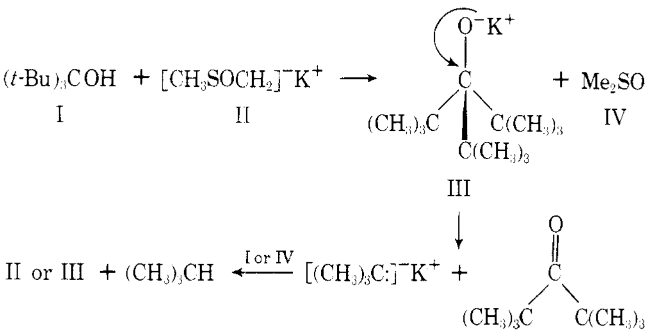
sodium hydroxide and its failure to titrate with $K^+Me_2SYL^-$ in Me_2SO in the predicted pK_a range. (c) Recovery experiments, which retrieved neopentyl alcohol and di-*tert*-butylcarbinol quantitatively after deprotonation in Me_2SO, show that tri-*tert*-butylcarbinol is converted completely and instantly to di-*tert*-butyl ketone and isobutane.

We propose that this reaction occurs through the expulsion of a *tert*-butyl carbanion in accordance with the following mechanistic scheme:



This mechanism is entirely analogous to the retro-Grignard addition proposed by Zook[7] for the cleavage of di-*tert*-butylneopentylcarbinol with sodium hydride in ether. Cram[6] likewise observed cleavage of some heavily substituted tertiary alcohols in the course of his classic investigations of electrophilic aliphatic substitution. The striking feature in the present case is the instantaneous expulsion of a completely aliphatic moiety under relatively moderate conditions in strongly basic solution. Zook's cleavage required reaction times of 1 to 6 h at 200 to 400 °C. Cram's leaving groups carried resonance stabilizing aromatic or cyano groups.

Schleyer[14] has calculated the strain energy for tri-*tert*-butylmethane as 40.4 kcal/mol and that for 1,1-di-*tert*-butylethane is 15.0 kcal/mol. The heat of reaction of tri-*tert*-butylcarbinol with $K^+Me_2SYL^-$, −23.2 kcal/mol, is close to the difference (−25 kcal/mol) in strain energy for these compounds and is probably the driving force for the reaction.

We can produce no iron-clad evidence against a radical cleavage pathway[8,15] through *tert*-butyl radical or di-*tert*-butylketyl. Tri-*tert*-butylmethyl radical and di-*tert*-butylmethyl radical are remarkably stable because of steric hindrance against dimerization.[16] One might reasonably presume that di-*tert*-butylketyl would also be fairly long lived for the same reason. However, the lack of coupling products[6] in our product mixture and the initiation of the reaction by strong base make a radical pathway seem much less likely than the carbanion mechanism.[17] In view of the high rate of the reaction and the high melting point of Me_2SO, CIDNP or ESR experiments to test for *tert*-butyl radicals at low temperatures would be difficult, but not impossible.[18,19]

Acknowledgments. We are glad to acknowledge support of this work by NSF Grant GP-6550-X.

Registry No.—Tri-*tert*-butylcarbinol, 41902-42-5; di-*tert*-butylcarbinol, 14609-79-1; neopentyl alcohol, 75-84-3; dimethyl sulfoxide, 67-68-5.

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(17) The editor has pointed out that the absence of isobutene in the gaseous product argues against radical disproportionation of *tert*-butyl radicals. Correspondingly, the absence of di-*tert*-butylcarbinol in the worked-up solution argues against formation and disproportionation of an intermediate ketyl.
(18) We do not plan to do such experiments and invite other workers with suitable equipment to try them.
(19) R. Breslow and J. L. Grant, *J. Am. Chem. Soc.*, **99**, 7746 (1977), have just reported strong evidence that the pK_a of isobutane lies between 66 and 71 in a variety of solvents. That of Me_2SO is 35.1.

