Alkylation and Subsequent Decomposition of Arenesulfonylhydrazone Dianions

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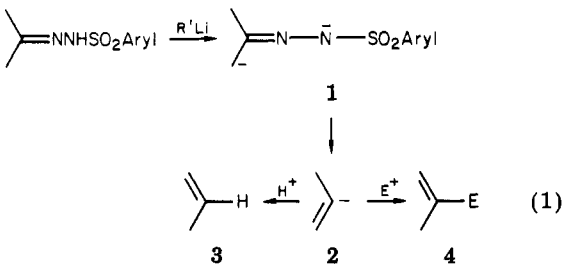
Trisyl- or tosylhydrazones of a variety of ketones containing an α-methylene group have been converted into dianions by treatment with alkyllithium bases at −78 °C. Alkylation of these dianions with 1-iodobutane occurs readily and can be followed by a second base treatment to give an alkylated dianion that decomposes to a vinyl carbanion in the normal manner. These vinyl carbanions can be trapped with a variety of electrophiles. The sequence allows regiospecific alkylation of a ketone, followed by regiospecific generation of a vinyl carbanion and trapping thereof.

Thermal decomposition of dianions 1 derived from arenesulfonylhydrazones constitutes a valuable olefin (3) synthesis[2] (eq 1). Typically, tosylhydrazones have been



(1)

used in either ether or hydrocarbon solvents. It has been shown[3] that the use of TMEDA as solvent along with excess base allows the vinyl carbanion 2 to be trapped with a variety of electrophiles to give 4, thus greatly expanding the utility of the sequence. By employment of triisopropylbenzenesulfonylhydrazones (trisylhydrazones),[4] the need for excess base is eliminated, and formation of 2 is accelerated to the point where THF may be employed as solvent. Under these conditions, 2 is not protonated by THF and can be trapped in reasonable yield with common electrophiles.

The use of THF as solvent facilitates further study[5] of dianion 1. In a previous report[6] it was shown that the dianion of acetone trisylhydrazone could be alkylated on carbon and the resulting anion reconverted regiospecifically into a new dianion which underwent the expected decomposition to vinyl carbanion and products therefrom.

We now report extension of this work to the alkylation of secondary systems, followed by further decomposition and trapping to give a variety of substituted olefins. It should be noted that arenesulfonylhydrazone dianions (1) can be trapped with electrophiles other than alkyl iodides as reported here. Among the reagents which have been employed are aldehydes and ketones,[7] disulfides,[8] and chlorotrimethylsilane,[9] although in only two cases,[7a,9] have the subsequent vinyl carbanions been trapped with electrophiles other than protons.

The variety of products available by this double electrophilic substitution is demonstrated by the sequences

Scheme I. Products Obtained from Camphor Trisylhydrazone via Dianion Alkylation, Elimination, and Subsequent Vinyl Carbanion Trapping

