ence of Florisil.—Florisil (0.50 g) was added to a solution of **3** (0.20 g) in 10 ml of benzene, and the mixture was refluxed for 15 hr. The mixture was then cooled and filtered, and the solvent was evaporated to give 0.15 g of a pale yellow oil. Vpc on column A at 175° showed the presence of three peaks with retention times of 2.6, 3.0, and 8.3 min, with relative areas in the ratio 10:52, respectively. The three products were isolated by preparative vpc on column B at 200°. The two components with lower retention times were identified as **5** and **6** by comparison of their nmr and ir spectra and vpc retention times with those of samples previously prepared.

The component with the highest retention time showed maxima in its ir spectrum at 3.35 (s), 6.3 (w), 6.8 (s), 6.9 (s), 7.05 (m), 7.17 (m), 7.3 (m), 7.35 (s), 7.98 (m), 8.25 (s), 8.4 (m), 8.75 (w), 9.45 (w), 9.7 (w), 10.05 (m), 10.35 (s), 10.55 (m), 11.5 (m), 12.7 (w), and 12.9 μ (w). On the basis of its nmr spectrum (see Table I) it was assigned the structure **3-(*trans*-2-butenyl)-2,6-di-*tert*-butyl-*p*-xylene (7)**.

A suspension of Florisil (0.20 g) in a solution of **4**[3] (0.20 g) in 10 ml of benzene was refluxed for 24 hr. Work-up as above gave 0.18 g of pale yellow oil. Vpc analysis on column A at 150° showed the presence of three components, with retention times of 2.6, 3.0, and 8.2 min, with relative areas of 9:3:1 The three products were isolated by preparative vpc on column B, and identified as **5**, **6**, and **7** by their ir and nmr spectra.

Rearrangement of 4-Allyl-2,6-di-*tert*-butyl-4-methyl-1-phenylcyclohexa-2,5-dien-1-ol (9) in Acid.—Dienol **9** (0.20 g) was dissolved in 4 ml of a 10% (by volume) solution of sulfuric acid in acetic acid. An insoluble layer immediately separated above the acetic acid layer. The mixture was allowed to stand at room temperature overnight, and the two layers then separated. The upper layer was dissolved in *n*-pentane, washed with water, sodium bicarbonate solution, and water, and dried over magnesium sulfate. The mixture was filtered and the filtrate was evaporated to give 0.16 g of a clear oil. Vpc analysis on column A at 200° showed the presence of only one peak with a retention time of 9.5 min. The ir and nmr spectra and vpc retention time of the product showed it to be 2-allyl-3,5-di-*tert*-butyl-4-phenyltoluene (**11**). The acetic acid layer was extracted with *n*-pentane, and the pentane layer was washed with water and sodium bicarbonate solution. It was dried over magnesium sulfate and the solvent was evaporated to give 0.05 g of brown oil. Vpc on column A at 200° showed the presence of two components with retention times of 3.6 and 9.6 min, with relative areas in the ratio 1:4. The two products were isolated by preparative vpc on column C at 175°. The major product was again shown to be **11**. The low retention time component had peaks in its ir spectrum at 3.4 (s), 6.1 (m), 6.2 (m), 6.75 (s), 6.85 (s), 6.95 (s), 7.15 (w), 7.35 (m), 8.05 (m), 8.3 (m), 9.35 (m), 9.7 (m), 10.5 (m), 11.0 (s), 11.4 (m), 13.0 (s), and 14.35 μ (s). On the basis of its nmr spectrum (see Table I) it was assigned the structure **2-allyl-5-*tert*-butyl-4-phenyltoluene (10)**.

Rearrangement of 9 in the Presence of Florisil.—A mixture of **9** (0.20 g) and Florisil (0.20 g) in 10 ml of benzene was refluxed overnight. After filtration evaporation of the solvent gave 0.17 g of a clear oil. Vpc analysis on column A at 200° showed the presence of three peaks with retention times of 3.4, 4.1, and 9.8 min, with relative areas in the ratio 3:1:11. The products were isolated by preparative vpc on column C at 175°. The product with lowest retention time was a pale yellow oil with ir peaks at 3.35 (s), 6.05 (m), 6.2 (m), 6.4 (w), 6.85 (w), 6.95 (s), 7.1 (w), 7.2 (w), 7.35 (m), 8.2 (m), 8.3 (m), 8.5 (w), 8.7 (w), 9.35 (m), 9.7 (w), 9.9 (m), 10.05 (w), 10.95 (s), 11.65 (s), 12.6 (w), 13.1 (s), and 14.2 μ (s). On the basis of its nmr spectrum (see Table I) it was assigned the structure **3-allyl-5-*tert*-butyl-4-phenyltoluene (13)**.