Periselectivity in the [4 + 2] and [6 + 4] Cycloadditions of Diphenylnitrilimine to Tropone

Debabrata Mukherjee,[1a] Charles R. Watts, and K. N. Houk*[1b]

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803

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The cycloaddition of diphenylnitrilimine, generated from the dehydrochlorination of α-chlorobenzylidenephenylhydrazine, to tropone gives a [6 + 4] adduct in 4% yield, a 2:1 adduct (4%) of unknown structure, and three partially aromatized [4 + 2] adducts in 54, 5, and 5% yield. Attempted photochemical decarbonylation of the [6 + 4] adduct gave only a mixture of rearranged products, while pyrolysis of the [6 + 4] adduct resulted in a [1,5]sigmatropic shift and formation of one of the partially aromatic [4 + 2] adducts. The periselectivity observed here is similar to that of nitrile oxide, but differs substantially from that observed with other dipoles and with dienes. Electronic origins of these differences are discussed.

Introduction

In 1970, we reported the first examples of [6 + 4] cycloadditions of 1,3-dipoles across the termini of trienes.[2,3] The [6 + 4] cycloaddition of diphenylnitrilimine to tropone[2] and the [6 + 4] cycloaddition of diazomethane to dimethylfulvene[3] were prototypes of a general method for the synthesis of new heterocyclic systems. However, in the interim, remarkably few

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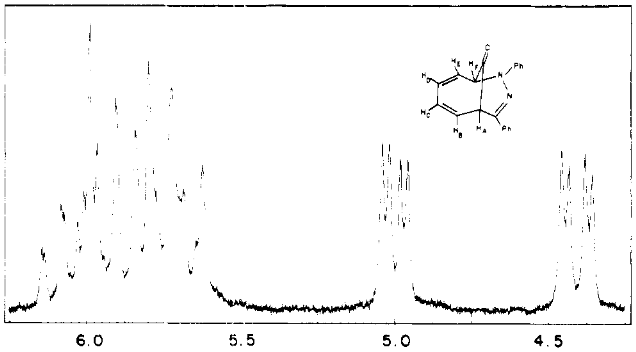


Figure 1. 100-MHz NMR spectrum of [6 + 4] adduct 1 (the aromatic region of the spectrum is not shown).

1,3-dipolar cycloadditions of this type have been discovered. The [6 + 4] cycloadditions of mesito- and benzonitrile oxide to tropone compete poorly with [4 + 2] cycloadditions.[4] The [6 + 4] dimerization of a cyclic azomethine ylide and its [6 + 4] cycloaddition to fulvenes have also been reported,[5] and we have found that diazomethane adds in a [6 + 4] fashion to 6-phenylfulvene.[6] We predicted in 1973 that nitrile ylides, a class of electron-rich 1,3-dipoles, would add in a [6 + 4] fashion to fulvenes,[7] and Padwa has recently confirmed this experimentally.[8] The formal [6 + 4] cycloaddition of cycloheptatriene to "S_3" is another possible example,[9] and the electron-rich 6-dimethylaminofulvene adds in a [6 + 4] fashion to nitrile oxides.[10]

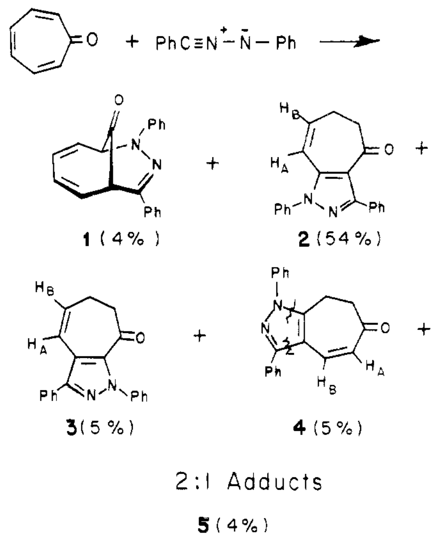
Thus, the [6 + 4] cycloadditions of diphenylnitrilimine and two aryl nitrile oxides, which compete poorly with [4 + 2] additions, are the only documented cases of 1,3-dipolar cycloadditions across the 2,7 positions of tropone. These results stand in marked contrast to the results of diene cycloadditions to tropone, where cyclopentadiene and cyclohexadiene,[11a] isobenzofulvenes,[11b] perhaps dimethyl-, methyl-, and phenylfulvenes,[11c,12] several acyclic dienes,[11d] cyclopentadienones,[11e] and a benzopyrone[11f] all react preferentially in the [6 + 4] fashion, tropone behaving as a 6π addend.

