# Reaction of *p*-Nitrobenzenesulfonyl Azide with Alkylidenecycloalkanes

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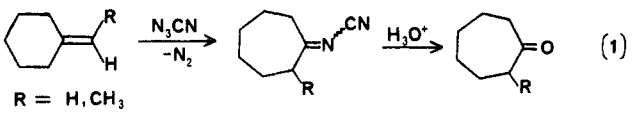
The 1,3-dipolar addition of *p*-nitrobenzenesulfonyl azide (PNBSA) to alkylidenecycloalkanes 1–3 was studied, and the products of hydrolysis were isolated and identified. The products from 1 and 2 suggest that these alkenes react to give a single triazoline intermediate. The tetrasubstituted derivatives 3, however, give both possible reaction modes. The products initially derived from 3 were the two sulfonimides expected from ring expansion (4, R = R′ = Me) and methyl migration (5). Upon hydrolysis, the respective ketones, 8 and 9, were obtained in excellent overall yields. The ring-expanded sulfonimides 4 (R = R′ = Me, $n$ = 6–8) were found to be less reactive under hydrolytic conditions than their respective isomers 5. Thus, subjecting the PNBSA adducts to mild hydrolysis conditions allowed the isolation of pure 9 ($n$ = 6–8). Also, in two cases (i.e., $n$ = 7, 8), the pure imides 4 (R = R′ = Me, $n$ = 7, 8) crystallized from the hydrolysis solutions. Dipolar cycloaddition of *p*-nitrobenzenesulfonyl azide to 2-isopropylidenebicyclo[2.2.1]heptane followed by acid hydrolysis gives *endo*-2-acetyl-*exo*-2-methylbicyclo[2.2.1]heptane (4.1%), *exo*-2-acetyl-*endo*-2-methylbicyclo[2.2.1]heptane (16.3%), 2,2-dimethylbicyclo[3.2.1]octan-3-one (2.1%), and 3,3-dimethylbicyclo[3.2.1]octan-2-one (36.8%), thus providing evidence that electronic factors are much more important than steric effects in controlling regioselectivity.

Hermes and Marsh[2] reported that cyanogen azide and olefins react to give addition products which, in some cases, are rearranged ketone precursors. Their study was followed by those of McMurry,[3,4] who investigated the synthetic utility of the ring enlargement following the addition of cyanogen azide to alkylidenecycloalkanes, e.g., eq 1.

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Other groups have also studied the synthetic applicability of this ring expansion using various types of exocyclic olefins and other azides.[5-8] The dipolar cycloadditions are regiospecific,[2] and their rates are greatly affected by steric factors in the olefin.

In connection with our studies of the reaction of sulfonyl azides with olefins[9] and with dienes,[10] a systematic study of the addition of sulfonyl azides to a wider range of alkylidenecycloalkanes was of interest. Isopropylidenecycloalkanes were considered to be of special interest because the electronic effects of the olefinic carbons are more or less constant but the steric factors vary. Isopropylidenebicyclo[2.2.1]heptane (IPBH) is especially interesting in this respect. The regioselectivity was therefore not easily predicted. To provide the necessary data for our evaluation, we investigated the addition of *p*-nitrobenzenesulfonyl azide (PNBSA) to olefins 1–3 (Scheme I) and to IPBH (Schemes II and III). The ketones formed upon hydrolysis of the intermediate sulfonimides were identified and their yields determined.

## Results and Discussion

**Reaction Procedure.** Benzene solutions of the olefins and PNBSA were prepared in an olefin–azide molar ratio of 2:1 in Fisher-Porter thick-walled tubes. These vessels were sealed and heated at 90 °C until PNBSA was not detectable by IR analysis. The sulfonimide intermediates 4 and, in the case of 3, 5 were characterized by their strong IR absorption at about 1635–1590 cm$^{-1}$. Hydrolysis of the intermediate gave the ring-enlarged ketones 6–8 and, in the case of 3, the methyl rearrangement product 9.

Scheme I

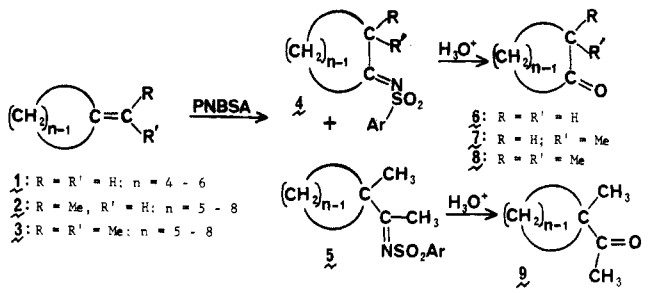


Table I. Reaction of PNBSA with Methylenecycloalkanes 1

| $n$ | reaction time,[a] days | % yield of 6 by GLC | % yield of 6 as 2,4-DNP |
|---|---|---|---|
| 4 | 4.5 | 21 | 26.5 |
| 5 | 5 | 45 | 53 |
| 6 | 7.5 | 92 | 61 |

[a] Approximate time for disappearance of azide.

The identity and yields of products were determined by GLC when authentic samples were available for comparison. Alternatively, the structures of the products and yields were determined by preparation and isolation of product 2,4-dinitrophenylhydrazone (2,4-DNP) derivatives from the whole reaction mixture.

**Methylenecycloalkanes.** Research on the addition of various azides to methylenecycloalkanes[3-5] has shown that the additions are regiospecific, giving only dipolar addition such that the electrophilic terminus of the dipole adds to the least substituted carbon (Markovnikov addition). Triazolines were not isolated although they were suspected to be intermediates.[2,10] Despite nonbonding interactions between the arylsulfonyl group and ring protons, PNBSA behaves similarly, and as the size of the ring decreased, the reactivity increased, the yield of the enlarged ketone 6 decreased, and the amount of tars increased (Table I).

(1) (a) The University of Alabama in Huntsville. (b) Abstracted in part from the dissertation presented by M.O., in partial fulfillment of the degree requirements of the degree of Doctor of Philosophy, The University of Alabama, 1979. (c) Clemson University.
(2) Hermes, M. E.; Marsh, F. D. *J. Org. Chem.* **1972**, *37*, 2969.
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(10) Abramovitch, R. A.; Ortiz, M.; McManus, S. P. *J. Org. Chem.*, preceding paper in this issue.

