5-Nitro-6-substituted-2-norbornenes: determination of Diels-Alder isomer ratios from nuclear magnetic resonance spectra

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Received July 31, 1967

The nuclear magnetic resonance spectra of representative 5-nitro-6-substituted-2-norbornenes (II–VII) are described. From the spectra, ratios of the two possible *endo–exo trans* stereoisomers derived from the Diels–Alder reaction of cyclopentadiene with the appropriate *trans* nitroölefin are estimated as shown in Table II. For all cases, there was predominance (3:1 to 9:1) of the 5-*endo*-nitro *trans* stereoisomer. The synthesis of the 6-(*p*-nitrophenyl) (V), 6-(2-furyl) (VI), and 6-(2-thienyl) (VII) derivatives is reported and the 6-ethyl derivative (III) has been characterized.

Canadian Journal of Chemistry. Volume **45**, 2969 (1967)

Roberts, Lee, and Saunders (1) noted that the Diels–Alder adduct (I) of cyclopentadiene and nitroethylene was a mixture of *endo-* (I*a*) and *exo-* (I*b*) nitro stereoisomers, which they suggested might contain > 90% of the *endo*-nitro stereoisomer. Fraser (2) subsequently deduced from the nuclear magnetic resonance (n.m.r.) spectrum that the adduct is the 5-*endo*-nitro isomer (I*a*). His published spectrum is that of a pure isomer and he made no mention of the presence of another stereoisomer. Ouellette and Booth (3) showed that under alkaline equilibration conditions the ratio of I*a* to I*b* was 0.64 at 75°. The two isomers could be separated cleanly by preparative vapor phase chromatography (v.p.c.) on a 20 ft 30% SE-30 column, with the 5-*endo*-nitro stereoisomer (I*a*) having the longer retention time. The ratio of stereoisomers present in the original Diels–Alder adduct (I) was not reported.

Van Tamelen and Thiede (4) showed by a series of degradative experiments that the adduct (II, an oil) of cyclopentadiene and 1-nitropropene contains an *exo*-methyl and an *endo*-nitro group, thus accounting for the stereochemistry of the major isomer (II*a*) in what is now seen to be a mixture of *trans* stereoisomers. Poos and co-workers (5) showed the adduct (IV, also an oil) of cyclopentadiene and *trans*-β-nitrostyrene to be a 3:1 mixture of the 5-*endo*-nitro-6-*exo*-phenyl (IV*a*) and 5-*exo*-nitro-6-*endo*-phenyl (IV*b*) *trans* stereoisomers. We have essentially confirmed this observation by analysis of the n.m.r. spectrum of the mixture, which indicates a 4:1 mixture of the two stereoisomers. Because of the anticipated reversal of the Diels–Alder reaction at the high temperatures required for v.p.c. analysis (which we have confirmed does occur), Poos and co-workers (5) carried out the analysis by v.p.c. on the hydrogenated nitro derivatives and their corresponding amine reduction products, which were characterized as crystalline benzenesulfonamide derivatives. At about the same time, Weinstock and co-workers (6) also proved, by another series of degradative experiments, that IV*a* is the major component of the adduct IV. The adduct of cyclopentadiene and *cis*-β-nitrostyrene has also been reported to be an oil (7) but nothing was said about the ratio of the two possible *endo-* or *exo*-5,6-*cis* stereoisomers present in the oil.

The preparation and a reaction of 6-ethyl-5-nitro-2-norbornene (III) are described in a patent by Weinstock (8), but no analyses or physical properties are reported. We have obtained the compound

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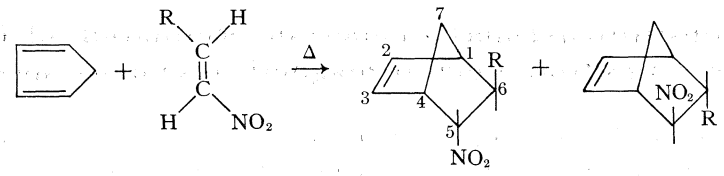
[1]Taken in part from the *summa cum laude* senior thesis of J. W. Manthey, June 1964.
[2]Students in the advanced organic chemistry laboratory course at the University of Minnesota, winter quarter 1965.
[3]Taken in part from senior thesis research of G. L. Eian, winter quarter 1965.



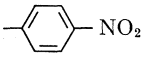
endo-nitro series, I*a*–VII*a* *exo*-nitro series, I*b*–VII*b*

I*a*, *b* R = H

II*a*, *b* R = CH_3

III*a*, *b* R = CH_2CH_3

IV*a*, *b* R = 

V*a*, *b* R = 

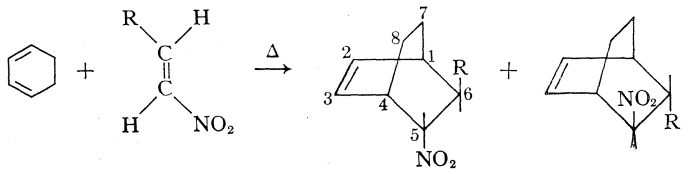
VI*a*, *b* R = 

VII*a*, *b* R = 

from 1-nitro-2-butyl acetate by the *in situ* method (9) for generating the nitroölefin, which was also employed for preparation of the 6-methyl derivative (II). Analysis of the n.m.r. spectra of the 6-methyl (II) and 6-ethyl (III) derivatives shows the ratio of major (II*a*,III*a*) to minor (II*b*, III*b*) stereoisomers to be about 9:1 and 6:1 in the two cases (see Table II). With the only solid adduct examined in the present work, the 6-(*p*-nitrophenyl) derivative (V), the ratio of the major (V*a*) to minor (V*b*) stereoisomers was the lowest observed, 3:1. With the 6-(2-furyl) (VI) and 6-(2-thienyl) (VII) derivatives, which were prepared in a manner similar to the 6-phenyl (IV) and 6-(*p*-nitrophenyl) (V) derivatives, the corresponding ratios were 6:1 in both cases. Attempted reaction of 3-(2-nitrovinyl)indole with refluxing cyclopentadiene was unsuccessful. Apparently, this was due to the lower electrophilicity of the nitroölefin and its greater steric requirements. Solid nitroölefin partially dissolved in refluxing cyclopentadiene, but when reflux was continued until all of the cyclopentadiene had dimerized, the solid crystallized out upon cooling and was recovered unchanged in quantitative yield.[4]

