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The Photolysis of 1-Phenylbicyclo[*n*.1.0]alkanes in Acidic Media

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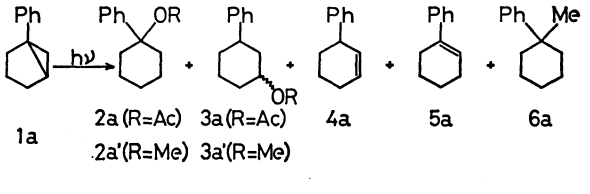
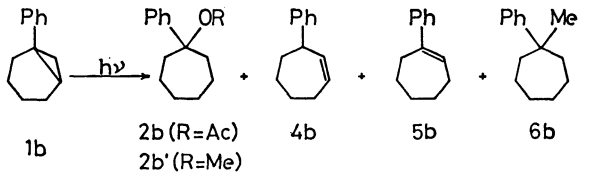
In continuation of our studies of the photochemical polar addition of acetic acid to 1-phenylcycloalkenes,[1] we have been interested in the title reaction of phenylcyclopropanes (**1a**, **1b**). This has been disclosed to involve proton addition to the cyclopropane ring and to give products, **2**—**6**, as a result of the expansion of the original $n+2$ rings to $n+3$ rings, where $n=3$ or 4. Such a photoinduced heterolysis is rare[2] and forms a sharp contrast to the previously recorded formation of carbenes in this kind of photolysis.[3]





The irradiation of 1-phenylbicyclo[3.1.0]hexane (**1a**) was performed in acetic acid, and the resulting photoproducts were separated by preparative-scale thin layer (TLC) and gas chromatography (GC). The acetate fraction of TLC consisted of 5 components, among which 1-acetoxy-phenylcyclohexane (**2a**) and *cis* and *trans* isomers of 3-acetoxy-1-phenylcyclohexane (**3a**) were identified. The three hydrocarbons isolated were 1-(**5a**) and 3-phenylcyclohexene (**4a**) and 1-methyl-1-phenylcyclohexane (**6a**). The photolysis of 1-phenylbicyclo[4.1.0]heptane (**1b**) in acetic acid proceeded in a similar way to afford the corresponding acetate (**2b**), two isomerization products (**4b** and **5b**), and 1-methyl-1-phenylcycloheptane (**6b**). Methanol also added to the cyclopropane ring of **1a** or **1b** on UV irradiation in the presence of sulfuric acid. On the other hand, the photolysis of **1a** and **1b** under neutral conditions gave no ionic photoadducts, but only isomerization products in rather low yields.

The formation of acetates and ethers is ionic in nature, and protonated cyclopropanes[4] are plausible intermediates, as the attack of solvent molecules occurred on the both sides of cyclopropane rings. However, the possibility of the intermediary of **5a** and **5b** in the polar addition can not be excluded.[1] It should be emphasized that the C_1–C_{n+2} bonds of 1-phenylbicyclo[*n*.1.0]alkanes (**1**) were cloven exclusively. The alkylation products (**6a** and **6b**) can be explained as secondary photoprodncts arising from **2a** and **2b** respectively.[1]

Experimental

The mass spectra were determined on a Hitachi RMU-6L spectrometer, and the NMR data, on a JEOL C-60-H spectrometer in carbon tetrachloride at 60 MHz. Prepara-

TABLE 1. PHOTOLYSIS OF 1-PHENYLBICYCLO[*n*.1.0]ALKANES[a]

Substrate	Solvent	1%	Acetate or Ether			Hydrocarbons		
			R	2%	3%	4%	5%	6%
1a	AcOH	4	Ac	28	3[b]	15	7	4
	MeOH(H$^+$)[c]	4	Me	35	3[b]	4	2	d
	MeOH	78	Me	d	d	e	11	d
1b	AcOH	40	Ac	24	d	10	2	1
	MeOH(H$^+$)[c]	18	Me	47	d	10	4	d
	MeOH	75	Me	d	d	4	2	d

a) Direct irradiation was effected on 0.05 M solutions placed in quartz tubes with an external 200 w high pressure mercury arc under nitrogen atomosphere at room temperature during 5 hr. The reaction did not proceed in the dark at room temperature.
b) This is a mixture of *cis* and *trans* isomers.
c) Methanol contains 0.3% sulfuric acid.
d) Not detected.
e) The presence of a trace amount was detected.

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tive TLC was performed on silica-gel G (20×20×0.3 cm), using benzene as the solvent and as an eluant. Preparative GC was carried out using High Vacuum Silicone Grease 20% on Celite 545 (2 m, 180°C, helium as the carrier gas). The hydrocarbon contents were determined by GC.

