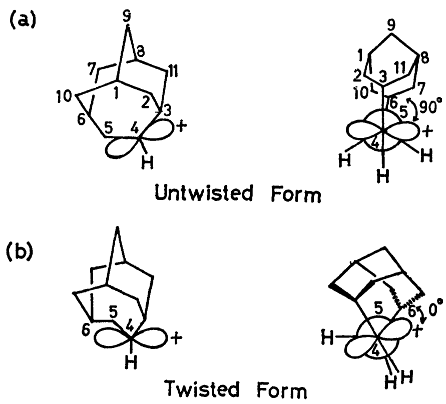
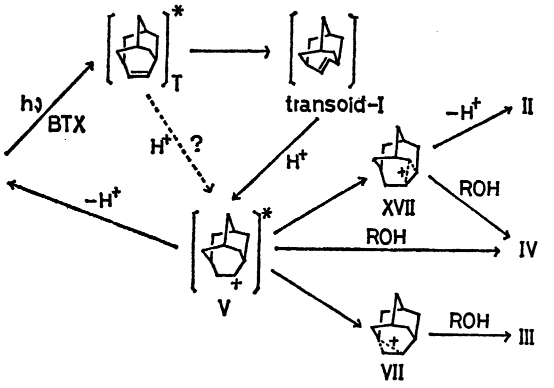


Fig. 2. Conformations of V.

produced in the solvolysis.[5,6] The possibility that II would be formed in the acetolysis and would subsequently react with acetic acid, thus giving I and IVa, can be ruled out, since II was stable under the acetolysis conditions (70 °C for 3 hr[6]). Thus, the formation of II should be due to the "hot," *i.e.*, vibrationally excited, nature of V. Therefore, V must have the enhanced nature of the non-classical cation (XVII), which is nicely deprotonated to give II (Scheme 3).



Scheme 3.

Although III was produced in the photochemical reaction, no III was detected in the diazotization or in the acetolysis[5,6] (Scheme 2, Eq. 3). Under thermodynamic controlled conditions, as are shown in Scheme 2, Eqs. 1 and 2,[7,8] the formation of XI is not surprising, because the homoadamantyl skeleton is known to be about 10 kcal/mol more strained than the adamantyl skeleton.[18] Therefore, III should be thermodynamically more stable than IV.[19] However, the photochemical reaction, the diazotization, and the buffered acetolysis[5,6] should be kinetically controlled. The cation (V) generated in the solvolysis must be in the ground state and, therefore, would not have enough energy to produce II. On the other hand, the cation (V) generated in the diazotization as well as the photochemical reaction would have enough energy to produce II. Although the reason why III is produced only in the case of the photochemical reaction is still not clear, in this rearrangement not only a energetic factor but also a stereochemical one would be operative.[20]

In summary, the total pathway of the photosensitized polar addition of protic solvents to I can be depicted as is shown in Scheme 3. Additionally, it should be noted that no 1,2-hydride shift in V forming a 3-homoadamantyl cation is observed in any of the three different ways so far as the product analysis is concerned.

Experimental

All the temperatures are uncorrected. The IR spectra were obtained on a Shimadzu IR-27 spectrometer. The mass spectra were taken by using a Hitachi RMS-4 mass spectrometer. The NMR spectra were obtained on a Varian EM-360 spectrometer, TMS being chosen as the internal standard. The microanalyses were performed in the Kyoto University Elemental Analysis Center.

Photosensitized Polar Addition of Acetic Acid to I. In an analytical-scale experiment, a solution of I (50 mg, 0.34 mmol) in 5 ml of glacial acetic acid containing 1 ml of benzene (xylene) was irradiated by means of a 300 W medium-pressure mercury lamp under nitrogen for 7 days. The reaction mixture was then poured onto water, neutralized by sodium hydrogen carbonate, and extracted by CH_2Cl_2. The organic layer was washed with aq. $NaHCO_3$ and water, and dried (Na_2SO_4). The solvent was removed, and the residue was analyzed by glc (PEG 20 M, 160 °C). Each product was isolated by preparative glc and was identical with the corresponding authentic sample (II, IIIa, and IVa) in glc retention time and in IR and NMR spectra.

