# An Addition Reaction of Indane with Nitric Acid in Acetic Anhydride

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*cis*- and *trans*-5-Acetoxy-7*a*-nitro-5,7-dihydroindane are formed as well as the 4- and 5-nitroindanes when indane is reacted with nitric acid and acetic anhydride. These adducts both decompose on standing by loss of nitrous acid forming 5-acetoxyindane. The *cis* isomer is obtained in greater amount and it undergoes elimination less readily than the *trans*.

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Les acétoxy-5 nitro-7*a* dihydro-5,7 indanes *cis* et *trans* sont formés ainsi que les nitro-4 et -5 indanes quand l'indane est mis en réaction avec l'acide nitrique et l'anhydride acétique. Ces produits d'addition se décomposent au repos par perte d'acide nitreux en donnant l'acétoxy-5 indane. L'isomère *cis* est obtenu en plus grosse quantité et subit l'élimination moins facilement que le *trans*.

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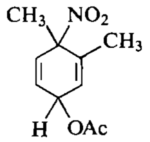
Reaction of indane with nitric acid and acetic anhydride has been reported to give 5-acetoxyindane as well as the expected 4- and 5-nitroindanes (1). The similar formation of 3,4-xylyl acetate (4-acetoxy-*o*-xylene) and of 3,4,5-trimethylphenyl acetate (5-acetoxyhemimellitene) when *o*-oxylene and 1,2,3-trimethylbenzene (hemimellitene) are treated with nitric acid and acetic anhydride (2) has recently been shown to occur via the 1,4-diene adducts, **1** and **2**, each of which occurs in *cis* and *trans* diastereoisomeric forms (3, 4). It is these dienes, together with the nitroarenes, that are the primary products of the reactions of the arenes. Thermolysis of the dienes, or heating them in acetic acid causes the elimination of nitrous acid and the formation of the aryl acetate which is thus a product of secondary reaction. These results have prompted us to re-examine the reaction of indane.

When indane was reacted with nitric acid in acetic anhydride at temperatures below −20° the product isolated after removal of the anhydride exhibited n.m.r. absorption in the region ($\tau$) 3.5–4.6 p.p.m., indicative of the presence of a diene, as well as absorption in the aromatic region. The predominant diene **3** crystallized when the product was allowed to stand overnight at −20°. The diastereoisomer **4** was obtained when the residue was subjected to low temperature chromatography on alumina. The structures assigned to the dienes are based on spectral and chemical evidence. The i.r. absorptions at 1540 and 1380 $cm^{-1}$ and at 1735 and 1230 $cm^{-1}$ establish the presence of nitro and acetoxy groups in **3**. Diene **4** has corresponding i.r. absorptions at 1550 and 1375 and at 1750 and 1225 $cm^{-1}$. The n.m.r. absorption in the region $\tau$ 3.5–4.5 p.p.m., which integrated for four protons, and the absence of absorption in the aromatic region show that **3** and **4** are dienes. That they are 1,4- rather than 1,3-dienes is indicated by the u.v. absorption: $\lambda_{max}$ is 202 nm ($\varepsilon$ 980 $m^2$ $mol^{-1}$) for **3** and 199.5 nm ($\varepsilon$ 1440 $m^2$ $mol^{-1}$) for **4**. 1,3-Cyclohexadienes absorb above 250 nm (5). There are three structurally isomeric 1,4-diene adducts (**3**/**4**, **5**, and **6**), each of which is potentially capable of existing as *cis–trans* diastereoisomers, which might be obtained by addition of nitro and acetoxy groups to indane. Structure **6** is not compatible with the coupling constants derived from the n.m.r. spectra (see below) and on chemical grounds is an unlikely structure since it contains an acid proton $\alpha$ to the nitro group. Such a proton would be readily removed by the basic reagents used during work-up with concomitant elimination of the acetate group and formation of 4-nitroindane. Structures **3**/**4** and **5** are consistent with the spectral information, but **5** should readily eliminate acetic acid, like **6**, to form 5-nitroindane. However, elimination of acetic acid does not occur under the strongly basic work-up conditions, and the elimination which does occur on standing results in the loss of nitrous acid and the formation of 5-acetoxyindane. Thus only the structure **3**, and its diastereoisomeric structure **4** are consistent with both the spectral evidence and the chemistry of the dienes.