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Scheme II

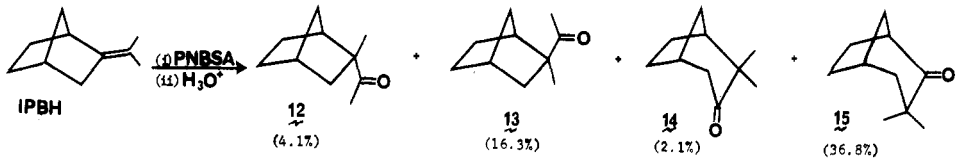
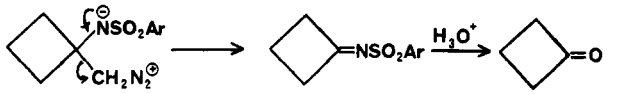



Table II. Reaction of PNBSA with Ethylidenecycloalkanes 2

| n | reaction time,[a] days | % yield of 7 by GLC | % yield of 7 as 2,4-DNP |
|---|---|---|---|
| 5 | 6 | 44 | 44 |
| 6 | 8 | 63 | 69 |
| 7 | 5 | 76 | 98 |
| 8 | 7 | 66 | 72 |

[a] Approximate time for disappearance of azide.

It is possible that other products, formed by an alternate mechanism, could be present. For example, McMurry found that the decomposition of the betaine intermediate also takes place by C–C bond cleavage,[3] which would lead to eq 2 if it occurred here. However, we were unable to

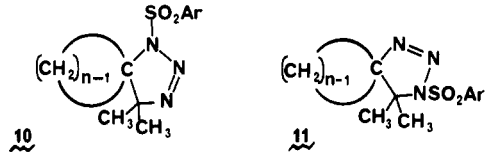



(2)

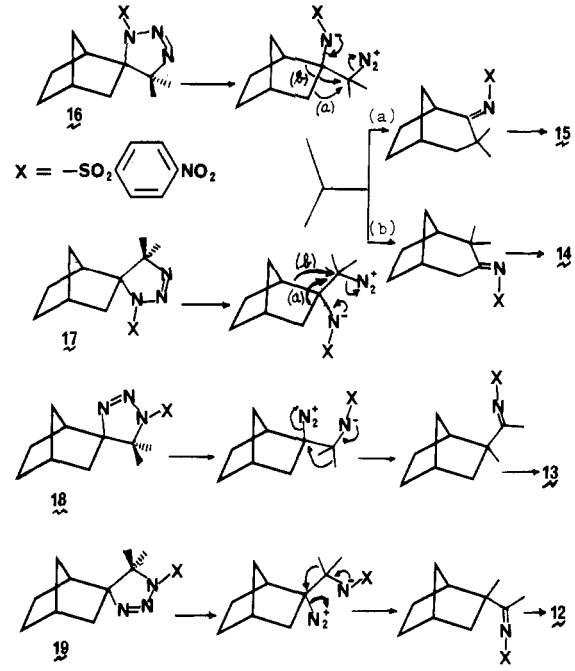
detect any cyclobutanone by GLC of the reaction products of PNBSA and methylenecyclobutane.

**Ethylidenecycloalkanes.** The reactions of PNBSA with ethylidenecycloalkanes proceeded much in the same manner as those of the methylene analogues, with electronic effects in the alkene controlling regiospecificity. On the basis of following the disappearance of the azide (IR analysis) qualitatively, the reaction times of the derivatives 2 were found to be just slightly longer than those of the parent exocyclic olefins, but yields of the enlarged 2-methylcycloalkanone 7 were in the same range (Table II).

**Isopropylidenecycloalkanes.** The reaction of PNBSA with isopropylidenecycloalkanes 3 gave the sulfonimide 5 resulting from methyl migration as well as the ring-enlarged sulfonimide 4. These products are undoubtedly produced via the unstable triazoline intermediates 10 and 11 which are the two possible regioadducts of the azide with the unsymmetrically tetrasubstituted olefin.




Scheme III




Under mild conditions the PNBSA–isopropylidenecyclopentane adducts 4 (R = R′ = Me, $n$ = 5) and 5 ($n$ = 5) were completely hydrolyzed to give the ketones 8 and 9 ($n$ = 5; Table III). However, under these mild conditions, the hydrolysis of the sulfonimide intermediates from the other isopropylidenecycloalkanes ($n$ = 6, 7, or 8) gave only the ketones 9. The unhydrolyzed sulfonimides 4 (R = R′ = Me, $n$ = 7 and 8) could be isolated as crystalline compounds from the hydrolysis product mixtures and their structures confirmed by their IR and NMR spectra and elemental analysis. It was confirmed that these imides were more resistant to hydrolysis than were their isomers 5 ($n$ = 7 and 8) and required stronger conditions to drive the reaction to completion. This could possibly be attributed to the steric hindrance of the two methyl groups which shield the imide carbon from attack by water, although their poor solubility in aqueous ethanol may be a contributing factor.

In Table III are presented the observed approximate reaction times and product analyses for the additions of

Table III. Reaction of PNBSA with Isopropylidenecycloalkanes 3

| n | reaction time,[a] days | hydrolysis conditions: t, days | hydrolysis conditions: temp, °C | product ratio (8:9) by NMR | product ratio (8:9) by GLC | % yield of 8 + 9 as 2,4-DNP |
|---|---|---|---|---|---|---|
| 5 | 6.5 | 1 | 50 | 1.7:1 | 2.1:1 | 75 |
| 6 | 10.5 | 1 | 50 | 0:1 | 0:1 | 33 |
| | | 3 | 50 | 1.5:1 | 1.7:1[b] | 92[c] |
| 7 | 6.5 | 1 | 50 | 0:1 | | 49 |
| | | 2 | 100 | 1.1:1 | | 89 |
| 8 | 10 | 3 | 50 | 0:1 | 0:1 | 52 |
| | | 4 | 100 | 1:1.7 | 1:2.2[b] | 95[b] |

[a] Approximate time for the disappearance of azide. [b] Approximate ratios (based on analysis of overlapping peaks) for the remaining unhydrolyzed product 4. [c] Corrected for unhydrolyzed sulfonimide indicated by NMR to be present along with 8 and 9 in the hydrolysis product mixture.

PNBSA to isopropylidenecycloalkanes. The ratio of the two major products, **8** and **9**, was determined from GLC peak area ratios and by NMR integration of the methyl signals at about $\delta$ 1.0 and 1.15 for compounds **8** and **9**, respectively. When unhydrolyzed imide **4** was present (e.g., with **3**, $n$ = 6–8), the *gem*-dimethyl protons for **4** were integrated along with those of **8** to give the proper ratio of completely hydrolyzed products. However, the GLC ratios shown are only semiquantitative, since equal molar responses for compounds **8** and **9** were assumed, and unhydrolyzed sulfonimide **4** was not taken into account. The GLC retention times for compounds **9** were shorter than those for **8** for $n$ = 5 and 6, while for $n$ = 7 both had the same retention time. The total yield of carbonyl products from the reactions was determined by isolation of the 2,4-DNP derivatives. The total yield of 2,4-DNP derivatives from the reaction of isopropylidenecyclooctane was slightly lower than that for the lower homologues, and an estimated 5% yield of unidentified side products was detected by GLC for this reactant.