In a preparative-scale run, a solution of I (1.00 g, 6.75 mmol) in 45 ml of glacial acetic acid containing 5 ml of xylene was irradiated by means of a 300 W medium-pressure mercury lamp under nitrogen for 30 days. The usual work-up (see above) gave a crude oil, from which xylene was quickly removed under reduced pressure, but the high subliming property of II prevented the complete removal of the xylene. The glc analysis showed the complete disappearance of I. The residue (2.0 g) was chromatographed on silica gel (200 g). The eluting solvent was gradually changed from *n*-hexane to a mixture of *n*-hexane and ether (95 : 5). The eluent of *n*-hexane gave pure II (216 mg, 21.6%). The eluent of *n*-hexane with ether gave pure IIIa (25 mg, 1.8%), a mixture of IIIa and IVa (303 mg, 21.6%), and pure IVa (360 mg, 25.7%).

A solution of I (500 mg; 3.4 mmol) in 10 ml of AcOD containing 3 ml of xylene was irradiated for 14 days. The usual work-up and chromatography on silica gel gave a mixture of I and II (185 mg, I : II = 1 : 2.5 by glc analysis) and a mixture of III-d_1 and IV-d_1 (278 mg, 6 : 1 by glc analysis). The preparative glc gave pure I and pure II, which contained 12% d_1 and 41% d_1 respectively, as determined by mass spectrometry. The mixture of III-d_1 and IV-d_1 (150 mg) was treated with $LiAlH_4$ (75 mg) in refluxed ether for 10 hr, the subsequent usual work-up gave a crude solid (140 mg) which contained IX-d_1 and VIII-d_1 (*ca.* 1 : 6 by glc analysis). The preparative glc gave pure VIII-d_1 and pure IX-d_1, which contained 45% d_1 and 49% d_1 respectively, as determined by mass spectrometry.

The products, II, IIIa, and IVa, were shown by control experiments to be stable under the present photochemical reaction conditions.

Photosensitized Polar Addition of Pivalic Acid to I. A mixture of I (50 mg; 0.34 mmol), 2.5 ml of pivalic acid, and 2.5 ml of benzene was irradiated by means of a 300 W medium-pressure mercury lamp under nitrogen for 7 days.

The usual work-up gave a crude oil, which was then analyzed by glc (PEG 20 M, 160 °C). Each product, when isolated by preparative glc, was found to be identical with the corresponding authentic sample (II, IIIb, and IVb) in glc retention time and in IR and NMR spectra.

The authentic samples were prepared as follows:

2,4-Dehydrohomoadamantane (II)[21] and 4-homoadamantyl acetate (IVa)[5] were synthesized by the reported method.

4-Homoadamantyl Pivalate (IVb). To a solution of 4-homoadamantanol (VIII) (166 mg; 1.0 mmol) in 1 ml of pyridine, we added pivaloyl chloride[22] (180 mg; 1.5 mmol) in an ice-water bath. The reaction mixture was stirred at room temperature for 24 hr and then poured onto aq. HCl (5%) and extracted with CH_2Cl_2. The CH_2Cl_2 solution was washed successively with 5% aqueous HCl, aqueous $NaHCO_3$, and water, and then dried (Na_2SO_4). The subsequent removal of the solvent gave a crude oil, which was chromatographed on silica gel. The eluent of *n*-hexane with ether (5%) gave pure IVb (204 mg, 81.6%); bp 140 °C/40 mmHg (bath temp.); IR (neat) 2980, 1750, 1160, cm^{-1}; NMR δ (CCl_4) 1.13 (s, 9H), 1.30—2.30 (complex m, 16H), 4.93 (m, 1H). Found: C, 76.49; H, 10.55%. Calcd for $C_{16}H_{26}O_2$: C, 76.75; H, 10.14%.

