Alkyl Azides, Diazides, Haloazides and Bridged Polycyclic Diazides

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A series of monoazido alkanes and diazido alkanes have been synthesized. Specifically, 1-azidobutane (100.0 g), 1-azidopentane (100.0 g), 1-azidoheptane (100.0 g), and 1-azidodecane (100.0 g) were synthesized and characterized completely both analytically and spectroscopically. Among cyclic examples 1,2-diazidocyclopentane, 1,2-diazidocyclohexane, and 1,2-diazidocycloheptane were synthesized. Norbornene was converted into a regioisomeric mixture of 2,3-diazo and syn and anti-2,7-diazidonorbornanes. The photodimer of norbornadiene was synthesized and converted to the tetraazido analog. These compounds were transmitted to C.K. Law, Princeton, for droplet combustion experiments. Dihydrobenzylidene was synthesized and preliminary developmental work has been initiated. A sample has been transmitted to C.K. Law for combustion experiments.
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ALKYL AZIDES, DIAZIDES, HALOAZIDES AND BRIDGED POLYCYCLIC DIAZIDES

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Abstract

A series of monoazido alkanes and diazido alkanes have been synthesized. Specifically, 1-azidobutane (100.0 g), 1-azidopentane (100.0 g), 1-azidohexane (100.0 g), 1-azidoctane (100.0 g), and 1-azidoheptane (100.0 g), 1,3-diazidopropane (200.0 g), 1,4-diazidobutane (200.0 g), 1,5-diazidopentane (200.0 g), 1,6-diazidohexane (200.0 g), 1,7-diazidoheptane (200.0 g), 1,8-diazidoctane (200.0 g) were synthesized and characterized completely both analytically and spectroscopically. Among cyclic examples 1,2-diazidocyclopentane, 1,2-diazidocyclohexane and 1,4-diazocyclohexane were synthesized. Norbornene was converted into a regioisomeric mixture of 2,3-diazo and syn and anti-2,7-diazidonorbornanes. The photodimer of norbornadiene was synthesized and converted to the tetraaza analog. These compounds were transmitted to C.K. Law, Princeton, for droplet combustion experiments.

Dihydrobenzvalene was synthesized and preliminary developmental work has been initiated. A sample has been transmitted to C.K. Law for combustion experiments.
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1. **Introduction**

In continuation of our original concept, namely, the thermal decomposition of alkyl azides in the liquid phase of droplets exothermically releases nitrogen, we extended the scope of work to include long chain diazides and strained polycyclic polyazides. The decomposition of a monoazide is represented by equation 1:

$$\text{R} \equiv \text{N}_3 \xrightarrow{\Delta} \text{R} - \text{N} + \text{N}_2 \quad \text{Equation 1}$$

In the case of a diazide the release of nitrogen would be stepwise:

$$\text{N}_3(\text{CH}_2)_n\text{N}_3 \xrightarrow{\Delta} \text{N}_3(\text{CH}_2)_n - \text{N} + \text{N}_2$$

$$\downarrow \Delta$$

products \quad \xleftarrow{} \quad \text{N} - (\text{CH}_2) - \text{N} + \text{N}_2 \quad \text{Equation 2}$$

In the case of a bridged polycyclic system the strain energy of the carbocyclic framework would contribute additionally to the exothermic fragmentation.

**Method of Synthesis**

The generic equation for the synthesis of linear aliphatic diazides is as follows:

$$\text{Br}(\text{CH}_2)_n\text{Br} + \text{NaN}_3 \xrightarrow{\text{CH}_3\text{OH/H}_2\text{O}} \text{N}_3(\text{CH}_2)_n\text{N}_3 \quad \text{Equation 3}$$

$$n = 4,5,6,7,8,9$$

*Table 1* presents a list of the various alkyl diazides which have been synthesized.
### Table I  Mono and Diazidoalkanes Synthesized

