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PREPARATION OF CYCLONONA-1,2,5-TRIENE, CYCLONONA-1,2,5,7-TETRAENE AND CYCLODECA-1,2,5,6-TETRAENE

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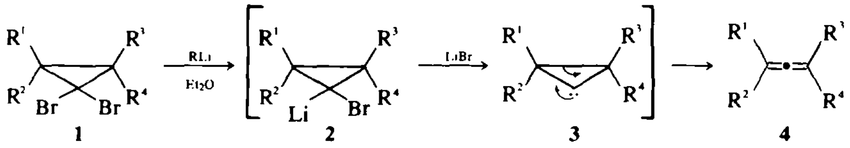
Abstract—Cyclonona-1,2,5-triene (**13a**) and 7-methoxycyclonona-1,2,5-triene (**13b**) have been prepared in satisfactory yields by the action of MeLi on (**12a**) and (**12b**), respectively; cyclodeca-1,2,5,6-tetraene (**29**) has similarly been prepared from **16**. Cyclonona-1,2,5,7-tetraene (**22**), which was prepared from **20** at below −40°, readily dimerizes to give **21**; the half-time of the reaction is 10–20 min in $CDCl_3$ solution at 0°.

Olefins can usually be converted into the corresponding allenes containing one more C atom by a simple two-step process:[1,2] the olefin is first converted into its dibromocarbene adduct (**1**) which is then treated with a lithium alkyl in ether or hexane solution to give the allene (**4**). Yields are often high and this represents one of the best general methods for the preparation of both acyclic and cyclic allenes. A possible mechanism[1,2] (Scheme 1) for the second step of this process involves initial lithiation to give the intermediate (**2**) followed by elimination of lithium bromide. The carbene (**3**) thus obtained can then collapse as indicated to give the allene (**4**). Products other than allenes are sometimes obtained[1,3–6] and their formation may also be rationalized in terms of intermediates of the types **2** and **3**.

boiling methanol solution gave a 45% yield of a 9:1 mixture (as estimated by GLC) of **15** and *cis,cis*-cycloocta-1,5-diene. The latter mixture was treated with bromoform and potassium t-butoxide and the desired dibromocarbene adduct (**12a**) isolated from the products as a colourless liquid in 40% yield. A small amount (*ca.* 1%) of a crystalline bis-adduct (**16**) was also obtained. Reaction between **12a** and an excess of methyl lithium at 20° gave cyclonona-1,2,5-triene (**13a**) as the sole volatile product: the latter compound, which was characterized on the basis of its spectroscopic properties, was isolated as a colourless mobile liquid in 63% yield. Cyclonona-1,2,5-triene (**13a**) is a relatively stable compound; a sample of it underwent only partial decomposition when it was allowed to stand at room temperature for several weeks.



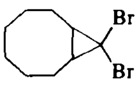
Scheme 1.

Cyclic allenes with the allene group situated in a ring larger than 8-membered appear to be relatively stable. Thus cyclonona-1,2-diene (**6**) was obtained[2] as the sole product in 93% yield when 9,9-dibromobicyclo[6,1,0]nonane (**5**) was treated with methyl lithium in ether solution and cyclonona-1,2,6-triene (**8**) was similarly obtained[2] from **7** in 80% yield. However, treatment of **9** with methyl lithium gave[4c] a 2:1 mixture of the tricyclic hydrocarbons (**10** and **11**) and no allenic products. The latter compounds (**10** and **11**) appear to result from intramolecular insertion of an intermediate carbene (corresponding to **3**). We now report that 9,9-dibromobicyclo[6,1,0]non-3-ene (**12a**) reacts with methyl lithium in the normal manner to give cyclonona-1,2,5-triene (**13a**) in satisfactory yield.

The starting olefin required for the preparation of **13a** was *cis,cis*-cyclo-octa-1,4-diene[7,8] (**15**). Treatment of 5-bromo-*cis*-cyclo-octene[7] (**14**) with sodium methoxide in

Treatment of 9,9 - dibromo - 5 - methoxybicyclo[6,1,0] non - 3 - ene (**12b**) (see below) with methyl lithium under the same conditions gave 7-methoxycyclonona-1,2,5-triene (**13b**) in comparable yield.