Because of our interest in the development of understanding of periselectivity in cycloadditions,[12] and in order to obtain quantities of the [6 + 4] diphenylnitrilimine–tropone adduct to attempt transformations to other novel heterocyclic systems, we have reinvestigated the reaction of diphenylnitrilimine to tropone. We report here full details of the reaction reported in the earlier communication,[2] structures of three additional minor products formed in this reaction, and results of investigations of the thermal and photochemical behavior of the [6 + 4] adduct. After submission of this work, Gandolfi and co-workers published a parallel study in which the structure of the major adduct 2 (see below) was proven,[13] and was found to have a different regiochemistry from that assigned in our earlier communication.[2]

Cycloaddition Products

The reaction of tropone with diphenylnitrilimine, generated in situ from α-chlorobenzylidenephenylhydrazine and triethylamine in benzene at room temperature, produced a mixture of adducts (Scheme I). The major adduct, **2**, precipitates from the reaction mixture, and careful column chromatography of the remaining solution gave five reaction products (**1**–**5**). The first four of these proved to be 1:1 adducts, while the last was a 2:1 adduct of diphenylnitrilimine and tropone. The structures of the major adduct, **2**, and the [6 + 4] adduct, **1**, were reported earlier,[2] but the work of Gandolfi et al. indicates that our assignment of structure to 2 was incorrect.

Scheme I



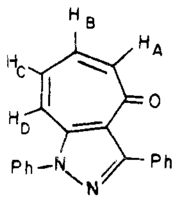
The structure of the [6 + 4] adduct **1**, mp 112–113 °C, formed in 4% yield, is clearly revealed from the NMR spectrum, shown in Figure 1, and the infrared spectrum. The bridging carbonyl is revealed by the stretching absorption at 5.79 μm, while the 100-MHz NMR spectrum, shown in Figure 1, is only compatible with the addition of the 1,3-dipole across the 2 and 7 positions of tropone. Thus, the two bridgehead protons (H_A and H_F) each appear as a sharp doublets of doublets. The doubly allylic bridgehead proton (H_A) (δ 4.52) has vicinal (J_{AB}) and "*W* (through carbonyl)"[14] (J_{AF}) couplings of 7.7 and 2.5 Hz, respectively, while the other bridgehead proton (H_F) is shifted downfield to δ 5.02 by the nitrogen and has vicinal (J_{EF}) and "*W*" (J_{AF}) couplings of 6.0 and 2.5 Hz. The olefinic protons appear as a complex multiplet between 5.5 and 6.4 ppm, which is the ABMN part of an ABMNXY system. Vicinal olefinic couplings (J_{BC} and J_{DE}) of approximately 11 Hz, and J_{CD} of approximately 6.5 Hz, along with smaller long-range couplings could be discerned from the spectrum.

Compound **5**, mp 216–217 °C, proved to be an inseparable mixture of 2:1 adducts **5a** and **5b**. The IR spectrum of this mixture revealed a bridging carbonyl stretching at 5.74 μm while the NMR spectrum indicated that **5** consisted of two closely related adducts, **5a** and **5b**, present in a 2:1 ratio. The major isomer, **5a**, gave a broadened AB resonance (δ_A 3.82, δ_B 4.54, J_{AB} = 0.1 Hz), while **5b** gave a similar pattern in the vinylic region, but with the chemical shifts more nearly identical (δ_A 4.06, δ_B 4.44, J_{AB} = 9.0 Hz). None of the remaining resonances are in the olefinic region of the spectrum. Reactions of the adducts, **1** or **4**, gave 2:1 adducts which were different from **5**. We cannot propose a structure of **5** consistent with all of the data.