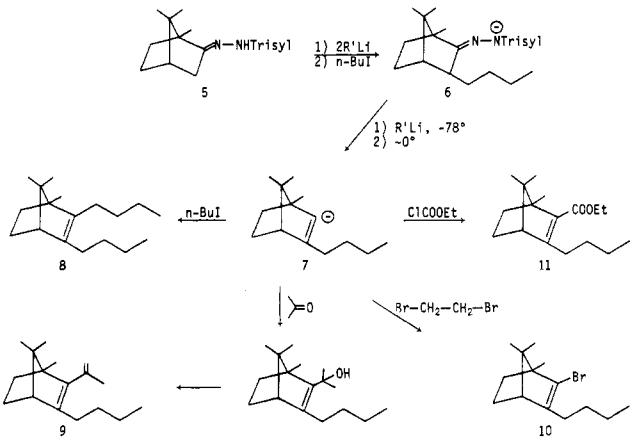


Table I. Products Derived from Camphor

compd[a]	yield,[b] %	^{1}H NMR ($CDCl_3$), δ
8	62	0.79 (s, 6 H), 0.90 (t, 6 H), 0.93 (s, 3 H), 1.1-2.2 (m, 16 H), 2.33 (d, 1 H)
9	33	0.70 (s, 3 H), 0.76 (s, 6 H), 0.8-2.2 (m, 11 H), 0.91 (t, 3 H), 1.76 (br s, 3 H), 4.54 (m, 1 H), 4.74 (m, 1 H)
10	72	0.80 (s, 3 H), 0.86 (s, 3 H), 0.93 (t, 3 H), 1.00 (s, 3 H), 1.1-2.2 (m, 10 H), 2.32 (d, 1 H)
11	54	0.79 (s, 3 H), 0.82 (s, 3 H), 0.9 (t, 3 H), 0.99 (s, 3 H), 1.1-2.3 (m, 13 H), 2.30 (d, 1 H), 4.13 (d of q, 2 H)

[a] All products had infrared and mass spectral data consistent with the assigned structures. All compounds except 9 gave microanalytical analyses for C and H within ±0.3% of theory. [b] Yields were determined by GLC using an external standard except for 9 which is an isolated yield.

(1) Abstracted in part from the M.S. thesis of R.A.D., University of California, San Diego, 1980.

(2) Shapiro, R. H. *Org. React.* **1976**, *23*, 405.

(3) (a) Stemke, J. E.; Chamberlin, A. R.; Bond, F. T. *Tetrahedron Lett.* **1976**, 2947. (b) Shapiro, R. H.; Lipton, M. F.; Kolonko, K. J.; Buswell, R. L.; Capuan, L. A. *Ibid.* **1975**, 1811. (c) Traas, P. C.; Boelens, H.; Takken, H. J. *Ibid.* **1976**, 2287. (d) Chan, T. H.; Baldassare, A.; Massuda, D. *Synthesis* **1976**, 801. (e) Taylor, R. C.; Degenhart, C. R.; Melega, W. P.; Paquette, L. A. *Tetrahedron Lett.* **1977**, 159.

(4) Chamberlin, A. R.; Stemke, J. E.; Bond, F. T.; *J. Org. Chem.* **1978**, *43*, 147.

(5) Shapiro and co-workers had previously reported[3b] alkylation of a dianion without trapping of the derived vinyl anion.

(6) Chamberlin, A. R.; Bond, F. T. *Synthesis* **1979**, 44.

(7) (a) Adlington, R. M.; Barrett, A. G. M. *J. Chem. Soc., Chem. Commun.* **1978**, 1071. (b) Lipton, M. F.; Shapiro, R. H. *J. Org. Chem.* **1978**, *43*, 1409.

(8) Nakai, T.; Mimura, T. *Tetrahedron Lett.* **1979**, 531.

(9) Liotta, E.; Bond, F. T., unpublished observations.

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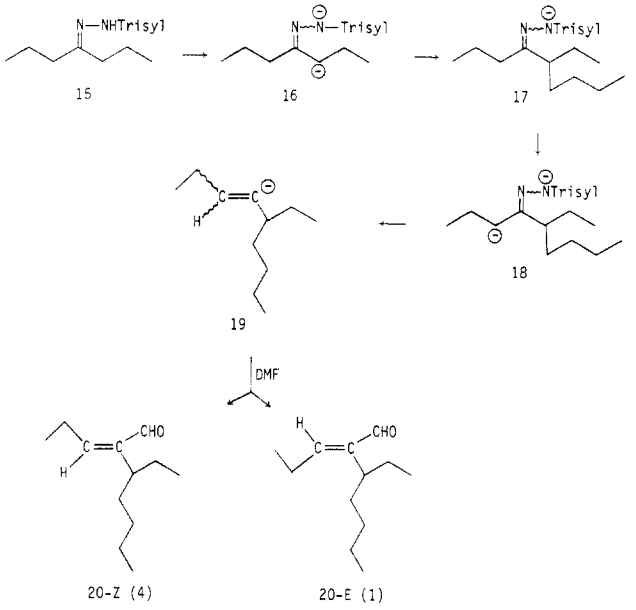
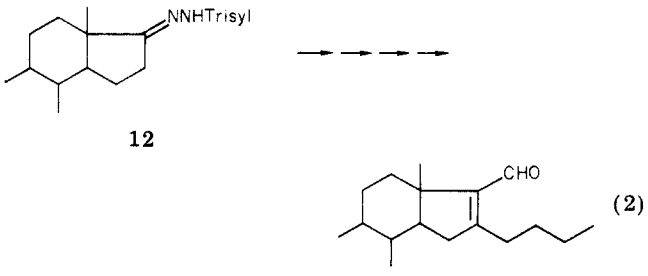
Scheme II. Products Obtained from 4-Heptanone Trisylhydrazone