The assignment of structure **3** to the diene produced in greater amount, *i.e.* that which crystallized preferentially from the reaction product, and of structure **4** to the less easily



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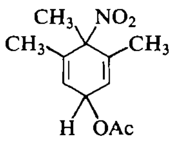

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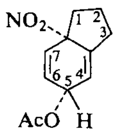

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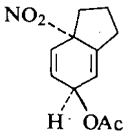

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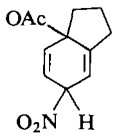

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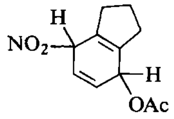

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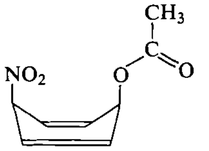

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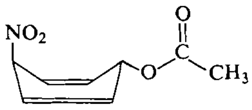

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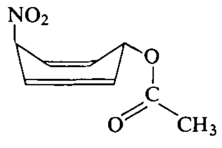

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isolated diene is based on the magnitudes and signs of the three- and four-bond vinyl-allylic proton coupling constants of each diene. Agreement between measured and calculated dipole moments provides independent support for these assignments. Dreiding models of the indane adducts show that the five-membered ring locks the six-membered diene ring into a fixed boat conformation.[1] The dihedral angle ($\phi$) between the $H_5$—$C_5$—$C_6$ and $C_5$—$C_6$—$H_6$ planes is $\sim 27°$ in the *cis* adduct **3** and $\sim 93°$ in the *trans* adduct **4**. The dependence of the three-bond and four-bond coupling constants of an allylic system on $\phi$ are given by Garbisch's equations (8) which are written in the following more simple equivalent forms.

$$\left.\begin{array}{ll}[1] & {}^3J = 4\cos^2\phi + 2.6 \\ [2] & {}^4J = 3.9\cos^2\phi - 2.6\end{array}\right\} 0^\circ \leqslant \phi \leqslant 90^\circ$$

$$\left.\begin{array}{ll}[3] & {}^3J = 9\cos^2\phi + 2.6 \\ [4] & {}^4J = 2.6\cos^2\phi - 2.6\end{array}\right\} 90^\circ \leqslant \phi \leqslant 180^\circ$$

For the specified angles, $J_{45}$ and $J_{56}$ (three-bond coupling constants) are predicted to be 5.8 Hz for the *cis* adduct **3** and 2.6 Hz for the *trans* adduct **4**. The four-bond coupling constant $J_{57}$ is predicted to be 0.5 Hz for the *cis* adduct and $-2.6$ for the *trans*. Comparison of these predicted values and those observed (Table 1) clearly shows that diene **3** is indeed the *cis* adduct and diene **4** is its *trans* isomer. The difference between the $J_{45}$ and $J_{56}$ values of **3**, together with the fact that these values are lower than predicted, may reflect a distortion of the diene ring caused by the repulsion between the diaxial nitro and acetoxy groups. Such distortion may be expected to be larger at C-6 than C-4 because the latter is closer to the restraining fused cyclopentene ring. The structural assignment is not affected by the choice of the particular set of coupling constants for each diene. Although there are two solutions in each case the only significant difference between the two pairs is in the sign of the $J_{46}$ value. In saturated systems coupling constants between protons in the equatorial "W" relationship (as are the H-4 and -6 in **3** and **4**) are positive and in the range 1–2 Hz (9) and we therefore suggest that the first (for **3**) and third (for **4**) solutions in Table 1 are the more likely.

Mention has been made above that structure **6** is inconsistent with the coupling constants of Table 1. For the purposes of the immediately following argument we take the subscripts in the headings of Table 1 as proton labels only and not

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[1] Dreiding models of 1,4-cyclohexadiene suggest that there are two rigid boat forms which are interconvertible by a ring flip. The models also suggest that there would be considerable angle strain in planar cyclohexadiene. Although the boat form for 1,4-cyclohexadiene has been supported, or at least assumed, by some authors (6) there is evidence which points to a planar structure (7). In the case of **3** and **4**, where the cyclohexadiene has a cyclopentene ring fused at the 3,4-bond, the requirement of planarity in the cyclopentene ring would force the cyclohexadiene ring into the boat form, even if this were not the preferred form in the unsubstituted 1,4-cyclohexadiene.

