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2-ETHYNYLINDENE BY REARRANGEMENT OF 2-VINYLIDENE-2H-INDENE AND 2-INDENYLVINYLIDENE

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Summary: 2-Ethynylindene is obtained by flash vacuum pyrolysis of naphtho[b]cyclopropene and 4-(2-indenylmethylidene)-3-methylisoxazol-5-(4H)-one

Studies on the thermal chemistry of benzocyclopropenes have been limited to the parent compound which, on flash vacuum pyrolysis above 500° gives fulvenallene (1) in good yields.[1] At higher temperatures (1) rearranges in part to ethynylcyclopentadienes (2).[2] 1 is also the major high temperature product of phenylcarbene and other C_7H_6 precursors.[2] Since the yields of 2 are generally

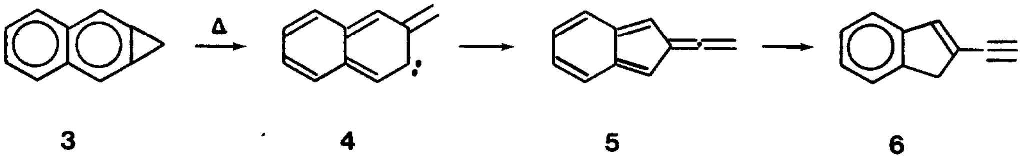
1 2

low, and 1 and 2 cannot be separated, an isolation of pure 2 has never been reported. The fact that 2 exists as a mixture of two isomers makes its identification even more tenuous.

We now wish to report the first isolation and unambiguous characterization of an acetylene in a rearrangement of this kind.

By analogy with the reaction shown above, naphtho[b]cyclopropene (3) was anticipated to generate 2-vinylidene-2H-indene (5). However, isoindene derivatives are generally unstable: 2,2-dimethylisoindene has been matrix isolated and characterized,[3] but simple isobenzofulvenes have till now resisted direct spectroscopic observation.[4] It could be expected, therefore, that 5 would be highly unstable compared with its 2-ethynylindene isomer (6).

Naphtho[b]cyclopropene[5] (3) was flash pyrolysed at 700°/10^{-3} Torr, using the apparatus previously described.[6] The products were collected in a liq. N_2 trap and then examined by infrared spectroscopy at -78°. The IR spectrum showed an intense absorption at 1950 cm^{-1}, typical for allenes, which indicates the presence of compound 5, formed by a Wolff-type rearrangement[2] of the carbene 4.

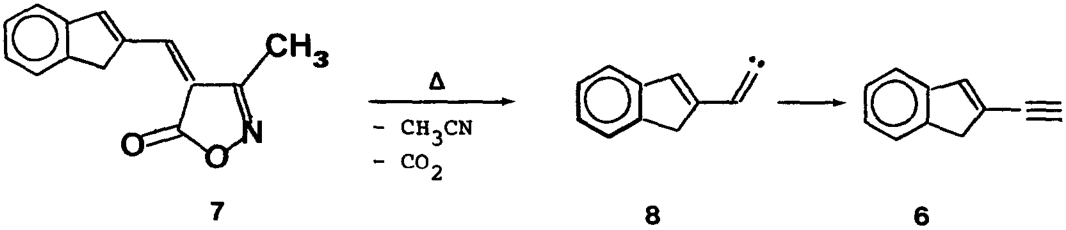


A medium absorption at 2110 cm^{-1} and a strong one at 3320 cm^{-1}, corresponding to the acetylene 6, were also present. While it was not possible to isolate the allene component, column chromatography ($SiO_2/CHCl_3$) furnished the acetylene (6) in 20-25% yield (IR (film): 3300 (C≡C-H), 2110 (C≡C), 1465, 1400, 875, 760, 720, 615 cm^{-1}; ^1H-NMR ($CCl_4/(CD_3)_2CO$): δ 3.30 (s, 1H), 3.51 (dd, J=1.5 and 0.3 Hz, 2H (indene-CH_2)), 7.0-7.8 (m, 5H); MS: m/e 140 (M^+, 100%), 139 ($(M-1)^+$, 78%)).

Since 6 is a new compound, an independent synthesis was desirable. Flash pyrolysis of 4-arylmethylideneisoxazol-5(4H)-ones is known to produce arylvinylidenes which efficiently isomerise to arylacetylenes.[7] The required 4-(2-indenylmethylidene)-3-methylisoxazol-5(4H)-one (7) was prepared in 95.5%

yield by stirring 300 mg of inden-2-al together with 200 mg of 3-methylisoxazolone and one drop of piperidine in 50 ml dry $CHCl_3$ under N_2 for 24 h at room temperature. 7 (yellow crystals, mp 187-188°) had IR (KBr): 1730, 1610, 1590, 1520, 1380, 1105, 1000, 875, 765 cm^{-1}; ^1H-NMR ($CDCl_3$): δ 2.1 (s, 3H), 4.1 (m, 2H), 7.3-7.7 (m, 5H), 7.8 (m, 1H); MS: m/e 225 (M^+, 100%); and correct elemental analysis.

Due to the low volatility of 7, a normal flash vacuum pyrolysis gave only low yields of 6, the major part of 7 decomposing before subliming.
However, a 60% yield of 6 (determined by NMR) was obtained by allowing powdered 7 to drop slowly into a vertical quartz pyrolysis tube (30 x 2 cm) fitted with a loose plug of quartz wool 10 cm below the top of the heated zone. The lower end of the tube led directly into a U-shaped cold trap, thus providing a very short path between hot and cold zones. In this manner, 1.5 g of 7 was pyrolysed at 685° at a pressure varying between 0.01 and 1 Torr in the course of 1 h. The crude pyrolysate was distilled at 100°/0.08 Torr, and then separated by preparative gas chromatography (3m x 6 mm Apiezon M column at 130°)



The following products were identified by their retention times, ^1H-NMR, IR, and mass spectra: indene, naphthalene, 2-methylindene, and 2-ethynylindene (6) (relative area by GC: 0.25:0.20:0.15:1.0). The isolated 6 had spectral properties in complete agreement with the sample obtained above by pyrolysis of 3.

In conclusion, the pyrolysis of 7 constitutes a viable synthesis of acetylene 6. 6 is the thermodynamically most stable of the $C_{11}H_8$ isomers 3, 4, 5, 6, and 8. Further work aimed at a complete characterization of the allene 5 will be reported in due course.

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