Comparison of the observed reaction times for the addition of PNBSA to the alkylidenecycloalkanes suggests that, for a given ring size, the less substituted olefins **1** are more reactive than **2** and **3**, with methylenecyclobutane being the most reactive single compound. Wohl[5] has previously suggested that relief of angular strain (I strain) may facilitate the addition while nonbonding interactions may act to retard it. These suggestions are supported by our qualitative data on the reaction times. It is interesting to note that the six-membered ring in each series is observed to be the slowest reacting in the series. On the basis of the disappearance of the azide, the five- and seven-membered rings appear to have similar rate characteristics, and they each give nearly complete reaction in 60–75% of the time required for the six-membered rings.

**Isopropylidenebicyclo[2.2.1]heptane.** The addition off PNBSA to IPBH was complete after 16 days, compared to ca. 6–11 days for the less sterically hindered derivatives **3**. The formation of the imine intermediate was evident by the strong absorption at 1610–1600 $cm^{-1}$ (small amounts of enamines were also evident); the NMR also indicated the aromatic moiety, a singlet at $\delta$ 2.6 assigned as the $CH_3C{=}N$ group and two singlets at $\delta$ 1.25 and 1.04 for $sp^3$-bound methyl groups. As with the reactions of isopropylidenecycloalkanes, hydrolysis of the imine required stronger conditions than other less hindered imino products. Hydrolysis of the intermediates was nearly complete after the mixture was stirred for 3 h in boiling 2 N HCl in 50% aqueous ethanol. The NMR of the hydrolyzed reaction products indicated a $CH_3C{=}O$ absorption at $\delta$ 2.08 and overlapping methyl singlets at $\delta$ 1.15 and 1.01. Unambiguous NMR analysis of the mixture of products was not possible because of the overlapping peaks.

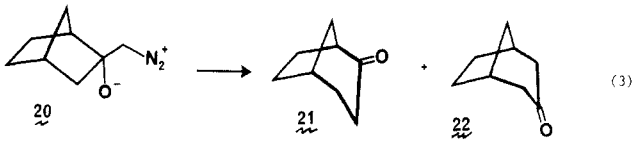
GLC analysis indicated the presence of four major products and traces of four other components (less than 1%). The retention times and yields of the four major products are shown in Scheme II. With cycloheptanone as the internal standard and with the assumption of equal molar response factors, the yields were determined by integration of the GLC curves. Ketones **12**, **13**, and **15** were isolated by preparative GLC and identified as *endo*-2-acetyl-*exo*-2-methylbicyclo[2.2.1]heptane, *exo*-2-acetyl-*endo*-2-methylbicyclo[2.2.1]heptane, and 3,3-dimethylbicyclo[3.2.1]octan-2-one, respectively, by NMR analysis of the pure ketones and by isolation and characterization of their 2,4-DNP derivatives.

Surprisingly, the $CH_3C{=}O$ proton chemical shifts for **12** and **13** were very close [$\delta$ 2.05 (endo), 2.06 (exo)], and the methyl on the ring had the same chemical shift for both isomers ($\delta$ 1.16). Therefore, the melting points of the 2,4-DNP derivatives of these isomers were the key to the structure assignments; the 2,4-DNP of **13** had a melting point of 155–156 °C (lit.[11] mp 155.5–156.6 °C), while the 2,4-DNP of **12** had a melting point of 165–166 °C.

Because it was present in small amounts, 2,2-dimethylbicyclo[3.2.1]octan-3-one (**14**) was not isolable by preparative GLC. Therefore, a firm assignment of a structure to **14** is not possible on the basis of our data. However, **14** can form by either exo or endo addition, and because all the modes of addition appear to be occurring, **14** is an expected product.

Because of severe and unsymmetrical steric factors in the rigid olefin, the reaction between PNBSA and IPBH was expected to be slow and to proceed with nearly exclusive attack on the olefins' less sterically hindered[12,13] exo face. While a relatively slow reaction occurred [$k$(isopropylidenecycloalkanes)/$k_{IPBH} \simeq$ 1.5–2.5), a surprising amount of endo attack (e.g., $k_{exo}/k_{endo} \simeq 13/12 = 4$) was observed. This is apparently the result of a conflict between electronic and steric control in the addition. Steric control would favor exo attack to give the regioisomer **18** (Scheme III) where the nonbonding interactions between the arylsulfonyl group and the syn C-7 hydrogen are minimized. However, exo regioisomer **16** is the product favored electronically,[12,13] but it should have to overcome severe nonbonding interactions on approaching the transition state. Despite the steric factors, the ring-expansion products **14** and **15** (via **16** and **17**) are formed about twice as readily as the methyl migration products **12** and **13** (via **18** and **19**). This confirms the previously demonstrated importance of electronic factors in these additions.[3] Regardless of the electronic factors favoring **16**, nonbonding interactions apparently slow the formation of **16**, making the formation of **18** and **19** competitive.

For the ring-expanded products, a preference for methylene migration (less substituted C-2,C-3 bond) over methine migration (more substituted C-1,C-2 bond) was observed, as expected from studies of similar rearrangements.[14,15] However, the dominance of methylene group migration (17:1) was not expected. Sauers and Tucker[15] found that the betaine **20**, formed by the addition of diazomethane to norcamphor, rearranges to a mixture of the ketones **21** and **22** (eq 3) with a 2:1 preference for




20 21 22 (3)

methylene over methine group migration. Because our intermediates leading to **14** and **15** are similar to **20**, our results were expected to be similar. Therefore, a much greater preference for methylene group migration in our work suggests that the additional steric factors present in our intermediates may influence the migratory aptitudes. Since both **14** and **15** may be derived from the intermediates from exo and endo attack, it is impossible for us, from our data, to perform a detailed analysis that could

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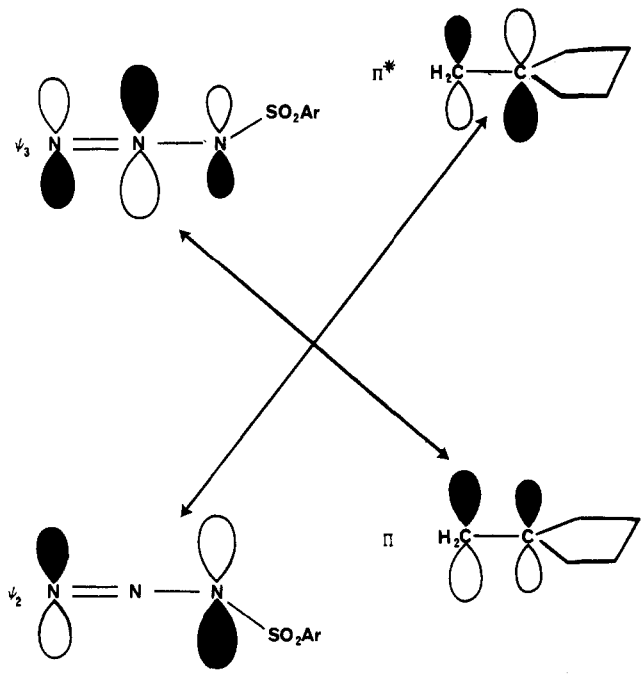



**Figure 1.** Qualitative view of the frontier molecular orbital interactions of PNBSA and methylenecyclopentane.

establish the reasons for the large preference for methylene group migration.