Anal. Calcd for $C_{20}H_{24}$: C, 90.9; H, 9.15. Found: C, 90.9; H, 9.17.

The other two products were identified by their ir and nmr spectra and vpc retention times as **12** and **11**.

Reaction of 4-(*trans*-2-Butenyl)-2,6-di-*tert*-butyl-4-methyl-1-phenylcyclohexa-2,5-dien-1-ol (14) with Acid.—Dienol **14** (0.20 g) was dissolved in 10% sulfuric acid in glacial acetic acid solution. A white solid formed immediately. Water was added and the mixture was extracted with *n*-pentane. The pentane solution was washed with water and sodium bicarbonate solution, dried over magnesium sulfate, and evaporated to give 0.18 g of oily crystals. Vpc on column A at 200° showed the presence of two components with retention times of 4.1 and 11.0 min, in the area ratio 10:1. Recrystallization from methanol gave white crystals, mp 122–124°, which were identified by their vpc retention time and ir and nmr spectra as **12**. The oil obtained from the mother liquor after recrystallization showed two peaks with the same retention times as before recrystallization. The peak with the higher retention time was isolated as a pale yellow oil by preparative vpc. The ir spectrum of the product had peaks at 3.35 (s), 5.8 (w), 6.22 (m), 6.3 (w), 6.75 (s), 6.95 (s), 7.1 (m), 7.2 (m), 7.65 (w), 7.9 (w), 8.15 (w), 8.3 (s), 8.4 (m), 8.6 (w), 9.3 (m), 9.7 (m), 9.85 (m). 10.3 (s), 10.7 (w), 10.8 (w), 11.4 (m), 12.75 (s), 13.55 (w), and 14.05 μ (s). On the basis of its nmr spectrum (see Table I) this compound was assigned the structure **2-(*trans*-2-butenyl)-3,5-di-*tert*-butyl-4-phenyltoluene (15)**.

Anal. Calcd for $C_{25}H_{34}$: C, 89.7; H, 10.2. Found: C, 89.9; H, 9.86.

Reactions of 14 in the Presence of Florisil.—A mixture of **14** (0.20 g) and Florisil (0.20 g) in 10 ml of benzene was refluxed overnight and then filtered. The filtrate was evaporated to give 0.15 g of colorless oil. Vpc on column A at 200° showed the presence of two components with retention times of 4.1 and 10.1 min, with areas in the ratio 2:1. The two components were isolated by preparative vpc on column C at 175°. Comparison of their vpc retention times and ir spectra with those of the products previously showed them to be **12** and **15**, respectively.

Registry No.—**3**, 34731-37-8; **6**, 34731-38-9; **7**, 34731-39-0; **9**, 34712-56-6; **10**, 34731-40-3; **11**, 34014-53-4; **12**, 34014-54-5; **13**, 34014-56-7; **14**, 34712-57-7; **15**, 34731-44-7.

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The Reaction of 1-Azirines with 1,3-Diphenylisobenzofuran. Ring Expansion to Isoquinoline, Dihydroisoquinoline, and Azanorcarane Derivatives

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Under appropriate reaction conditions advantage can be taken of the inherent reactivity of the rigid C=N bond of 1-azirines to effect cycloadditions. The 2-π electrons of this system can participate in thermally allowed [$_\pi 4 + {}_\pi 2$] reactions as dienophiles[1,2] or as dipolarophiles.[3-5] Thus, reaction of 1-azirines with cyclopentadienones proceeds *via* the cycloadduct to furnish after decarbonylation, valence tautomerism, and 1,5-sigmatropic shift, 3*H*-azepine derivatives. 1,3-Dipolar cycloaddition to the three-orbital 4-π electron system of diazomethane and nitrile oxides transforms these 1-azirines into allylic azides and carbodiimides, respectively. The apparent photochemical [2 + 2] cycloaddition with electron-deficient olefins actually proceeds through thermal addition of a 1,3-dipolar species generated by cleavage of the electronically excited singlet state of the appropriate azirine.[6]