TABLE 1. Computed coupling constants (Hz) and chemical shifts* ($\tau$)

| Compound | $J_{45}$ | $J_{46}$ | $J_{47}$ | $J_{56}$ | $J_{57}$ | $J_{67}$ | $\nu_4$ | $\nu_5$ | $\nu_6$ | $\nu_7$ | r.m.s.† |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **3** | 5.03 | 1.37 | −0.12 | 4.38 | −0.02 | 9.71 | 3.94 | 4.36 | 3.83 | 3.60 | 0.14 |
| **3** | 5.11 | −1.42 | 0.00 | 4.31 | −0.02 | 9.72 | 3.94 | 4.36 | 3.83 | 3.60 | 0.14 |
| **4** | 2.28 | 1.86 | −0.33 | 2.37 | −2.48 | 9.78 | 4.08 | 4.15 | 3.84 | 3.75 | 0.09 |
| **4** | 2.34 | −2.00 | 0.39 | 2.33 | −2.44 | 9.78 | 4.08 | 4.15 | 3.84 | 3.75 | 0.10 |

*Subscripts are both proton labels and position indicators.
†Deviation (Hz) of the calculated line positions from those observed.

as position indicators and the compound numbers in that table as labels of parameter sets. The large coupling ($J_{67}$) must be assigned to the vinyl protons of **6**. The other two protons are thus 4 and 5. Either $J_{47}$ or $J_{57}$ must be a three-bond allylic coupling constant the minimum value for which is 2.6 Hz according to Garbisch's equations. This requirement, which is clearly inconsistent with the $J_{47}$ and $J_{57}$ values of Table 1, follows from the structural requirement of **6** that either protons 4 and 7 or 5 and 7 be adjacent. Structure **6** is therefore ruled out.

The measured dipole moment of **3** (2.56 D) is markedly lower than that of **4** (4.09 D). Dipole moments for **3** and **4** were calculated on the assumption that the hexadiene ring is in the rigid boat form. The calculations assume that (*i*) the acetoxy group is in the *s-trans* conformation (10) and that the group moment of the CH—$OCOCH_3$ fragment is the same as the dipole moment of methyl acetate (1.70 D orientated at 66° to the C—O bond with the negative end towards carbon (10)); (*ii*) the group moment of the C—$NO_2$ fragment is the same as the dipole moment of nitromethane (3.10 D directed along the C—N bond with the positive end towards carbon (10)); (*iii*) the group moment of the rest of the molecule, involving only C—H and C—C bonds, is negligible; (*iv*) the angle between the 1,4-diaxial bonds, estimated from Dreiding models, is 10°. We suggest that the predominant conformation of **3** is as depicted in partial structure **7** with the carbonyl oxygen at the extreme position from the nitro group. Severe steric interactions between carbonyl and nitro oxygens should prevent free rotation above the acetate C—O bond and destabilize structures in which the carbonyl oxygen approaches closely to the nitro group. In contrast conformations **8** and **9** of **4** should both be allowed as there are no marked steric interactions introduced as the acetate group rotates. Thus **4** would be expected to be a free rotation mixture. There is excellent agreement between the calculated dipole moments for these conformations and the measured values for **3** and **4** (Table 2) confirming the structural assignments of **3** and **4** based on the n.m.r. coupling constants.

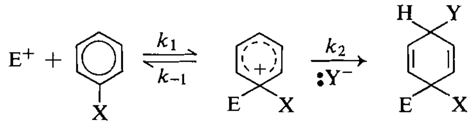
TABLE 2. Measured and calculated dipole moment values ($\mu$)

| Compound | $\mu$* | $\mu$† | $\mu_{calcd}$‡ |
|---|---|---|---|
| **3** | 2.56 | 2.51 | 2.54 |
| **4** | 4.09 | 4.04 | 3.91 |

*Derived using [6] and [7].
†Derived using [8].
‡Calculated from group moments as described in the text.

