BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (2), 641—642 (1979)

The Reaction of 1-(1-Pyrrolidinyl)acenaphthylene with Electrophilic Acetylenes[1)]

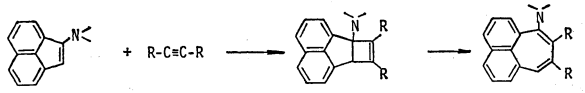
Otohiko TSUGE* and Haruyuki WATANABE

Research Institute of Industrial Science, Kyushu University 86, Hakozaki, Higashi-ku, Fukuoka 812

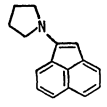
(Received August 25, 1978)

Synopsis. 1-(1-Pyrrolidinyl)acenaphthylene (**1**), which was prepared from acenaphthenone and pyrrolidine, reacted with dimethyl acetylenedicarboxylate to give the dihydrocyclohepta[*de*]naphthalene and dihydrofluoranthene. The reaction of **1** with methyl propiolate in benzene afforded the dihydrocyclohepta[*de*]naphthalene (**8**) and its isomeric cyclohepta[*de*]naphthalenol (**9**), whereas the Michael type adduct was formed in methanol. An interconversion between **8** and **9** was also described.

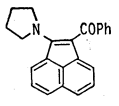
It is known that enamines derived from cyclic ketones react with activated acetylenes to yield intermediate cyclobutene adducts which undergo rearrangement with expansion of the carbocyclic ring by two carbon atoms.[2)] Application of this process to 1-aminoacenaphthylene derivatives, which might exhibit enamine-like properties, seems to provide a one-pot synthesis of cyclohepta[*de*]naphthalene compounds which are nonalternant hydrocarbons. However, no 1-aminoacenaphthylenes appeared in the literature. We now report the preparation of 1-(1-pyrrolidinyl)acenaphthylene (**1**) and its reaction with electrophilic acetylenes.



When a benzene solution of acenaphthenone was refluxed with a slight excess of pyrrolidine in the presence of *p*-toluenesulfonic acid for 1 h, the expected enamine **1** as reddish violet viscous oil was obtained quantitatively. Benzoylation of **1** with benzoyl chloride afforded 1-benzoyl-2-(1-pyrrolidinyl)acenaphtylene (**2**), mp 178—180 °C, in 87% yield.



1



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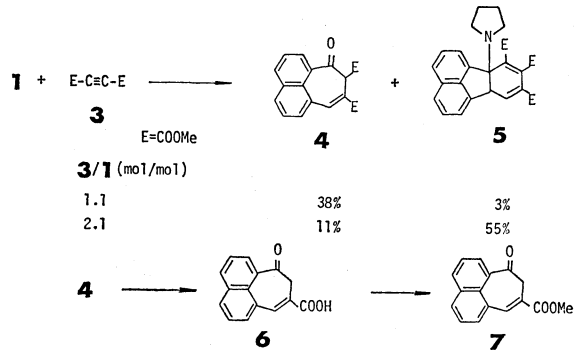
The reaction of **1** with dimethyl acetylenedicarboxylate (**3**) in benzene at room temperature for 3 h gave dimethyl 7-oxo-7,8-dihydrocyclohepta[*de*]naphthalene-8,9-dicarboxylate (**4**), mp 131—132 °C, and the dihydrofluoranthene (**5**), mp 191—192 °C, together with tarry materials. The compound **4** was evidently formed by hydrolysis of an initial cyclohepta[*de*]naphthalene. As shown in Scheme 1, the yields of **4** and **5** depended on the amounts of **3** used. Structural elucidation of **4** and **5** was accomplished on the basis of their spectral data.

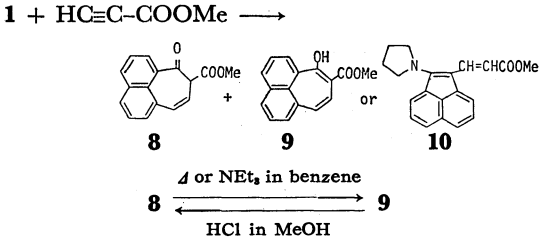
Treatment of **4** with 3% aqueous sodium hydroxide solution under reflux for 30 min gave 7-oxo-7,8-dihydrocyclohepta[*de*]naphthalene-9-carboxylic acid (**6**), mp



Scheme 1.