*1-Phenylbicyclo[3.1.0]hexane (**1a**).* A solution of bromoform (135 g, 0.53 mol) in *n*-hexane (200 m*l*) was added, under 5°C, to a mixture of 1-phenylcyclopentene (40 g, 0.28 mol), potassium *t*-butoxide (59 g), and *n*-hexane (400 m*l*). The mixture was allowed to stand overnight at room temperature, poured into water, extracted with ether, and dried over sodium sulfate. After concentration, the unchanged olefin was recovered by distillation. The resulting residue (60 g) was subjected to reduction without further purification.

The crude dibromide was added to a solution of sodium metal (30 g) in liquid ammonia (*ca.* 500 m*l*) under −40°C for 2 hr. After stirring for an additional 2 hr, solid ammonium chloride was added and the solvent was allowed to evaporate at room temperature. The residue was diluted with water, extracted with ether, and dried over sodium sulfate. Subsequent concentration and fractional distillation gave **1a** (22 g, 50%) as a colorless liquid; bp. 69°C/1 mmHg. IR (neat): 3035, 3007, 2940, 2920, 2850, 1604, 1498, 1476, 1452, 1101, 1072, 1024, 935, 868, 799, 756 and 698 cm^{-1}. NMR (CCl_4): δ 7.12 (5H, s), 2.25—1.40 (7H, m) and 0.80—0.57 (2H, m). MS *m/e* (relative abundance): 158 (100), 143 (65), 130 (91), 129 (99), 128 (48), 117 (63), 115 (79), 104 (55), 91 (63), 77 (35), 51 (34), 39 (35).

Found: C, 91.1; H, 8.8%. Calcd for $C_{12}H_{14}$: C, 91.1; H, 8.9%.

1-Phenylbicyclo[4.1.0]heptane (**1b**)[5] was similarly prepared from 1-phenylcyclohexane.

*Direct Irradiation of **1a** and **2b** in Acetic Acid.* A 0.05 M solution (200 m*l*) of 1-phenylbicyclo[*n*.1.0]alkane (**1**) in acetic acid was placed in eight quartz tubes (1.5ϕ×19 cm) and irradiated with a high-pressure mercury are under a nitrogen atmosphere for 5 hr. The combined photolysates were then neutralized with aqueous sodium hydrogen carbonate, extracted with ether, and dried over sodium sulfate. Concentration *in vacuo* and subsequent preparative TLC gave a mixture of hydrocarbons (**1**, **4**, **5** and **6**) and the corresponding esters (**2** and **3**). These two separated fractions were weighed and subjected directly to GC analyses. The results are summarized in Table 1. The preparative GC of the hydrocarbon fraction gave the starting material (**1**), 1- (**5**) and 3-phenylcycloalkene (**4**)[6] and 1-methyl-1-phenylcycloalkane (**6**).[1] All the hydrocarbons were identified by comparison with known samples. The esters (**2**) were distilled and subjected to spectrometric analyses. The *cis* and *trans* isomers of **3a** were isolated by preparative GC and compared with the authentic specimens to be described below.

*Direct Irradiation of **1a** and **1b** in Methanol Containing Sulfuric Acid.* A 0.05 M solution (200 m*l*) of **1** in methanol containing 0.3% sulfuric acid was irradiated as has been described above. The photolysate was analyzed by GC (Table 1). The ethers (**2a′** and **2b′**) were identical with the authentic samples.[1] The *cis* and *trans* isomers of **3a′** isolated by preparative GC were identical with the authentic samples described below.

*Direct Irradiation of **1a** and **1b** in Methanol.* A 0.05 M solution (200 m*l*) of **1** in methanol was irradiated. A usual work-up gave a mixture of hydrocarbons (**1**, **4**, and **5**) which was then analyzed by GC. The results are summarized in Table 1.

cis-*3-Acetoxy-1-phenylcyclohexane (*cis-***3a***).* The reduction of 3-phenylcyclohexanone with lithium aluminum hydride gave a *cis*-rich mixture of 3-phenylcyclohexanol, from which the *cis* isomer was isolated by recrystallization from *n*-hexane. mp 78—79°C (lit,[7] 79—80°C).

