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Novel Dimerization of 3-(2-Nitroethenyl)guaiazulene. A Convenient Route to Cyclopenta[ef]heptalene

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Dimerization of 3-(2-nitroethenyl)guaiazulene with sodium methylate gave 5-(1-guaiazulenyl)-5,6-dihydro-9-isopropyl-1-methyl-4-nitrocyclopenta[ef]heptalene (**3**). On treatment with formic acid, **3** was converted into 9-isopropyl-1-methyl-4-nitrocyclopenta-[ef]heptalene quantitatively. A combination of the reactions provides a convenient route to the cyclopenta[ef]heptalene derivatives.

Cyclopenta[ef]heptalenes (aceheptylenes) have drawn attention due to their unique properties to selectively absorb laser, which are required for data medium of optical recording disk.[1] A series of the compounds was synthesized by introducing a suitable C_3-unit between 3-position and 4-methyl group of 4,6,8-trimethylazulene in order to build up a seven-membered ring.[2-6] These methods need special reagents and/or involve many reaction steps. Recently, it was found that the reaction of 3-formylguaiazulene (**1**) with 3-(2-acylethenyl)guaiazulene afforded 5,6-dihydro-aceheptylenes, one of which was converted into an aceheptylene derivative in a low yield.[7] Herein we describe a simple and convenient synthetic method of 9-isopropyl-1-methyl-4-nitroaceheptylene (**4**), which is attained by treating 3-(2-nitroethenyl)guaiazulene (**2**) successively with base and acid.

The reaction of **1** with nitromethane for 4 h in the presence of piperidine[8] yielded **2** (49%), **4** (0.4%) and the 5-(1-guaiazulenyl)-5,6-dihydro derivative (**3**) (17%). The new compounds **3** and **4** were characterized by spectral data and elemental analyses (Table 1). The use of piperidine - acetic acid (1 : 1, volume ratio) as the base[9] led to the better yield of **2** (60%). Then, **3** (50%) was obtained by stirring **1** and **2** (1 : 1, mole ratio) in piperidine for 24 h at ambient temperature. Formally it seemed that **3** was formed either by the addition of both 3-formyl and 4-methyl groups of **1** to the nitroethenyl double bond of **2** or by linking 3-nitroethenyl and 4-methyl groups of **2** to formyl carbon of **1**. However, this speculation was denied since the treatment of **2** with bases such as piperidine and sodium methylate also gave **3** (Table 2). Further, the base-catalyzed dimerization of **2** was facilitated by

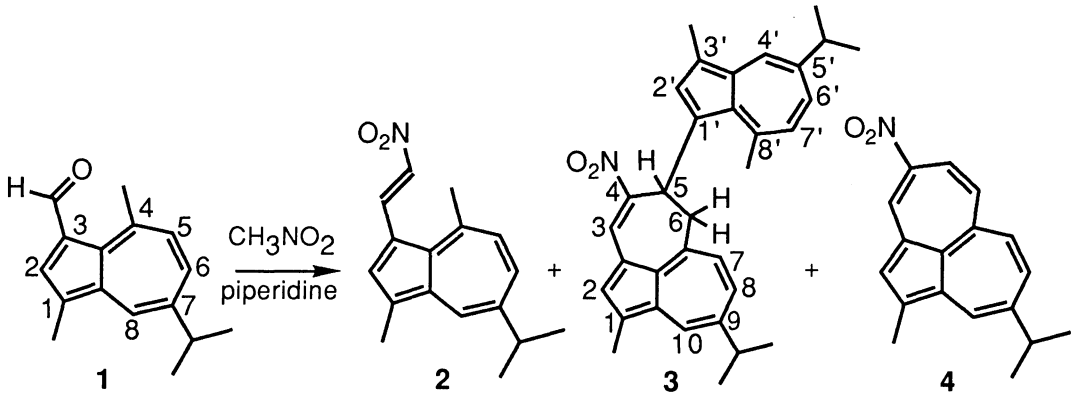


Table 1. Selected Physical Data and Elemental Analyses of **3** and **4**

3: Violet crystals, mp 118 - 119 °C; IR ($CHCl_3$) 1280 and 1500 cm^{-1} (NO_2).
Found: C, 82.90; H, 7.40; N, 2.94%; M^+, 477.2661. Calcd for $C_{33}H_{35}NO_2$: C, 82.98; H, 7.39; N, 2.93%; M^+, 477.2666.

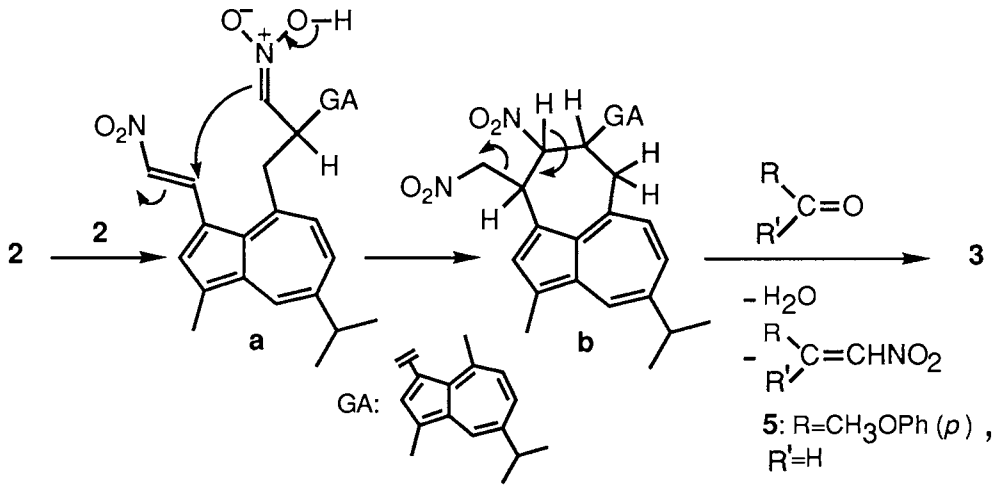
4: Violet crystals, mp 209 - 210 °C; IR ($CHCl_3$) 1260 and 1287 cm^{-1} (NO_2).
Found: C, 77.14; H, 6.04; N, 4.96%; M^+, 279. Calcd for $C_{18}H_{17}NO_2$; C, 77.40; H, 6.13; N, 5.01%; M^+, 279.