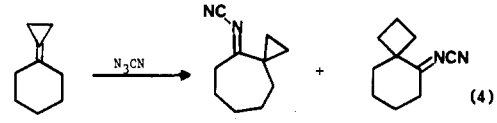
**Mechanism of Azide–Olefin Cycloadditions.** In the past several years, the reactions of azides with olefins have been described as concerted 1,3-dipolar additions, and, in that context, their properties are generally well described by perturbational molecular orbital (PMO) theory.[16] While quantitative data on the MO's of the specific addends are not available, we can treat these reactions qualitatively by assuming they follow the reaction pattern of similar systems. Thus, in Figure 1 is shown the frontier MO interactions expected for PNBSA and methylenecyclopentane. The alkene has the larger coefficient at the exocyclic carbon in the HOMO and the endocyclic carbon in the LUMO.[16e] For the sulfonyl azide, the terminal N has a larger coefficient than the sulfonyl-substituted N in the LUMO while the largest coefficient is on the more substituted N in the HOMO.[16b] The interaction of the LUMO of the azide and HOMO of the alkene is predicted to dominate because of the relatively small gap as compared with the azide HOMO–alkene LUMO interaction (which would produce the same regioisomer). The same diagram would qualitatively serve to rationalize the regiospecificity observed for all of the methylene- and ethylidenecycloalkanes.

With the isopropylidenecycloalkanes **3** the situation is more complex. Because the degree of substitution at the olefinic carbons is equal, any difference in the alkene coefficients must arise because of secondary electronic effects such as inductive effects of the β-alkyl groups in the ring and that caused from differential angle strain at the endocyclic and exocyclic olefinic carbons. Following the line of reasoning given for the unsymmetrical alkenes, the added donor ability of the ring methylene groups should favor the same net pertubation and hence the same ordering of the coefficients as for **1** and **2**. Therefore, on the basis of inductive effects alone, the regioisomer predicted to form in the cases of **1** and **2** is also favored for **3**. However, Houk and co-workers[17] have recently carried out calculations of methyl-substituted alkenes that suggest that approach of a nucleophilic reactant may cause reversal of the small orbital polarization difference that is predicted for the alkene without any perturbation by a reactant. This effect could obviously be a factor with **3** since the C=C coefficients are expected to be very similar.

The CC=C angle distortion because of ring strain also should complicate the situation. Kao and Radom[18] have calculated that a change in CC=C bond angle in cyclopropene or cyclopentadiene is accompanied by a change in the energies of the C=C HOMO and LUMO. Also, the restricted rotational freedom of the carbons flanking the endocyclic olefinic C and the differential strain in the C=C angles should affect σ–π mixing and hence the orbital coefficients. Since both the orbital energies and coefficients are expected to be affected, both reaction rates and regioselectivity should be affected, as is observed (Table III).

An alternate mechanistic description of these reactions is possible. Firestone[19] has been a proponent of a radical rather than a concerted pathway.[16a] Since the ring-expansion products **4** resulting from PNBSA addition to **1** and **2** are the result of Markovnikov addition, either the stepwise or the concerted mechanism serves to adequately describe the product regioselectivity. More research is, therefore, required before a clear mechanistic choice for these reactions can be confirmed.

In the only other reported examples of addition of azides to tetrasubstituted olefins, McMurry and Coppolino[4] added cyanogen azide to cyclopropylidenecyclohexane to get a mixture of the expected regioisomers with only a slight excess (1.5:1 ratio) of the first product shown in eq 4. In a related report, Fitjer[7] reported that PNBSA reacts



(4)

with members of the novel spirocyclic series **23** to give the ring-expanded adducts **24** free of their regioisomers (eq 5).

(5)

While this selectivity difference may be the result of electronic and steric influences of the spirocyclic rings, it is possible that cyanogen azide is too reactive to show significant selectivity with cyclopropylidenecyclohexane.

In summary, the addition of PNBSA to exocyclic olefins **1** and **2** gives only the ring-expanded sulfonimide **4**. On hydrolysis, the imides provide good yields of the ketones **6** and **7**. The addition of PNBSA to the isopropylidenecycloalkanes **3** or to IPBH gives the sulfonimides expected from the various modes of addition. A cursory consideration of the factors which affect the regioselectivity of the concerted dipolar addition did not allow a prediction of the preferred regioisomer in any case. However, it is assumed that the influence of angle strain on the iso-

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propylidenecycloalkane HOMO and LUMO is a significant factor in the observed result in each case. For practical application of the latter reactions to synthesis, it was noticed that the methyl migration product **5** was the more sensitive to hydrolysis when $n = 7$ and 8. In those cases, the ring-expanded sulfonimide was crystallized and purified. The procedure thus affords a route to each of the pure ketones 8 and 9.

## Experimental Section

**General Methods.** Melting points are uncorrected. The IR spectra were recorded on a Beckman Acculab I. NMR spectra were obtained with a Varian EM-360 or a Bruker HFX-10 90 MHz spectrometer using $CDCl_3$ as solvent, unless otherwise specified. Chemical shifts ($\delta$) are expressed in parts per million relative to internal $Me_4Si$. Gas chromatographic (GLC) analyses were carried out on a $^1/_8$ in. × 6 ft column packed with 5% FFAP (Carbowax 20M/2-nitroterephthalic acid product) on Chromosorb W by using a Varian Model 1520 instrument with He carrier and flame-ionization detector. Elemental analyses were performed by Galbraith Laboratories, Inc.

**Materials.** The methylene- and ethylidenecycloalkanes were purchased from Chem Samples Co. and were used without additional purification. The isopropylidenecycloalkanes were prepared by the Wallach procedure[20,21] and had the characteristics described below.

**Isopropylidenecyclopentane** was prepared in 19% overall yield from cyclopentanone: bp 135–136 °C; $n^{20}_D$ 1.4589 (lit.[20a] bp 136–137 °C, $n^{20}_D$ 1.4581); NMR $\delta$ 2.1 (m, 4 H, $CH_2C{=}C$), 1.62 (m, 10 H, $CH_3C{=}C$ and $CH_2$), no C=CH. The purity was >99% (GLC).

