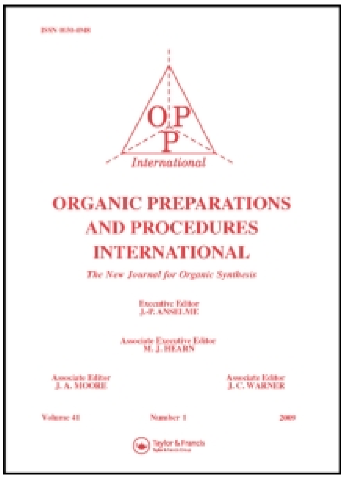

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

3-NITRO-1,3,5-HEXATRIENE

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To cite this Article Spangler, Charles W. and Hennis, Ronald P.(1970) '3-NITRO-1,3,5-HEXATRIENE', Organic Preparations and Procedures International, 2: 1, 75 — 78

To link to this Article: DOI: 10.1080/00304947009458424

URL: http://dx.doi.org/10.1080/00304947009458424

ORGANIC PREPARATIONS AND PROCEDURES 2(1), 75-78 (1970)

3-NITRO-1,3,5-HEXATRIENE[1]

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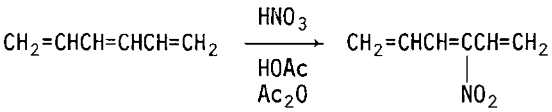

$$CH_2{=}CHCH{=}CHCH{=}CH_2 \xrightarrow[\substack{HOAc\\ Ac_2O}]{HNO_3} CH_2{=}CHCH{=}\underset{\substack{|\\ NO_2}}{C}CH{=}CH_2$$

The chemistry of 1,3,5-hexatriene, which can be considered to be the open chain π-electron analog of benzene, has been studied extensively during the past few years. Woods and coworkers[2] had reported earlier an apparent electrophilic nitration of 1,3,5-hexatriene, but were unable to determine the position or positions of attack in the "nitrohexatriene" product. Their structural assignment was based entirely on a carbon-hydrogen analysis and the similarity of the ultraviolet spectrum to that of nitrobenzene. Since many structures can be envisaged for an empirical formula of $C_6H_7NO_2$, most of which could correspond to the observed ultraviolet spectrum, their assignment must be considered to be very tenuous.

Nitration was accomplished in a mixture of concentrated nitric acid, acetic acid and acetic anhydride, and the highly unstable product isolated by a combination of steam and vacuum distillations. Infrared analysis and comparison to a spectrum of authentic 1,3,5-hexatriene was consistent with nitro substitution in a highly conjugated system. Nmr analysis was consistent with substitution at the three position by an electronegative grouping compared to both 1,3,5-hexatriene and 3-methyl-1,3,5-hexatriene. Continuous nmr monitoring of the reaction mixture for a twenty-four hour period showed initial and continuous substitution on the interior carbon skeleton as opposed to the terminal carbons. Reduction of a pentane solution of nitrohexatriene in a Parr apparatus in the presence of Adams catalyst, followed by acid extraction and neutralization, yielded 3-aminohexane as the main hydrogenation product.

We conclude on the basis of this evidence that nitration of 1,3,5-hexatriene yields 3-nitro-1,3,5-hexatriene as the primary product. As such, this represents an exception to the general theory of acyclic polyene substitution reactions; for example, Fukui and coworkers predict on the basis of the "Frontier electron" method that 1,3,5-hexatriene should undergo electrophilic substitution (nitration) exclusively at the 1-position[3].