No derivative of cyclonona-1,2-diene (**6**) containing two additional endocyclic double bonds has been described previously. In another investigation,[9] we found that treatment of 9,9 - dibromobicyclo[6,1,0]nona - 2,6 - diene (**17**) with methyl lithium gave homosemibullvane (**18**) as the sole product in 89% isolated yield. We now report that when **20** was treated with methyl lithium in ether solution at 25–30°, a hydrocarbon, with molecular formula $C_{18}H_{20}$, which is believed to be the allene dimer[10] (**21**) was obtained in *ca.* 80% yield. No trace of the monomeric allene (**22**) was detected. However, when the reaction between **20** and methyl lithium was carried out at below −40° and the products worked-up at low temperature, **22** was obtained as the major product. The structure of the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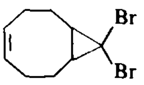
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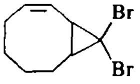
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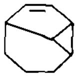
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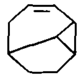
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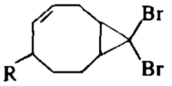
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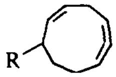
a: R = H
b: R = OMe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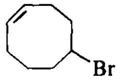
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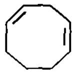
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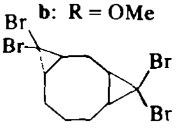
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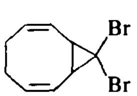
a: R = H
b: R = OMe

latter compound (**22**) was based on its NMR spectrum (at −30°, Experimental) and on the presence of a medium to weak band at 1950 cm^{-1} in its IR spectrum. This structural assignment was further confirmed when sodium–liquid ammonia reduction of the crude products of the reaction between **20** and methyl lithium gave *cis,cis*-cyclonona-1,5-diene (**23**) (70%) as the main volatile product.[11] Cyclonona-1,2,5,7-tetraene (**22**) is a relatively unstable allene: the half-time of its dimerization[13] to **21** was found to be between 10 and 20 min in deuteriochloroform solution at 0°. 9,9 - Dibromobicyclo[6,1,0]nona - 3,5 - diene (**20**) was itself obtained in 45% yield, together with 9,9 - dibromo - 5 - methoxybicyclo[6,1,0]non - 3 - ene (**12b**) (21% see above), by the action of sodium methoxide on 4,5,9,9 - tetrabromobicyclo[6,1,0]nonane (**19**) in boiling methanol solution. Treatment of the latter compound (**19**),† which was in turn prepared by the action of bromine on **7** in carbon tetrachloride solution, with a large excess of sodium hydroxide in methanol solution gave **20** in higher yield.

The bis-allene, cyclodeca-1,2,6,7-tetraene (**25**) was obtained[2] when **24** was treated with methyl lithium. However, treatment of the isomeric tetrabromo-compound (**26**) with methyl lithium did not give the conjugated bis-allene (**27**) but a bicyclic valence tautomer (**28**).[14] We now report that when 4,4,10,10-tetrabromotricyclo[7,1,0,0^{3,5}]decane (**16**) was treated with methyl lithium in ether solution at 25–30°, cyclodeca-1,2,5,6-tetraene (**29**) was obtained. The latter compound (**29**) was isolated in 75% yield by molecular distillation and characterized on the basis of its spectroscopic properties. From the complexity of its NMR spectrum, it seems likely that the cyclodeca-1,2,5,6-tetraene (**29**) obtained was a mixture of two possible diastereoisomers.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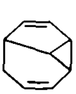
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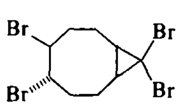
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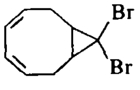
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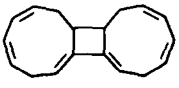
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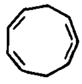
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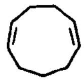
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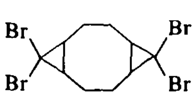
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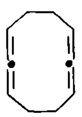
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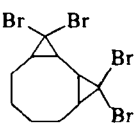
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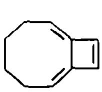
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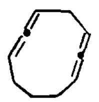
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The present study was undertaken mainly to obtain more information about the scope of this very useful and convenient method for the preparation of allenes. It seems that allenes are obtained, and usually in good yields, unless (a) the allenes themselves are unstable [e.g. cyclo-octa-1,2-diene[4b] which dimerizes readily and **27** which apparently isomerizes[14] to **28**, or (b) alternative reactions of the putative intermediates (**2** and **3**, see Scheme 1) such as intramolecular insertion and dimerization are more favourable.