shown in Scheme I with camphor trisylhydrazone[4] **5**. The trisylhydrazone was converted into its dianion at −78 °C and alkylated at that temperature with 1-iodobutane.[10] Without isolation, **6** was treated with an additional 1 equiv of base and allowed to warm to 0 °C. During this warming the generation of **7** can be easily monitored by nitrogen evolution. Trapping of **7** after nitrogen evolution ceases, with the indicated electrophilic reagents, gave the products shown.[11] Nonoptimized yields ranged from 33% to 72%. Synthesis of **8** demonstrates tetrasubstituted olefin formation. Acetone presumably gives the tertiary allylic alcohol, as its dehydration product, **9**, was obtained upon workup. The facile formation of vinyl bromide **10** and substituted acrylate **11** demonstrates further the broad synthetic utility of the sequence. The properties of these products are shown in Table I. Use of dimethylformamide (DMF)[3c,4] was not successful in this case as the product could not be separated from an arenesulfinate-derived side product. Use of iodomethane as the original alkylating agent was successful, and subsequent DMF trapping afforded 3-methylbornene-2-carboxaldehyde in 46% yield.

In a similar sequence, dehydroepiandrosterone trisylhydrazone **12** could be converted into **14** (eq 2). Butyla-



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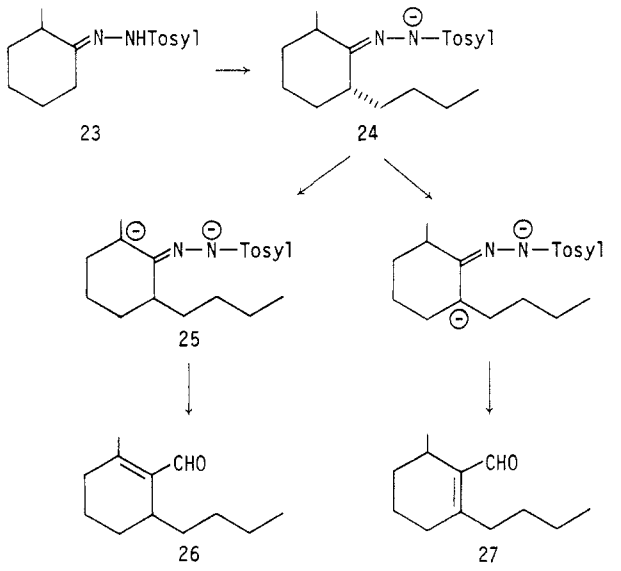
tion of the dianion from **12** did not go to completion, requiring in this case isolation and purification of the butylated trisylhydrazone **13**, before conversion to **14**.

Scheme III



In the two cases already discussed, alkylation and subsequent reformation of dianion could only occur in one direction, leading ultimately to a tetrasubstituted olefin. Ring size also precludes formation of trans olefins. Acyclic and less substituted alicyclic ketones are potentially more complicated. 4-Heptanone trisylhydrazone **15** was converted (Scheme II) into dianion **16** and alkylated to **17**. In situ reconversion to the dianion occurred exclusively at the secondary position, C-5, anti to the original directing group, to give **18**. We do not know if this involves antideprotonation[12] or isomerization around the carbon–nitrogen double bond, but DMF trapping gives only products derived from **19**. The aldehydes formed are (*Z*)-**20** and (*E*)-**20** in a 4:1 ratio, their stereochemistry being easily defined by their characteristic proton NMR spectra.[13] The crude reaction mixture has a proton spectrum showing aldehydic protons only for (*Z*)- and (*E*)-**20** with no evidence for the fully substituted aldehyde which would have resulted from tertiary proton removal in **17**. In general, tertiary proton removal in such systems is slow[4,14] although possible.