It was possible to detect the presence of each diene in the reaction product by n.m.r. However, because the spectra of the dienes overlap, it was not possible to determine the ratio in which the dienes were produced, although it was obvious that **3** was formed in greater amounts than **4**. The **3**:**4** ratio (4:1) was determined by measurement of the dielectric constant of the product diene mixture, after separation from nitroindanes and a small amount of acetoxyindane by chromatography. Both dienes decompose on standing by elimination of nitrous acid to give 5-acetoxyindane. Decomposition is accelerated by acids. The relative reactivity of **4**:**3** in carbon tetrachloride containing 1% trifluoroacetic acid is 2.6:1. The greater reactivity of the *trans* adduct parallels the observations of Cristol *et al.* (11) on the thermal and base-catalyzed decompositions of *cis*- and *trans*-1,5-dichloro-9,10-dihydro-9,10-anthradiols and their derivatives. Thus, the *trans* diacetate and dibenzoate decomposed at their melting points to give the 1,5-dichloro-9-anthryl acetate and benzoate respectively while the *cis* isomer did not decompose. Similarly, in the base-catalyzed 1,4-conjugate elimination, the *trans* isomer was much more reactive than the *cis*.

It seems likely that the dienes are formed via attack of the nitrating electrophile at the position of attachment of the five-membered ring (*ipso* attack). Perrin and Skinner (12) have discussed the possible reaction paths from a $\sigma$ complex (Wheland) intermediate formed by attack at the *ipso* position, but they have not explicitly recognized the possibility encountered in the present work, *viz.* combination of a nucleophile with the $\sigma$ complex leading to an overall addition reaction, eq. 5. It is consistent with this two-step mechanism that a mixture of diastereoisomeric dienes is obtained. What is not obvious is why the *cis* diene should predominate: Dreiding models suggest that steric interactions in **3** (*cf.* partial structure **7**) should be more marked than in **4** (partial structures **8** and **9**) and this should also be true for the respective transition states leading to **3** and **4**. Exclusive formation of *cis* adduct (**3**) could be accounted for by a one-step concerted cycloaddition mechanism but this mechanism cannot account for the formation of the *trans* isomer (**4**). We therefore regard the two-step mechanism, [5], as being the more likely. Earlier work (13) on the kinetics of the acetoxylation reaction of *o*-xylene demonstrated that nitration and acetoxylation (*i.e.* diene formation) have a common intermediate whose formation is rate determining.[2] It is now clear that a nitrating electrophile, and in particular, nitronium ion, the most likely species, would be a common intermediate if the addition followed the two-step path. Addition, by this mechanism, is a nitration which has been diverted in the final step. It would be more difficult to propose a common intermediate if the addition were a concerted process with a mechanism necessarily quite different from that of nitration.

[5]


Using the product ratios of Vaughan *et al.* (1) (27 mol % 5-acetoxyindane, 19 mol % 4-nitroindane, and 54 mol % 5-nitroindane) and making the assumption that the fraction of acetoxy product is equal to the fraction of dienes initially formed, the relative reactivity of the 3*a*, 4, and 5 positions of indane to attack by the nitrating electrophile is 1.4:1:2.8. Change of the electrophile will change the relative reactivity of the positions because of change in reaction constant (Hammett $\rho$) but, unless there are large changes in the relative steric effects, the reactivity order $5 > 3a > 4$ should be the same. Thus a significant fraction of *ipso* attack is to be expected in other electrophilic substitution reactions of indane which give detectable amounts of the 4-substituted indane. Products of *ipso* attack, *e.g.* diene products or products involving diene intermediates, were not observed in the bromination of indane (1). It is possible that such products were formed but not detected but it is more likely that in [5] for bromination $k_{-1} > k_2[\mathrm{Y}^-]$ and thus the *ipso* $\sigma$ intermediate dissociates to reactants before combination with the nucleophile occurs to form an addition product. Bromination, in contrast to nitration, is normally reversible. We attribute the apparent ease with which addition occurs in the course of nitration to the slowness of the reverse reaction of the initial electrophilic attack, *i.e.* $k_2[\mathrm{AcOH}] \gg k_{-1}$. Addition does not occur when the electrophile attacks the 4 or 5 positions because in these cases the $\sigma$ complex is readily deprotonated to give the aromatic substitution product, a reaction pathway not open to the complex formed by *ipso* attack.