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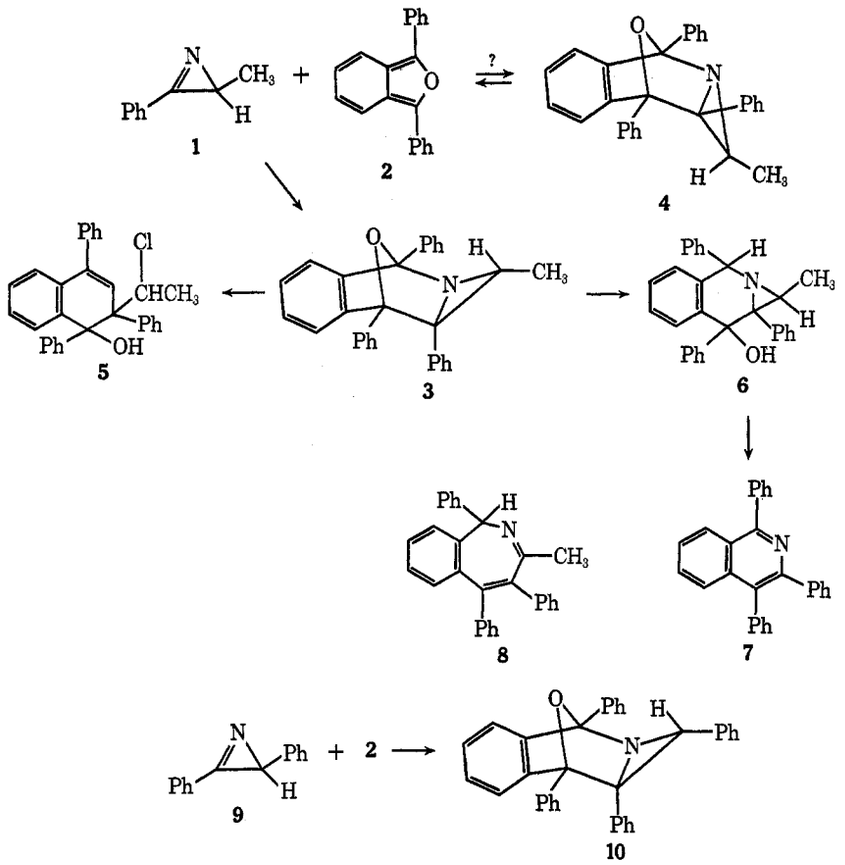

As part of this program, we embarked on some further cycloadditions of 1-azirines with dienes. We were particularly interested in the isolation and examination of the initially formed cycloadduct, a feature that had been absent from our previous studies on cycloadditions due to the inherent instability of these adducts. We selected to examine the cycloaddition of the reactive diene[7] 1,3-diphenylisobenzofuran (**2**)[8] with a model azirine, 3-methyl-2-phenyl-1-azirine (**1**).[8] When azirine **1** was treated with **2** in toluene at reflux temperatures for 18 hr, column chromatography and crystallization furnished a white, crystalline compound in 73% isolated yield. Mass spectral data and elemental analysis were consistent with the molecular formula $C_{29}H_{23}NO$. The nmr spectrum (in $CDCl_3$) showed absorptions at δ 1.05 (d, J = 5.8 Hz, 3 H) and 3.52 (q, J = 5.8 Hz, 1 H) and multiplets in the aromatic region between δ 6.48 and 7.96 (19 H, aromatic).

On the basis of the spectral evidence and the chemical transformations discussed below, the compound was assigned the cycloadduct structure **3**. The exo stereochemistry was inferred from its nmr spectrum, which showed considerable deshielding (>1 ppm) of the aziridine hydrogen (δ 3.52) by the oxido bridge, implying that this hydrogen is syn to the oxygen. Further support for this assignment comes from work on cyclopropene adducts with 1,3-diphenylisobenzofuran by Cava,[9] Breslow,[10] Battiste,[11] and coworkers.

The lone pair of electrons on the nitrogen of the cycloadduct **3** undergoes protonation readily in anhydrous HCl–benzene and the protonated species suffers subsequent cleavage to furnish the HCl salt of **5**, from which the free base **5** can be easily obtained. No dihydroazepine derivatives were isolated or detected. The protonated species resulting from **3** undergoes C–N and not C–C bond cleavage. There is discrimination between the two C–N bonds and cleavage of presumably the weaker aziridine bond takes place, giving the dihydroisoquinoline derivative **5**. That **5** is indeed the product of this ring cleavage was substantiated further by examination of the nmr spectrum of **5** HCl, which showed a downfield shift for both the H and CH_3 (of $ClCHCH_3$) consistent with a positive center situated β to the carbon carrying them.