**Isopropylidenecyclohexane** was prepared in 16% overall yield from cyclohexanone: bp 159–160 °C; $n^{20}_D$ 1.4720 (lit.[20b] bp 160–161 °C; $n^{20}_D$ 1.4723); NMR $\delta$ 1.52 (m, 6 H, $CH_2$), 1.67 (s, 6 H, $CH_3C{=}C$), 2.16 (m, 4 H, $CH_2C{=}C$), no C=CH.

**Isopropylidenecycloheptane** was prepared in 20% overall yield from cycloheptanone: bp 180–183 °C; $n^{20}_D$ 1.4788 (lit.[22] bp 180–181 °C; $n^{20}_D$ 1.4765); NMR $\delta$ 2.17 (m, 4 H, $CH_2C{=}C$), 1.64 (s, 6 H, $CH_3C{=}C$), 1.46 (m, 10 H, $CH_2$), no C=CH.

**Isopropylidenecyclooctane** was prepared in 18% overall yield from cyclooctanone: bp 208–210 °C; $n^{20}_D$ 1.4839 (lit.[22] bp 206 °C; $n^{20}_D$ 1.4874); NMR $\delta$ 2.17 (m, 4 H, $CH_2C{=}C$), 1.64 (s, 6 H, $CH_3C{=}C$), 1.46 (m, 10 H, $CH_2$), no C=CH.

**2-Isopropylidenebicyclo[2.2.1]heptane (IPBH).** Isopropylmagnesium bromide and norcamphor afforded *exo*-2-isopropylbicyclo[2.2.1]heptan-*endo*-2-ol (**25**) in a yield of 76.4%. Heating the alcohol with potassium bisulfate (1:1 w/w) at 180 °C and direct distillation of the product at 90 mm[23] gave a mixture of the starting alcohol, an unidentified ketone, and a mixture of olefins. Attempted separation by fractional distillation failed. The olefinic mixture was separated by column chromatography on neutral alumina and the components were tentatively identified as IPBH and 2-isopropylbicyclo[2.2.1]hept-2-ene: IR (neat) 3060 (C=CH), 790 $cm^{-1}$ (s, trisubstituted olefin); NMR $\delta$ 5.9 (s, C=CH).[24]

Under milder dehydration conditions (150–160 °C) with potassium bisulfate (1:2 w/w) for 4 h, the desired olefin, free of its isomer, was obtained along with unreacted alcohol and traces of ketone. Attempted separation of the olefin by distillation failed, but column chromatography on neutral alumina gave the olefin in high purity in 26% yield. Final purification by fractional distillation gave the product as a colorless liquid: bp 70 °C (28 mm); $n^{20}_D$ 1.4852 (lit.[26] bp 78 °C (30 mm); $n^{20}_D$ 1.4854); IR 1640 (vw, C=C), no significant absorption > 3000, 790, or 890 $cm^{-1}$; NMR 2.8 (br s, 1 H, allylic bridgehead H), 2.24 (br s, 1 H, bridgehead H), 1.53 and 1.43 (d, $C{=}C(CH_3)_2$).

**General Procedure for the Addition Reaction.** A solution of the azide (2.28 g, 10 mmol) and the olefin (20 mmol) in dry benzene (30 mL) was sealed and heated in a 3-oz Fisher-Porter aerosol tube at 90 ± 4 °C (protected from light) until all the azide had reacted, as determined by an IR analysis of an aliquot of the evaporated solution on a NaCl plate. The formation of the imino product was indicated by the strong IR absorptions at about 1600 $cm^{-1}$.

**General Procedure for Hydrolysis and Product Analysis. Reaction of PNBSA with Methylene- and Ethylidenecycloalkanes.** The crude *p*-nitrobenzenesulfonimidocycloalkane was mixed with ethanol (10 mL) and 4 N HCl (10 mL) and stirred at room temperature for 24 h. The reaction mixture was neutralized with sodium bicarbonate, and the precipitate was filtered. The solution was extracted with ether until an aliquot gave a negative 2,4-DNP test. The combined ether extracts were dried ($MgSO_4$), and the ether was distilled at atmospheric pressure. The residue was transferred to a volumetric flask and diluted with absolute ethanol.

**2,4-DNP Derivatives.** An aliquot from each ethanol solution of the hydrolysis residues was treated with 2,4-DNP reagent and subsequently allowed to stand until precipitation was complete. The precipitated hydrazone was filtered, washed with cold ethanol, and air-dried. The yields of hydrolysis product based on the crude 2,4-DNP products are indicated in Tables I and II. The structures of the isolated 2,4-DNP derivatives in each case were verified by comparisons with authentic compounds.

Because no authentic sample was available, the hydrolysis product from the reaction of PNBSA with ethylidenecyclooctanone was identified as 2-methylcyclononanone (**7**, $n = 8$) by analysis of its 2,4-DNP: IR (KBr) 3310 (m, NH), 3110, 3080 (w, aromatic CH), 2960, 2920, 2850 (s, CH), 1620 (s, C=N), 1590 (s, NH), 1540 (m, $NO_2$), 1510 (s, $NO_2$), 1475, 1420 (m, CH), 1340 (s, $NO_2$), 1312 (s), 1270, 1218, 1130, 1070, 920, 835 (s), 740 (s) $cm^{-1}$; NMR $\delta$ 11.02 (s, 1 H, NH), 9.1 (s, 1 H, aromatic CH), 8.2 and 7.94 (dd, 2 H, aromatic CH), 2.4 (m, 3 H, $CH_2$–CN–CH), 1.67–1.26 (m, 10 H, ring $CH_2$), 1.07 (d, 3 H, $CH_3CH$). Anal. Calcd for $C_{16}H_{22}N_4O_4$: C, 57.47; H, 6.63. Found: C, 57.36; H, 6.70.

**GLC Analysis.** The sole significant product in each chromatogram was identified as the ring-expanded product by comparing its retention time with that of an authentic sample. Yields were determined by comparing peak areas with an internal standard which had been compared for molar response with authentic samples of the respective products.

***Hydrolysis and Product Analysis. From Isopropylidenecyclopentane.*** The crude sulfonimide product was partially dissolved in ethanol (5 mL) and 4 N HCl (5 mL) and allowed to stir overnight at 50 °C. The resulting mixture was neutralized with sodium carbonate and extracted several times with carbon tetrachloride until no ketone was detected by the 2,4-DNP test. The combined extracts were washed with water, dried ($MgSO_4$), and concentrated by distillation through a fractionating column at atmospheric pressure. The residue was transferred to a volumetric flask, diluted with carbon tetrachloride, and set aside for analysis.