The major adduct, **2**, mp 188–189 °C, could be isolated in a total yield of 54% by combining the material which precipitated from the reaction mixture with that obtained by chromatography. The strong carbonyl stretch at 6.07 μm was indicative of an α,β-unsaturated ketone moiety, while the multiplets at 2.3–3.0 (4 H) and 6.2–6.5 ppm (2 H) were indicative of the absence of protons on the unsaturated carbons α and β to the carbonyl. On this basis, the major isomer must have either the structure **2** or **3**. We earlier assigned to the major isomer structure **3**[2] on the basis of similar regioselectivity in other nitrile imine cycloadditions to α,β-unsaturated carbonyl compounds.[15]

The 100-MHz NMR spectrum has an AA′BB′ multiplet between 2.5 and 2.8 ppm and an ABX_2 pattern centered at 6.4 ppm. In a further attempt to simplify the NMR spectrum of **2**, deuterium exchange with NaOEt in EtOD was attempted. However, under conditions required for exchange, all of the protons other than the phenyl protons were replaced by deuterium. Although this is compatible with the structure of 2 shown, it was of no aid in distinguishing 2 from 3.

Adduct 2 could be dehydrogenated with chloranil in refluxing n-amyl alcohol. The resulting pyrazolotropone (6) had



6

tropone-like carbonyl absorptions at 6.05 and 6.2 μm and the NMR spectrum gave a complex multiplet between 6.5 and 7.2 ppm. Aromatic character is reflected in the closeness of these resonances and their downfield shifts with respect to resonances in α,β-unsaturated ketones.

The compound to which we assign structure 3, mp 152 °C, was obtained in 5% yield. The IR spectrum of this compound has a carbonyl stretch at 5.99 μm, indicative of an α,β-unsaturated ketone structure, and an upfield multiplet in the NMR at 2.3–2.9 ppm very similar in appearance to that of 2. However, the olefinic protons form a resolved AB pattern, with one proton (H_B) appearing at δ 6.18 as a doublet of triplets (J_{AB} = 11.0 Hz, J_{BC} = 6.0 Hz) and the second (H_B) appearing as a broadened doublet at δ 6.68 (J_{AB} = 11.0 Hz, $J_{AC} \leq 0.5$ Hz). The main NMR spectral difference between 2 and 3 is the downfield shift of one of the olefinic resonances in 3 as compared to 2.

The structural assignments shown in Scheme I, rather than the opposite, have been shown to be correct by the work of Gandolfi et al., who prepared the dihydro analogue of 3 by independent synthesis, and degraded 3 to a compound of unequivocal structure.[13]

Both 2 and 3 must arise from the initial [4 + 2] cycloaddition of the 1,3-dipole to the 2,3-double bond of tropone, followed by a hydrogen shift, probably base catalyzed, since triethylamine was present in the reaction mixture. Hydrogen shifts ultimately result in the formation of the aromatized pyrazole rings.

Finally, adduct 4, mp 134 °C, formed in 5% yield, was clearly an α,β-unsaturated ketone with protons on the α and β carbons. The carbonyl stretch at 6.05 μm and the AB pattern (δ_A 6.10, δ_B 7.00, J_{AB} = 12.0 Hz) in the NMR spectrum are fully in accord with expectation for structure 4, although no evidence for the orientation of the diphenylnitrilimine moiety relative to the cycloheptadiene moiety has been obtained. The protons on saturated carbons appear as a narrow multiplet between 2.6 and 3.3 ppm. Compound 4 arises from 1,3-dipolar cycloaddition to the γ,δ double bond of tropone, with subsequent isomerization to only one of the two possible aromatized products.