Reductive cleavage of the exo adduct **3** with $LiAlH_4$ gave a compound to which we have assigned the benzoazanorcarane structure **6** on the basis of its spectral and analytical data. Its nmr spectrum showed considerable deshielding of the benzylic hydrogen (δ 5.68), suggesting that the central six-membered ring retains its boat conformation, the deshielding being from the hydroxyl group. When **6** was treated with anhydrous HCl at room temperature, a white, crystalline compound precipitated out of the reaction mixture within a few minutes. Its nmr spectrum was consistent with its being the hydrochloride salt of **6**. Treatment of **6** with anhydrous HCl in refluxing benzene converted it to the triphenylisoquinoline **7**.

When 2,3-diphenyl-1-azirine (**9**) was treated with 1,3-diphenylisobenzofuran (**2**), conversion to the exo adduct **10** occurred in ~70% yield.

The isolation of the exo adducts exclusively from these Diels–Alder reactions may be explained in terms

(7) Attempted cycloaddition with furan and with butadiene derivatives, such as methyl *trans*-2,4-pentadienoate, were unsuccessful.

(8) M. S. Newman, *J. Org. Chem.*, **26**, 2630 (1961).

(9) M. P. Cava and K. Narasimhan, *ibid.*, **36**, 1419 (1971).

(10) R. Breslow, G. Ryan, and J. T. Groves, *J. Amer. Chem. Soc.*, **92**, 988 (1970).

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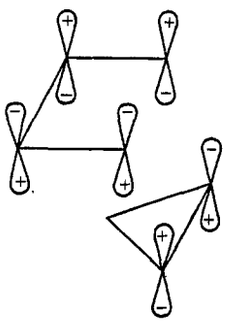
of an unfavorable increase in energy for the endo transition state as a result of secondary orbital interactions (**11**).[5] In **11**, a mixing of the highest occupied diene



11

orbital with the lowest unoccupied cyclopropene or azirine orbital occurs.

It is possible that the endo adduct **4** is formed to a small extent but is unstable and undergoes a retro Diels–Alder reaction.[9]

We are currently examining the possible dehydrative rearrangement of the azanorcarane **6** to the 2*H* azepine **8**.

Experimental Section

Reaction of 3-Methyl-2-phenyl-1-azirine with 1,3-Diphenylisobenzofuran. Formation of Exo Adduct 3.—A solution of 1.048 g (8 mmol) of 3-methyl-2-phenyl-1-azirine (**1**)[8,12] in 10 ml of toluene was treated with a solution of 1.620 g (6 mmol) of 1,3-diphenylisobenzofuran (**2**)[8] in 15 ml of toluene. The reaction mixture was heated under reflux for 18 hr and then chromatographed over silica gel. Unreacted 1,3-diphenylisobenzofuran was eluted with pentane and the adduct with 10% ether–pentane. Crystallization from ether–pentane gave the exo adduct **3** as white plates (1.75 g, 73%): mp 192–194°; nmr $\delta_{TMS}^{CDCl_3}$ 1.05 (d, J = 5.8 Hz, 3 H), 3.52 (q, J = 5.8 Hz, 1 H), 6.48–7.96 (m, 19 H).

Anal. Calcd for $C_{29}H_{23}NO$: C, 86.75; H, 5.77; N, 3.49. Found: C, 86.43; H, 5.51; N, 3.53.

Thermal Stability of Exo Adduct 3.—The adduct **3** in $CDCl_3$ was heated in a sealed nmr tube at 100° and the reaction was monitored by periodic nmr spectral determinations. Even after 1 week, about 85 ± 5% of **3** remained undestroyed.

3-Chloroethyl-4-hydroxy-1,3,4-triphenyl-3,4-dihydroisoquinoline (5).—A solution of 500 mg of the adduct **3** in 5 ml of anhydrous benzene was treated with 10 ml of a saturated solution of anhydrous HCl in benzene. The reaction mixture darkened immediately. After the mixture was stirred for 3 hr, the yellow crystalline compound that precipitated out (**5**·HCl) was collected (510 mg): mp 168°; nmr $\delta_{TMS}^{CD_3OD}$ 1.43 (d, J = 6.2 Hz, 3 H), 5.24 (s, broad, 2 H), 6.06 (q, J = 6.2 Hz, 1 H), 6.58–7.95 (19 H).

The product from the foregoing reaction was dissolved in 5 ml of methanol and treated with 20 ml of 2 *N* aqueous NaOH. The reaction mixture was diluted with 100 ml of water and extracted with benzene (3 × 50 ml). The combined organic extract was washed with water and dried (Na_2SO_4). The solution was concentrated and treated with pentane when pale yellow plates of the dihydroisoquinoline **5** crystallized out (335 mg, 76%): mp 178–180°; nmr $\delta_{TMS}^{CDCl_3}$ 1.28 (d, J = 6.2 Hz, 3 H), 4.10 (s, 1 H), 4.72 (q, J = 6.2 Hz, 1 H), 6.84–8.00 (m, 19 H).