A. Monoazidoalkanes

<table>
<thead>
<tr>
<th></th>
<th>Name</th>
<th>Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1-Azidobutane</td>
<td>100.0 g</td>
</tr>
<tr>
<td>2</td>
<td>1-Azidopentane</td>
<td>100.0 g</td>
</tr>
<tr>
<td>3</td>
<td>1-Azidohexane</td>
<td>100.0 g</td>
</tr>
<tr>
<td>4</td>
<td>1-Azidoheptane</td>
<td>100.0 g</td>
</tr>
<tr>
<td>5</td>
<td>1-Azidoctane</td>
<td>100.0 g</td>
</tr>
</tbody>
</table>

B. Diazidoalkanes

<table>
<thead>
<tr>
<th></th>
<th>Name</th>
<th>Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1,3-Diazidopropane</td>
<td>200.0 g</td>
</tr>
<tr>
<td>2</td>
<td>1,4-Diazidobutane</td>
<td>200.0 g</td>
</tr>
<tr>
<td>3</td>
<td>1,5-Diazidopentane</td>
<td>200.0 g</td>
</tr>
<tr>
<td>4</td>
<td>1,6-Diazidohexane</td>
<td>200.0 g</td>
</tr>
<tr>
<td>5</td>
<td>1,7-Diazidoheptane</td>
<td>200.0 g</td>
</tr>
<tr>
<td>6</td>
<td>1,8-Diazidoctane</td>
<td>200.0 g</td>
</tr>
</tbody>
</table>
2. Synthesis of Vicinal Diazides. Hypervalent Iodine Method

In this process (Eqn 4) a double bond is converted into a 1,2-diazide:

\[
\text{R-CH=CH-R'} \xrightarrow{(\text{PhIO})_n/\text{NaN}_3, \Delta} \text{R-CH-CH-R'} + \text{R-CH-C-R'}
\]

Eqn. 4

\( R = R' = \text{H or alkyl or aryl} \)

Using this method we have synthesized some cycloalkyl diazides which will be evaluated by CK Law in combustion experiments. Specifically cyclopentene and cyclohexene have been converted to 1,2-diazidocyclopentane and 1,2-diazidocyclohexane, respectively.

5.
3. **Synthesis of Norbornadiene Dimers**

Using the method shown in Eqn. 7 norbornadiene was converted into exo-trans-exo and exo-trans endo dimer.

\[
\text{Exo-trans-exo-diene (84\%)} \quad \text{Exo-trans-endo-diene (8\%)}
\]

The dimer mixture was purified by column chromatography and converted directly to a mixture of the corresponding tetraazido derivatives.

\[
\text{(84\%)} \quad \text{(8\%)} + \text{other products (8\%)}
\]

The mixture of isomeric tetraazides was transmitted to CK Law for combustion experiments.
4. **References:**


5 EXPERIMENTAL
Synthesis of Monoazidoalkanes

General Procedure:

1-Bromo-octane [96.5 g, 0.5 mol] was dissolved in methanol (500 ml). To this solution sodium azide [65.0 g, 1.0 mol] in water (300 ml) was added in one portion and the contents were refluxed for 2 days. The reaction mixture was cooled to room temperature and concentrated in vacuo to ~400 ml. Water (500 ml) was added to the concentrate and extracted with ether (3 x 500 ml), dried over anhydrous magnesium sulfate, filtered and concentrated in vacuo to yield the product (70 g, 90%).

Synthesis of Diazidoalkanes

General Procedure:

1,4-Dibromobutane [64.5 g, 0.3 mol] was dissolved in methanol (500 ml). To this solution sodium azide [97.5 g, 1.5 mol] in water (300 ml) was added in one portion and the contents were refluxed for 2 days. The reaction mixture was cooled to room temperature and concentrated in vacuo to ~400 ml. Water (500 ml) was added to the concentrate and extracted with ether (3 x 500 ml), dried over anhydrous magnesium sulfate, filtered and concentrated in vacuo to yield the product (40.0 g, 95%).