EXPERIMENTAL

NMR spectra were measured at 60 and 100 MHz with a Perkin Elmer R10 and a Varian HA100 spectrometer, respectively. TMS was used as an internal standard. IR spectra were measured with Perkin Elmer spectrometers (models 21 and 257). Mass spectra were measured with an A.E.I. MS9 spectrometer, using heated insertion. GLC was carried out with an F. & M. model 720 chromatograph with hydrogen as carrier gas. Columns containing 10% of the following stationary phases on Celite were used: silicone gum rubber, polyphenyl ether and LAC (ethylene glycol adipate, cross-linked with pentaerythritol).

Ethereal MeLi was either purchased from Ventron (2 M) or else prepared from methyl bromide; in the latter case, its concentration was determined by the addition of an excess of water followed by titration with 0.1 M HCl.

cis,cis-*Cyclo-octa-1,4-diene* (**15**). A soln of *cis*-5-bromocyclo-octene[7] (135 g, 0.71 mole) and NaOMe (1.52 mole, from 35 g Na) in MeOH (500 ml) was heated, under reflux, for 8 hr. The products were then distilled and the residue partitioned between ether and water. The dried ($MgSO_4$) ether layer was combined with the distillate and the resulting soln fractionated (Fenske column) until only *ca*. 75 ml remained. This residual liquid was then distilled as rapidly as possible with precautions being taken to avoid excessive frothing. The distillate was fractionated (spinning-band column) to give **15** (35 g, 45%), b.p. 146–147°. GLC of this material revealed that it was *ca*. 90% pure and that it was contaminated with *ca*. 10% of *cis,cis*-cyclo-octa-1,5-diene.

A sample of pure **15** was obtained by preparative GLC. NMR spectrum (CCl_4): τ 4.25–4.85 (4H, m), 7.15 (2H, m), 7.75 (4H, m), 8.62 (2H, m); mass spectrum: M^+ at $m/e = 108$ (35% of base-peak at $m/e = 79$).

Reaction between cis,cis - *cyclo - octa* - 1,4 - *diene and dibromocarbene*. An *M*-soln of t-BuOK in t-BuOH (500 ml, 0.50 mole) was added dropwise over a period of 4 hr to a stirred soln of *cis,cis* - cyclo - octa - 1,4 - diene (27 g, 0.25 mole) and bromoform (120 g, 0.47 mole) at 20°. The products were then partitioned between ether (400 ml) and water (4 × 200 ml). The dried ($MgSO_4$) ether layer was evaporated and the residual liquid distilled to give cis - 9,9 - *dibromobicyclo*[6,1,0]*non* - 3 - *ene* (28 g, 40%) [Found: C, 38.4; H, 4.6; Br, 57.2. $C_9H_{12}Br_2$ requires: C, 38.5; H, 4.3; Br, 57.1%], b.p. 118–120°/2 mmHg; NMR spectrum (CCl_4): τ 4.40 (2 H, m), 7.4–8.8 (10 H, m); mass spectrum: M^+ at $m/e = 278$ (1), 280 (2), 282 (1) (peak at $m/e = 280$ is 3% of base-peak at $m/e = 91$).