GLC analysis indicated two products in a peak area ratio of ~1:2 (assuming equal molar responses). On the basis of analogy with the other reactions in the series, a mixture of 1-acetyl-1-methylcyclopentane (**9**, $n = 5$) and 2,2-dimethylcyclohexanone (**8**, $n = 5$) was expected and was indicated by the NMR spectrum of the reaction solution: $\delta$ 2.3 (t, $CH_2CO$), 2.07 (s, $CH_3CO$), 1.73 (m, $CH_2$), 1.19 (s, $CH_3CCO$), 1.06 (s, $(CH_3)_2CCO$) (lit.[27] $\delta$ 1.02). By integration of the singlets at $\delta$ 1.19 and 1.06, the ratio of products was calculated (Table III).

An aliquot of the hydrolysis reaction mixture was distilled through a fractionating column, and the product fraction was diluted with ethanol, treated with 2,4-DNP reagent, and allowed to stand. The precipitate was filtered, washed with cold ethanol,

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dried, and weighed. A mixture of two products was indicated by TLC, and the total yield of both reaction products, assumed to be 2,4-DNP derivatives of the ketones above, was calculated from the crude weight (Table III).

**From Isopropylidenecyclohexane.** After treatment of the crude sulfonimide with 2 N HCl in 50% aqueous ethanol solution for 24 h at 50 °C and workup, GLC analysis indicated only one product which was indicated by GLC comparison with an authentic sample and confirmed by $^1$H NMR to be 1-acetyl-1-methylcyclohexane (**9**, $n$ = 6), which was further confirmed by its 2,4-DNP derivative: mp 130–131 °C (lit.[28] mp 131–132 °C); NMR $\delta$ 11.07 (s, NH), 9.11 (s, aromatic), 8.20 and 7.93 (dd, $J$ = 10 Hz, aromatic), 2.0 (s, $CH_3CN$), 1.5 (m, $CH_2$), 1.26 (s, $CH_3$). Anal. Calcd for $C_{15}H_{20}N_4O_4$: C, 56.24; H, 6.29. Found: C, 56.39; H, 6.13.

After hydrolysis was continued for 3 days, GLC analysis indicated the presence of the ketones **9** ($n$ = 6) and **8** ($n$ = 6) in an approximate ratio of 1:1.7 based on relative areas of the overlapping peaks. A molar ratio of **9** to **8** of 1:1.5 was calculated from the NMR spectrum of the mixture by integration of the methyl singlets at $\delta$ 1.11 ($CH_3CC$=O) and 1.05 ($(CH_3)_2CC$=O) (lit.[28] $\delta$ 1.0). However, the presence of a small amount of the unhydrolyzed imide **4** (R = R' = Me, $n$ = 6) was indicated by the absorptions at $\delta$ 8.18 (dd, aromatic $A_2B_2$ system) and 3.04 (t, $CH_2C$=N). Thus the product yield was corrected accordingly and is as indicated in Table III.

**From Isopropylidenecycloheptane.** After the crude sulfonimido product was stirred with 2 N HCl in 50% ethanol for 24 h at 50 °C and the mixture worked up, GC analysis indicated the presence of only one peak. The NMR spectrum was consistent with the structure of 1-acetyl-1-methylcycloheptane (**9**, $n$ = 7): $\delta$ 2.03 (s, $CH_3CO$), 1.53 (m, $CH_2$), 1.07 (s, $CH_3$). Its 2,4-DNP derivative was obtained from the crude hydrolysis product and was extracted free of unhydrolyzed sulfonimides: mp 132–133 °C; NMR $\delta$ 11.2 (s, NH), 9.13 (s, aromatic), 8.32 and 8.1 (dd, aromatic), 2.01 (s, $CH_3CN$), 1.52 (m, $CH_2$), 1.2 (s, $CH_3$). Anal. Calcd for $C_{16}H_{22}N_4O_4$: C, 57.47; H, 6.63. Found: C, 57.50; H, 6.63.

From the hydrolysis solution was isolated by crystallization a 22.5% yield of 2,2-dimethyl(*p*-nitrobenzenesulfonimido)cyclooctane (**4**; R = R' = Me, $n$ = 7): mp 115–116 °C (from $CCl_4$); IR (KBr) 3100 (w, aromatic CH), 2920 (w, CH), 1590 (s, C=N), 1530 (s, $NO_2$), 1470, 1450, 1380 (m, CH), 1345 (s, $NO_2$), 1320 (s), 1305 (s), 1150 (s), 870 (w), 850 (s), 785 (s); NMR $\delta$ 8.3 (dd, 4 H, aromatic CH), 3.1 (t, 2 H, CHC=N), 2.2–1.48 (m, 12 H, ring $CH_2$), 1.11 (s, 6 H, $CH_3$). Anal. Calcd for $C_{16}H_{22}N_2O_4S$: C, 56.78; H, 6.55. Found: C, 56.59; H, 6.38.

After the hydrolysis was continued for 2 days at 100 °C, no sulfonimide was detected by NMR, and **8** ($n$ = 7) and **9** ($n$ = 7) were indicated: $\delta$ 2.48 (t, $CH_2CO$), 2.08 (s, $CH_3CO$), 1.83 (m), 1.5 (m), 1.19 (s, $CH_3CCO$), 1.05 (s, $(CH_3)_2CCO$). The ratios calculated by integration of the peaks at $\delta$ 1.19 and 1.05 are presented in Table III. Unfortunately, both ketones had the same GC retention time, and resolution could not be achieved by use of various GLC conditions.

**From Isopropylidenecyclooctane.** After the crude sulfonimido product was stirred with 2 N HCl in 50% ethanol for 3 days at 50 °C, 1-methyl-1-acetylcyclooctane **9** ($n$ = 8) was selectively formed as indicated by the NMR signals at $\delta$ 2.01 (s, $CH_3CO$) and 1.08 (s, $CH_3CCO$) and by the isolation of its 2,4-DNP derivative: mp 103–104 °C (by column chromatography on and recrystallization from ethanol); IR (KBr) 3325 (m, NH), 3110 (w, C=CH), 1620 (s, C=N), 1590 (s, NH); NMR $\delta$ 11.33 (s, 1 H, NH), 920 (s, 1 H, aromatic), 8.44 and 8.16 (dd, 2 H, aromatic), 2.03 (s, 3 H, $CH_3$), 1.56 (m, 14 H, $CH_2$), 1.11 (s, 3 H, $CH_3$). Anal. Calcd for $C_{17}H_{24}N_4O_2$: C, 58.61; H, 6.94. Found C, 58.56; H, 6.78.