Similar results were obtained with a cyclic system, 4-*tert*-butylcyclohexanone. With this and other conformationally flexible ketones, the trisylhydrazone dianion decomposes too rapidly, even at −78 °C, to allow alkylation. Fortunately in such cases the tosylhydrazone dianions can be used, and their subsequent decomposition to vinyl carbanions is sufficiently facile to allow THF to still be used as the solvent. As in the acyclic case above, alkylation of the dianion from **21** and subsequent olefin formation occur in opposite directions to afford, upon DMF workup, only **22** (eq 3). Trans stereochemistry was assigned to the alkyl substituents on the basis of expected axial alkylation of the dianion from **21**. This would be consistent with the results of Fraser, Banville, and Dhawan,[12b] who observed exclusive axial alkylation of the *N*-benzyl ketimine from

(10) Use of *n*-butyl bromide resulted in alkylation, but in significantly lower yield.

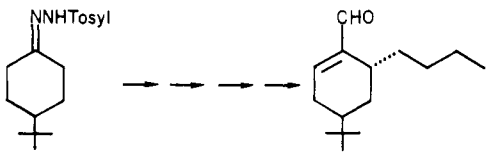
(11) For typical reactions of alkenyllithium reagents generated by metal–halogen exchange, see: Cahiez, G.; Bernard, D.; Normant, J. F. *Synthesis* **1976**, 245.

(12) (a) Syn deprotonation is usually observed in such systems although in hexane–TMEDA we have observed anti deprotonation.[6] For a possible explanation for the preference for syn deprotonation and leading references, see: Houk, K. N.; Strozier, R. W.; Rondau, N. G.; Fraser, R. R.; Chuaqui-Offermanns, N. *J. Am. Chem. Soc.* **1980**, *102*, 1426; (b) Fraser, R. R.; Banville, J.; Dhawan, K. L. *Ibid.* **1978**, *100*, 7999.

(13) Chan, K. C.; Jewell, R. A.; Nutting, W. H.; Rapoport, H. *J. Org. Chem.* **1968**, *33*, 3382.

(14) Kolonko, K. J.; Shapiro, R. H. *J. Org. Chem.* **1978**, *43*, 1404.

(15) Beak, P.; Reitz, D. B. *Chem. Rev.* **1978**, *78*, 275. Corey, E. J.; Enders, D. *Tetrahedron Lett.* **1976**, 3.



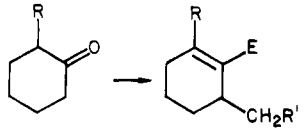
(3)

21 22

4-*tert*-butylcyclohexanone even in the formation of the diaxial derivative of 2,6-dimethyl-4-*tert*-butylcyclohexanone. Equatorial attack is disfavored for both steric and stereoelectronic reasons. None of the other electrophiles shown in Scheme I were used to trap the precursor to **22**, although no problems would be anticipated.

The final system studied was the tosylhydrazone **23** of 2-methylcyclohexanone. Original dianion formation and alkylation would be expected to yield **24** (Scheme III). In situ generation of dianion from **24** requires removal of a tertiary proton. If one assumes axial alkylation to **24** and conformational stability at −78 °C, however, only the original anti proton is now axial, and formation of **25** and ultimately **26** would be predicted.[16] This is the result of an in situ experiment which yields **26** containing less than 5% of **27**. If, however, **24** is protonated and the tosylhydrazone isolated, equilibration can occur, and upon completion of the sequence one obtains the same products in a 7:3 ratio.