Synthesis of Norbornadiene Dimers

Norbornadiene [135.0 g, 1.46 mol], hexacarbonyl bis(triphenyl phosphine) dicobalt [3.0 g, 0.0037 mol] and benzene (120 ml) were stirred together under reflux for 48 hours. The reaction mixture was cooled to room temperature and then washed with dil HCl (2N, 500 ml) and separated, and the aqueous portion was extracted with ether (2 x 500 ml). The combined organic portions were washed with saturated sodium carbonate (2 x 500 ml), dried over anhydrous MgSO₄, filtered and concentrated in vacuo to yield the product (98.0 g, 73%).

Synthesis of Polyazidonorbornane Dimers

Iodosobenzene [26.4 g, 0.12 mol] was added to acetic acid (500 ml) followed by the addition of norbornadiene dimers [9.2 g, 0.05 mol] at 0°C. The reaction mixture was stirred at 0°C for 15 min., then sodium azide [26.0 g, 0.4 mol] was added to the reaction
mixture and the contents were heated at 40° C for 2 hours. The reaction mixture was cooled to room temperature and then poured into water (1000 ml) and extracted with chloroform (3 x 500 ml). The organic phase was then washed with saturated sodium bicarbonate solution (3 x 500 ml), dried over anhydrous MgSO₄, filtered, concentrated in vacuo to give the crude product (30 g). The crude product was then passed through a silica gel column using 20% ethyl acetate in hexane as an eluant. Yield 8.0 g.
6. **Dihydrobenzvalene**

Work was initiated during the current project on the synthesis of dihydrobenzvalene.

During the contract period this synthesis was standardized, and currently we are producing 30g/wk of 80:20% dihydrobenzvalene:benzene.
7. **Preparation of Dihydrobenzvalene**

Methyllithium (457.2 ml, 640 mmol, Aldrich, 1.4 M solution in diethyl ether) was cannulated into a dropping funnel (500 ml) under an N\textsubscript{2} atmosphere. The methyllithium was slowly introduced into a 5 L three necked flask. An aspirator outlet was adopted to remove ethyl ether from the methyllithium. After all the ethyl ether was removed under reduced pressure, dry N\textsubscript{2} gas was introduced and the flask was cooled to -78 °C (dry ice-acetone bath). Methyl ether gas was introduced slowly through the adaptor while cooling until approximately 1200 ml of methyl ether was collected. The dry ice-acetone bath was replaced with a dry ice-acetonitrile bath (-42 °C). Freshly distilled cyclopentadiene (40 g, 605 mmol) was slowly added from a dropping funnel into the stirred solution. After vigorous evolution of methane subsided, dry dichloromethane (104 g, 1.22 moles) was added dropwise with stirring. The slurry turned yellow. An ether solution containing methyl lithium (900 ml, 1.26 moles, Aldrich, 1.4 M solution in diethyl ether) was added very slowly with stirring. After complete addition, the solution was slowly warmed to room temperature. Most of the methyl ether was removed during this process. The ethyl ether was distilled from the reaction mixture using a water aspirator into a receiver cooled in a dry ice-acetone bath. The benzvalene was codistilled with ethyl ether and some benzene. (Note: distillation was carried out until all of the ether was removed. The ether solution of benzvalene was used as such for the reduction without further purification).

**Step II**

Hydrazine hydrate (175 g, 3.5 mol), ethanol amine (175 g, 2.87 mol), and 2-methoxy ethanol (750 ml, 9.51 mol) were added to approximately 18 g of benzvalene (230.8 mmol) which was in 1500 ml of ether and methylene chloride. An aqueous solution of potassium ferricyanide (385 g, 1.17 mol, dissolved in 900 ml of water) was added dropwise with stirring (Note: a mechanical stirrer was used). During the reaction, N\textsubscript{2} gas was eliminated. The gas was passed through a condenser cooled with dry ice-acetone (-78 °C). Most of the volatiles were condensed and went back into the mixture. After complete addition of the potassium ferricyanide solution, the mixture was stirred for an additional 30 minutes. The total time of the reduction was 4-5 hours. Then the ether was distilled using a water aspirator into a receiver cooled in a dry ice-acetone bath. While distilling, slowly warm the solution with hot water until a temperature of 35 °C is reached. Wash the ether layer with distilled water (3 x 100ml) and dried over anhydrous sodium sulfate. The dried ether was then distilled. The dihydrobenzvalene comes with ether and methylene chloride at 35-60, 60-70 and 70-75 °C. All the fractions were again fractionally distilled. (Note: most of the benzene was removed from the reaction mixture by first
freezing and then by distillation of the decanted liquid).

