BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (1), 319—320 (1977)

Synthesis of New Heptacyclic Propellanes

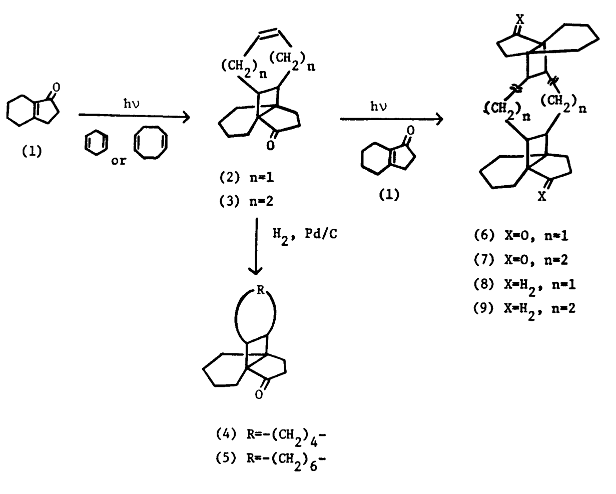
Yoshito Tobe, Hirofumi Omura, Atsutaka Kunai, Koji Kimura,
and Yoshinobu Odaira
Department of Petroleum Chemistry, Faculty of Engineering, Osaka University, Suita-shi, Osaka 565

(Received June 28, 1976)

Synopsis. The heptacyclic propellanes, **8** and **9**, having two propellane rings in each molecule, were synthesized by the stepwise photocycloaddition of bicyclo[4.3.0]non-1(6)-en-7-one (**1**) to cyclohexadiene or cyclooctadiene followed by the Wolff-Kishner reduction of the resulting propellanones **6** and **7**. The photosolvolytic behavior of some of the cycloadducts is also described.

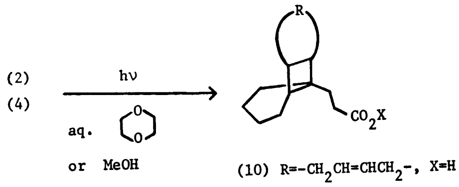
As part of a study of the synthesis of polycyclic propellanes,1) we report that the tetracyclic *trans*-fused cycloadduct (**4** or **5**) was easily derived from the photocycloaddition of bicyclo[4.3.0]non-1(6)-en-7-one (**1**) to cyclohexene or cyclooctene.2) The present investigation was undertaken to synthesize some new heptacyclic propellanes, having two propellane rings in each molecule, by a similar but stepwise photocycloaddition between the enone (**1**) and two kinds of alicyclic dienes.

First, **1** was irradiated in the presence of 10 molar excess of 1,4-cyclohexadiene or 1,5-cyclooctadiene through a Pyrex filter, until it was almost consumed, giving the sole cycloadduct, **2** or **3**, respectively in 74% or 80% yield. Catalytic hydrogenation of **2** and **3** over Pd/C led to the formation of **4** and **5**, respectively, compounds identical with the cycloadducts. The stereochemistry around the junction of the cyclobutane ring in the compounds **2**, **3**, and **4** has been determined to be *trans* by means of X-ray analysis.3) Next, the cycloadduct (**2** or **3**) was irradiated with 4 molar excess of the enone (**1**), under similar conditions to those described above, to afford the heptacyclic cycloadduct, **6** or **7**, respectively in 25% or 31% yield. Thus, it seems reasonable to assume that the stereochemistry about the second cyclobutane ring in **6** and **7** is also *trans*, though the stereochemical relation between two bicyclo[4.3.0]-nonan-7-one skeltons in each molecule is still uncertain. Finally, the heptacyclic propellanes (**8** and **9**), having two propellane rings in each molecule, were obtained by the Wolff-Kishner reduction of the corresponding propellanones (**6** and **7**), in 37% and 56% yields, respectively.4)

