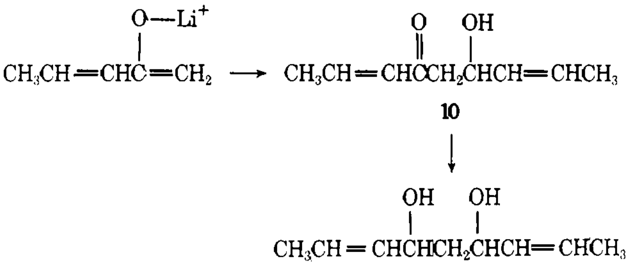
in THF) with ethyl iodide; and (b) by dehydration (*p*-toluenesulfonic acid, refluxing benzene) to the known[14] unsaturated ketone **8**.

The kinetic lithium enolates of α,β-unsaturated ketones[15] can also be used in regiospecific aldol condensation. The lithium enolate from 3-penten-2-one was prepared and condensed, as described above, with crotonaldehyde to give the dienolone **10** in 70% yield (after preparative tlc on silica gel with 4:1 methylene chloride–ether): ir (film) 3.0, 5.9 μ; nmr ($CDCl_3$) δ 5.9–7.1 (m, $CH_3CH{=}CH{=}C{=}O$) 5.5–5.7 (m, $CH_2CH{=}CHCHOH{-}$), 4.4–4.6 (m, HCOH), 2.6 (d, J = 6 Hz, $-CH_2C{=}O$), 1.98 (d, b, J = 6 Hz, $O{=}CC{=}CCH_3$), 1.85 (d, J = 5 Hz $CH_3C{=}CCHOH$). Analysis was performed on the bis(trimethylsilyl) ether of the doubly unsaturated diol **11** from reduction (bis(2-methoxyethoxy)aluminum hydride in benzene): m/e 300.1938 (calcd 300.1940). Catalytic hydgenation of **10** gave the saturated aldol **1** identical (*vide supra*) with the product of the aldol condensation of butyraldehyde and the kinetic lithium enolate of 2-pentanone.



$$CH_3CH{=}CH\overset{\overset{\displaystyle O^-Li^+}{|}}{C}{=}CH_2 \longrightarrow CH_3CH{=}CH\overset{\overset{\displaystyle O}{\|}}{C}CH_2\overset{\overset{\displaystyle OH}{|}}{C}HCH{=}CHCH_3$$

10

$$\downarrow$$

$$CH_3CH{=}CH\overset{\overset{\displaystyle OH}{|}}{C}HCH_2\overset{\overset{\displaystyle OH}{|}}{C}HCH{=}CHCH_3$$

11

The ability of regiospecifically produced lithium enolates to maintain their integrity in aldol condensations should greatly extend the usefulness of the reaction.[16,17]

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(1) *Cf.* H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Menlo Park, Calif., 1972.

(2) "No examples (of successful aldol condensation under nonequilibrating conditions) involving methyl ketones are known": A. T. Nielsen, *Org. React.*, **16**, 37 (1968).

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(6) Except, of course, when the kinetic enolate is also the more stable one.

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(8) "Selective alkylation of the methyl group of ketones RCH_2COCH_3 by any method which involves generation of the enolate $RCH_2C(O^-){=}CH_2Li^+$ in an ethereal solvent will not be a good synthetic procedure": H. O. House, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **36**, 2361 (1971).

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(11) The linear isomer had the longer retention time.

(12) By reduction of the enol ether of 4,6-nonanedione with bis(2-methoxyethoxy)aluminum hydride in benzene, followed by aqueous acid hydrolysis.

(13) In a paper (ref 3) which was published after the completion of our own work, the statement is made (without experimental details) that direct preparation of lithium enolates with lithium diisopropylamide in tetrahydrofuran had not given satisfactory results. In the absence of experimental details, the reason for this difference with our own results is unclear.

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(15) For the structure of the kinetic enolates of *cyclic* α,β-unsaturated ketones, see R. A. Lee, C. McAndrews, K. M. Patel, and W. Reusch, *Tetrahedron Lett.*, 965 (1973); G. Stork and R. L. Danheiser, *J. Org. Chem.*, **38**, 1775 (1973).

(16) We have, for instance (G. Stork and J. D'Angelo, in preparation), shown that the synthetically versatile α-hydroxymethyl ketones can be produced regiospecifically by trapping enolate ions with formaldehyde.

(17) We thank the National Institutes of Health and the National Science Foundation for their support of this work.

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Capillary Techniques in Organic Synthesis

Summary: Some reactions such as nucleophilic displacements and additions have been found to be considerably accelerated if allowed to take place inside the pores of high surface area materials (silica gel, aluminum oxide and others).