2-Adamantylmethanol (IX).[23] This compound was prepared by the reported methods. Adamantane-2-carboaldehyde[24] was synthesized by the treatment of adamantyleneoxirane[25,26] with BF_3-etherate.[26] The aldehyde was oxidized by Jones' reagent to give adamantane-2-carboxylic acid,[24,26] which was then reduced with $LiAlH_4$ to furnish IX.[23]

2-Adamantylmethyl Acetate (IIIa). To a solution of IX (50 mg; 0.30 mmol) in 1 ml of pyridine, we added 0.5 ml of acetic anhydride, after which the reaction mixture was stirred for 19 hr at room temperature. The usual work-up gave crude IIIa (60 mg, 96%); bp 135 °C/40 mmHg (bath temp.); IR (neat) 2930, 1750, 1455, 1370, 1220, 1035 cm^{-1}; NMR δ(CCl_4) 1.87 (broad s, 15H), 2.00 (s, 3H), 4.17 (d, 2H, J=7.5 Hz). Found: C, 75.09; H, 9.75%. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68%.

2-Adamantylmethyl Pivalate (IIIb). To a solution of IX (50 mg; 0.30 mmol) in 0.5 ml of pyridine, we added pivaloyl chloride (60 mg; 0.5 mmol) in an ice-water bath. The reaction mixture was then stirred at room temperature for 19 hr, after which the usual work-up gave a crude oil, which was subsequently chromatographed on silica gel. The eluent of *n*-hexane with ether (5%) gave pure IIIb (64 mg, 85%); bp 135 °C/30 mmHg (bath temp.); IR (neat) 2940, 1745, 1480, 1460, 1290, 1150 cm^{-1}; NMR δ (CCl_4) 1.17 (s, 9H), 1.83 (broad s, 15H), 4.14 (d, 2H, J= 7.5 Hz). Found: C, 77.02; H, 10.85%. Calcd for $C_{16}H_{26}O_2$: C, 76.75; H, 1047%.

Diazotization of 4-Homoadamantylamine (XV). The amine was synthesized by a previously reported method.[27] Some typical examples will be described.

Diazotization by Isopentyl Nitrite: A solution of XV (80 mg; 0.48 mmol) and isopentyl nitrite (65 mg; 0.55 mmol) in 5 ml of glacial acetic acid was stirred at room temperature for 72 hr. The reaction mixture was then poured onto water, neutralized with $NaHCO_3$, and extracted with CH_2Cl_2. The CH_2Cl_2 solution was washed with aq. $NaHCO_3$ and water, and dried (Na_2SO_4). After the removal of the solvent, the residue was analyzed by glc (PEG 20 M, 160 °C). Each product, when isolated by preparative glc, was found to be identical with the corresponding authentic sample (I, II, and IVa) in glc retention time and in mass and IR spectra.

Diazotization via *XVI*: The triazene (XVI) was synthesized by the usual method.[28] Since XVI could not be isolated, the crude XVI was used immediately after its preparation. To the crude XVI (100 mg) we added glacial acetic acid (4.5 ml); nitrogen evolved. The reaction mixture was then stirred at room temperature for 1 hr and poured onto water. The solution was neutralized with $NaHCO_3$ and extracted with CH_2Cl_2. The extract was washed with aqueous $NaHCO_3$ and water, and dried (Na_2SO_4). After the removal of the solvent the residue was analyzed by glc (PEG 20 M, 160 °C). Each product, when isolated by preparative glc, was found to be identical with the corresponding authentic sample (I, II, and IVa) in glc retention time and in mass and IR spectra.

Stability of II under the Buffered Solvolysis Conditions. A mixture of II (50 mg; 0.34 mmol), NaOAc (60 mg; 0.73 mmol), and 1 ml of glacial acetic acid was heated at 70 °C for 3 hr.[6] No change was observed by glc analysis.

The authors are indebted to Mr. S. Arimatsu for the preliminary studies.

References and Footnotes

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4) For pertinent data as to the chemistry of carbocation, *cf.* G. A. Olah and P. v. R. Schleyer, eds., "Carbonium Ions," Vols. 1—4, Wiley-Interscience, New York, N.Y. (1968, 1970, 1972, 1973).

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8) K. M. Majerski and Z. Majerski, *Tetrahedron Lett.*, **1972**, 4915

9) A preliminary account on this subject has been reported: R. Yamaguchi, S. Arimatsu, and M. Kawanisi, *Chem. Lett.*, **1973**, 121.