addition of methyl ketones giving **4** as a major product (Table 2). Acidity of 4-methyl protons of **2** would be enhanced by the nitroethenyl group, so that the methyl group could, in the presence of the base, have enough reactivity to add to the nitroethenyl double bond of another molecule of **2** to afford **a** (Scheme 1). Subsequent intramolec-

Table 2. Effect of Carbonyl Compounds on Dimerization of **2**

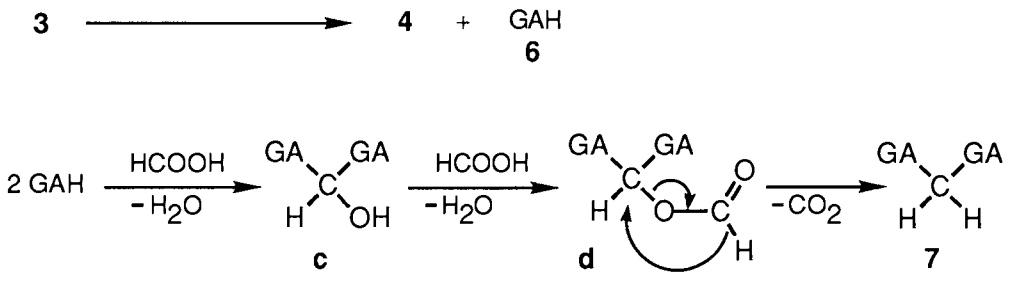
Carbonyl compound	Base	Time/h	Yield/%	
			3	**4**
——	Piperidine	72	6	——
$(CH_3)_2NCHO$	Piperidine	72	4	——
——	$NaOCH_3$	5	31	——
Benzaldehyde	$NaOCH_3$	24	37	——
$(CH_3)_2CO$	$NaOCH_3$	3	23	32
$CH_3COCH_2COCH_3$	$NaOCH_3$	24	24	41

ular 1,4-addition of the α-nitromethylene to the nitroethenyl group gives **b**, from which nitromethane is eliminated to yield **3**. The latter reaction should be assisted by the intermediation of carbonyl compounds. This process was proved by isolation of 2-(4-methoxyphenyl)-1-nitroethene (**5**)[10] (1%), in addition to **3** (0.1%) and **4** (0.3%), when **2** was reacted with *p*-anisaldehyde for 24 h using potassium hydroxide as the base. Moreover, **3** may be deprotonated by the enolate of methyl ketones to afford **4** with the elimination of guaiazulenide (Table 2).



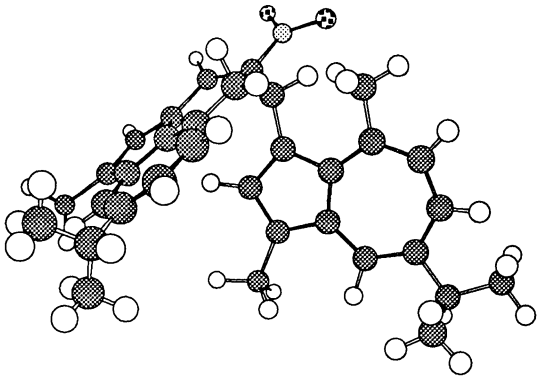
Scheme 1.

DDQ treatment or pyrolysis of a dihydroaceheptylene derivative has been reported to form corresponding aceheptylene in 3 and 33% yields, respectively.[7] In the case of **3**, the production of **4** and guaiazulene (**6**) was observed by treatment of **3** with acids such as 85% phosphoric acid, trifluoroacetic acid, perchloric acid, *etc.* The best result was noted in the reaction of **3** with formic acid for 2 h, which yielded **4** (90%) and 3,3-methylenebis(guaiazulene) (**7**)[11] (93%) without formation of **6**. The production of **7** is explained in Scheme 2, where two molecules of **6** formed from **3** were reacted with formic acid, followed by esterification and decarboxylation.



Scheme 2.

Facile decomposition of **3** would be attributed to its conformation. When ^1H NMR of **3** was compared with that of **6**, a large deviation of chemical shifts (δ [**3**-**6**]) was observed in 2'-H (-0.96 ppm) and 3'-CH_3 (-0.52 ppm) toward up-field, and in 7'-H (0.11 ppm) and 8'-CH_3 (0.57 ppm) to down-field. The deviation was well interpreted by the conformation **e**, which was also supported by a MM2 calculation.



e

The guaiazulene moiety of **e** is almost perpendicular to the dihydroaceheptylene skeleton, and a mutual repulsion between them may not be negligible. It explains the reason why elimination of **6** occurs from **3** so easily.

A combination of dimerization and elimination enables a simple and convenient access to **4**. In a typical experiment, a solution of **2** in acetone was mixed with 10 equivalents of sodium methylate in methanol, and the mixture kept for 3 h at ambient temperature. After removal of the solvent, a large excess of formic acid was added with ice-cooling, and the mixture stirred for 2 h at ambient temperature. The reaction mixture was diluted with ice-water, taken up in chloroform, and submitted to silica-gel chromatography (benzene) yielding **4** (50%). Extension of the present study to other 3-ethenylguaiazulene system is in progress in our laboratory.

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