From the crude hydrolysis workup solution was recovered 11.3% of 2,2-dimethyl(*p*-nitrobenzenesulfonimido)cyclononane (**4**; R = R' = Me, $n$ = 8): mp 136–137 °C ($CCl_4$); IR (KBr) 3100 (w, aromatic CH), 2930 (s, CH), 1590 (s, C=N), 1540 (s, $NO_2$), 1465 (m), 1382 (w, CH), 1342 (s, $NO_2$), 1316 (s), 1295 (s), 1160 (s), 1158 (s), 1085 (m), 1000 (m), 890 (w), 850 (s), 900, 790, 745, 778 (m); NMR $\delta$ 8.3 (dd, 4 H, aromatic $A_2B_2$ system), 3.06 (t, 2 H, $CH_2C$=N), 1.88, 1.54 (m, 14 H, $CH_2$), 1.08 (s, 6 H, $(CH_3)_2CC$=N). Anal. Calcd for $C_{17}H_{24}N_2O_4S$: C, 57.93; H, 6.86. Found: C, 57.73; H, 6.79.

After hydrolysis of the original reaction mixture at 100 °C for 4 days, two products in a ratio of 1:2.3 were indicated by GLC. Since the second peak was identified by comparison with an authentic sample as 1-acetyl-1-methylcyclooctane, the first peak was tentatively assigned to 2,2-dimethylcyclononanone (**8**, $n$ = 8). Other minor peaks in the GLC accounted for less than 5% of the total composition. The NMR of the reaction products confirmed the presence of both ketones [$\delta$ 2.0 (s, $CH_3CO$), 1.05 (s, $CH_3CCO$), 0.92 (s, $(CH_3)_2CCO$)] in a ratio of 1:1.7. Since a small amount of unhydrolyzed product remained, the ratio was corrected as indicated in Table III.

**From Isopropylidenebicyclo[2.2.1]heptane.** After hydrolysis of the reaction mixture by heating to reflux in 2 N HCl in 50% aqueous ethanol for 3 days and then the normal workup procedure, the product residue was dissolved in $CCl_4$. The NMR spectrum of the hydrolyzed product was complex due to the interference of unreacted olefin and some unhydrolyzed imine: $\delta$ 8.38 (q, aromatic, minor component), 7.2 (br s), 2.08 (s, $CH_3CC$=O).

Using a 6 ft × $^1/_8$ in. column of FFAP on Chromosorb W, with a column temperature of 100 °C and a 25 psi helium flow (flame-ionization detector), the chromatogram of the solution containing the mixture of products showed four major products with retention times of 3.85, 4.35, 5.05 and 5.68 min in a peak ratio of 1:4.0:0.4:8.97, respectively. The ratios were also determined with a thermal-conductivity detector using a 10 ft × $^1/_4$ in. FFAP column at 122 °C and a 30 psi helium flow; the ratios obtained were 1:4.0:0.52:9.3, respectively. Cycloheptanone was used as the internal standard for the quantitative analysis.

By use of the 10 ft × $^1/_4$ in. column, the product was separated preparatively, giving three major products in pure form. The first fraction (retention time 3.85 min, >98% pure) was tentatively assigned either structure **12** or **13** on the basis of its NMR spectrum: $\delta$ 2.05 (s, 3 H, $CH_3C$=O), 1.16 (s, 3 H, $CH_3CC$=O), and a complex pattern of peaks at 2.23, 2.17, 1.73, 1.62, 1.43, and 1.3. The second fraction (retention time 4.35 min, >98% pure) also was assigned as either **12** or **13**: $\delta$ 2.06 (s, 3 H, $CH_3C$=O), 1.16 (s, 3 H, $CH_3CC$=O), and a complex pattern of peaks at 2.36, 2.2, 1.57, and 1.52. The third fraction [retention time 5.68 min, >95% pure; $\delta$ 2.47 (br s, C$^1$H), complex pattern with peaks at 2.31, 2.16, 2.05, 1.7, 1.6, 1.15 s, 3 H, $CH_3CC$=O), 1.05 (s, 3 H, $CH_3CC$=O)] was tentatively identified by its NMR spectrum as 3,3-dimethylbicyclo[3.2.1]octan-2-one [lit.[12] $\delta$ 2.8–2.7 (m, bridgehead C-1 H), 2.4–2.3 (m, bridgehead CH), 1.1 and 1.0 (d, sharp, $COC(Me_2)_2$]. The reported peak at $\delta$ 2.8–2.7, assigned as the C-1 H, was not present in our spectrum.

The samples obtained by preparative GLC were each allowed to react with 2,4-DNP reagent, and the derivatives were recrystallized from ethanol prior to IR and NMR analysis and melting point determination. Fraction 1 ($t_r$ = 3.85 min): mp 165–166 °C; IR (KBr) 3330 (m, NH), 3110 (w, aromatic H), 2960–2880 (m, CH), 1920 (s, C=N), 1590 (s, NH), 1518–1500 (s, $NO_2$), 1455, 1420 (m, CH), 1335 (s, $NO_2$); NMR ($CDCl_3$, $Me_4Si$), the signals at $\delta$ 2.03 (br s, $CH_3C$=N) and 1.16 (br s, $CH_3CC$=N) were clear. Anal. Calcd for $C_{16}H_{20}N_4O_4$: C, 57.82; H, 6.07. Found: C, 57.71; H, 6.23. On the basis of the identity of fraction 2 below as the 2,4-DNP of ketone **13**, this component was assigned as the 2,4-DNP of *endo*-2-acetyl-*exo*-2-methylbicyclo[2.2.1]heptane (**12**). Fraction 2 ($t_r$ = 4.35 min): mp 155–156 °C; identified as the 2,4-DNP of *exo*-2-acetyl-*endo*-2-methylbicyclo[2.2.1]heptane (**13**; lit.[11] mp 155–156 °C); IR (KBr) 3320 (m, NH), 3105 (w, aromatic CH), 2978–2855 (m, CH), 1620 (s, C=N), 1590 (s, NH), 1580–1500 (s, $NO_2$), 1455 and 1425 (m, CH), 1335 (s, $NO_2$); NMR ($CDCl_3$, $Me_4Si$) $\delta$ 1.98 (s, $CH_3C$=N), 1.15 (s, $CH_3CC$=N). Fraction 3 ($t_r$ = 5.68 min) gave only an oily derivative that failed to crystallize.

An aliquot of the original solution of the reazction products (2 mL) was concentrated on a steam bath, and the residue was allowed to react with 2,4-DNP reagent (10 mL). The brown gummy precipitate was filtered and air-dried, giving 0.485% g (72.9%) of the crude 2,4-DNP mixture. Column chromatography on neutral alumina (Brockman activity I) with elution with pentane–benzene (1:1 v/v) gave, after 500 mL of eluant, a yellow oily compound that, after recrystallization twice from ethanol–ethyl acetate, gave small orange beads (mp 103–105 °C) identified

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as the 2,4-DNP of 3,3-dimethylbicyclo[3.2.1]octan-2-one (lit.[12] mp 103-105 °C): IR (KBr) 3320 (m, NH), 3118, 3080 (w, ArCH), 2980-2880 (s, CH), 1620 (s, C=N) (s, NH), 1510-1500 (s, $NO_2$), 1460, 1420 1375 (m, CH), 1340 (s, $NO_2$); NMR ($CDCl_3$, $Me_4Si$) 11.2 (br s, 1 H, NH), 9.2 (s, 1 H, aromatic), 8.34 and 8.02 (d, 2 H, aromatic), 2.52 and 2.47 (overlapped s, 2 H, bridgehead), complex pattern with peaks at 2.22, 2.05, 1.69, 1.56 (8 H, $CH_2$), 1.3 and 1.24 (d, 6 H, $(CH_3)_2CC{=}N$). Further elution produced additional colored bands, but there was no clear separation. Identification of the other 2,4-DNP components by TLC also failed as all three of the major products had the same $R_f$ value upon elution with petroleum ether and benzene mixtures.