Nitrous acid is a weak acid and nitrite anion is not a good leaving group. It is therefore not surprising that the loss of nitrous acid from the diene adduct should be acid-catalyzed. Present information does not allow a distinction to be made between a two-step mechanism involving a $\sigma$ complex intermediate (E1 type) and a concerted elimination (E2 type).

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[2] The kinetics were followed by shaking samples of the reaction mixture with 2 *M* sodium hydroxide solution and extraction of the nitroarenes with carbon tetrachloride. The concentrations of phenoxide ion, in the aqueous phase, and nitroarenes, in the extract, were determined by u.v. spectroscopy. The phenoxide ion was formed by hydrolysis of the phenyl acetate. The latter was presumably formed by elimination of nitrous acid from the diene adduct. The diene adduct could not have eliminated nitrous acid before the sample for analysis was added to the sodium hydroxide since the product, 3,4-dimethylphenylacetate, reacts further with nitric acid to give a nitrodienone (14). Considerable heat was evolved when the sample (acetic anhydride solvent) was added to the sodium hydroxide solution and it is not surprising that decomposition of adduct to phenyl acetate and further hydrolysis of the latter to phenoxide was substantially quantitative. In ref. 13, it is observed that the ratio of the rate of formation of phenyl acetate to that of nitroarenes is constant when the absolute rates vary over a wide range. The observation should be restated that there is a constant ratio of the rate of formation of diene adduct to that of nitroarene.

## Experimental

The u.v. spectra were determined on a Unicam SP 700 spectrometer. The i.r. spectra were determined on a Perkin–Elmer Model 337 spectrometer calibrated with polystyrene. The n.m.r. spectra were determined on Varian HA-60-IL, Varian XL-100, and Perkin–Elmer R12A spectrometers with tetramethylsilane as internal standard. Molecular weights were determined in methylene dibromide using a Hitachi Perkin–Elmer Model 115 molecular weight apparatus. Microanalyses were by Mr. M. Yang, Simon Fraser University, Burnaby, B.C. Melting points are uncorrected. Alumina was deactivated with 3% of 10% acetic acid.

### *cis (3) and trans (4) 5-Acetoxy-7a-nitro-5,7-dihydroindane*

Fuming nitric acid (300 $cm^3$) was distilled at 1 mm from urea (10 g) and sulfuric acid (500 $cm^3$). Distilled nitric acid (3.2 $cm^3$, 0.075 mol) was added to acetic anhydride (20 $cm^3$) at $-30°$. The solution was allowed to warm to 0° to complete the formation of acetyl nitrate (15) and then re-cooled to $-30°$. This solution was added slowly, with stirring, to a solution of indane (6 $cm^3$, 0.05 mol) in acetic anhydride (20 $cm^3$) maintained at a temperature below $-60°$. The mixture was allowed to warm to $-30°$ and maintained at that temperature for 10 min. It was then cooled in Dry Ice – acetone, ether (100 $cm^3$) added, and ammonia condensed into the solution. The cooling bath was removed, excess ammonia allowed to evaporate, and the residue poured onto ice and extracted with ether. The ether extract was washed ($\times 6$) with water, dried over magnesium sulfate, and the ether evaporated at 14°. The residue was allowed to stand overnight at $-20°$ and the crystals which formed were washed with cold pentane and recrystallized from pentane to give white crystals of **3**, m.p. 61.5–62.5°, u.v. max ($CH_3OH$) 202 nm ($\varepsilon$ 980 $m^2\ mol^{-1}$); i.r. (Nujol) 1735 and 1230 ($OCOCH_3$), 1540 and 1380 $cm^{-1}$ ($NO_2$); n.m.r. ($CCl_4$) $\tau$ 3.60 (d, 1, H-7), 3.83, 3.94 (m, 2, H-6 and -4), 4.4 (m, 1, H-5), 7.3, 8.2 (m, 6, $CH_2CH_2CH_2$), 7.99 p.p.m. (s, 3, $OCOCH_3$).

Anal. Calcd. for $C_{11}H_{13}NO_4$ ($M_r$ 223): C, 59.19; H, 5.87; N, 6.28. Found (218): C, 59.28; H, 6.03; N, 6.19.