The oily Diels–Alder adducts of cyclopentadiene and nitroölefins are exceedingly difficult to free from some impurities (eg. dicyclopentadiene). The adducts II and III derived from the lower aliphatic nitroölefins tend also to be contaminated with diphenyl ether carried along through the nitroacetate from the original co-distillation (10) of the nitroalcohol with diphenyl ether. The adducts IV, VI, and VII derived from β-nitrostyrene and the heterocyclic nitroölefins tend to be contaminated with the nitroölefin, which accounts for the ultraviolet absorption in the 309 mμ (log ε 4.22 for β-nitrostyrene) (11) or 345–350 mμ regions (for the heterocyclic nitroölefins). This probably also accounts for most of the yellow color of the oils since the nitroölefin ultraviolet absorption tails into the visible region. Poos and coworkers (5) have noted that a sample of the adduct IV containing 5.8% β-nitrostyrene was freed of the β-nitrostyrene by two careful fractionations through a jacketed column with removal of the head fractions. Our experience with the adducts from β-nitrostyrene and the heterocyclic nitroölefins suggests that dissociation of these higher molecular weight adducts into the starting components seems to occur more rapidly at the high pot temperatures normally employed for vacuum distil-

[4]This experiment was performed by Patrick G. McCormick at the University of Minnesota.



endo-nitro series VIII*a* and IX*a*

exo-nitro series, VIII*b* and IX*b*

VIII*a*, *b* R = H

IX*a*, *b* R = C_6H_5

lation, just as it contributed to the failure to separate by v.p.c. the stereoisomeric adducts of IV*a* and IV*b*.

The Diels–Alder reaction of nitroethylene with 1,3-cyclohexadiene gives an adduct, 5-nitrobicyclo[2·2·2]oct-2-ene(VIII), in 33% yield (12). The Diels–Alder reaction of β-nitrostyrene with 1,3-cyclohexadiene, without added solvent, is also reported to give, in 20 (reference 13) – 25 (reference 14) % yield, an adduct, 5-nitro-6-phenylbicyclo[2·2·2]oct-2-ene (IX), which was characterized solely by boiling point and satisfactory elemental analytical data. Under the conditions we tried, we were unable to confirm this report.[5] In our hands, refluxing a solution of β-nitrostyrene (60 g, 0.40 mole) in 1,3-cyclohexadiene (40 g, 0.50 mole) at 84–85° (bath temperature) for 6 h gave only unchanged 1,3-cyclohexadiene (30 ml, 63% recovery), n_D^{22} 1.4712, and β-nitrostyrene (58 g, 97% recovery), b.p. 138–140° at 1 mm, isolated as yellow crystals in the condenser, which were identified by their melting point and mixture melting point, 55–56°, and infrared spectrum in Nujol. The pot residue did not exceed 5 ml. As might be anticipated, since 1-nitropropene is more sterically hindered than nitroethylene and would be expected to be less electrophilic than β-nitrostyrene, the attempted Diels–Alder reaction of 1-nitropropene, when used either directly or when generated *in situ* (15) from 1-nitro-2-propyl acetate, with refluxing 1,3-cyclohexadiene gave no product which could be identified as a Diels–Alder adduct (16).

The stereochemistry of 1-nitropropene, a liquid, was determined by van Tamelen and Thiede (4) to be *trans* on the basis of the stereochemistry of the predominant stereoisomer of its adduct with cyclopentadiene (II*a*), as noted previously. The stereochemistry of 1-nitrobutene, which is also a liquid, is assumed to be *trans* by analogy with 1-nitropropene and β-nitrostyrene. The normal, crystalline form of β-nitrostyrene is known to have the *trans* configuration from dipole moment studies (17) and the stereochemistry of its Diels–Alder adduct with 1,3-butadiene (18). The coupling constants for the vinyl protons in the n.m.r. spectra of crystalline β-nitrostyrene (14 Hz), 2-(2-nitrovinyl)-furan (13.5 Hz), and 2-(2-nitrovinyl)thiophene (13.5 Hz) also indicate that these nitroölefins have the *trans* configuration. Dailey and Shoolery (19) have shown that there is a linear relationship between the electronegativity (E) of a substituent in an ethane, and the difference in chemical shift (ΔCH_3–ΔCH_2) between the methyl and ethyl protons of the ethyl group. Thus, for nitroethane E_{NO_2} = 0.02315(91 Hz) + 1.71 = 3.82. Banwell, Sheppard, and Turner have shown (20, 21) for substituted ethylenes that the vicinal proton coupling constants J_{trans} and J_{cis} are related to the difference in electronegativity (ΔE) between the electronegative substituent (in

[5]Higher temperatures and a much longer retention time are apparently required. Prof. C. F. H. Allen, now at the Rochester Institute of Technology, has kindly provided the following statement: "The best conditions for bringing about the adduct formation from cyclohexadiene and β-nitrostyrene were as follows. A mixture of 15 g of the hydrocarbon and 25 g of the nitro compound was heated at 100° for 5 days and distilled at 3 mm. Three cuts, totalling 17 g, were made up to 159° ····· these were mainly β-nitrostyrene. The pay cut, b.p. 159–163°, amounted to 11.5 g. Thank you for noting the error in giving the wrong boiling point (reported for the product, b.p. 138–142° at 1 mm (13, 14)); we agree with yours on the β-nitrostyrene."

TABLE I

Chemical shifts and multiplicities of the 5-and 6-protons in the n.m.r. spectra of 5-nitro-6-substituted-2-norbornenes*

	Major (*a*) stereoisomer		Minor (*b*) stereoisomer	
Compound	5-*Exo*	6-*Endo*	5-*Endo*	6-*Exo*
II	5.43t	7.93‡	6.19cm	7.20cm
	(0.86)	(1.04)	(0.10)	(0.18)
III	5.57t	>7.83§	6.21bp‖	7.13bp‖
	(0.69)	(8.32)§	(0.18)	(0.17)
IV	5.19t	6.63bp¶	5.59f	6.19t
	(0.78)	(1.70)¶	(0.20)	(0.18)
V	4.99t	6.45bp**	5.43f	5.98t
	(0.71)	(1.62)	(0.26)	(0.27)
VI	4.97t	6.63††	5.63‡‡	6.13t
	(0.85)	(0.95)	(0.15)	(0.16)
VII	5.04t	6.47§§	5.66f	5.95t
	(0.85)	(1.80)§§	(0.14)	(0.15)

*Chemical shifts are given as τ values† followed by the multiplicity (bp = broad peak, cm = complex multiplet, f = four-line multiplet, t = triplet). Areas relative to the total number of protons in the molecule (with major and minor stereoisomers grouped as one) are given in parentheses.

