

A New Synthesis of Semibullvalenes *via* Photodecarbonylation of Norsnoutanones

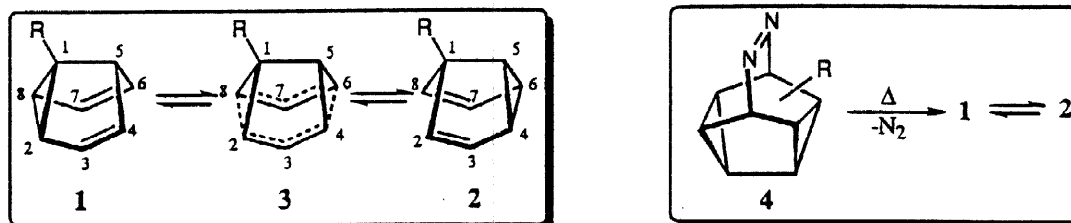
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Abstract: A new and simple approach to C1(5) monosubstituted semibullvalenes from 4-substituted pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonan-9-ones (norsnoutanones) *via* photo-mediated cheletropic ejection of CO is reported. © 1998 Elsevier Science Ltd. All rights reserved.

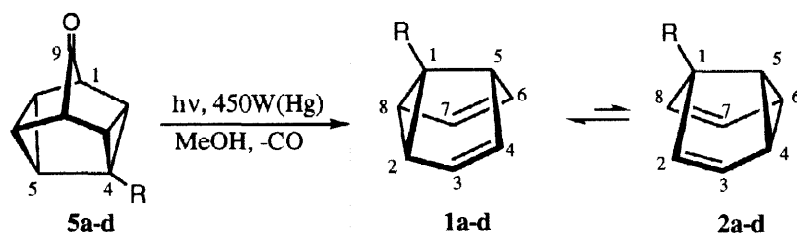
Key words: Photochemistry; Cheletropic reactions; Decarbonylation; Polycyclic aliphatic compounds.

Semibullvalene **1** continues to arouse intense interest among organic chemists, ever since its first preparation by Zimmerman *et al.*¹ in 1966, primarily on account of the low barrier to the degenerate Cope rearrangement in it and the experimentally verifiable theoretical predictions that substitution or annulation can exert profound equilibrium influences (**1** *vs* **2**), to the extent that the delocalized bishomoaromatic transition state **3** can become an energy minima.² In depth study of the dynamical behaviour of **1** necessitated ready and regiospecific access to its mono- and multi-functionalized derivatives and a variety of synthetic routes to the semibullvalene nucleus have been developed.³ Among these, the approach based on the ejection of nitrogen from diazasnoutenes **4** is the most versatile for the preparation of monofunctionalized **1**.^{3c,d} However, this strategy failed to install efficient electron acceptor groups like cyano and carboalkoxy at the key C1(5) position and recourse had to be taken to a more circuitous route emanating from barrelene.^{3g} We report here a new, simple and general route to monofunctional derivatives of **1**, including those bearing electron acceptor groups like cyano and carboalkoxy, via the cheletropic ejection of CO from 4-substituted 9-norsnoutanones **5a-d**, under photo-irradiation regime. This seemingly obvious and straightforward approach to **1** became feasible in view of our recent synthesis⁴ of diverse 4-substituted 9-norsnoutanones from the readily available homocubanone derivatives.



Irradiation of methanolic solution of pentacyclic ketones **5a-d**,^{4,5} through a 450W medium pressure lamp, in a quartz reaction vessel, resulted in smooth decarbonylation to deliver semibullvalenes **1a-d** \rightleftharpoons **2a-d** respectively, in good yield, Table.⁶ In each case, formation of small amounts (>10%) of the corresponding cyclooctatetraene was also observed^{3c}. The ¹H NMR spectral data, summarized in the Table, in conjunction with the COSY derived coupling constants, indicated that

valence isomers **1a-d** with the substituent residing on cyclopropane C1 dominated the equilibrium **1a-d** \rightleftharpoons **2a-d** in all the cases^{3d,g}.



Table

Starting Material	Product ^a (yield %) ^b	Irradiation Time	¹ H NMR Data ^c			
			H ₅	H _{2,8}	H _{3,7}	H _{4,6}
5a R=COOCH ₃	1a \rightleftharpoons 2a (72)	3h	3.69	3.50	5.18	5.80
5b R=CN	1b \rightleftharpoons 2b (65)	1h	3.54	3.49	5.21	5.73
5c R=Phenyl	1c \rightleftharpoons 2c (70)	1h	3.42	3.52	5.31	5.52
5d R=CH ₂ OCH ₃	1d \rightleftharpoons 2d (60)	50 min.	3.12	3.43	5.19	5.19

(a) Products were purified by column chromatography (SiO₂-gel). (b) Yields based on recovery of starting material. (c) ¹H NMR spectra were recorded at 200 MHz in CDCl₃.

In summary, we have presented a new and convenient route of general utility to C1(5) monosubstituted semibullvalenes through light-mediated cheletropic ejection of CO from nornorsnoutanones.⁷

References & Notes

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- 4-Phenylnorsnoutanone **5c** was prepared from nornorsnoutanone carboxylic acid⁴ via decarboxylative arylation with Pb(OAc)₄ in benzene.
- While **1b-d** \rightleftharpoons **2b-d** have been prepared earlier,^{3d,g} **1a** \rightleftharpoons **2a** are reported here for the first time. The ¹H NMR spectral data for **1b-d** \rightleftharpoons **2b-d** recorded here are in agreement with reported values.
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