The residue from the above distillation crystallized from acetone to give 4,4,10,10 - *tetrabromotricyclo*[7,1,0,0^{3,5}]*decane* (1.0 g, 1%) [Found: C, 26.7; H, 2.7; Br, 70.8. $C_{10}H_{12}Br_4$ requires: C, 26.6; H, 2.7; Br, 70.9%]; m.p. 121–122°; NMR spectrum (CCl_4):

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†It has been assumed, without proof, that **19** is the *trans*-4,5-dibromo compound.

τ 7.56 (3 H, m), 8.0–9.4 (9H, m); ν_{max}^{KBr} 2920 m, 2850 m, 1465 s, 1440 m, 1180 m, 1120 s, 968 m, 885 s, 800 m, 750 s, 696 s; mass spectrum: M^+ at $m/e = 448$ (1), 450 (3), 452 (4), 454 (3), 456 (1); base-peak at $m/e = 129$.

4,5,9,9-*Tetrabromobicyclo*[6,1,0]*nonane* (**19**). A soln of Br_2 (16.0 g, 100 mmole) in CCl_4 (30 ml) soln was added dropwise over a period of 30 min to a cooled (ice-water bath), stirred soln of 9,9-dibromobicyclo[6,1,0]non - 4 - ene (27 g, 96 mmole) in CCl_4 (125 ml). After a further 15 min, the products were evaporated and the solid residue recrystallised from petroleum ether (b.p. 60–80°) to give 4,5,9,9-tetrabromobicyclo[6,1,0]nonane (28 g, 66%). [Found: C, 24.75; H, 2.8. Calc. for $C_9H_{12}Br_4$; C, 24.55; H, 2.7%], m.p. 76–77° (lit. 64–65°); NMR spectrum (CCl_4): τ 5.32 (2 H, m), 7.36 (2 H, m), 7.6–8.6 (8 H, m).

9,9 - *Dibromobicyclo*[6,1,0]*nona* - 3,5 - *diene* (**20**) *and* 9,9 *dibromo* - 5 - *methoxybicyclo*[6,1,0]*non* - 3 - *ene* (**12b**)

(a) A soln of 4,5,9,9-tetrabromobicyclo[6,1,0]nonane (20.0 g, 45.5 mmole) and NaOMe (25 g, 0.46 mole) was heated, under reflux, in anhyd MeOH (200 ml) soln. After 4.5 hr, GLC revealed two products (in the approximate proportions of 2:1) and no starting material. The products were treated with water (500 ml) and then extracted with ether (3 × 250 ml). The dried ($MgSO_4$) ether extracts were evaporated and the residue distilled to give a lower-boiling and a higher boiling fraction. The lower-boiling fraction was identified as 9,9 - *dibromobicyclo*[6,1,0]*nona* - 3,5 - *diene*. [Found: C, 39.1; H, 3.5; Br, 57.1. $C_9H_{10}Br_2$ requires: C, 38.9; H, 3.6; Br, 57.6%]; it was obtained as a colourless liquid (5.8 g, 45%), b.p. 78–79°/0.9 mmHg; UV absorption [hexane: λ_{max} 233 nm (ϵ 4400)]; NMR spectrum (CCl_4): τ 4.30 (4 H, m), 7.5 (4 H, m), 8.16 (2 H, m); ν_{max}^{film} 3020 s, 760 s cm^{-1}; mass spectrum: M^+ at $m/e = 276$ (1.1%), 278 (2.2%), 280 (1.1%), base-peak at $m/e = 117$.

The higher-boiling fraction was identified as 9,9 - *dibromo* - 5 - *methoxybicyclo*[6,1,0]*non* - 3 - *ene*. [Found: C, 38.4; H, 4.7; Br, 51.7. $C_{10}H_{14}Br_2O$ requires: C, 38.7; H, 4.55; Br, 51.6%]; it was obtained as a colourless liquid (2.9 g, 21%), b.p. 95°/0.9 mmHg; NMR spectrum (CCl_4); τ 4.4 (2 H, m), 6.3 (1 H, m), 6.84 (3 H, s), 7.6 (2 H, m), 7.9–8.5 (6 H, m); ν_{max}^{film} 3020 m, 975 m, 932 m, 880 m, 758 s, 715 s; mass spectrum: M^+ at $m/e = 308$ (0.2%), 310 (0.4%), 312 (0.2%), base-peak at $m/e = 71$.