†G. V. D. Tiers. J. Phys. Chem. **62**, 1151 (1958); 1τ = 60 Hz (c.p.s.).

‡Broad multiplet; $w_{1/2}$ = 14 Hz.

§An extremely complex pattern from 7.83–9.25 (8.32) must include the 6-*endo* proton of the major stereoisomer as well as the bridge CH_2 and 6-ethyl protons of both stereoisomers.

‖The analysis of the major stereoisomer is clear, but owing to the presence of some impurity peaks of comparable intensity, analysis of the minor stereoisomer peaks is much less certain, though the assignments given are consistent with those reported for the minor stereoisomer of the 6-methyl derivative.

¶Broad multiplet ($w_{1/2}$ = 18 Hz) in which the bridgehead H-4 at 6.52 and the 6-*endo* proton of the major stereoisomer at 6.63 overlap. The area includes both protons.

**Broad multiplet ($w_{1/2}$ = 18 Hz) in which the bridgehead H-4 at 6.32 and the 6-*endo* proton of the major stereoisomer at 6.45 overlap. The area includes both protons.

††A minor multiplet at 6.79 (0.10), possibly attributable to the bridgehead H-1 of the minor stereoisomer, overlaps the very rough triplet ($w_{1/2}$ = 8 Hz) at 6.63 (0.95) due to the 6-*endo* proton of the major stereoisomer.

‡‡Eight-line multiplet.

§§The bridgehead H-4 and the 6-*endo* proton of the major stereoisomer appear as a rough triplet ($w_{1/2}$ = 8 Hz) at 6.47 (1.66), with a small shoulder at 6.60 (0.14). The area includes both protons.

this case NO_2, E = 3.82) and the hydrogen atom (E=2.1 (reference 22)) it replaces by the following equations:

$$J_{trans} = 19(1\text{–}0.17\Delta E) = 13.4 \text{ Hz}$$

$$J_{cis} = 11.7(1\text{–}0.34\Delta E) = 4.9 \text{ Hz}$$

If it is assumed that the phenyl, 2-furyl, or 2-thienyl substituents which have replaced a vinyl proton in the nitroölefins have a negligible effect on the coupling constant, then J_{trans} is in excellent agreement with the observed vicinal coupling constants of the nitroölefins which indicates that they have the *trans* configuration. It was not possible to determine the vicinal coupling constant of the vinyl protons of *p*-β-dinitrostyrene because of overlap between the vinyl and phenyl proton signals, but this crystalline nitroölefin is assumed to have the *trans* configuration by analogy with the stereochemistry of crystalline β-nitrostyrene and the other nitroölefins.

In the n.m.r. spectra of the 5-nitro-6-substituted-2-norbornenes (II–VII), the vinyl proton absorption is centered at τ 3.51–3.84. The highest field signals occur with the 6-methyl (II*a*, τ 3.80) and 6-ethyl (III*a*, 3.84) derivatives, whereas the lowest field signals occur with the 6-(2-thienyl) (VII*a*, 3.55) and 6-(*p*-nitrophenyl) (V, 3.58) derivatives. These compare with values of τ 3.91 (or 3.87)[6] (I*a*) and 3.90 (I*b*) for the 6-unsubstituted case, as estimated from the published n.m.r. spectra (3). In all the cases where the vinyl proton absorption of the minor (5-*exo*-nitro) stereoisomer can be differentiated (I*b* (3), II*b*, III*b*, and VII*b*), it is centered slightly downfield (τ 0.01 (reference 3) – 0.05) from that of the major (5-*endo*-nitro) stereoisomer (I*a* (3), II*a*, III*a*, and VII*a*). The vinyl proton absorption of the homologous 5-nitrobicyclo[2·2·2]oct-2-ene (VIII)

TABLE II

Stereoisomer ratios in the 5-nitro-6-substituted-2-norbornenes

Compound	Stereoisomer % composition		Ratio
	Major (*a*)	Minor (*b*)	
II	90*	11†	9:1
III	78‡	14§	6:1
IV	78‖	19¶	4:1
V	71‖	26¶	3:1
VI	85‖	15¶	6:1
VII	83‡	14§	6:1

*Based on the two vinyl, 5-*exo*, 6-*endo*, and 6-*exo* methyl protons.
†Based on the two vinyl, 5-*endo*, 6-*exo*, and 6-*endo* methyl protons.
‡Based on the two vinyl and 5-*exo* protons.
§Based on the two vinyl, 5-*endo*, and 6-*exo* protons.
‖Based on the 5-*exo* proton.
¶Based on the 5-*endo* and 6-*exo* protons.

appears as a complex multiplet from τ 3.43–4.10, in the same general region as with I.

The electron-withdrawing inductive and field effects of the nearby 5-nitro group are assumed to cause the bridgehead H-4 absorption to occur farther downfield (from τ 6.32 in V to 6.62 in III) than with the relatively remote bridgehead H-1 (which occurs from τ 6.75 in V to 7.43 in II). These compare with values of 6.53 and 7.05 in I*a* (3)[6] and τ 6.75 and 7.09 in I*b* (3). With 5-nitrobicyclo[2·2·2]oct-2-ene (VIII) the corresponding peaks occur at τ 6.72 and 7.29. The absorption due to methylene bridge H-7 is best resolved into a clean AB pattern in the case of the 6-(2-furyl) derivative (VI*a*), although a similar but more compressed pattern is also present in II*a* and VII*a* and probably in the rest of the derivatives as well, although in the 6-phenyl cases (IV, V) there appear to be one or two additional weak downfield peaks. In II*a*, VI*a*, and VII*a* the AB pattern is centered at τ 8.23–8.36, with a geminal coupling constant of 9–10 Hz. The A portion, which appears as two peaks at τ 8.10–8.24, is relatively unsplit, and is attributed to the proton *anti* to the double bond, which is in a favorable position for coupling only with bridgehead H-1 and H-4. Any coupling (< 0.5 Hz) (23) of the *anti* proton with the vinyl protons was not sufficiently marked to be observed under our conditions. The B portion, at τ 8.32–8.49, is hyperfinely split into two four-line multiplets ($J_{1,7\text{-}syn} = J_{4,7\text{-}syn} = J_{6\text{-}endo,7\text{-}syn} = 2$ Hz), and is attributed to the proton *syn* to the double bond because of the presence of long range coupling (23) involving the 6-*endo* proton. The pattern of hyperfine splitting of the upfield half of the methylene bridge absorption is present in the n.m.r. spectra of all the derivatives II*a*–VII*a*.