Sir: Solids such as activated charcoal, silica gel, and aluminum oxide having high surface areas promote reactions which would otherwise require much higher temperatures or would not take place at all. Innumerable examples of such reactions in the vapor phase are well known.

In the liquid phase, catalytic effects of the adsorbent were frequently observed during adsorption chromatography when polymerization, isomerization, hydrolysis, dehydration,[1] dehydrohalogenation,[2] reduction,[3] and similar alterations[1] of the chromatographed substances were occasionally recorded. In some instances, the adsorbent was pretreated with certain chemicals to achieve reactions which would not occur over the pure adsorbent.[4]

In all these instances, the reactions take place between the compound and the adsorbent which reacts by virtue of its chemical properties (acidity, dehydrating power, etc.).

It was of interest to find out whether porous materials could be used just to bring two or more compounds together in the liquid phase inside the pores where the minimum pore size is of the order of several molecular diameters. For this purpose, several displacement and addition reactions have been carried out.

When a column of acid aluminum oxide was soaked with a solution of benzyl chloride in chloroform containing hydrazoic acid, and after 16 hr at room temperature the column was eluted with hexane and ether, 49.5% conversion and 68.5% yield of benzyl azide was obtained.

Similar treatment of dialkyl α-bromo-α'-fluorosuccinate or α,α'-dibromosuccinate with a solution of hydrazoic acid gave dialkyl azidofumarate. Preparation of the same compound required refluxing of the halogenated esters with sodium azide in methanol for 12 hr.[5]

The Diels–Alder reaction between 1-acetoxy-1,3-butadiene and fluoranil (tetrafluoro-*p*-benzoquinone) requires heating of the benzene solution of the two compounds at 98° for several hours.[6] When the same solution was placed in a column of silica gel at room temperature for 60 hr, the product, 5-acetoxy-2,3,4a,8a-tetrafluoro-4a,5,8,8a-tetrahydro-1,4-naphthoquinone, was obtained by chloroform elution in 49.5% conversion and 67–78% yield.

Similar reaction of 1-acetoxy-1,3-butadiene with *p*-benzoquinone was described taking place at a reflux temperature of carbon tetrachloride and diisopropyl ether after at least 1 hr.[7] When a solution of 1-acetoxy-1,3-butadiene and *p*-benzoquinone in benzene was allowed to react for 40 hr at room temperature in a column of silica gel presoaked with hexane, not only did the addition occur, but the product, 5-acetoxy-4a,5,8,8a-tetrahydro-1,4-naphthoquinone, eliminated acetic acid, and the intermediate dihydro compound 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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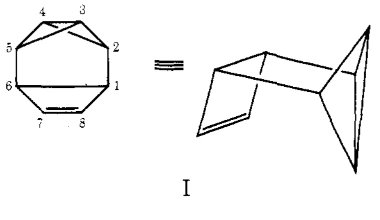
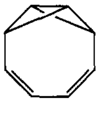
A New (CH)$_8$ Isomer, Tetracyclo[4.2.0.0^{2,4}.0^{3,5}]oct-7-ene

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.

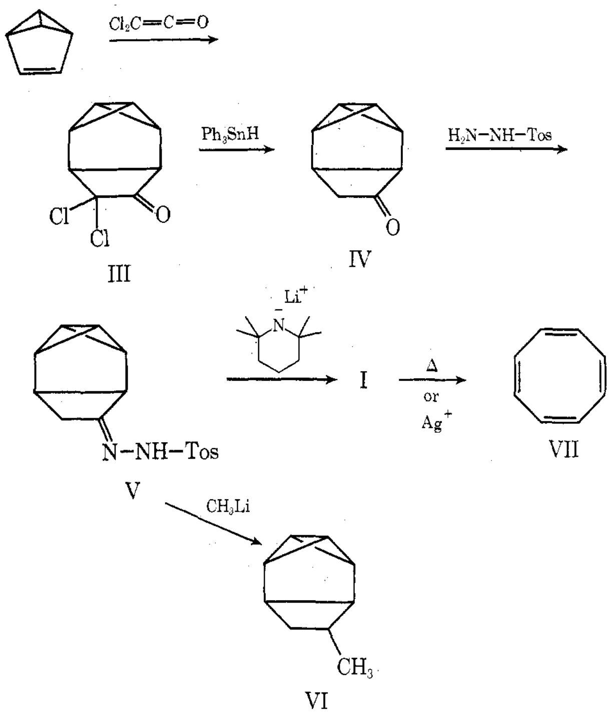


I



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$_4$) δ 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 δ 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°