(b) Crude 4,5,9,9-tetrabromobicyclo[6,1,0]nonane, obtained as above from 9,9 - dibromobicyclo[6,1,0]non - 4 - ene (16.0 g, 57 mmole) and Br_2 (9.6 g, 60 mmole), was heated under reflux with NaOH (30 g, 0.75 mole) in MeOH (150 ml) soln for 2.5 hr. The cooled products were then poured into water (500 ml) and extracted with ether (3 × 150 ml). The combined ether layers were washed with water (3 × 100 ml), dried ($MgSO_4$), concentrated under reduced pressure and the residue distilled to give 9,9 - dibromobicyclo[6,1,0]nona - 3,5 - diene (10.5 g, 66%); b.p. 108–118°/3 mmHg.

Cyclonona-1,2,5-*triene* (**13a**). Ethereal MeLi (2.1 M, 30 ml) was added dropwise over a period of 20 min to a magnetically-stirred soln of 9,9 - dibromobicyclo[6,1,0]non - 3 - ene (13 g, 46 mmole) in anhyd ether (20 ml) at 20°. After water (25 ml) had been added carefully to the products the ethereal layer was separated, washed with water and dried ($MgSO_4$). Evaporation of the ether and distillation of the residual liquid gave *cyclonona*-1,2,5-*triene* (3.5 g, 63%) as a GLC homogeneous, colourless liquid, b.p. 62°/14 mmHg; NMR spectrum (CCl_4): τ 4.6 (2 H, m), 4.94 (2 H, m), 7.35 (2 H, dt, J 4.5 and 8.5 Hz), 7.8–8.5 (6 H, m); ν_{max}^{film} 3000s, 1950s, 1650w, 910w, 856m, 840w, 820w, 780m, 750w, 730m, 710s, cm^{-1}; mass spectrum: M^+ at $m/e = 120.0927$ (Calc. for C_9H_{12}: 120.0939), base-peak at $m/e = 91$.

7-*Methoxycyclonona*-1,2,5-*triene* (**13b**). Ethereal MeLi (2.1 M, 4 ml) was added over a period of 5 min to a magnetically stirred soln of 9,9 - dibromo - 5 - methoxybicyclo[6,1,0]non - 3 - ene (1.0 g, 3.23 mmole) in anhyd ether (15 ml) at 25–35°. The products were worked-up as above to give a colourless oil (0.30 g) which was shown by GLC to consist of a major (*ca.* 90%) and a minor (*ca.* 10%) component. The major component was identified as 7-*methoxycyclonona*-1,2,5-*triene* (yield *ca.* 55%); NMR spectrum (CCl_4): τ 4.64 (2 H, m), 4.90 (2 H, m), 6.53 (1 H, m), 6.9 (3 H, s), 7.33 (2 H, m), 8.0 (2 H, m), 8.2 (2 H, m); ν_{max}^{film} 3005m, 2970m, 1950m, 1090s, 1070s, 865m, 860m, 940m, 765m, 720m; mass spectrum: M^+ at $m/e = 150.1036$ (Calc. for $C_{10}H_{14}O$: 150.1044), base-peak at $m/e = 92$.

Cyclodeca-1,2,5,6-*tetraene* (**29**). Ethereal MeLi (0.6 M, 4 ml) was added over a period of 5 min to a magnetically-stirred soln of 4,4,10,10-tetrabromotricyclo[7,1,0,0^{3,5}]decane (0.50 g, 1.1 mmole) in anhyd ether (10 ml) at 20°. The products were worked-up as above and then purified by molecular distillation to give *cyclodeca*-1,2,5,6-*tetraene* (0.109 g, 75%); NMR spectrum (CCl_4): τ 4.7–5.5 (4 H, m), 7.2–7.6 (2 H, m), 7.6–8.2 (4 H, m), 8.4–8.8 (2 H, m); ν_{max}^{film} 2960s, 2910s, 2840s, 1960s, 1435s, 860s, 780m, 710m, 670m; mass spectrum: M^+ at $m/e = 132.0936$ (Calc. for $C_{10}H_{12}$: 132.0939), base-peak at $m/e = 59$.