As shown in Table I, the 5-*exo* proton of the major stereoisomer occurs downfield (from τ 4.97 in VI*a* to 5.57 in III*a*) from the 5-*endo* proton of the minor stereoisomer (from τ 5.43 in V*b* to 6.21 in III*b*). Similarly, the 5-*exo* proton of I*a* occurs at 5.06 (3),[6] whereas the 5-*endo* proton of the epimer I*b* occurs at τ 5.78 (3). The average $\Delta\tau_{5\text{-}endo\text{-}5\text{-}exo}$ for I–VII is 0.61. With the homolog VIII, the 5-*exo* proton of the major isomer (VIII*a*), which appears as a complex multiplet from τ 5.27–5.83, also occurs downfield from the 5-*endo* proton of the minor isomer (VIII*b*), also a complex multiplet, from 5.87–6.13. The downfield *endo* to *exo* shift is also observed with the H-6 in II and IV–VII. Thus, the 6-*exo* proton of the minor stereoisomer appears in the region from 5.95 in VII*b* to 7.20 in II*b*, whereas the 6-*endo* proton of the major stereoisomer appears in the region from τ 6.45 in V to 7.93 in II*a*. The

[6]Fraser (2) reports for I*a* peaks at 3.87, 5.07 6.47, and 7.01. We have arbitrarily used the values for I*a* estimated from the published spectrum of Ouellette and Booth (3) because spectra for both stereoisomers of I*a* and I*b* were available under comparable conditions.

average $\Delta\tau_{6\text{-}endo\text{-}6\text{-}exo}$ for II and IV–VII is 0.53. The downfield *endo* to *exo* shift is also observed with the 6-methyl group, which appears as a doublet (J = 7 Hz), at τ 8.94 (*endo*) in II*b* and τ 8.72 (*exo*) in II*a*, giving a $\Delta\tau_{endo-exo}$ = 0.22. Flautt and Erman (24) have pointed out that the downfield *endo* to *exo* shift in the proton signal, which we have observed with the 5-nitro-2-norbornenes, is a general phenomenon with bornanes, analogous to the axial–equatorial shift in cyclohexanes.

The n.m.r. spectra of the derivatives II–VII were subjected to first order analysis. Coupling of the vinyl and bridgehead H-4 and H-1 gives an ABXY pattern as two four-line multiplets, the B portion of which contains two or three unexplained additional lines[7] in the 6-phenyl derivatives IV and V. Constants for coupling of the bridgehead H-4 and H-1 with the vinyl protons are all about 3 Hz, while the coupling constants for the 2,3-vinyl proton interaction lie in the range of 5–6 Hz. The 5-*exo* protons in II*a*–VII*a* all appear as triplets. This results from the fortuitous equivalence of the coupling constants for the 4,5-*exo* and 5-*exo*, 6-*endo* interactions, which lie in the range of 4–5 Hz. This is in agreement with the coupling constants of 3.9 Hz reported by Fraser (2) for the corresponding interactions involving the 5-*exo* proton in I*a*. In contrast, the 5-*endo* protons, in those cases where sufficient resolution exists (IV*b*, V*b*, and VII*b*), appear as four-line multiplets, resulting from non-equivalence of the coupling constants for the 5-*endo*, 6-*exo* (4–5 Hz) and long range (23) 5-*endo*,7-*syn* (2 Hz) interactions. An apparent exception is the 6-(2-furyl) derivative (VI*b*), in which additional coupling (0.7 Hz; 4,5-*endo* ?) is sufficiently marked so that the usual four-line multiplet for the 5-*endo* proton is hyperfinely split into an eight-line multiplet. In IV*b*–VII*b*, where sufficient resolution exists, the 6-*exo* proton appears as a triplet. This results from the fortuitous equivalence of the coupling constants (4–5 Hz) for the 1,6-*exo* and 5-*endo*,6-*exo* interactions.

[7]Drs. George I. Poos and Harold R. Almond, Jr., of the McNeil Laboratories, Inc., Fort Washington, Pennsylvania (to whom we are indebted for having read and criticized the manuscript) have suggested that allylic couplings ($J_{1,3} = J_{2,4}$ = 0.5 to 1.0 Hz) (23) might account for some of these extra peaks.

EXPERIMENTAL

Melting points were determined on calibrated Fisher–Johns hot stages. Ultraviolet spectra were determined on Cary model 11 or Bausch and Lomb Spectronic 505 spectrophotometers; infrared spectra were determined on Unicam SP.200, Beckman IR5, or Perkin–Elmer model 21 spectrophotometers; and n.m.r. spectra were determined on a Varian Associates A-60 spectrometer. Microanalyses were performed by Dr. T. S. Prokopov and his assistants, George E. Davis, Robert E. Johnson, and Mrs. Kathleen Nelson Juneau at the University of Minnesota.

6-Methyl-5-nitro-2-norbornene (II)

The compound was prepared in 44–59% yield[8] from 1-nitro-2-propyl acetate and cyclopentadiene by the *in situ* method (9) for generation of the nitroölefin according to the procedure of Hart (15). The sample used for n.m.r. analysis had the following properties: pale-yellow oil, b.p. 103–105° at 13 mm, n_D^{23} 1.4884; ν_{NO_2} (neat) 1 540 (strong) 1 380 (medium strong) cm^{-1}; lit. b.p. 94–95° at 15 mm (25), 91.5–92.5° at 11–12 mm (4), and n_D^{21} 1.4871 (4).