Experimental[4]

Nitric acid (4.1 g, 0.065 mole) was added dropwise to a solution of 1,3,5-hexatriene[5] (5.0 g, 0.0625 mole), acetic acid (60 ml) and acetic anhydride. The temperature was maintained below 40°. After the solution had stood at room temperature for 0.5 hour, it was added dropwise to a flask from which steam distillation was in progress. The pale yellow distillate was saturated with salt and extracted with pentane. The pentane solution was washed with $NaHCO_3$ solution and dried with anhydrous $MgSO_4$. Distillation at reduced pressure yielded a highly unstable yellow liquid[6] (1 g) b.p. 46-52° (1 mm), λ_{max} (isooctane) 302 mμ [lit.[2] λ_{max} (ethanol) 305 mμ b.p. 60-70° (6mm)] ir 6.65 and 7.55μ (conj $-NO_2$), nmr compared to both 1,3,5-hexatriene and 3-methyl-1,3,5-hexatriene:

$C_6H_7NO_2$	τ	3.95 - 4.8	(m, 4H, $CH_2=$)
	τ	2.3 - 3.6	(m, 3H, $-CH=CH-$)
C_6H_8	τ	4.6 - 5.1	(m, 4H, $CH_2=$)
	τ	3.35 - 4.0	(m, 4H, $-CH=CH-$)
$(3\text{-}CH_3)\ C_6H_7$[7]	τ	4.6 - 5.1	(m, 4H, $CH_2=$)
	τ	2.8 - 4.15	(m, 3H, $-CH=CH-$)
	τ	8.15	(s, 3H, CH_3-)

Nitro-1,3,5-hexatriene (ca. 1g) was dissolved in 250 ml of pentane and mixed with 0.5 g Adams catalyst. Reduction was carried out in a Parr apparatus and was essentially complete after 2 hours. The clear, colorless solution had an ammonia-like odor. After removal of the catalyst by filtration, the amine was extracted by washing the pentane solution several times with small portions of dilute HCl (3N). The combined HCl extracts were then neutralized with NaOH and the liberated amine extracted in pentane. The bulk of the pentane was removed by fractional distillation and the residue submitted to glpc which revealed the presence of essentially one component (plus residual pentane, ca. 50-60% recovery of the theoretical yield of aminohexane). This was shown to be 3-aminohexane by comparison to a known mixture of the three isomeric aminohexanes.[8]

In one reduction carried out under identical conditions, a small quantity of n-hexylamine was also obtained (3-NH_2: 87%, 1-NH_2: 13%). This product was obtained from a large scale nitration-hydrogenation process (10 g 1,3,5-hexatriene); however n-hexylamine has never been observed as a final product in the small scale (5 g 1,3,5-hexatriene or less) sequence.

3-Nitro-1,3,5-hexatriene is a highly unstable substance, and is especially labile to both polymerization and thermal decomposition. It can be stored for periods up to 24 hours at 0° in dilute ($< 1\%$) pentane solution in the presence of hydroquinone. Glpc analysis of a freshly prepared sample indicates a probable mixture (9:1) of geometric or positional isomers. At this time however assignment of isomeric identity is not possible.

Aliquots taken from a nitration reaction mixture identical to the one described above (from 5 g 1,3,5-hexatriene) were continuously monitored by nmr for a twenty-four hour period. The progress of nitration could be followed by observing the disappearance of the intense triplet portion of the τ3.35-4.0 1,3,5-hexatriene multiplet (assigned to the -CH=CH- protons). The rapid disappearance of this absorption (totally absent in 3-nitrohexatriene) indicates that initial attack occurs at the 3-position, as does comparative integrations (3 interior : 4 terminal protons).

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1. Support of this research by Research Corporation is gratefully acknowledged.
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4. Gas-liquid partition Chromatography was performed with an Aerograph Model 202-1B dual column instrument. Ultraviolet spectra were obtained with a Bausch and Lomb Model 505 Spectrophotometer, infrared spectra with a Beckman IR-8. Nmr spectra were obtained with a Varian A60-A spectrometer using TMS (τ= 10) as an internal standard ($CDCl_3$ solvent).

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6. A reliable refractive index was not obtained due to the extreme rapidity of polymerization of a thin film.

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8. Identical retention times as determined with a Hewlett-Packard Model 3370-A electronic integrator on both 6'-15% Carbowax 20M-on-60/80 mesh Chromosorb W and 6'-15% SE-30-on-60/80 mesh Chromosorb W columns both as separate samples and upon admixture of authentic 3-aminohexane sample. Both the 2-amino and 1-amino hexanes are well separated and distinguishable on these columns.

(Received October 20, 1969)