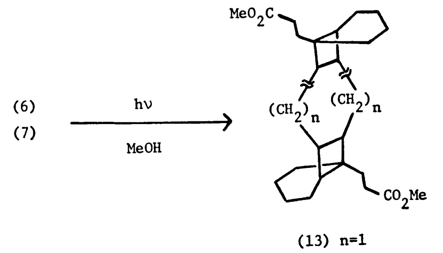


(1)
(2) n=1
(3) n=2
(4) R=-$(CH_2)_4$-
(5) R=-$(CH_2)_6$-
(6) X=O, n=1
(7) X=O, n=2
(8) X=H_2, n=1
(9) X=H_2, n=2

Photolyses of the propellanones **2**, **4**, **6**, and **7** were carried out, in an attempt to transform the cycloadducts of [4.3.2]propellane system into polycyclic compounds of another system. Photolyses of **2** and **4** in aqueous dioxane gave the acids, **10** and **11**, respectively, almost quantitatively. Irradiation of **4**, **6**, and **7** in methanol gave the esters **12**, **13**, and **14**, respectively.



(10) R=-$CH_2CH=CHCH_2$-, X=H
(11) R=-$(CH_2)_4$-, X=H
(12) R=-$(CH_2)_4$-, X=Me



(13) n=1
(14) n=2

Experimental

Bicyclo[4.3.0]non-1(6)-en-7-one(1). Enone (**1**) was prepared according to the procedure of Dev.5)

Photocycloaddition of 1 with 1,4-Cyclohexadiene. A solution of **1** (0.800 g, 5.88 mmol) in 1,4-cyclohexadiene (59 mmol) was irradiated through a Pyrex filter under nitrogen at room temperature until enone (**1**) was almost comsumed. After removal of the diene, distillation gave 0.938 g of the cycloadduct (**2**) (74%), as the sole adduct (GLPC). Recrystallization from methanol gave an analytical sample, mp 80—81 °C; ν_{max} 1725, 660 cm^{-1}; δ (CCl_4) 0.60—2.65 (m, 18H), 6.55 (s, 2H); *m/e* 216 (M^+), 137; 2,4-dinitrophenylhydrazone, mp 174—175 °C; Found: C, 63.47; H, 6.03; N, 14.30%. Calcd for $C_{21}H_{24}O_4N_4$: C, 63.62; H, 6.10; N, 14.13%.

Photocycloaddition of 1 with 1,5-Cyclooctadiene. A solution of **1** (0.493 g, 3.62 mmol) in 1,5-cyclooctadiene (36 mmol) was irradiated and work-up as above gave 0.711 g of the cycloadduct (**3**) (80%), mp 88—89.5 °C; ν_{max} 1715, 725 cm^{-1}; δ (CCl_4) 0.60—1.75 (m, 14H), 1.90—2.50 (m, 8H), 6.40—6.65 (m, 2H); *m/e* 244 (M^+), 137; Found: C, 83.59; H, 9.95%. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90%.

Photocycloaddition of 1 with 2. A solution of **1** (2.825 g, 28.1 mmol) and **2** (1.355 g, 6.27 mmol) in 50 ml of pentane was irradiated as above. After removal of the solvent, the residue was chromatographed on silica gel. The benzene eluate was collected and recrystallized from ethanol to give 0.55 g of the cycloadduct (**6**) (25% based on **2** used), mp 265—267 °C; ν_{max} 1720 cm^{-1}; δ (CCl_4) 0.60—2.40 (m, 28H), 2.40—2.70 (m, 4H); *m/e* 352 (M^+), 137; Found: C, 81.41; H, 9.05%. Calcd for $C_{24}H_{32}O_2$: C, 81.77; H, 9.15%.

*Photocycloaddition of **1** with **3**.* A solution of **1** (5.20 g, 38.2 mmol) and **3** (2.39 g, 9.80 mmol) in 50 ml of pentane was irradiated and work-up as above gave 1.15 g of the cycloadduct (**7**) (35% based on **3** used), mp 239—240 °C; ν_{max} 1715 cm^{-1}; δ ($CDCl_3$) 0.40—2.30 (m, 32H), 2.30—2.70 (m, 4H); *m/e* 380 (M^+), 137; Found: C, 81.79; H, 9.56%. Calcd for $C_{26}H_{36}O_2$: C, 82.06; H, 9.54%.