The high regiospecificity of the in situ sequence should prove synthetically valuable regardless of its origin. The sequence allows transformations of the type shown in eq 4. This combines regiospecific alkylation of an unsym-



(4)

metrical ketone, regioselective conversion of the ketone to a vinyl anion, and subsequent trapping by a variety of electrophilic reagents. We are continuing our investigations in this area.

Experimental Section[17]

3-*n*-Butyl-2-lithiobornene (7). A dry, 100-mL round-bottomed flask was charged with 20 mL of dry THF and 2.00 g (0.005 mol) of camphor trisylhydrazone **5**[4] and fitted with a rubber septum and the mixture stirred magnetically until all solid had dissolved. The temperature was lowered by using a dry ice–acetone bath, and 8.21 mL (0.012 mol) of *sec*-butyllithium was added dropwise from a syringe over a 10-min period. The solution was then treated dropwise with 2.58 g (0.014 mol) of *n*-butyliodide and stirred at −78 °C for 7 h, after which time the yellow solution, still at −78 °C, was treated with 11.4 mL (0.016 mol) of additional *sec*-butyllithium, restoring the dark color of the dianion. The dry ice–acetone bath was replaced with a room-temperature water bath, and the solution was stirred while it was allowed to come to room temperature. During this period nitrogen evolution was monitored by a mineral oil bubbler. When vigorous nitrogen evolution ceased (internal temperature for this system about 0 °C), an excess (0.02 mol or greater) of the appropriate electrophile was added and the solution stirred at room temperature for 1 h. The reaction mixture was worked up in the usual manner and concentrated to a known volume, and an aliquot was taken for GLC analysis. For electrophiles *n*-butyl iodide, acetone, *n*-butyl bromide, and ethyl chloroformate, the products shown in Table I could be obtained by preparative GLC. In most cases the crude product contained small amounts (0–10%) of the corresponding unalkylated product, e.g., 2-*n*-butylbornene in the case of **8**, as well as small amounts of triisopropylbenzene.

3-Methyl-2-bornenecarboxaldehyde. The dianion of camphor trisylhydrazone (4.50 g, 0.010 mol) was prepared in 25 mL of THF with 20 mL (0.028 mol) of *sec*-butyllithium as described above and treated with 2.56 g (0.018 mol) of freshly distilled methyl iodide. After the mixture was stirred for 2 h at −78 °C, 24 mL (0.034 mol) of *sec*-butyllithium was added and the stirred solution allowed to warm toward room temperature until vigorous nitrogen evolution ceased, at which time 4 mL of DMF was added and the solution stirred for 5 min. A standard workup and short-path distillation afforded 0.82 g (46%) of product as a light yellow liquid, bp 69–70 °C (0.05 mm).

The infrared spectrum shows characteristic bands at 2980, 2745, 1675, 1612, 1345, and 760 cm^{-1}. The NMR spectrum shows δ 0.80 (s, 6 H), 0.90–2.3 (m, 5 H), 1.26 (s, 3 H), 2.12 (s, 3 H), and 9.87 (s, 1 H). Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.92; H, 10.27.

16-*n*-Butyl-3β-hydroxy-5,16-androstadiene-17-carboxaldehyde (14). A 300-mL, three-necked flask, equipped with a mechanical stirrer and 50-mL addition funnel, was thoroughly dried and charged with 5.00 g (0.009 mol) of dehydroepiandrosterone trisylhydrazone **12** and 135 mL of THF. After all the solid dissolved, the stirred flask was cooled at −78 °C and 28.6 mL (0.04 mol) of *sec*-butyllithium added dropwise over a 30-min period. To the stirred heterogenous mixture was then added 4.0 mL (0.036 mol) of *n*-butyl iodide, dropwise, by syringe. After the mixture had been stirred 8.5 h at −78 °C, the original deep red color had become almost white, and 5 mL of water was added. The mixture was poured into water, the organic layer separated, and the aqueous layer adjusted to pH ~5 and extracted twice with ether. The combined organic extracts were thoroughly washed with water, dried, and concentrated to yield 5.42 g of crude material. Crystallization from methanol afforded 4.34 g (80%) of **13** as white crystals, mp 206–208 °C dec.