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**Registry No.** 1 ($n$ = 4), 1120-56-5; 1 ($n$ = 5), 1528-30-9; 1 ($n$ = 6), 1192-37-6; 2 ($n$ = 5), 2146-37-4; 2 ($n$ = 6), 1003-64-1; 2 ($n$ = 7), 10494-87-8; 2 ($n$ = 8), 19780-51-9; 3 ($n$ = 5), 765-83-3; 3 ($n$ = 6), 5749-72-4; 3 ($n$ = 7), 7087-36-7; 3 ($n$ = 8), 30718-63-9; 4 (R = R′ = Me; $n$ = 5), 75600-20-3; 4 (R = R′ = Me; $n$ = 6), 75600-21-4; 4 (R = R′ = Me; $n$ = 7), 75600-22-5; 4 (R =R′ = Me; $n$ =8), 75600-23-6; 5 ($n$ = 5), 75600-24-7; 5 ($n$ = 6), 75600-25-8; 5 ($n$ = 7), 75600-26-9; 5 ($n$ = 8), 75626-84-5; 6 ($n$ = 4), 120-92-3; 6 ($n$ = 4) 2,4-DNP derivative, 2057-87-6; 6 ($n$ = 5), 108-94-1; 6 ($n$ = 5) 2,4-DNP derivative, 1589-62-4; 6 ($n$ = 6), 502-42-1; 6 ($n$ = 6) 2,4-DNP derivative, 3349-73-3; 7 ($n$ = 5), 583-60-8; 7 ($n$ = 5) 2,4-DNP derivative, 5138-30-7; 7 ($n$ = 6), 932-56-9; 7 ($n$ = 6) 2,4-DNP derivative, 970-95-6; 7 ($n$ = 7), 10363-27-6; 7 ($n$ = 7) 2,4-DNP derivative, 73674-39-2; 7 ($n$ = 8), 73674-37-0; 7 ($n$ = 8) 2,4-DNP derivative, 73674-40-5; 8 ($n$ = 5), 1193-47-1; 8 ($n$ = 5) 2,4-DNP derivative, 5212-74-8; 8 ($n$ = 6), 7228-52-6; 8 ($n$ = 6) 2,4-DNP derivative, 22612-83-5; 8 ($n$ = 7), 42393-51-1; 8 ($n$ = 7) 2,4-DNP derivative, 42393-52-2; 8 ($n$ = 8), 75600-27-0; 8 ($n$ = 8) 2,4-DNP derivative, 75600-28-1; 9 ($n$ = 5), 13388-93-7; 9 ($n$ = 5) 2,4-DNP derivative, 75600-29-2; 9 ($n$ = 6), 2890-62-2; 9 ($n$ = 6) 2,4-DNP derivative, 2890-63-3; 9 ($n$ = 7), 75600-30-5; 9 ($n$ = 7) 2,4-DNP derivative, 75600-31-6; 9 ($n$ = 8), 75600-32-7; 9 ($n$ = 8) 2,4-DNP derivative, 75600-33-8; 12, 75658-54-7; 12 2,4-DNP derivative, 75600-34-9; 13, 75658-55-8; 13 2,4-DNP derivative, 75600-35-0; 14, 55682-09-2; 15, 42393-53-3; 15 2,4-DNP derivative, 42393-54-4; PNBSA, 4547-62-0; IPBH, 4696-14-4; 26, 75600-36-1; isopropyl bromide, 75-26-3; norcamphor, 497-38-1.

# Investigation of Thermally Induced α-Deoxysilylation of Organosilylated Hydroxylamine Derivatives as a General Method for Nitrene Production

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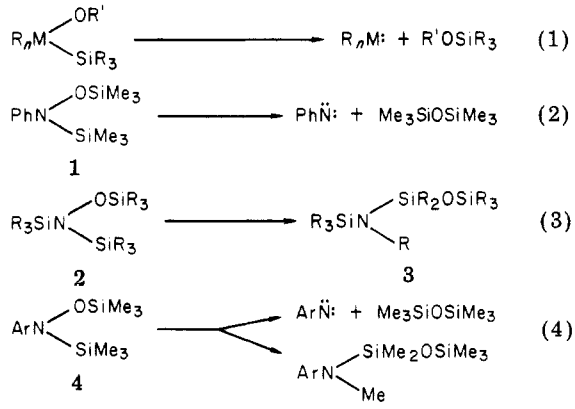
A variety of organosilylated hydroxylamine derivatives have been synthesized and studied as possible nitrene generators by thermally induced α-deoxysilylaton: $GN(OR')SiR_3 \rightarrow G\ddot{N}: + R'OSiR_3$, where G = $EtO_2C$, ArCO, $ArSO_2$, Me, H, and $Ph_2PO$. The methods used to assess nitrene formation include trapping product characterization, substitutent variation, kinetic activation parameter measurements, Hammett studies, and solvent effects. While the latter two types of precursors were only briefly investigated because of their marked resistance to fragmentation, the combined data for the remaining compounds are consistent with the intermediacy of a nitrene. The existence of alternative deoxysilylation pathways is discussed in some cases, and for comparison with the nitrogen systems reported herein, kinetic activation parameters for α-deoxysilylation about carbon and silicon have been determined.

We have previously reported[3,4] that the thermally induced α-deoxysilylation reaction (eq 1) known for carbon[5] (M = C) and silicon[6] (M = Si) systems also obtains for the nitrogen case where M = N and G = Ph. Thus, as shown in eq 2, heating *N*-phenyl-*N*,*O*-bis(trimethylsilyl)-hydroxylamine (1) leads to formation of hexamethyldisiloxane and phenylnitrene, which may be intercepted by various trapping agents.[3,4] This fragmentation contrasted markedly with the rearrangement (eq 3) of structurally related tris(organosilyl)hydroxylamines (2) to (silylamino)disiloxanes (3) discovered by West and coworkers;[7] however, our subsequent studies with phenyl-




substituted derivatives of 1 (4) have shown that partitioning between the fragmentation and rearrangement pathways is controlled by the aryl group electronic interactions with nitrogen (eq 4).[8] The effect is illustrated by

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