The combined mother liquors were evaporated at 14° and the residue chromatographed on alumina maintained below $-30°$. Elution with pentane gave a mixture of 4- and 5-nitroindane.

4-Nitroindane has two triplets in the benzylic region (16) with the characteristic lower field one centered at $\tau$ 6.7 p.p.m. 5-Nitroindane crystallized from the mixture, i.r. (Nujol) 1550 and 1340 $cm^{-1}$ ($NO_2$); n.m.r. ($CDCl_3$) $\tau$ 2.3 (m, 2, Ar-*H*), 2.92 (m, 1, Ar-*H*), 7.2 (t, 4, Ar$CH_2$), 8.0 p.p.m. (m, 2, $CH_2CH_2CH_2$). The benzylic protons were decoupled from the aromatic protons by irradiation at 7.2 p.p.m. Coupling constants and chemical shifts were evaluated for the decoupled spectrum following the procedure described below for the dienes and gave the data $\nu_4 = 2.26$, $\nu_6 = 2.30$, $\nu_7 = 2.95$, $J_{46} = 2.20$, $J_{47} = 0.65$, $J_{67} = 8.15$. The chemical shift values show that there are two low field protons which must therefore be ortho to the nitro group and that the compound must be 5-nitroindane rather than its 4 isomer. The coupling constants show that the aromatic protons are in the *ortho*, *meta*, and *para* relationship which is consistent only with a 5-substituted indane.

Further elution was with ether–pentane mixtures. Trace amounts of 5-acetoxyindane were eluted with 10% ether–pentane, i.r. (film) 1750 and 1220 $cm^{-1}$ ($OCOCH_3$), n.m.r. ($CCl_4$) $\tau$ 3.2 (m, 3, Ar-*H*), 7.2 (t, 4, Ar-$CH_2$), 7.90 (s, 3, $OCOCH_3$), 7.9 p.p.m. (m, 2, $CH_2CH_2CH_2$). The benzylic protons were decoupled from the aromatic protons by irradiation at 7.19 p.p.m. Coupling constants and chemical shifts were evaluated from the decoupled spectrum and gave $\nu_7 = 2.99$, $\nu_6 = 3.34$, $\nu_4 = 3.22$, $J_{67} = 7.90$, $J_{47} = 0.50$, $J_{46} = 2.15$. The coupling constants show that the three protons are in the *ortho*, *meta*, and *para* relationship and are thus only consistent with a 5-substituted indane.

The dienes **3** and **4** were eluted with 20% ether–pentane. The diene fraction was rechromatographed using an alumina:substrate ratio of 150:1 and pure diene **4** was eluted with 18% ether–pentane. Diene **4** gave white crystals from pentane, m.p. 57.5–58.5°, u.v. max ($CH_3OH$) 199.5 nm ($\varepsilon$ 1440 $m^2\ mol^{-1}$); i.r. (Nujol) 1750 and 1225 ($OCOCH_3$), 1550 and 1375 $cm^{-1}$ ($NO_2$); n.m.r. ($CCl_4$) $\tau$ 3.75, 3.84 (m, 2, H-7 and -6), 4.08, 4.15 (m, 2, H-4 and -5), 7.4, 8.15 (6, $CH_2CH_2CH_2$), 7.97 p.p.m. (s, 3, $OCOCH_3$).

Anal. Calcd. for $C_{11}H_{13}NO_4$: C, 59.19; H, 5.87; N, 6.28. Found: C, 58.76; H, 5.70; N, 6.46.

The n.m.r. spectrum of each diene was taken at 100 MHz with the cyclopentane ring protons decoupled from the diene protons by irradiation at $\tau$ 7.50 for **3** and $\tau$ 7.52 for **4**. Line positions for the diene protons were measured and corrected for Bloch–Siegert shift (17). The computer program UEAITR (18) was used to refine estimated coupling constants and chemical shifts. Two sets of parameters (Table 1) led to good agreement between the calculated and the observed spectra. Not all of the peaks in the diene region could be resolved and this difficulty was compounded by the broadening of the spectrum caused by the decoupling of the cyclopentane ring protons. For these reasons $J_{47}$ and $J_{57}$ of **3** are not significantly different from 0.