A portion (1.20 g, 0.002 mol) of **13** was added to a 250-mL, three-necked flask containing 100 mL of THF. The solution was stirred at −78 °C, and 8.0 mL (0.010 mol) of *sec*-butyllithium was added dropwise over a 5-min period. The stirred red solution was allowed to warm until vigorous nitrogen evolution ceased, whereupon 0.5 mL of DMF was added and the uncooled solution stirred for 0.5 h.

After a standard workup, evaporation of the solvent afforded a viscous yellow material which was dissolved in 20 mL of hot methanol and stored at 0 °C overnight. Collection of the resulting white precipitate afforded 0.44 g (64%) of **14**, mp 116–118 °C; concentration of the mother liquor afforded an additional 0.15 g of less pure material.

The NMR spectrum shows δ 3.50 (s, 1 H), 5.30 (d, 1 H), and 9.92 (s, 1 H) in addition to the aliphatic envelope. Anal. Calcd for $C_{24}H_{36}O_2$: C, 80.85; H, 10.18. Found: 80.62; H, 10.31.

(*Z*,*E*)-5-Ethyl-3-nonene-4-carboxaldehyde (20). In the manner described above, 2.0 g (0.005 mol) of 4-heptanone trisylhydrazone in 25 mL of THF was treated at −78 °C with 8.9 mL (0.013 mol) of *sec*-butyllithium and 1.1 mL (0.01 mol) of *n*-butyl iodide. After being stirred 6 h at −78 °C, the pale yellow solution was treated with 10.7 mL (0.015 mol) of additional *sec*-butyllithium and allowed to warm toward room temperature. Upon cessation of nitrogen evolution, excess (1.5 mL) DMF was added, and the solution was stirred and worked up in the usual manner. GLC analysis of an aliquot indicated a mixture (yield

(16) House, H. O.; Kramar, V. *J. Org. Chem.* **1963**, *28*, 3362. Huff, B. J. L.; Tuller, F. N.; Caine, D. *Ibid.* **1969**, *34*, 3070.

(17) Capillary melting points were determined on a Mel-Temp apparatus and are uncorrected. Infrared spectra were taken as neat films or $CHCl_3$ solutions on a Beckman IR-18 A-X. Proton magnetic resonance (NMR) spectra were recorded in $CDCl_3$ solution on an EM-390 instrument. Chemical shifts are reported as parts per million (δ) downfield from tetramethylsilane. Reagent grade hexane was distilled from lithium aluminum hydride prior to use. 2,4,6-Triisopropylbenzenesulfonylhydrazide was prepared as reported.[18] Alkyllithium reagents were obtained from Alfa-Ventron Corp. and standardized prior to use. "Standard workup" consisted of pouring the mixture into water, separating the organic layer, and reextracting the aqueous layer with ether. The combined organic layers were washed to neutrality with water and dried over magnesium sulfate. After concentration of the filtered solution in vacuo, it was diluted to known volume and an aliquot taken for GLC analysis. The aliquot was analyzed on a $^1/_8$ in. × 15 ft, 6% SE-30 on Chromosorb W column by using solutions of purified product as the standard. Preparative GLC was done on a $^1/_4$ in. × 5 ft 20% SE-30 on Chromosorb W. Microanalyses were performed by Galbraith Laboratories, Inc. Trisylhydrazones were stored in a freezer prior to use.

(18) Cusack, N. C.; Reese, C. B.; Risius, A. C.; Roozpeikar, B. *Tetrahedron* **1976**, *32*, 2157.

86%) of (*Z*)- and (*E*)-**20** in a 4:1 ratio as determined by integration of the NMR peaks at δ 10.12 and 9.32. Short-path distillation afforded a fraction [bp 60–61 °C (0.08 mm)] of (*Z*)-**20** of greater than 95% purity.