Thermal and Attempted Photochemical Transformations of [6 + 4] Adduct 1. One feature of 1 which prompted this study was the possibility that photochemical or thermal extrusion of CO would provide an additional entry into nine-membered 10π-electron heterocyclic systems,[16] as shown on the left of Scheme II. However, photolysis of 1 under various conditions (see Experimental Section) produced a complex mixture of compounds with a prominent broad carbonyl stretching region in the IR at 5.99 μm. Although interesting transformations of the type observed in [6 + 4] adducts of tropone with dienes[17] are no doubt occurring, the lack of evidence for decarbonylation has discouraged us from further investigations of the photolysis of 1.

However, heating 1 at 150 °C in Me_2SO solution caused formation of the previously elucidated adduct 3 in 50% yield.

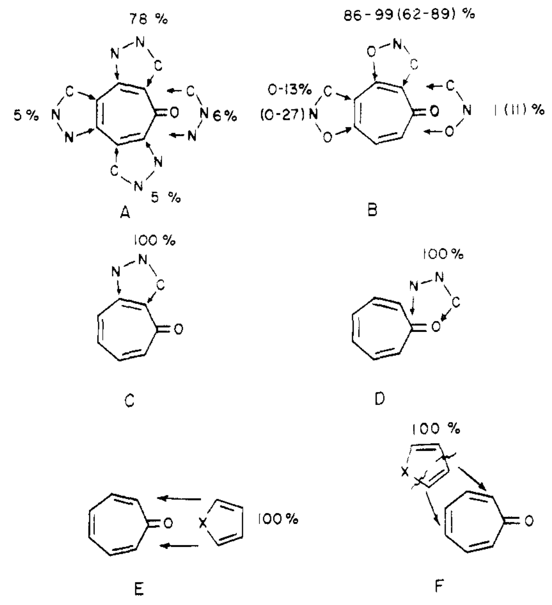


Figure 2. Summary of regio- and periselectivity observed in cycloadditions of 1,3-dipoles and dienes to tropone: A, diphenylnitrilimine (this work and ref 13); B, mesitonitrile oxide (benzonitrile oxide) (ref 4); C, diazomethane (ref 9) and dimethyldiazomethane (ref 20); D, N-phenylsydnone (ref 21); E, cyclopentadienones (ref 11e), cyclopentadiene and cyclohexadiene (ref 11a), isobenzofulvenes (ref 11b); benzopyrone, (ref 11d); F, 5-substituted cyclopentadienes (ref 22), cycloheptatriene (ref 23), fulvenes (ref 11c, 12).

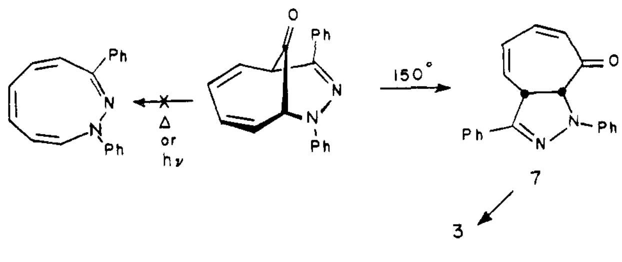
This transformation can be envisioned as a [1,5] sigmatropic shift to form 7, followed by subsequent [1,5] sigmatropic (or base-catalyzed] hydrogen shifts to form the aromatized product 3.

In the [6 + 4] adduct 1, two different [1,5] sigmatropic shifts could occur, one involving cleavage of a double allylic CN bond and the other of a CC bond which is allylic at one terminus and vinylic on the second. The first migration would lead to formation of the compound we have called 3, while the second cleavage would ultimately give 2. The surprising migration of the vinyl group, rather than the allylic nitrogen terminus, has some analogy in the rearrangements of spirononatriene, where the vinyl carbon, rather than allylic carbon, migrates preferentially.[18]

Discussion

In Figure 2, we have summarized the regio- and periselectivity results found in this work, with percentages normalized to 100%. The figure also summarizes the results of other 1,3-dipolar and diene cycloadditons to tropone. The periselective [4 + 2] cycloadditions of 1,3-dipoles (A–D) to tropone are puzzling, since unhindered dienes generally undergo periselective [6 + 4] cycloadditions (E) to tropone. This is all the more remarkable since both electron-rich (butadiene, isoprene, cyclopentadiene, cyclohexadiene, isobenzofulvenes, and perhaps fulvenes) and electron-deficient (cyclopentadienones, benzopyrone) dienes undergo [6 + 4] cycloadditions (E) to tropone, while electron-rich (diazoalkanes)[19,20] (C) and