229—230 °C, in a 78% yield, evidently by hydrolysis and followed by decarboxylation. The carboxylic acid **6** was converted into the methyl ester **7**, mp 102—103 °C.

In the reaction of **1** with an equimolar amount of methyl propiolate in benzene at room temperature for 1 h, two isomers were isolated. The minor product (2.3 %), mp 115—125 °C (turned to red), as colorless prisms was proven to be methyl 7-oxo-7,8-dihydrocyclohepta[*de*]naphthalene-8-carboxylate (**8**), which is an isomer of **7**, and the major product (21%), mp 87—88 °C, as red needles was assigned to be a tautomer of **8**, methyl 7-hydroxycyclohepta[*de*]naphthalene-8-carboxylate (**9**). On the other hand, the same reaction in methanol at room temperature for 3 h gave the Michael type adduct **10**, mp 157—158 °C, in a 49% yield. (Scheme 2).



Scheme 2.

As mentioned above, dihydrocyclohepta[*de*]naphthalene **8** melted at 115—125 °C with color change to red, which suggests the transformation into red colored cyclohepta[*de*]naphthalenol **9**. In fact, heating of **8** at 130 °C for 3 h afforded **9** in a 73% yield. When treated with silica gel or triethylamine in benzene at room temperature, **8** was also converted into **9**. On the treatment with catalytic amounts of hydrochloric acid in methanol, however, **9** was partially converted into **8**.

In contrast to **8**, attempts to isomerize **7** to a cyclohepta[*de*]naphthalenol under various conditions were unsuccessful.

Experimental

1-(1-Pyrrolidinyl)acenaphthylene (1). A solution of acenaphthenone (9.1 g, 0.054 mol), pyrrolidine (4.6 g, 0.065 mol), and *p*-toluenesulfonic acid (0.9 g) in benzene (100 ml) was boiled with azeotropic removal of water. After being boiled for 1 h, the reaction mixture was concentrated *in vacuo*, and the residue was extracted with petr. ether. The extract was concentrated to give 11.8 g (*ca.* 100%) of the enamine **1** as reddish violet viscous oil. Bp 185 °C/4 mmHg; NMR (CCl_4) δ 1.85—2.25, 3.40—3.75 (each 4H, m), 5.26 (1H, s, =CH), 6.85—7.86 (6H, m); MS *m/e* 221 (M^+). Picrate of **1**: mp 164—166 °C. Found: C, 58.60; H, 4.05; N, 12.19%. Calcd for $C_{22}H_{18}N_4O_7$: C, 58.66; H, 4.03; N, 12.44%.

Benzoylation of the Enamine 1. A solution of **1** (1.3 g, 0.006 mol) and benzoyl chloride (1.3 g, 0.009 mol) in benzene (20 ml) was stirred with NEt_3 (0.9 g, 0.009 mol) at room temperature for 3 h. The reaction mixture was filtered to remove triethylamine hydrochloride, and the filtrate was evaporated *in vacuo*, followed by addition of petr. ether to give crystals. Recrystallization from EtOH afforded 1.7 g (87%) of 1-benzoyl-2-(1-pyrrolidinyl)acenaphthylene (**2**), mp 178—180 °C, as red prisms. IR (KBr) 1600 cm^{-1} ($\nu_{C=O}$); MS *m/e* 325 (M^+). Found: C, 84.89; H, 5.88; N, 4.30%. Calcd for $C_{23}H_{19}NO$: C, 84.89; H, 5.89; N, 4.30%.