The NMR spectrum shows a broad envelope from δ 0.67 to 1.67 and δ 2.3–2.8 (m, 3 H), 6.33 (t, 1 H), and 10.12 (s, 1 H). Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 78.81; H, 12.31.

4-*tert*-Butyl-6-*n*-butylcyclohexene-1-carboxaldehyde (22). By use of the procedure described above, 5.20 g (0.016 mol) of 4-*tert*-butylcyclohexanone tosylhydrazone in 30 mL of THF was treated at −78 °C with 22.0 mL (0.0321 mol) of *sec*-butyllithium and 2.4 mL (0.02 mol) of *n*-butyl iodide. After the mixture was stirred at −78 °C for 5 h, 50.0 mL (0.040 mol) of *sec*-butyllithium was added and the stirred mixture warmed to room temperature until nitrogen evolution ceased, at which time 1.5 mL of DMF was added. A standard workup and short-path distillation afforded 1.53 g (43%) of **22** [bp 104–106 °C (0.35 mm)], presumably the trans isomer as discussed in the text.

The NMR spectrum shows, in addition to a broad aliphatic envelope, peaks at δ 0.88 (s, 9 H), 6.67 (t, 1 H), and 9.34 (s, 1 H). Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 80.78; H, 11.88.

6-*n*-Butyl-2-methylcyclohexene-1-carboxaldehyde (26). A solution of 2.00 g (0.011 mol) of 2-methylcyclohexanone tosylhydrazone in 35 mL of dry THF was treated at −78 °C with 18.0 mL (0.026 mol) of *sec*-butyllithium and 1.2 mL (0.02 mol) of *n*-butyl iodide. After being stirred 24 h at −78 °C, the solution was treated with 35.0 mL (0.05 mol) of *sec*-butyllithium and allowed to warm to room temperature with stirring. Excess (1.5 mL) DMF was added, and the reaction mixture was stirred 0.5 h and worked up by the standard method. Preparative GLC afforded **26**. The NMR spectrum shows δ 0.87 (s, 3 H), 1.10–2.73 (m, 16 H including a singlet at 2.10), and 10.10 (s, 1 H). An aliquot of the crude reaction mixture showed the yield to be 47%. Both crude GLC and NMR spectroscopy suggested the presence of a small (<5%) amount of **27**.

When the alkylated tosylhydrazone dianion in a separate experiment was quenched with water and worked up as described above, 1.40 g of the alkylated tosylhydrazone (mp 96–102 °C) could be isolated. When this material was converted into the dianion, allowed to decompose, and then trapped with DMF in the usual manner, the crude GLC showed the presence of **26** and another product, **27**, in a 7:3 ratio. Preparative GLC afforded **27**, the NMR spectrum of which shows δ 0.78–1.08 (2 overlapping t, 6 H), 1.16–2.93 (m, 13 H), and 10.06 (s, 1 H).

Registry No. **5**, 63883-67-0; **7**, 76421-17-5; **8**, 76421-18-6; **9**, 76421-19-7; **10**, 76421-20-0; **11**, 76421-21-1; **12**, 76421-22-2; **13**, 76421-23-3; **14**, 76421-24-4; **15**, 63883-82-9; (*E*)-**20**, 76421-25-5; (*Z*)-**20**, 76421-26-6; **21**, 41780-53-4; **22**, 76421-27-7; **23**, 52826-41-2; **26**, 76421-28-8; **27**, 76421-29-9; 3-methyl-2-borenecarboxaldehyde, 76421-30-2.