Scheme II



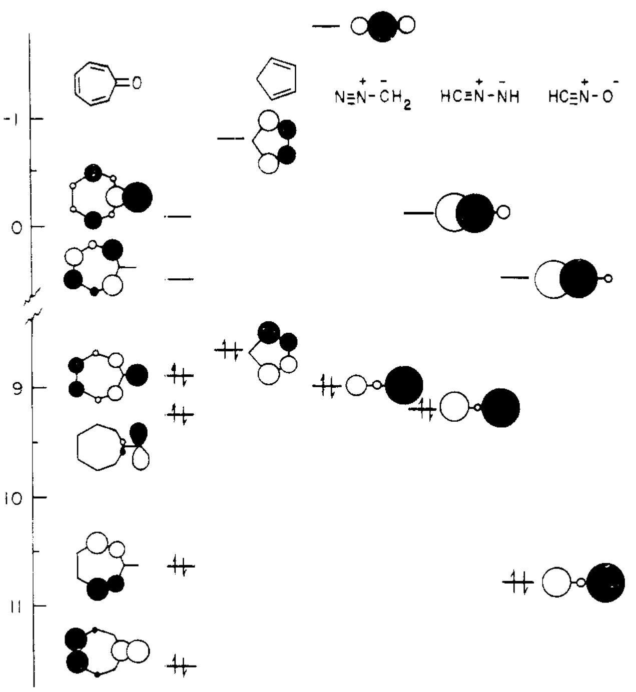


Figure 3. The π molecular orbitals of tropone (STO-3G), cyclopentadiene, and several 1,3-dipoles.[27] Filled and vacant MO energies are negatives of ionization potentials (from PES)[26] and negatives of estimated electron affinities, respectively.

electron-deficient (nitrile oxide, nitrile imine, and sydnone)[21] (A, B, D) dipoles prefer [4 + 2] cycloadditions.

In order to attempt a rationale of this divergent behavior of dienes and 1,3-dipoles, 4π-electron systems which are otherwise similar in their cycloaddition behavior, we turn to the molecular orbitals of tropone, which are shown in Figure 3. The MO's shown are calculated by an ab initio method[24] using the STO-3G basis set.[25] The orbital coefficients are those obtained from the calculations, while the occupied orbital energies are negatives of photoelectron ionization potentials[26] and the vacant orbital energies are negatives of estimates of electron affinities.

This figure also includes the frontier orbitals of cyclopentadiene, which adds in a [6 + 4] fashion to tropone, diazomethane, the parent nitrilimine, and fulminic acid, three 1,3-dipoles whose frontier orbital energies have been measured or closely estimated.[27]

The reactivity of tropone toward electrophilic species should be dominated by the HOMO, a π orbital, which is 1.75 eV higher in energy than the second highest π orbital. Particularly "hard" electrophiles may also react at the relatively negative oxygen. In reactions with dienes, the tropone HOMO should favor [6 + 4] cycloaddition or cycloaddition to the 4,5 double bond. The third occupied orbital will, however, lead to stabilization of cycloaddition to the 2,3 double bond.

The LUMO of tropone is a normal, somewhat polarized, triene orbital. It also would appear to favor [6 + 4] cycloaddition or [4 + 2] addition to the 4,5 double bond. The presence of the relatively low-lying SLUMO complicates this picture, since reaction at C-3 is favored here. However, the propensity for cyclopentadienes and other simple dienes to add in a [6 + 4] fashion to tropone can be used as empirical evidence in favor of the importance of the HOMO and LUMO in determining the periselectivity of reactions of dienes.