Reaction between 9,9 - *dibromobicyclo*[6,1,0]*nona* - 3,5 - *diene* (**20**) *and methyl lithium*

(a) Ethereal MeLi (2 M, 3 ml) was added dropwise, with stirring, over a period of 2 min to a soln of 9,9 - dibromobicyclo[6,1,0]nona - 2,5 - diene (0.50 g, 1.8 mmole) in anhyd ether (10 ml) at 25–35°. Water (10 ml) was then added cautiously to the products. The organic layer was separated, washed with water (2 × 10 ml), dried and evaporated to give a pale yellow oil (0.17 g) which showed no detectable absorption in the region of 1950 cm^{-1}. TLC [petroleum ether (b.p. 60–80°) on sensitized alumina] revealed a major component, contaminated with a higher R_f minor component which was removed by flash distillation (at *ca.* 45°/15 mmHg); the residue was characterised as **21** which showed τ (CCl_4): 4.0–5.0 (10 H, m) 7.0–8.5 (10 H, m); ν_{max}^{film} 2990s, 2890s, 1635m, 1445s cm^{-1}; M^+ (10% of base-peak at $m/e = 39$) = 236.1541 (Calc. for $C_{18}H_{20}$: 236.1565).

(b) The experiment described in (a) above was repeated on the same scale but the reaction temp was kept below −40°. After 1 min, water (10 ml) was added carefully so that the temp. of the products remained below −20°. The products were washed with ice-cold water, decanted into a cooled flask and the solvent removed at −30°/1 mmHg to give an oil ($\nu_{max}^{CCl_4}$ 1950m cm^{-1}) with NMR spectrum ($CDCl_3$, −40°): τ 3.7–4.1 (2 H, br.d., $J = 9.5$ Hz), 4.3–4.5 (2 H, m), 4.5–4.9 (2 H, m), 7.0–7.4 (4 H, m). The soln was then warmed up to 0° and its NMR spectrum measured at intervals of time: absorption in the regions τ 3.7–4.1, 4.3–4.8 and 7.0–7.4 was found to decrease and absorption in the regions 4.1–4.4 and 7.4–7.9 was found to increase with time. From an examination of a number of NMR spectra it was estimated that the putative cyclonona-1,2,5,7-tetraene had a half-life of 10–20 min in $CDCl_3$ soln at 0°. After the solution had been allowed to stand at 25° for 16 hr, its NMR spectrum corresponded to that of the product obtained in (a) above.

(c) Ethereal MeLi (2 M, 5 ml) was added dropwise, with stirring, over a period of 2 min to a soln of 9,9-dibromobicyclo[6,1,0]nona - 2,5 - diene (0.8 g, 2.9 mmole) in ether (10 ml) at below −40°. After 1 min, water (5 ml) was added carefully so that the temperature of the products remained below −20°. The products were washed with ice-cold water, cooled to −50°, and the ether layer decanted into a cooled flask and added, with stirring, over a period of 2 min to a soln of sodium (350 mg) in liquid ammonia (25 ml). After 2 min, the excess of sodium was destroyed by careful addition of solid NH_4Cl. Ether (20 ml) and water (20 ml) were then added and the products allowed to warm up to 25°. The ether layer was then separated, washed with water (25 ml) and dried ($MgSO_4$). After removal of the solvent at 14 mmHg, the residue was flash distilled at 30–40°/1 mmHg to give a major volatile product (~95% by GLC, 4′ SE30, 60°) (238 mg, 70%) which was shown to be *cis,cis* - cyclonona - 1,5 - diene, identical (NMR and IR spectroscopy) to an authentic sample.[12]

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