Overall yield from cyclopentadiene: 12.9 g, 27%

B.P.: 69-70 °C; $^1$H NMR δ 1.25 (s, 4H), 1.67 (br. s, 2H) and 2.05 (br. s, 2H). NMR spectral data agrees with the reported data in literature.¹

8. **ADENDUM**

1. $^1$H NMR [400 MHz] OF 1,5-DIBROMOPENTANE
2. $^{13}$C NMR [100 MHz] OF 1,5-DIBROMOPENTANE
3. IR SPECTRUM OF 1,5-DIBROMOPENTANE
4. $^1$H NMR [400 MHz] OF 1,5-DIAZIDOPENTANE
5. $^{13}$C NMR [100 MHz] OF 1,5-DIAZIDOPENTANE
6. IR SPECTRUM OF 1,5-DIAZIDOPENTANE
7. HPLC OF 1,5-DIAZIDOPENTANE
8. $^1$H NMR [400 MHz] OF 1,6-DIBROMOHXANE
9. $^{13}$C NMR [100 MHz] OF 1,6-DIBROMOHXANE
10. $^1$H NMR [400 MHz] OF 1,6-DIAZIDOHEXANE
11. $^{13}$C NMR [100 MHz] OF 1,6-DIAZIDOHEXANE
12. MASS SPECTRUM OF 1,6-DIAZIDOHEXANE
13. IR SPECTRUM OF NORBORNADIENE DIMERS
14. $^1$H NMR [400 MHz] OF NORBORNADIENE DIMERS
15. IR SPECTRUM OF TETRAAZIDONORBORNANE DIMERS
16. $^1$H NMR [400 MHz] OF TETRAAZIDONORBORNANE DIMERS
17. MASS SPECTRUM OF TETRAAZIDONORBORNANE DIMERS
18. $^1$H NMR OF DIHYDROBENZVALENE
19. GAS CHROMATOGRAPH OF DIHYDROBENZVALENE
$^1H$ NMR [400 MHz] of 1,5-Dibromopentane

Br $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$
$^{13}$C NMR [100 MHz] of 1,5-Dibromopentane

Br CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$Br
IR Spectrum of 1,5-Dibromopentane
$^1$H NMR [400 MHz] of 1,5-Diazidopentane

$\text{N}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}_3$
$^{13}$C NMR [100 MHz] of 1,5-Diazidopentane

$\text{N}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}_3$
IR Spectrum of 1,5-Diazidopentane
HPLC of 1,5-Diazidopentane

Solvent: Hexane : Ethyl acetate (3:1)
Flow Rate: 1.0 ml / min
Wavelength: 280 nm
Column: Zorbax, CN
$^1$H NMR [400 MHz] of 1,6-Dibromohexane

Br $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$
$^{13}\text{C} \text{NMR [100 MHz]} \text{ of 1,6-Dibromohexane}$

$\text{Br CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$
$^{1}H$ NMR [400 MHz] of 1,6-Diazidohexane

$N_3CH_2CH_2CH_2CH_2CH_2CH_2N_3$
$^{13}$C NMR [100 MHz] of 1,6-Diazidohexane

$N_3CH_2CH_2CH_2CH_2CH_2CH_2N_3$
Mass Spectrum of 1,6-Diazidohexane
IR Spectrum of Norbornadiene Dimers
$^1H$ NMR [400 MHz] of Norbornadiene Dimers
IR Spectrum of Tetraazidonorbornane Dimers
$^{1}H$ NMR [400 MHz] of Tetraazidonorbornane Dimers
Mass Spectrum of Tetraazidonorbomane Dimers