A mixture of *cis*-3-phenylcyclohexanol (0.15 g, 0.85 mmol), acetic anhydride (5 m*l*), and pyridine (10 m*l*) was heated at 90—100°C for 2 hr. A work-up gave *cis*-**3a** (0.16 g, 86%), bp 75—80°C (bath temperature)/0.04 mmHg, which was contaminated with 1.6% of *trans* isomer. An authentic specimen of *cis*-**3a** was purified by preparative GC. IR (neat): 3030, 3010, 2900, 2840, 1737, 1603, 1497, 1451, 1367, 1242, 1200, 1029, 967, 756, and 699 cm^{-1}. NMR (CCl_4): δ 7.17 (5H, s), 4.97—4.48 (1H, m), 2.87—0.80 (12H, m+s (δ 1.97, 3H)). MS *m/e* (relative abundance): 218 (7), 158 (100), 143 (37), 130 (52), 129 (35), 117 (31), 104 (54), 91 (49).

Found: C, 77.2: H, 8.1%. Calcd for $C_{14}H_{18}O_2$: C, 77.0; H, 8.3%.

trans-*3-Acetoxy-1-phenylcyclohexane (*trans-***3a***).* The Meerwein-Ponndorf reduction of 3-phenylcyclohexanone (4.2 g, 24 mmol) gave a mixture (3.4 g, 81%) of *cis*- and *trans*-3-phenylcyclohexanol (*cis* : *trans*=2.5 : 1),[7] from which the *cis* isomer was then removed by recrystallization.

A *cis-trans* mixture of 3-phenylcyclohexanol (0.034 g, 0.19 mmol, *cis*:*trans*=1:3), acetic anhydride (5 m*l*), and pyridine (10 m*l*) was refluxed. Distillation gave a mixture (0.035 g, 81%) of *cis*- and *trans*-**3a** (*cis*:*trans*=5:4). The analytical sample of *trans*-**3a** was purified by preparative GC. IR (neat): 3030, 3010, 2900, 2845, 1739, 1604, 1496, 1440, 1376, 1249, 1232, 1115, 1018, 958, 753, and 698 cm^{-1}. NMR (CCl_4): δ 7.16 (5H, s), 5.30—5.00 (1H, m), 2.95—0.90 (12H, m+s (δ 2.06, 3H)). MS *m/e* (relative abundance): 218 (3), 158 (100), 143 (38), 130 (39), 129 (32), 117 (16), 104 (28), 91 (32).

Found: C, 77.3; H, 8.5%. Calcd for $C_{14}H_{18}O_2$: C, 77.0; H, 8.3%.

cis- *and* trans-*3-Methoxyl-1-phenylcylohexane (**3a′**).* To a solution of 3-phenylcyclohexanol (1.0 g, 5.7 mmol, *cis*: *trans* =2.5: 1) in ether (50 m*l*), boron trifluoride etherate (5 m*l*) was added, drop by drop; then, a solution of diazomethane (from 20 g of *N*-methyl-*N*-nitrosourea) in ether (50 m*l*) was added. Subsequent concentration and distillation gave a mixture (0.80 g, 74%) of *cis*- and *trans*-**3a′** (*cis*:*trans*=7:1). The analytical samples of both the isomers were obtained by preparative GC.

The pure *cis* isomer **3a′** showed the following spectra. IR (neat): 3027, 3010, 2920, 2860, 2820, 1602, 1498, 1450, 1371, 1139, 1128, 1098, 756, and 702 cm^{-1}. NMR (CCl_4): δ 7.13 (5H, s), 3.35—0.80 (13H, m+s (δ 3.27, 3H)). MS *m/e* (relative abundance): 190 (66), 158 (75), 147 (100), 143 (67), 130 (41), 129 (37), 117 (62), 115 (41), 105 (29), 104 (98), 91 (87), 77 (28), 71 (43), 58 (46).

Found: C, 82.1; H, 9.6%. Calcd for $C_{13}H_{18}O$: C, 82.1; H, 9.5%.

The pure *trans*-**3a′** showed the following spectra. IR (neat): 3027, 3010, 2910, 2860, 2810, 1602, 1498, 1450, 1362, 1140, 1115, 1088, 756, 704 cm^{-1}. NMR (CCl_4): δ 7.13 (5H, s), 3.65—3.45 (1H, m), 3.30 (3H, s), 3.00—1.00 (9H, m).

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b) A. C. Cope and S. S. Hecht, *ibid.*, **89**, 6920 (1967).

7) M. Balasubramanian and A. D'Souza, *Tetrahedron Lett.*, **1963** 1891.

MS *m/e* (relative abundance): 190 (2), 158 (100), 143 (37), (37), 130 (45), 129 (30), 117 (22), 115 (22), 104 (36), 91 77 (15), 71 (12), 58 (17).

Found: C, 81.9; H, 9.6%. Calcd for $C_{13}H_{18}O$: C, 82.1; H, 9.5%.

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