1-Nitro-2-butanol

The compound was prepared according to the procedure of Hurd and Nilson (26) except that the reaction solution was warmed in the manner employed by de Montmollin and Achermann (27) and, for reasons of safety, the product was co-distilled with diphenyl ether (28) under reduced pressure, according to the method of Roy (10). Propionaldehyde (100 g, 1.72 moles) was added to a well-stirred solution of nitromethane (181.1 g, 2.96 moles) and water (50 ml). Sodium carbonate was added to keep the solution alkaline to litmus paper. The solution was warmed on a water bath to initiate the reaction and was kept at 60° for 4.5 h. The solution was allowed to cool and was extracted with ether. The ether extract was washed with water, dried over Na_2SO_4, and the ether and excess nitromethane were removed in a rotary evaporator after removal from the drying agent. The resulting oil was co-distilled with diphenyl ether (200 g) under reduced pressure. The distillate, b.p. 63–69° at 0.25–0.5 mm, was extracted with petroleum ether (b.p. 60–68°) to remove most of the diphenyl ether. The lower layer was evaporated in a rotary evaporator to remove dissolved petroleum ether, and a crude colorless oil (183.0 g, 89%), $n_D^{24.2}$

[8]Charles M. Hall, Phillip D. Hammen, and Eng C. Wang at the University of Minnesota prepared this compound in the aforementioned yield.

1.4682; lit. 67% (26), 82% (27), b.p. 75° at 2 mm, n_D^{25} 1.4425 (29) remained. The high refractive index of our product indicates that it probably still contains some diphenyl ether (n_D^{24} 1.5826).

1-Nitro-2-butyl Acetate (31)

The compound was prepared in 73% yield (b.p. 80–82° at 0.2–0.25 mm, $n_D^{22.5}$ 1.4463) by acetylation of 1-nitro-2-butanol with acetic anhydride according to the method used by Tindall (30) for preparation of other nitroacetates; lit. (31) n_D^{20} 1.4285, b.p. 105–106° at 11 mm. The high refractive index of our product suggests that it contains some diphenyl ether carried over from co-distillation with the 1-nitro-2-butanol.

6-Ethyl-5-nitro-2-norbornene (III)

The preparation is patterned after that of Hart (15) for 6-methyl-5-nitro-2-norbornene involving generation of the nitroölefin *in situ* (9). A mixture of 1-nitro-2-butyl acetate (54.8 g, 0.340 mole which contained some diphenyl ether), anhydrous sodium acetate (27.9 g, 0.340 mole), and absolute ethanol (200 ml) was stirred for 2.5 h. Freshly prepared (32) cyclopentadiene (45.0 g, 0.680 mole) was then added in a steady stream to the yellow lachrymatory mixture, and the resulting mixture was heated at 48° with vigorous stirring for 14 h. The two-phase liquid mixture was filtered through a sintered glass funnel and the solid sodium acetate was washed with absolute ethanol until the washings were colorless. The filtrate and washings were combined, and unreacted cyclopentadiene and the ethanol were removed by distillation under reduced pressure. The residual pale-yellow oil was fractionally distilled, giving a pale-yellow oil (16.24 g, 29%), b.p. 80–96° at 3.25–3.1 mm, n_D^{26} 1.4855. Fractional redistillation gave an analytical sample, also as a pale-yellow oil (4.02 g, 7%), b.p. 48–49°, n_D^{21} 1.4881; ν_{NO_2} (neat) 1 545 strong, 1 380 medium strong cm^{-1}.

Anal. Calcd. for $C_9H_{13}NO_2$ (167.20): C, 64.65; H, 7.84; N, 8.38. Found: C, 64.85; H, 7.47; N, 8.41.

Trans-β-nitrostyrene (32)

The n.m.r. spectrum of a 25% (by weight) solution in $CHCl_3$-*d* contains (using the τ scale, 1 τ = 60 Hz, *J* in Hz ± 1 Hz, areas relative to seven protons are given in parentheses) the vinyl proton α to the nitro group as the downfield doublet of an AB pattern (J_{trans} = 14) at 2.10 (1.0 proton) and the vinyl proton α to the phenyl ring as the upfield doublet of the AB pattern at 2.48, the upfield member of which is superimposed on the phenyl peak at 2.57 (total of 6.0 protons).

5-Nitro-6-phenyl-2-norbornene (IV)

The sample[9] (5, 34, and 35) used for n.m.r. analysis had the following properties: yellow oil, b.p. 124–125° at 0.15 mm, n_D^{22} 1.5641; λ_{max} (95% ethanol) 253mμ (log ε 2.86), 259 (2.82), 265 (2.74), λ(not a maximum) 309 (2.39, indicating < 1% *trans*-β-nitrostyrene present as a contaminant); ν_{NO_2} (neat) 1 550 (strong), 1 385 (medium strong) cm^{-1}; lit. b.p. 121–122° at 0.03 mm, n_D^{24} 1.5660 (5); b.p. 136–138° at 1–2 mm, n_D^{20} 1.5641 (34); b.p. 142-145° at 1-2 mm, n_D^{20} 1.5640 (35). Vapor-phase chromatography separated *trans*-β-nitrostyrene from 5-nitro-6-phenyl-2-norbornene which was accompanied by some thermal decomposition; however, separation of the latter into its component stereoisomers was not achieved.

p-β-Dinitrostyrene (36)

The general procedure of Worrall (33) for *trans*-β-nitrostyrene was used, except that 2.8 times the volume of methanol was found desirable and 8–9 times as much ice water was neded to dissolve the sodium salt as in the case of β-nitrostyrene. A cold mixture of *p*-nitrobenzaldehyde (54.0 g, 0.357 mole), nitromethane (19.3 ml, 0.357 mole), and methanol (200 ml) to which a solution (36 ml) of sodium hydroxide (15.0 g, 0.375 mole) was added dropwise with stirring at 5° gave, after acidification and work-up, a 34% yield, m.p. 199–204°. Recrystallization from acetone–water gave yellow crystals, m.p. 196–199°; lit. 26% (37), 78% (38), m.p. 196–199° (36), 199–200° (39), 203–204° decomp. (37), 203–204.5°(38); λ_{max} (95% ethanol) 217 mμ (log ε 3.99) and 306 (4.35); lit. λ_{max} (CH_3OH) 304 (4.34) (40); $\nu_{C=C}$(Nujol) 1 640 (medium), 1 605 (medium strong), ν_{NO_2} 1 535 (strong), 1 350 (very strong) cm^{-1}. The n.m.r. spectrum of an 8% by weight solution in dimethyl sulfoxide-d_6 contains a complex multiplet from τ 1.61–2.01 containing both the vinyl and aromatic protons.