Returning to the problem at hand, the orbital diagram makes even more apparent the difficulty of explaining the lack of substantial amounts of [6 + 4] adducts in reactions of 1,3-dipoles with tropone. Diazomethane, which has an IP similar to cyclopentadiene, and fulminic acid, which has a similar electron affinity, both avoid the [6 + 4] route, as does nitrile imine, which is only slightly more electrophilic than cyclopentadiene.

There also do not seem to be large differences in geometrical factors between dienes and 1,3-dipoles. Thus, the distance between termini is 2.44 Å in diazomethane, while the 1,4-distance is 2.24 Å in cyclopentadiene. Both should be easily able to span the 2,7 distance of tropone (2.55 Å).

The only compelling difference between dienes and 1,3-dipoles which might explain the failure of the latter to undergo [6 + 4] cycloaddition is the relatively large positive charge on the central atom of 1,3-dipoles (0.10–0.47), which must come in close proximity to the partially postively charged carbon of tropone (charge = +0.16) in the transition state of a concerted [6 + 4] 1,3-dipolar cycloaddition. However, for a charge of +0.16 on the carbonyl carbon, +0.5 on the central nitrogen of the 1,3-dipoles, and an assumed separation of 2.2 Å in the transition state, the Coulombic repulsion amounts to only 0.5 kcal/mol, and this seems insufficient to account for the exclusive [6 + 4] cycloaddition in the absence of this interaction and only small amounts of [6 + 4] adduct in the presence of this interaction. An effect worth at least several kilocalories per mole is required to explain the difference between 1,3-dipoles and carbocyclic dienes.

Turning to the various [4 + 2] routes observed, we note first that the preferential addition of the nitrilimine to the 2,3 double bond of tropone can be rationalized by frontier orbital predictions. For both nitrile oxides and imines, the interaction of the LUMO of these species with the HOMO of tropone determines the preferred regioselectivity. With the highly nucleophilic diazomethane, maximum transition-state stabilization occurs when the more nucleophilic carbon terminus (site of highest HOMO coefficient) becomes united with the C-2 of tropone, which has a larger LUMO coefficient than C-3.

We are continuing to explore the origins of periselectivity in this and related cycloadditions by both experimental and theoretical techniques.

Experimental Section

Melting points are uncorrected. Elemental analyses were performed by Mr. Ralph Seab at L.S.U.

Reaction of Tropone with Diphenylnitrilimine. Tropone (10 g) and α-chlorobenzylidenephenylhydrazine (4.6 g) were dissolved in benzene (60 mL), and triethylamine (6 mL) in benzene (25 mL) was added over a period of 6 h with stirring under nitrogen. The mixture was left at room temperature for 12 h. The precipitated $Et_3N{\cdot}HCl$ was filtered off and the benzene solution was washed thoroughly with water. Concentration of the solution and cooling afforded crystals (3.2 g), mp 180–185 °C. Recrystallization from methanol furnished pure material (2.8 g) **2**, mp 188–189 °C. The residual gummy material was chromatographed on alumina (50 g). Elution with 1:3–2:3 benzene/petroleum ether gave a fraction which consisted of three components on TLC. These components were separated on thick-layer plates. Two elutions with 8:2 benzene/cyclohexane gave three fractions.

Fraction I consisted of 250 mg of **1**, mp 112–113 °C (from methanol). Anal. Calcd for $C_{20}H_{16}N_2O$: C, 79.97; H, 5.37; N, 9.32. Found: C, 79.73; H, 5.41; N, 9.35.

Fraction II consisted of 250 mg of **5**, mp 216–217 °C (from methanol). Anal. Calcd for $C_{33}H_{26}N_4O$: C, 80.14; H, 5.30; N, 11.33. Found: C, 79.86; H, 5.52; N, 11.00.

Fraction III consisted of 300 mg of **3**, mp 152 °C (from methanol). Anal. Calcd for $C_{20}H_{16}N_2O$: C, 79.97; H, 5.37; N, 9.32. Found: C, 80.18; H, 5.36; N, 9.32.