Total yield of reaction products (nitro compounds and dienes) was in the range 75–85%. Gas–liquid chromatography of the decomposition product of each diene (SE 30 column at 200°) showed only 5-acetoxyindane and none of the nitroindanes. Integration of the n.m.r. spectrum of the product mixture in the diene and aromatic regions indicated that about 48% of the mixture was dienes. This is rather larger than the 26% of 5-acetoxyindane obtained by Wright after thermolysis of the reaction product. It is likely that analysis of dienes by n.m.r. is less accurate than Wright's chromatographic analysis of the acetate.

The relative reactivity of **3** and **4**, at 27° in carbon tetrachloride containing 1% trifluoroacetic acid as catalyst, was determined by following the rate of disappearance of the acetate peak of each (7.99 and 7.97 p.p.m., respectively) in the HA 60 spectrometer. At the same time the appearance of the acetate peak (7.90 p.p.m.) in the product 5-acetoxyindane was also followed. First order plots (in which concentration was taken as proportional to measured peak height) gave the rate constants $10^5k_3 = 3.7 \pm 0.6\ s^{-1}$; $10^5k_4 = 9.6 \pm 0.9\ s^{-1}$; $10^5k_{ArOAc} = 12 \pm 1\ s^{-1}$. Within experimental error the rate constant for formation of the acetoxyindane is equal to the sum of the rate constants for disappearance of **3** and **4** and the relative reactivity of **4** to **3** is 2.6:1.

### *Dielectric Constant Measurements and Dipole Moment Calculations*

Dielectric constants of benzene solutions of each diene were determined using a Sargent Chemical Oscillometer Model V with inductive cell-compensator. The compensator was adjusted so that a linear relationship between oscillometer reading (capacitance) and ($\varepsilon - 1$) for benzene, chlorobenzene, and dichloroethane was obtained. Diene (100 mg) was added in weighed increments (15 mg) to a known weight (7 g) of benzene in the capacitance cell and the instrument reading determined after each addition. The slope and intercept of the linear plot of instrument reading *vs.* mole fraction of diene ($n_2$) was obtained by a least squares fit and the ratio of these is

$$\frac{1}{\varepsilon_1 - 1}\cdot\frac{\Delta\varepsilon}{\Delta n_2} = \frac{\alpha}{\varepsilon_1 - 1}$$

(subscript 1 refers to solvent benzene and subscript 2 to solute diene). The density of the solution after each addition of diene was measured with a Westphal balance and a plot of specific volume ($v$) *vs.* $n_2$ gave the slope $\beta$. The dipole moments were then evaluated using the expression (19)

$$[6] \qquad \mu = 0.01281\ (P_{2\infty} - P_e - P_a)^{1/2}T^{1/2}$$

where

$$[7] \qquad P_{2\infty} = \frac{3\alpha v_1 M_1}{(\varepsilon_1 + 2)^2} + (v_1 M_2 + \beta M_1)\frac{\varepsilon_1 - 1}{\varepsilon_1 + 2}$$

$P_e$ was calculated from bond contributions (20) and $P_a$ was taken as zero (21). The dipole moment was also evaluated from Higasi's simple formula, for benzene solvent at 25° (22, 23).

$$[8] \qquad \mu = 0.828\alpha^{1/2}$$

Dipole moments are shown in Table 2. Dipole moments determined in solution are normally reported to ±0.05 to 0.1 D. Values of α were precise to 2% leading to a 1% precision of the derived moment and we therefore believe that the measured moments are within the accepted normal precision. It is to be noted that the values obtained using Higasi's simple expression agree with those evaluated from the more elaborate formula within the accepted precision.

For the mixture of isomers the polarization is related to the polarizations of each isomer by the expression,

$$[9] \qquad P = n_3 P_3 + n_4 P_4$$

where $n_3$ is the mole fraction of **3** in the mixture of **3** and **4**. Since $\beta$ has the same value for **3** and **4** it follows from [7] that $dP/dn$ is proportional to $d\alpha/dn$ and hence the isomer ratio is given by

$$[10] \qquad \frac{n_3}{n_4} = \frac{\alpha - \alpha_4}{\alpha - \alpha_3}$$

Using [10] and the measured values of α for the mixture and for each isomer the ratio $n_3 : n_4$ was found to be 4 : 1.

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