5-Nitro-6-(p-nitrophenyl)-2-norbornene (V)

p-β-Dinitrostyrene (11.35 g, 0.0584 mole) was dissolved by heating in a solution of freshly distilled cyclopentadiene (32) (b.p. 38–40°, 15 ml, 0.182 mole) in benzene (200 ml). The solution was refluxed for 3.5 h and then kept at room temperature overnight. Unreacted cyclopentadiene and the benzene were removed in a rotary evaporator. The resulting yellow solid was crystallized from methanol giving white needles (14.58 g, 96%), m.p. 103–104.5°; λ_{max} (95% ethanol) 220 mμ inflection (log ε 3.94) and 274 (4.06); $\nu_{C=C}$ (Nujol) 1 600 (medium), ν_{NO_2} 1 550 (very strong), 1 515 (strong), 1 350 (very strong) cm^{-1}. The analytical sample, m.p. 99–100.5°, was obtained by two recrystallizations from petroleum ether (b.p. 60–68°); ν_{NO_2} (CCl_4) 1 550 (very strong), 1 530 (strong), 1 355 (medium strong) cm^{-1}.

Anal. Calcd. for $C_{13}H_{12}N_2O_4$ (260.24): C, 59.99; H, 4.65; N, 10.77. Found: C, 59.76; H, 4.67; N, 10.97.

Trans-2-(2-nitrovinyl)furan (41, 42)

The compound was obtained (42) in 71% yield, m.p. 73–75°; λ_{max} (95% ethanol) 237 mμ (log ε 3.63), 345 (4.27); $\nu_{C=C}$ (Nujol) 1 635 (medium strong), ν_{NO_2} 1 505 (strong), 1 330 (very strong) cm^{-1}. The n.m.r. spectrum of a 25% (by weight) solution in

[9]Prepared by Edward M. Felien and James H. Houchens at the University of Minnesota.

$CHCl_3$-*d* contains (using the τ scale, 1 τ = 60 Hz, J in Hz ± 1 Hz, areas relative to five protons are given in parentheses) the vinyl proton α to the nitro group as the downfield doublet of an AB pattern (J_{trans} = 13.5) at 2.23 (0.9); the vinyl proton α to the furan ring as the finely split upfield doublet of the AB pattern at 2.50, the central member of which is partially superimposed on the finely split multiplet at 2.42 attributed to the furan H-5 (total 2.0 protons); the furan H-3 as a doublet (J=3.5) at 3.07 (1.0); and the furan H-4 as a four-line multiplet ($J_{3,4}$ = 3.5; $J_{3,5}$ = 1.8) at 3.42 (1.1 protons).

6-(2-Furyl)-5-nitro-2-norbornene (VI)

Trans-2-(2-nitrovinyl)furan (120 g, 0.86 mole) was added, with stirring, to cold cyclopentadiene (32) (200 ml, 2.44 moles). The resulting mixture was allowed to warm up to room temperature and was refluxed for 4 h, causing the mixture to become homogeneous after 1 h of refluxing. The solution was kept for 2 days and then distilled, giving a forerun of dicyclopentadiene, b.p. 40–60° at 0.8 mm and then the product as an orange oil (80 ml, 54%), b.p. 100–101° at 0.8 mm. Redistillation again gave an orange oil (19.85 g, 11%), b.p. 80–84° at 0.2–0.3 mm, $n_D^{21.5}$ 1.5345, having an infrared spectrum identical with the spectra of the analytical samples. Fractional distillation gave a yellow forerun (0.87 g), b.p. 75–94° at 0.38–0.5 mm, shown by v.p.c. to be a mixture, from which *trans*-2-(2-nitrovinyl)furan separated as a yellow solid, m.p. 63–70°. The product was collected as three yellow liquid fractions, each of which was shown to be essentially identical by infrared comparison and homogeneous by v.p.c. on a 5 ft × 1/8 in. 5% SE-30 on Chromosorb W column at 165° with a flow rate of 25 ml/min of carrier gas (Linde high purity nitrogen) and a flame ionization detector:

Fraction (*a*): 2.91 g, b.p. 94–96° at 0.5 mm, n_D^{16} 1.5408, d_4^{26} 1.22. The n.m.r. spectrum of a 20% (by weight) solution in CCl_4 is similar to that of fraction *b*.

Anal. Calcd. for $C_{11}H_{11}NO_3$ (205.21): C, 64.38; H, 5.40; N, 6.83. Found: C, 64.67; H, 5.59; N, 6.68.

Fraction (*b*): 0.87 g, b.p. 96–100° at 0.5 mm, n_D^{16} 1.5350; λ_{max} (95% ethanol) 214 mμ (log ε 3.93), 254 diffuse inflection (2.9), 342 (2.2), indicating < 0.6% *trans*-2-(2-nitrovinyl)furan present as a contaminant; ν_{NO_2} (neat) 1 545 (strong), 1 375 (strong) cm^{-1}. The n.m.r. spectrum is summarized in Table I.

Anal. Found: C, 64.64; H, 5.59; N, 6.86.

Fraction (*c*): 7.39 g, b.p. 96–100° at 0.5–0.3 mm, n_D^{16} 1.5342, d_4^{26} 1.22.

Anal. Found: C, 65.63, 64.10; H, 6.46, 5.60; N, 6.96, 6.82.

As in the previous distillations, there was a large pot residue resulting from thermal decomposition of the product during distillation.