Further elution of the alumina column using benzene and then 1:1 benzene/chloroform gave a fraction consisting of two components on TLC. These were separated by preparative TLC using 5:1 cyclohexane/ethyl acetate to give two fractions.

Fraction I′ consisted of 300 mg of **4**, mp 134 °C (from methanol). Anal. Calcd for $C_{20}H_{16}N_2O$: C, 79.97; H, 5.37: N, 9.32. Found: C, 79.70; H, 5.39; N, 9.27.

Fraction II′ consisted of **2**, mp 188–189 °C (from methanol). This material was identical with the crystalline material **2** initially obtained. Anal. Calcd for $C_{20}H_{16}N_2O$: C, 79.97; H, 5.37; N, 9.32. Found: C, 79.76; H, 5.23; N, 9.19.

Chloranil Treatment of Adduct 2. A solution of **2** (100 mg) in *n*-amyl alcohol (5 mL) was refluxed under nitrogen for 3 h with chloranil (500 mg). Excess *n*-amyl alcohol was distilled off under vacuum and the residue was taken up in chloroform and shaken with 4% NaOH solution to remove chloranil. Removal of the solvent in vacuo left a solid residue which was purified by eluting through a column of alumina (6 g) with 1:1 benzene/chloroform. Recrystallization from methanol afforded 50 mg of **6**, mp 175 °C. Anal. Calcd for $C_{20}H_{14}N_2O$: C, 80.52; H, 4.73; N, 9.39. Found: C, 80.40; H, 4.76; N, 9.28.

Deuteration Studies on 2. (a) A solution of **2** (100 mg) in tetrahydrofuran (3 mL) was stirred under nitrogen for 20 h with a solution of sodium (~10 mg) in D_2O (2 mL). The reaction mixture was extracted with methylene chloride. The NMR spectrum was identical with that of the undeuterated material.

(b) To a solution of Na (~10 mg) in EtOD (4 mL), **2** (100 mg) was added. The mixture was kept at 60 °C for 20 min under nitrogen and then D_2O (1 mL) was added. The reaction mixture was extracted with methylene chloride. The NMR spectrum of this material indicated exchange of all the protons except the phenyl protons.

Thermal Rearrangement of the [6 + 4] Adduct 1. A solution of **1** (100 mg) in Me_2SO (1 mL) was heated gradually to 150 °C and kept at that temperature for 1 h under N_2. The reaction mixture was diluted with water and extracted with methylene chloride. Removal of the solvent in vacuo gave a solid residue which was purified by filtration through a column of alumina with benzene eluent. Crystallization from methanol afforded 50 mg of a material, mp 150 °C, which was identical with the [4 + 2] adduct **3** already obtained.

Photolysis of the [6 + 4] Adduct 1. (a) A solution of **1** (100 mg) in benzene (350 mL) was irradiated with a Rayonet 3500 Å lamp in a Pyrex vessel under nitrogen. Even after 16 h of irradiation, the reaction mixture showed considerable starting material remaining (from NMR), besides a few spots having lower R_f than the original compound on TLC.

(b) A solution of the compound (100 mg) in benzene (350 mL) was irradiated with a Rayonet 3000 Å lamp in a quartz vessel under nitrogen. After 12 h of irradiation, the starting material was not visible by TLC. At least four spots were detectable by TLC having lower R_f values than the starting material. The infrared spectrum of this mixture indicated the presence of several α,β-unsaturated ketones.

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Registry No.—**1**, 32499-79-9; **2**, 63788-67-0; **3**, 31108-24-4; **4**, 64666-44-0; **6**, 63788-69-2; tropone, 539-80-0; α-chlorobenzylidenephenylhydrazine, 15424-14-3; diphenylnitrilimine, 15409-32-2.

References and Notes

(1) (a) On leave from the Indian Association for the Cultivation of Science, Jadavpur, Calcutta, 1976–1978; (b) Camille and Henry Dreyfus Teacher-Scholar Grant Recipient, 1972–1977; Fellow of the Alfred P. Sloan Foundation, 1975–1977.

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