Reaction of the Enamine 1 with Dimethyl Acetylenedicarboxylate (3). A solution of **1** (13.0 g, 0.059 mol) and the acetylene **3** (9.2 g, 0.065 mol) in benzene (100 ml) was stirred at room temperature for 3 h. The reaction mixture was concentrated *in vacuo*, and MeOH (20 ml) was added to the residue, giving 7.0 g (38%) of colorless crystals, mp 128—130 °C. Recrystallization from cyclohexane afforded dimethyl 7-oxo-7,8-dihydrocyclohepta[*de*]naphthalene-8,9-dicarboxylate (**4**), mp 131—132 °C, as colorless prisms. IR (KBr) 1680, 1720, 1780 cm^{-1} ($\nu_{C=O}$); NMR ($CDCl_3$) δ 3.25, 3.99 (each 3H, s), 5.46 (1H, s, >C**H**), 7.22 (1H, s, =C**H**), 7.30—8.20 (6H, m); UV λ_{max}^{EtOH} nm (log ε) 208 (4.5), 237 (4.5), 325 (4.0); MS *m/e* 310 (M^+). Found: C, 69.64; H, 4.58%. Calcd for $C_{18}H_{14}O_5$: C, 69.67; H, 4.55%.

The MeOH filtrate was concentrated *in vacuo*, and the residue was chromatographed on alumina using benzene as an eluent, giving 0.9 g (3%) of crystals. Recrystallization from MeOH afforded the dihydrofluoranthene **5**, mp 191—192 °C, as colorless prisms. IR (KBr) 1740, 1750 cm^{-1} ($\nu_{C=O}$); NMR ($CDCl_3$) δ 1.60—1.96, 3.20—3.60 (each 4H, m), 3.65, 3.72 (each 6H, s), 5.35 (1H, s, >C**H**), 7.25—8.20 (6H, m); UV λ_{max}^{EtOH} nm (log ε) 215 (4.8), 330 (3.8); MS *m/e* 505 (M^+). Found: C, 66.78; H, 5.45%. Calcd for $C_{28}H_{27}NO_8$: C, 66.52; H, 5.38%.

A similar reaction of **1** (11.7 g, 0.053 mol) with **3** (16.5 g, 0.116 mol) in benzene (100 ml) afforded 1.8 g (11%) of **4** and 14.8 g (55%) of **5**.

7-Oxo-7,8-dihydrocyclohepta[de]*naphthalene-9-carboxylic Acid (6) and Its Methyl Ester (7).* A suspension of dihydrocyclohepta-[*de*]naphthalene **4** (5.0 g) in 3% NaOH aq solution (200 ml) was refluxed for 30 min; during which time it turned to a red solution. The solution was acidified with hydrochloric acid to give brown precipitates, which extracted with hot EtOH (150 ml). The extract was concentrated *in vacuo* to leave the residue, which on recrystallization from EtOH using charcoal afforded 1.5 g (39%) of **6**, mp 229—230 °C, as yellow prisms. IR (KBr) 2700—3100 (ν_{OH}), 1690 cm^{-1} ($\nu_{C=O}$); NMR (DMSO-d_6) δ 3.80 (2H, s, C**H**$_2$), 7.60—8.45 (7H, m, Ar**H**+=C**H**); UV λ_{max}^{EtOH} nm (log ε) 225 (4.5), 243 (4.4), 320 (3.9); MS *m/e* 238 (M^+). Found: C, 75.90; H, 4.35%. Calcd for $C_{15}H_{10}O_3$: C, 75.62; H, 4.23%.

Esterification of **6** in MeOH containing H_2SO_4 afforded the methyl ester (**7**) in a 92% yield. Mp 102—103 °C; yellow prisms; IR (KBr) 1670, 1704 cm^{-1} ($\nu_{C=O}$), NMR ($CDCl_3$) δ 3.82 (2H, s, C**H**$_2$), 3.89 (3H, s), 7.30—8.20 (7H, m, ArH+=C**H**); MS *m/e* 252 (M^+). Found: C, 76.07; H, 4.78%. Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.80%.

Reaction of the Enamine 1 with Methyl Propiolate. i) A solution of **1** (2.65 g, 0.012 mol) and methyl propiolate (1.0 g, 0.012 mol) in benzene (20 ml) was stirred at room temperature for 3 h. The reaction mixture was concentrated *in vacuo*, and the residue was chromatographed on silica gel using benzene as an eluent to give crystals. The crystals were washed with hexane (50 ml) to leave red crystals. Recrystallization from petr. ether afforded 0.65 g (21%) of methyl 7-hydroxycyclohepta-[*de*]naphthalene-8-carboxylate (**9**), mp 87—88 °C, as red needles. IR (KBr) 1660 cm^{-1} ($\nu_{C=O}$); NMR ($CDCl_3$) δ 3.80 (3H, s), 6.02, 6.28 (each 1H, d, =C**H**, J=12 Hz), 6.85—8.20 (6H, m), 14.50 (1H, s, O**H**); UV λ_{max}^{EtOH} nm (log ε) 217 (4.5), 250 (4.2), 370 (3.7), 450 (3.3); MS *m/e* 252 (M^+). Found: C, 76.47; H, 4.79%. Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.80%.