*Wolff-Kishner Reduction of **6** and **7**.* The Wolff-Kishner reduction of **6** and **7** was carried out according to the procedure of Huang-Minlon.[6] The products were isolated by vacuum distillation and purified by preparative GLPC. They showed no carbonyl absorption in infrared spectra. Reduction of **6** gave **8** (37%), mp 173—175 °C; δ (CCl_4) 0.70—2.30 (m): *m/e* 324 (M^+), 122; Found: C, 88.81; H, 11.43%. Calcd for $C_{24}H_{36}$: C, 88.82; H, 11.18%. Reduction of **7** gave **9** (56%), mp 132—134 °C; δ (CCl_4) 0.70—2.00 (m); *m/e* 352 (M^+), 122; Found: C, 88.16; H, 11.77%. Calcd for $C_{26}H_{40}$: C, 88.56; H, 11.44%.

*Photolysis of **2** and **4** in Aqueous Dioxane.* A solution of **2** or **4** in 90% aq dioxane irradiated in a quartz vessel until the ketone was almost consumed. After removal of the solvent, distillation gave the acid, **10** or **11**, respectively. Recrystallization from hexane gave an analytical sample. **10** (78%); mp 97—99 °C; ν_{max} 3050, 1700, 660 cm^{-1}; δ (CCl_4) 0.80—2.50 (m, 19H), 5.65 (s, 2H), 10.30—11.60 (broad s, 1H); *m/e* 234(M^+). **11** (84%); mp 100—101 °C; ν_{max} 3050, 1700 cm^{-1}; *m/e* 236 (M^+); Found: C, 76.10; H, 10.25%. Calcd for $C_{15}H_{24}O_2$: C, 76.22; H, 10.24%. Catalytic hydrogenation of **10** over Pd/C gave **11**.

*Photolysis of **4**, **6**, and **7** in Methanol.* A solution of **4** or **6** or **7** in methanol was irradiated as above. After removal of the solvent, the ester (**12**) was isolated by distillation, and esters (**13** and **14**) were isolated by column chromatograph on silica gel. **12** (86%); ν_{max} 1740 cm^{-1}; δ (CCl_4) 0.80—2.30 (m, 23H), 3.55 (s, 3H); *m/e* 250 (M^+); Found: C, 77.06; H, 10.75%. Calcd for $C_{16}H_{26}O_2$: C, 76.75; H, 10.74%. **13** (43%); mp 159—161 °C; ν_{max} 1730 cm^{-1}; δ (CCl_4) 0.90—2.40 (m, 34H), 3.60 (s, 6H); *m/e* 416 (M^+); Found: C, 74.81; H, 9.72%. Calcd for $C_{26}H_{40}O_4$: C, 74.96; H, 9.68%. **14** (35%); ν_{max} 1740 cm^{-1}; δ (CCl_4) 0.80—2.40 (m, 38H), 3.60 (s, 6H); *m/e* 444 (M^+).

We are grateful to Prof. N. Kasai and co-workers for the X-ray analysis.

References

1) A. Kunai, T. Omori, T. Miyata, K. Kimura, and Y. Odaira, *Tetrahedron Lett.*, **1974**, 2517; A. Kunai, T. Omori, K. Kimura, and Y. Odaira, *Bull. Chem. Soc. Jpn.*, **48**, 731 (1975); A. Kunai, K. Kimura, and Y. Odaira, *ibid.*, **48**, 1677 (1975).

2) A. Kunai, K. Yorihiro, T. Hirata, and Y. Odaira, *Tetrahedron*, **29**, 1679 (1973); unpublished data, Y. Tobe, A. Doi, K. Kimura, and Y. Odaira.

3) M. Harada, Y. Kai, N. Yasuoka, and N. Kasai, *Acta Crystallogr., Sect. B* **32**, 625 (1976).

4) The propellanones (**2**)—(**5**) were also converted into the corresponding propellanes in similar yields.

5) S. Dev, *J. Indian Chem. Soc.*, **34**, 169 (1957).

6) Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).