pound was dehydrogenated by benzoquinone to 1,4-naphthoquinone in a 87% yield.

The general procedure for the "capillary technique" is as follows. A chromatographic tube (50 ml) is filled with silica gel (60–80 mesh), aluminum oxide (activity I), or other adsorbent (15–25 ml for 0.0005–0.002 *M* quantities). A solution of reactants (0.05–0.002 mol) in the least polar possible solvent (3–20 ml) is introduced into the column which is usually accompanied by very gentle warming. The mixture is allowed to react 12–72 hr at room temperature, and the products are isolated by conventional elution technique.

Alternately, the column filled with the adsorbent can be presoaked with a nonpolar solvent such as hexane or benzene before introducing the solution of the reactants, and this modification gives even better results. Also, the column may be presoaked with a solution of one reactant, and a solution of the other reactant can be passed through the column and allowed to react for a certain time.

The described technique is especially of advantage in such cases where conventional procedures require prolonged heating which could damage the reactants. Experiments are underway to find out the theoretical background of the reaction, in particular the function of the adsorbent, whether it is purely physical, or whether chemical aspects such as acid–base catalysis are involved.

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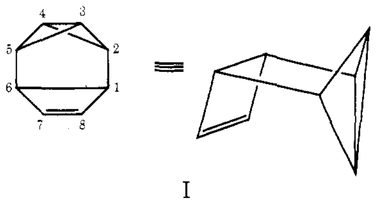
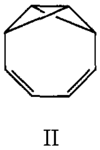
## A New $(CH)_8$ Isomer, Tetracyclo[4.2.0.0$^{2,4}$.0$^{3,5}$]oct-7-ene

*Summary:* Tetracyclo[4.2.0.0$^{2,4}$.0$^{3,5}$]oct-7-ene (I) has been prepared *via* a four-step reaction sequence, starting from benzvalene; the adduct (III) of dichloroketene and benzvalene was dehalogenated with triphenyltin hydride, and the resulting ketone (IV) was converted into I by the reaction of its *p*-toluenesulfonylhydrazone (V) with lithium 2,2,6,6-tetramethylpiperidide; preliminary experiments show that I is isomerized to cyclooctatetraene both thermally and in a silver ion catalyzed reaction.

*Sir:* As a consequence of our interest in $(CH)_8$ isomers and in highly strained molecules in general,[1] we have devised a synthesis of the as yet unreported title compound I, starting from benzvalene. It is hoped that this compound may serve as a precursor of the elusive "octavalene" (tricyclo[5.1.0.0$^{2,8}$]octa-3,5-diene), II, whose properties and possible rearrangements are expected to be of particular interest. After initial lack of success with approaches involving ozonolysis of benzvalene, sensitized photochemical addition of maleic anhydride to benzvalene, and the reaction of ethyl diazoacetate with benzvalene, the route outlined in Chart I proved fruitful.

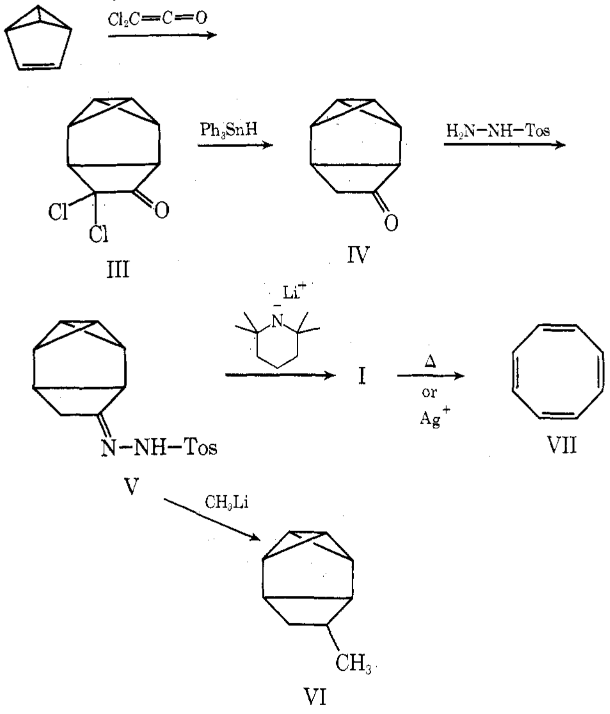


I



II

**Chart I**



Benzvalene in diethyl ether, prepared by the method of Katz,[2] was treated with just over 1 equiv of dichloroketene (generated *in situ* from dichloroacetyl chloride and triethylamine)[3] at 0° for 3.25 hr. After aqueous work-up and drying over potassium carbonate, the product was vacuum distilled (~0.1 Torr; oil bath heated to 80° after removal of ether) to yield up to 86% adduct III: ir (neat) 3145 (w), 3065 (w), 2990 (w), 1800 (s), 1110 (m), and 750 (s) cm$^{-1}$; nmr ($CCl_4$) $\delta$ 3.83, 3.72, 3.22, 3.10 (2H, "AB" pattern with $J_{AB}$ = 7 Hz), and 2.2–2.7 (4 H, br m); mass spectrum consistent with assigned structure. *Anal.* Calcd for $C_8H_6Cl_2O$: C, 50.84; H, 3.20. Found: C, 50.23; H, 3.12. Although benzvalene's addition reactions do not always follow "expected" paths,[4] the desired [2 + 2] cycloaddition is evidenced in this case by the characteristic carbonyl stretching frequencies exhibited by compounds III and IV.[3,5] The adduct III was reduced to the unhalogenated ketone IV by treatment with a small excess of triphenyltin hydride[3c,d,6] in refluxing cyclohexane for 4 hr, under nitrogen. After vacuum distillation (~0.1 Torr, bath temperature 70°), the yield of product was over 95% at its best (this includes ketone which codistilled with the cyclohexane): ir ($CCl_4$) 3060 (w), 1780 (vs), and 1119 (m) cm$^{-1}$; nmr $\delta$ 3.30 (1 H, m), 3.0–1.9 (7 H, very complex); mass spectrum (rel intensity) *m/e* 120 (15), 92 (15), 91 (54), 80 (20), 79 (26), and 78 (100). *Anal.* Calcd for $C_8H_8O$: C, 80.00; H, 6.71. Found: C, 80.14; H, 6.79.