Anal. Calcd for $C_{29}H_{24}NOCl$: C, 79.53; H, 5.52; N, 3.20. Found: C, 79.50; H, 5.32; N, 3.22.

Reductive Cleavage of Exo Adduct 3 with $LiAlH_4$. Isolation of Benzoazanorcarane (6).—A solution of 300 mg of the adduct **3** in 5 ml of anhydrous ether was reduced with $LiAlH_4$. Purification of the product by preparative layer chromatography on silica gel PF_{254} with 50% benzene–pentane as the developing solvent gave benzoazanorcarane (**6**) as a viscous, pale yellow oil which crystallized slowly from ether–pentane as pale yellow plates (280 mg, 93%): mp 85°; nmr $\delta_{TMS}^{CDCl_3}$ 0.95 (d, J = 5.5 Hz, 3 H), 2.32 (q, J = 5.5 Hz, 1 H), 2.52 (s, broad, 1 H), 5.69 (s, 1 H), 6.60–7.90 (m, 19 H).

Anal. Calcd for $C_{29}H_{25}NO$: C, 86.32; H, 6.24; N, 3.47. Found: C, 86.62; H, 6.41; N, 3.50.

Treatment of Benzoazanorcarane (6) with Anhydrous HCl in Benzene. Isolation of Isoquinoline (7).—A solution of 403 mg (1 mmol) of **6** in 20 ml of anhydrous benzene was treated with anhydrous HCl at reflux temperatures for 0.5 hr. The solution was concentrated and subjected to preparative layer chromatography using silica gel PF_{254} with 50% ether–pentane as the developing solvent. The isoquinoline (**7**) crystallized from ether–pentane as pale yellow plates (197 mg, 55%): mp 184–185; nmr $\delta_{TMS}^{CDCl_3}$ 7.08–8.18 (m, 19H).

Anal. Calcd for $C_{27}H_{19}N$: C, 90.72; H, 5.36; N, 3.92. Found: C, 90.79; H, 5.59; N, 3.83.

In a separate experiment the benzoazanorcarane (**6**) was treated with anhydrous HCl in benzene at 25°, and the precipitated white crystalline compound (**6** HCl) was collected: mp 178–181°; nmr $\delta_{TMS}^{CD_3OD}$ 1.45 (d, J = 5.8 Hz, 3 H), 5.12 (s, broad, 2 H), 5.94 (q, J = 5.8 Hz, 1 H), 6.60–8.13 (m, 20 H). Basification of this salt gave **6** quantitatively.

Reaction of 2,3-Diphenyl-1-azirine (9) with 1,3-Diphenylisobenzofuran. Formation of Exo Adduct 10.—A solution of 386 mg (2 mmol) of 2,3-diphenyl-1-azirine (**9**)[13] and 405 mg (1.5 mmol) of 1,3-diphenylisobenzofuran (**2**) was heated under reflux for 44 hr and then chromatographed using preparative plates (silica gel PF_{254}). Crystallization from ether–pentane gave the exo adduct **10** as white plates (490 mg, 70.5%): mp 198–200°; nmr $\delta_{TMS}^{CDCl_3}$ 4.52 (s, 1 H), 6.27–7.97 (m, 24 H).

Anal. Calcd for $C_{34}H_{25}NO$: C, 89.03; H, 5.00; N, 2.78. Found: C, 88.62; H, 5.22; N, 2.70.

Registry No.—**2**, 5471-63-6; **3**, 34806-16-1; **5**, 34806-17-2; **5** HCl, 34806-18-3; **6**, 34792-35-3; **6** HCl, 34792-36-4; **7**, 30081-56-2; **10**, 34806-20-7.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant No. 1871-G1), for partial support of this research.

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Selectivity in the Reaction of Azodicarboxylate Esters with Sulfides[1]

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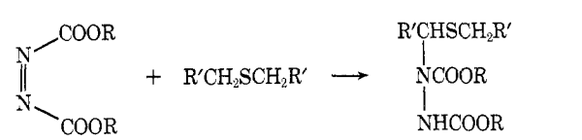
In the course of studies of other reactions which result in substitution at the α-carbon atom of sulfides, we have examined the reactions of azodicarboxylate esters with a number of sulfides. This reaction was used initially by Woodward in the synthesis of cephalosporin C.[2,3] The transformations, which proceed as



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