10) In a preliminary report[9] we assigned an incorrect structure, 3-homoadamantyl acetate, to the second product. Subsequent detailed studies confirmed the structure of the product to be IIIa instead of 3-homoadamantyl acetate. It is exactly the same as the structure of IIIb.

11) Another reason why Path B would be favored is as follows: The classical cation (VI) would be likely deprotonated to give methyleneadamantane,[29] which would be stable under the present photochemical reaction conditions. However, this compound was not detected by either glc or NMR analyses.

12) Recently evidence has been presented for the ground state *trans*-isomers as chemically reactive intermediates in the photo-induced polar addition of protic solvents to 7- and 8-membered cycloalkenones; R. Noyori and M. Kato, This Bulletin, **47**, 1460 (1974).

13) Scheleyer *et al.* have suggested that the C_4–C_5 ethylene bridge in homoadamantane system is so flexible that the dihedral angle can change from 0 to *ca.* 30°.[14] Therefore, it is not improbable to assume for geometrical reasons that considerably twisted *transoid*-4-homoadamantene is a chemically reactive intermediate.

14) E. M. Engler, L. Chang, and P. v. R. Schleyer, *Tetrahedron Lett.*, **1972**, 2525; T. M. Corrie, E. M. Engler, R. C. Bingham, and P. v. R. Schleyer, *ibid.*, **1972**, 3039.

15) Control experiments showed that the products, II, III, and IV, are stable under the present photochemical reaction conditions.

16) As to the nature of the carbocation generated in a photosensitized polar addition reaction, Kropp and Krauss described as follows: Caution must be urged against carrying the analogy too close to ground state chemistry, since the carbonium ion will, at least initially, have much more vibrational energy and probably a different geometry than an analogous carbonium ion generated by the simple protonation of a ground state *cis*-olefin; P. J. Kropp and H. J. Krauss, *J. Amer. Chem. Soc.*, **89**, 5199 (1967).

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19) It has been reported that 3-homoadamantyl acetate was converted into 1-adamantylmethyl acetate by treatment with *p*-toluenesulfonic acid in refluxed acetic acid (J. E. Nordlander, S. P. Jindal, P. v. R. Schleyer, R. C. Fort, Jr., J. J. Harper, and R. D. Nicholas, *J. Amer. Chem. Soc.*, **88**, 4475 (1966)). We have examined the similar treatment of IVa; we thus obtained IIIa and an additional acetate, the structure of which has not yet been determined. However, this result does not contradict our present discussion.

20) An important factor in skeletal rearrangement, especially under kinetically controlled conditions, may be the degree of overlap of the vacant orbital of the carbocation center and the C–C bond, which migrates. At this point, for the anticipated most stable geometry of V, which has an untwisted ethylene bridge (C_4–C_5), it would be unfavorable for V to being converted into VII (or VI), because the sp^2-vacant orbital at C_4 is orthogonal to the C_5–C_6 bond, which migrates (Fig. 2a). The more twisted the ethylene bridge is (Fig. 2b), the more favorable would be the rearrangement, because the overlap of the sp^2-vacant orbital at C_4 and C_5–C_6 bond increases. Since the geometry of V generated in the photochemical reaction would probably be a twisted one (Fig. 2b), at least initially,[16] the conversion of V into VII (or VI) would occur, while the geometry of the V generated in the solvolysis as well as in the diazotization would be an untwisted one (Fig. 2a).

Cf. R. Yamaguchi, T. Katsushima, and M. Kawanishi, This Bulletin, **47**, 2830 (1974).

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27) J. L. M. A. Schlatmann, J. G. Korsloot, and J. Schut, *Tetrahedron*, **26**, 949 (1970).

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* Throughout this paper we have adopted trivial nomenclature for simplicity. The IUPAC names for I, II, and IV are tricyclo[4.3.1.1^{3,8}]undec-4-ene, tetracyclo[5.3.1.0^{3,5}-0^{4,9}]undecane, and tricyclo[4.3.1.1^{3,8}]undec-4-yl acetate (pivalate), respectively.