The conversion of IV into its *p*-toluenesulfonylhydrazone[7] V is accomplished in high yield by dissolving the ketone and a slight excess of *p*-toluenesulfonylhydrazine in a minimum amount of anhydrous ethanol; the viscous solution is left at room temperature for 24 hr. The solvent is centrifuged from the resulting cream-colored solid mass. After recrystallization from ethanol, the product (apparently a mixture of geometrical isomers) gives mp 142–146°

dec; ir (KBr) 3200 (s), 3050 (w), 2930 (m), 1670 (m), 1590 (m), 1380 (s), 1325 (vs), 1170 (vs), 1083, 1020, 920, and 894 (m) cm$^{-1}$; nmr ($CDCl_3$) $\delta$ 8.10, 7.75 (combined 1 H, br s, removed by shaking with $D_2O$), 7.92, 7.78, 7.38, 7.25 (4 H, AA′BB′ pattern), 3.20–3.12 (1 H), and 2.8–1.7 (10 H, complex, containing s at 2.45). *Anal.* Calcd for $C_{15}H_{16}N_2O_2S$: C, 62.48; H, 5.59; N, 9.72. Found: C, 62.65; H, 5.60; N, 9.80.

The final transformation of V into I gave some initial difficulty. Treatment of V with excess methyllithium[8] in ether at room temperature for 10 hr gave as the major product (~25%) a compound whose mass spectrum suggests a $C_9H_{12}$ hydrocarbon bearing a methyl group, tentatively assigned structure VI, corresponding to methyl addition rather than to elimination to form an olefin.[8a,9] The use of other bases was therefore explored: potassium hydride (which seemed interesting because of its high reactivity),[10] *n*-butyllithium,[8b,c,d,11] and *sec*-butyllithium all failed to give appreciable amounts of the desired product. Finally, successful elimination was achieved by use of 2 equiv of lithium 2,2,6,6-tetramethylpiperidide[12] in THF–ether at room temperature for 8–10 hr under nitrogen; this gave yields of 35–55% I. To isolate the product, one adds pentane, removes THF and ether by repeated aqueous extraction, then removes the amine by rapid extractions with 1 *M* sodium dihydrogen phosphate; a final wash is carried out using aqueous ammonia. Pure I can be isolated by preparative gc, using a 6% SE-30 on Gas-Chrom Q column at room temperature. Lithium diisopropylamide in THF–ether at room temperature also gives I, but in only ~20% yield.

Tetracyclo[$4.2.0.0^{2,4}.0^{3,5}$]oct-7-ene (I) is characterized by the following spectral data: ir (vapor) 3100 (w), 3050 (s), 2950 (s), 2900 (w), 1570 (vw), 1380 (w), 1265 (m), 1180 (w), 1120 (m), 798, 755, and 705 (s) cm$^{-1}$; nmr ($CDCl_3$) $\delta$ 6.03 (s, 2 H), 2.80 (slightly broadened s, 2 H), 2.3–1.7 (m), and 2.1 (s, showing fine structure) (total 4 H);[13] $^{13}$C nmr[13c,14] ($\delta$ from TMS) 139.4 (assigned to vinylic C's), 47.7 and 37.2 (tentatively assigned to C-1,6 and C-2,5, respectively), and 16.2 and −0.7 (C-3,4, in indefinite order); uv end absorption, starting at ~230 nm; mass spectrum (EI) (rel intensity) *m/e* 105 (7), 104 (71), 103 (71), 102 (11), 79 (6), 78 (100), 77 (32), 76 (8), 75 (5), 74 (9), 52 (20), 51 (40), and 50 (25); mass spectrum (CI, with $CH_5^+$ as ionizing medium) (rel intensity) *m/e* 106 (10), 105 (100), 104 (12), 103 (20), 102 (1), 93 (4), 92 (2), 91 (28), 80 (2), 79 (33), 78 (3), 67 (2), 56 (3), and 51 (3).

In some preliminary experiments, samples of I were briefly pyrolyzed at 400–500°[15] in an attempt to open the cyclobutene ring to give II. The result of these pyrolyses was a very clean conversion to cyclooctatetraene (VII), as determined by the mass spectrum of the product and by coinjection with an authentic sample of VII on three different gc columns. Treatment of I with silver ion[16] (silver perchlorate or silver tetrafluoroborate in acetone or THF at room temperature for several minutes) also appears to yield some VII. Alternative ring opening techniques, as well as other reactions of the title hydrocarbon, are now being studied.

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