Trans-2-(2-Nitrovinyl)thiophene (43, 44)

The compound was obtained (43) in 74% yield, m.p. 79–80°; lit. m.p. 79–80° (43); λ_{max} (95% ethanol) 228mμ (log ε 3.65), 291 inflection (3.73), and 350 (4.25); $\nu_{C=C}$ (Nujol) 1 620 (medium strong), ν_{NO_2} 1 530 (medium), 1 330 (strong) cm^{-1}. The n.m.r. spectrum of a saturated solution in CCl_4 at 32° contains the 2-vinyl proton (α to the nitro group) as a doublet (J_{trans} = 13.5 Hz) at τ 1.82 and the remaining four protons as a complex multiplet ($w_{1/2}$ = 34 Hz) with center at τ 2.60.

5-Nitro-6-(2-thienyl)-2-norbornene (VII)

Cold cyclopentadiene (32) (30 ml, 0.365 mole) was added to *trans*-2-(2-nitrovinyl)thiophene (19.0 g, 0.122 mole). The mixture was stirred and allowed to warm up to room temperature, forming a yellow, viscous solution. The solution was refluxed for 4.5 h, forming a two-phase liquid. The small upper phase appeared to contain only product, whereas the larger, lower layer also contained product plus dicyclopentadiene and *trans*-2-(2-nitrovinyl)thiophene. These facts, and the progress of the reaction, were determined by thin-layer microchromatography (45) (t.l.mc.) on microscope slides prepared from E. Merck silica gel G (70 g) in a slurry with 3:2 chloroform–methanol (200 ml) and concentrated sulfuric acid (5 ml) and allowed to dry in air. The slides were spotted and then developed with 403: petroleum ether – ethyl acetate, dried in air and then on a hot plate. Dicyclopentadiene remained at the origin as a brown-black spot (R_f 0.04), the *trans*-2-(2-nitrovinyl)thiophene formed a black spot (R_f 0.72), and the product formed a deep violet spot (R_f 0.93). The reaction was terminated when it appeared to be 85% complete. Vacuum distillation of the two-phase liquid gave: (*a*) a little cyclopentadiene; (*b*) dicyclopentadiene (5.5 g, 23%), b.p. 36–37° at 0.05 mm which solidified to colorless crystals, m.p. 32.5–33.5°, the identity of which was confirmed by t.l.mc.; (*c*) *trans*-2-(2-nitrovinyl)-thiophene (4.3 g, 23% recovery), b.p. 114–118° at 0.65 mm, which solidified in the condenser, m.p. 78–80°, also identified by infrared and t.l.mc. comparison; and (*d*) the product as a yellow oil (20.3 g, 75%), b.p. 129–132° at 0.65 mm, which was collected in two fractions: (*d,i*) n_D^{21} 1.5760, the infrared spectrum of which ($\nu_{C=C}$ 1 621 (very weak) cm^{-1}) indicated the presence of a trace of *trans*-2-(2-nitrovinyl)thiophene, and (*d,ii*) n_D^{21} 1.5755; λ_{max} (95% ethanol) 234 mμ (log ε 3.94), 270 diffuse inflection (2.4), and 342 (2.2), indicating < 0.7% *trans*-2-(2-nitrovinyl)thiophene present as a contaminant; ν_{NO_2} (neat) 1 545 (strong), 1 375 (medium strong) cm^{-1}. The n.m.r. spectrum of fraction *d,ii* is summarized in Table I.

Anal. Calcd. for $C_{11}H_{11}NO_2S$ (221.35): C, 59.68; H, 5.01; N, 6.36; S, 14.49. Found: C, 59.86, 59.42; H, 5.97, 5.17; N, 6.72; S, 14.68.

5-Nitrobicyclo[2·2·2]oct-2-ene (VIII)

A sample (12, 16) which had been stored for a year was redistilled at reduced pressure in a short-path distillation apparatus, giving a pale-yellow oil in two fractions: (*a*) b.p. 55–60° at 0.7 mm, $n_D^{21.5}$ 1.4864; and (*b*) b.p. 61–65° at 0.7 mm, $n_D^{21.5}$ 1.5004, ν_{NO_2} (neat) 1 550 (very strong), 1 380 (strong) cm^{-1}, having an infrared spectrum identical with that of the distilled sample before being kept for a

year. First order analysis of the n.m.r. spectrum of a 31% (by weight) solution of fraction *b* in CCl_4 gave the results which follow (using the τ scale, $1\tau = 60$ Hz, J and $w_{1/2}$ in Hz $\pm$ 1 Hz, areas relative to 11 protons are given in parentheses). The vinyl protons appear as a complex multiplet from 3.43–4.10 (1.80 protons). The 5-*exo* proton of the major stereoisomer appears as a complex multiplet from 5.27–5.83 (1.16), whereas a small complex multiplet from 5.87–6.13 (0.23) is attributed to the 5-*endo* proton of the minor stereoisomer. The bridgehead H-4 appears as a broad peak ($w_{1/2} = 13$) at 6.72 with a broad secondary peak at 6.92 (total 0.99 protons). Bridgehead H-1 appears as a broad peak ($w_{1/2} = 12$) at 7.29 (0.97). The three methylene groups appear as a four-line multiplet ($w_{1/2} = 13$) at 7.99 (1.62) and a complex multiplet from 8.13–9.17 (4.22) with the major peak at 8.59. The n.m.r. spectrum suggests the presence of about 83% (based on the relative intensity of the 5-*exo* proton) of the 5-*endo*-nitro stereoisomer (VIII*a*) and about 17% (based on the relative intensity of the 5-*endo* proton) of the 5-*exo*-nitro minor stereoisomer (VIII*b*).

ACKNOWLEDGMENT

It is a pleasure to acknowledge helpful discussions concerning interpretation of the n.m.r. spectra with Prof. Edgar W. Garbisch, Jr. and Richard F. Sprecher. The senior author is grateful to the Chemistry Department of the University of Wisconsin at Madison for its hospitality during the writing of the latter part of this paper while he held a single quarter leave from the University of Minnesota.