Cycloaddition Reactions of Indenes. 3. 1:1 Adduct from 1,1-Dimethyl-1*H*-indene and Dimethyl Acetylenedicarboxylate[1]

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In contrast to 1*H*-indene (**1a**) and 1-methyl-1*H*-indene (**1b**), which give stable 1:2 adducts (**3a**, 34%; **3b**, 30%) and with **1a** also a 1:3 adduct (**4a**; 40% from **1a**; 71% from **3a**) with dimethyl acetylenedicarboxylate (DMAD), 1,1-dimethyl-1*H*-indene (**1d**) and DMAD gave as the only crystalline product a cycloadduct of different structural type, dimethyl 1a,7b-*cis*-dihydro-1,1-dimethyl-1*H*-cyclopropa[*a*]naphthalene-2,3-dicarboxylate (**5a**, 14%), the structure of which has been confirmed by X-ray crystallography.

1*H*-Indene (**1a**) and 1-methyl-1*H*-indene (**1b**), but not the more sterically hindered 1-ethyl-1*H*-indene (**1c**) react with dimethyl acetylenedicarboxylate (DMAD) in refluxing benzene (with **1a**)[3] or toluene (with **1b**)[1b] via a Diels–Alder [$4_\pi + 2_\pi$] cycloaddition across the 2- and 7a-positions to give 1:1 adducts **2** which undergo further, rapid, in situ [$2_\pi + 2_\pi$] cycloaddition across the 4- and 4a-positions (of **2**) to give solid 1:2 adducts (**3a**, 34%; **3b**, 30%).[1b] In refluxing xylene the reaction of **1a** goes further to give a 1:3 adduct (**4a**; 40% from **1a** and 71% from **3a**), formed by a Diels–Alder addition of a third molecule of DMAD across the remaining diene system of **3a**.[1b] 1,1-Dimethyl-1*H*-indene (**1d**) and DMAD, however, in a 1:2 molar ratio in refluxing xylene for 22 h gave as the sole crystalline product only a 1:1 adduct (**5a**, 14%), different from **2** and having ultraviolet (UV), infrared (IR), and ^1H nuclear magnetic resonance (NMR) spectra consistent with the structure dimethyl 1a,7b-*cis*-dihydro-1,1-dimethyl-1*H*-cyclopropa[*a*]naphthalene-2,3-dicarboxylate (**5a**) (Scheme I).

The UV spectrum of **5a** [(95% C_2H_5OH) λ_{max} 240 nm (log ε 4.17), 296 (3.89), 308 (3.90), 325 (sh, 3.61)] is similar to that of 1,2-dihydronaphthalene-3,4-dicarboxylic acid derivatives **6a–c** [longest wavelength band at 290–292 nm (log ε 4.18–4.22)[4]] but has additional conjugation such as that which comes from the cyclopropane ring in the 1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene derivatives **5b–l** [longest wavelength band or shoulder at 307–310 nm (log ε 3.0–3.35)], as shown in Table I. The ^1H NMR spectrum shows that the *gem*-dimethyl groups are retained in the adduct but are in widely different environments, as shown by the two methyl singlets (in $CDCl_3$) at δ 0.60 and 1.40. A similar difference in chemical shifts, averaging δ 1.65, has been noted for the 1-*endo* and 1-*exo* cyclopropyl protons in the methylene group at the corresponding position in the 2,3-benzonorcaradienes **5b–g** as shown in

(1) (a) Paper 1: Noland, W. E.; Landucci, L. L.; Kameswaran, V. *J. Org. Chem.* **1980**, *45*, 3456–3461. (b) Paper 2: Noland, W. E.; Kameswaran, V.; Landucci, L. L. *Ibid.* **1980**, *45*, 4564–4572.

(2) Taken in part from the Ph.D. thesis of Venkataraman Kameswaran, University of Minnesota, Minneapolis, MN, June 1971; *Diss. Abstr. B* **1972**, *32*, 6918–6919; *Chem. Abstr.* **1972**, *77*, 151725.

(3) (a) Alder, K.; Pascher, F.; Vagt, H. *Ber. Dtsch. Chem. Ges. B* **1942**, *75*, 1501–1514. (b) Muir, K. W.; Sim, G. A.; Strachan, P.; Huebner, C. F. *Chem. Ind. (London)* **1964**, 1581–1582.

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