The hexane washings were evaporated *in vacuo* to leave colorless crystals, which on recrystallization from hexane afforded 0.07 g (2.3%) of methyl 7-oxo-7,8-dihydrocyclohepta-[*de*]naphthalene-8-carboxylate (**8**), mp 115—125 °C (turned to red), as colorless prisms. IR (KBr) 1690, 1755 cm^{-1} ($\nu_{C=O}$); NMR ($CDCl_3$) δ 3.78 (3H, s), 4.48 (1H, dd, >C**H**, J=2, 5 Hz), 6.41 (1H, dd, =C**H**, J=5, 11 Hz), 6.98 (1H, dd, =C**H**, J=2, 11 Hz), 7.28—8.25 (6H, m); UV λ_{max}^{EtOH} nm (log ε) 220 (4.6), 317 (3.8), 340 (3.8), 355 (3.8); MS *m/e* 252 (M^+). Found: C, 76.29; H, 4.84%. Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.80%.

ii) A solution of **1** (2.65 g) and methyl propiolate (1.0 g) in MeOH (20 ml) was stirred at room temperature for 3 h; during which time crystals precipitated. Recrystallization of the crystals from EtOH afforded 1.8 g (49%) of the Michael type adduct **10**, mp 157—159 °C, as violet prisms. IR (KBr) 1690 cm^{-1} ($\nu_{C=O}$); NMR ($CDCl_3$) δ 1.69—2.05, 3.55—3.90 (each 4H, m), 3.79 (3H, s), 6.08, 8.17 (each 1H, d, =CH, J=15 Hz), 7.19—7.90 (6H, m); UV λ_{max}^{EtOH} nm (log ε) 227 (4.7), 254 (4.4), 320 (4.3), 357 (4.5), 390 (4.2), 520 (3.8); MS *m/e* 305 (M^+). Found: C, 78.04; H, 6.22; N, 4.69%. Calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27; N, 4.59%.

Isomerization of Dihydrocyclohepta[de]*naphthalene (8) to Cyclohepta-*[de]*naphthalenol (9). i)* Dihydrocyclohepta[*de*]naphthalene (**8**) (0.15 g) in a test tube was heated at 130 °C (bath temperature) under nitrogen for 3 h. The mixture was washed with hexane (20 ml) to leave 20 mg of unchanged **8**. From the hexane washing 0.11 g (73%) of **9** was obtained.

ii) A solution of **8** (80 mg) in benzene (20 ml) was stirred with NEt_3 (3 drops) at room temperature for 6 h. After the reaction mixture was evaporated *in vacuo* below 40 °C, a similar treatment of the residue with hexane gave 50 mg (62.5%) of **9**.

Isomerization of Cyclohepta[de]*naphthalenol (9) to Dihydrocyclohepta*[de]*naphthalene (8).* A solution of **9** (0.5 g) in MeOH (50 ml) was stirred with hydrochloric acid (1 drop) at room temperature for 7 days. The reaction mixture was poured into water, and extracted with $CHCl_3$. The extract was washed with water, dried over Na_2SO_4, and evaporated *in vacuo*. A similar treatment of the residue with hexane gave 0.15 g (30%) of **8**, together with recovery of **9** (0.3 g).

References

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2) G. A. Berchtold and G. F. Uhlig, *J. Org. Chem.*, **28**, 1459 (1963); K. C. Brannock, R. D. Burpitt, V. W. Goodlett, and J. G. Thweatt, *ibid.*, **28**, 1464 (1963); K. C. Brannock, R. D. Burpitt, V. W. Goodlett, and J. G. Thweatt, *ibid.*, **29**, 818 (1964).