REFERENCES

1. J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr. J. Am. Chem. Soc. **76**, 4501 (1954).
2. R. R. Fraser. Can. J. Chem. **40**, 78 (1962).
3. R. J. Ouellette and G. E. Booth. J. Org. Chem. **30**, 423 (1965).
4. E. E. van Tamelen and R. J. Thiede. J. Am. Chem. Soc. **74**, 2615 (1952).
5. G. I. Poos, J. Kleis, R. R. Wittekind, and J. D. Rosenau. J. Org. Chem. **26**, 4898 (1961).
6. J. Weinstock, N. Schwartz, and M. F. Kormendy. J. Org. Chem. **26**, 5247 (1961).
7. A. A. Dudinskaya, G. A. Shvekhgeĭmer, S. S. Novikov, and V. I. Slovetskiĭ. Bull. Acad. Sci. USSR Div. Chem. Sci. English Transl. 168 (1961).
8. J. Weinstock. U.S. Patent No. 2,931,805 (April 5, 1960) to Smith, Kline, and French Laboratories.
9. H. Feuer, R. Miller, and C. B. Lawyer. J. Org. Chem. **26**, 1357 (1961).
10. H. T. Roy, Jr. U. S. Patent No. 2,710,830 (June 14, 1955) to the General Tire and Rubber Co. W. E. Noland. Org. Syn. **41**, 67 (1961).
11. E. A. Braude, E. R. H. Jones, and G. G. Rose. J. Chem. Soc. 1104 (1947).
12. W. C. Wildman and D. R. Saunders. J. Org. Chem. **19**, 381 (1954). C. A. Grob, H. Kny, and A. Gagneux. Helv. Chim. Acta, **40**, 130 (1957).
13. C. F. H. Allen and A. Bell. J. Am. Chem. Soc. **61**, 521 (1939).
14. C. F. H. Allen, A. Bell, and J. W. Gates. J. Org. Chem. **8**, 373 (1943).
15. Richard B. Hart. Ph.D. thesis, University of Minnesota, Minneapolis, Minn. 1964. pp. 115–116; Dissertation Abstr. **26**, 695 (1965).
16. Susan M. Daluge. Unpublished results. University of Minnesota. 1965.
17. H. L. Goebel and H. H. Wenzke. J. Am. Chem. Soc. **60**, 697 (1938).
18. R. T. Arnold and P. N. Richardson. J. Am. Chem. Soc. **76**, 3649 (1954).
19. B. P. Dailey and J. N. Shoolery. J. Am. Chem. Soc. **77**, 3977 (1955).
20. C. N. Banwell, N. Sheppard, and J. J. Turner. Spectrochim. Acta, **16**, 794 (1960).
21. C. N. Banwell and N. Sheppard. Discussions Faraday Soc. **34**, 115 (1962).
22. L. Pauling. The chemical bond. Cornell Univ. Press, Ithaca, N. Y. 1967. p. 64. The nature of the chemical bond. Cornell Univ. Press, Ithaca, N. Y. 1939. p. 60.
23. P. Laszlo and P. von R. Schleyer. J. Am. Chem. Soc. **86**, 1171 (1964).
24. T. J. Flautt and W. F. Erman. J. Am. Chem. Soc. **85**, 3212 (1963).
25. K. Alder, H. F. Rickert, and E. Windemuth. Chem. Ber. **71**, 2451 (1938).
26. C. D. Hurd and M. E. Nilson. J. Org. Chem. **20**, 927 (1955).
27. M. de Montmollin and F. Achermann. Helv. Chim. Acta, **12**, 873 (1929).
28. W. E. Noland and R. Libers. Tetrahedron, Suppl. 1 **19**, 36 (1963).
29. D. V. Nightingale and J. R. Janes. J. Am. Chem. Soc. **66**, 352 (1944).
30. J. B. Tindall. Ind. Eng. Chem. **33**, 65 (1941).
31. E. Schmidt and G. Rutz. Chem. Ber. **61**, 2142 (1928).
32. R. B. Moffett. *In* Organic syntheses. Coll. Vol. 4. *Edited by* N. Rabjohn. John Wiley and Sons, Inc., New York. 1963. pp. 238–241; Org. Syn. **32**, 41 (1952).
33. D. E. Worrall. *In* Organic syntheses. Coll. Vol. 1. 2nd ed. *Edited by* A. H. Blatt. John Wiley and Sons, Inc., New York. 1941. p. 413; Org. Syn. **9**, 66 (1929).
34. W. E. Parham, W. T. Hunter, and R. Hanson. J. Am. Chem. Soc. **73**, 5068 (1951).
35. S. S. Novikov, G. A. Shvekhgeĭmer, and A. A. Dudinskaya. Bull. Acad. Sci. USSR Div. Chem. Sci. English Transl. 640 (1961).
36. J. Thiele. Chem. Ber. **32**, 1293 (1899).
37. T. Nishimura. Bull. Chem. Soc. Japan, **27**, 617 (1954); Chem. Abstr. **50**, 234e (1956).
38. S. Byrdy, Z. Eckstein, and J. Plenkiewicz. Bull. Acad. Polon. Sci. Ser. Sci. Chim. **9**, 627 (1961); Chem. Abstr. **60**, 4717a (1964).
39. T.Y. Yü and Y.I. Chia. Hua Hsueh Hsueh Pao, **25**, 417 (1959); Chem. Abstr. **54**, 19547e (1960).
40. M. J. Kamlet and D. J. Glover. J. Am. Chem. Soc. **77**, 5696 (1955).
41. B. Priebs. Chem. Ber. **18**, 1362 (1885). J. Thiele and H. Landers. Ann. Chem. **369**, 300 (1909). M. Okawara. Kogyo Kagaku Zasshi, **56**, 90 (1953): Chem. Abstr. **49**, 4618d

(1955). O. MOLDENHAUER, W. IRION, and R. PFLUGER. German Patent No. 918,148 (September 20, 1954) to Phrix–Werke A.G.; Chem. Abstr. **52**, 15590h (1958). H. SAIKACHI and H. HOSHIDA. Yakugaku Zasshi, **78**, 917 (1958); Chem. Abstr. **52**, 20113c (1958).
42. CHARLES E. MILLER. Unpublished results. Columbia University. 1964.
43. W. J. KING and F. F. NORD. J. Org. Chem. **14**, 405 (1949).
44. M. KOREMURA, H. OKU, H. NAKAO, T. SHŌNO, and Y. MORISAWA. Takamine Kenkyusho Nempo, **13**, 216 (1961); Chem. Abstr. **57**, 16451e (1962); V. S. EGOROVA, V. N. IVANOVA, and N. I. PUTOKHIN. J. Gen. Chem. USSR (English. Transl. **34**, 4142 (1964).
45. J. J. PEIFER. Microchim. Acta, 529 (1962).