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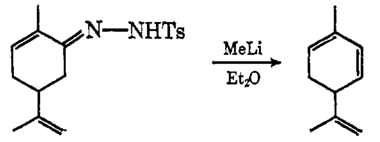
Preparation of Conjugated Dienes from Tosylhydrazones of α,β-Unsaturated Ketones and Alkyllithium Reagents[1,2]

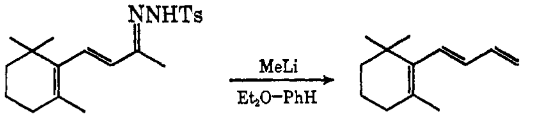
Sir:

The reaction of alkyllithium reagents with tosylhydrazones to yield the lesser substituted olefin without a carbon skeleton rearrangement has recently been reported.[3] This reaction finds great utility in the preparation of difficultly obtainable olefins such as 2-bornene[3a] and bicyclo[2.1.1]hexene.[3d]

An extension of this reaction using the tosylhydrazones of α,β-unsaturated ketones now permits the preparation of conjugated dienes in good to excellent yields. The reaction is of particular use in the synthesis of substituted 1,3-cyclohexadiene compounds which often are difficult to prepare in high purity and in quantity by other methods. Thus, in the presence of ≥ 2 equiv of methyllithium in ether or ether–benzene mixtures, carvone tosylhydrazone (I) gave in 80% yield, exclusively, 2-methyl-5-isopropenyl-1,3-cyclohexadiene (II),[4] showing that the elimination involved only the α hydrogen and that isomerization of other double bonds did not occur. A similar specificity is found in the preparation of the triene IV in a yield of 75–80% from β-ionone tosylhydrazone (III). Several other examples of the reaction are shown in Table I.

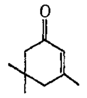
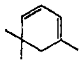
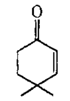
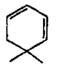
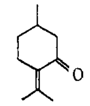
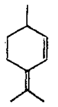
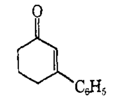
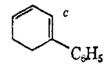
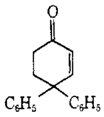
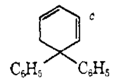
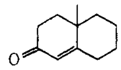
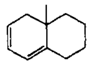
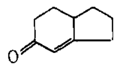
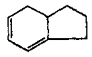
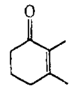
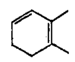
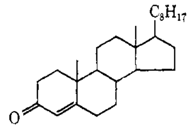
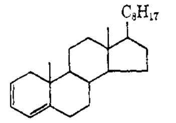


I II



III IV

Table I. Reaction of α,β-Unsaturated Tosylhydrazones with Methyllithium

Tosylhydrazone of	Product	Yield, %
		100^a
		85^b
		100^a
		40^b
		55^b
		$85^{b,d}$
		$60^{b,d}$
		87^b
		80^b

[a] Gas chromotographically pure. [b] Isolated yield. [c] Butyllithium used. [d] The reaetion and work-up were carried out below 10° to eliminate bond migration in the products.

In the course of the above investigation of dienes, the following features of the reaction were noted. In those cases where the tosylhydrazone, prepared in THF, did not precipitate from the reaction and permit ready isolation, excess benzene was added and the THF and benzene–water azeotrope were removed by distillation at atmospheric pressure. The resulting suspension of tosylhydrazone in benzene was allowed to react directly with methyllithium in ether. Methyllithium was found to be superior to *n*-butyllithium for the preparation of conjugated dienes, paralleling the behavior found for monoolefin production.[5] Dienes containing about 40% deuterium at the site of the original carbonyl group could be prepared by using deuterium oxide to decompose the reaction mixture. When the tosylhydrazone was added to *n*-butyllithium (inverse addition)[6] the deuterium content would be increased to approximately 60%. In some cases, sufficient toluene was found in the reaction mixture to make the isolation of the pure diene difficult. This toluene when formed in the presence of deuterium oxide contained deuterium only at the *para* position.

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[1] This work was supported at Berkeley, in part, by Public Health Service Grant 00709, National Institute of Arthritis and Metabolic Diseases, U.S. Public Health Service, and at Boulder by National Science Foundation Grant GP 5753.

[2] This paper is part VIII in the tosylhydrazone series of the Boulder group. For paper VII, see R. H. Shapiro and K. Tomer, *Chem. Commun.*, 460 (1968).

[3] (a) R. H. Shapiro and M. J. Heath, *J. Am. Chem. Soc.*, **89**, 5734 (1967); (b) G. Kaufman, F. Cook, H. Shechter, J. Bayless, and L. Friedman, *ibid.*, **89**, 5736 (1967); (c) R. H. Shapiro, *Tetrahedron Letters*, 345 (1968); (d) J. Meinwald and F. Uno, *J. Am. Chem. Soc.*, **90**, 800 (1968).

[4] All structures were assigned on the basis of spectral evidence (nmr, uv, and mass spectrometry). Nmr decoupling experiments were performed in some cases to establish the peak assignments.

[5] R. H. Shapiro, J. H. Duncan, E. C. Hornaman, and J. W. Serum, unpublished observation.

[6] The incorporation efficiency appeared to depend upon the age of the alkyllithium; this effect is now being evaluated.

An attempt to prepare an allene by this method proved unsuccessful. Upon reaction with methyllithium, cinnamaldehyde tosylhydrazone gave a mixture of 14 products, none of which has, as yet, been completely identified. Thus, it appears that, in order for the elimination reaction to be successful, the α-hydrogen atom must be attached to a saturated carbon atom. Also, when the tosylhydrazone of piperitone was allowed to react under the described conditions, no diene was found. Thus, the α-hydrogen atom must be a methylene or methyl group for the reaction to proceed under these conditions; a similar restriction has been noted for the preparation of alkenes.[3b]

The following procedure is representative. A 250-ml, three-necked flask was fitted with a condenser and a magnetic stirring bar. In the flask was placed 7.5 g (0.05 mol) of carvone and 9.3 g (0.05 mol) of *p*-toluenesulfonylhydrazine. Sufficient tetrahydrofuran (~25–50 ml) was added to bring the reactants into solution, three drops of concentrated HCl was added, and the solution was refluxed for 6 hr. Benzene was added and tetrahydrofuran was distilled at atmospheric pressure from the reaction mixture, bp 66–67°. The temperature of the distillate then rose to 70° and the benzene–water azeotrope was allowed to distil. The distillation was continued until the temperature was near 80°. The reaction mixture was then cooled in an ice bath and 0.11 *M* of methyllithium in ether was added, dropwise, over a 40-min period with stirring. The ice bath was removed and water was slowly added to the slurry. The mixture was extracted with pentane, the extract dried, and the solvent removed to yield 5.15 g of 2-methyl-5-isopropenyl-1,3-cyclohexadiene.

(7) National Institutes of Health Postdoctoral Fellow, 1967–present.
(8) NDEA Predoctoral Fellow, 1965–present.
(9) NASA Predoctoral Fellow, 1966–present.

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The Photochemical Conversion of Cyclooctatetraene to Semibullvalene. Mechanistic and Exploratory Photochemistry. XXXVII[1]

Sir:

A goal of considerable interest is the delineation of the excited-state pathways interrelating the C_8H_8 hydrocarbons and extension of the study to the benzo derivatives.[2] In the course of these studies we have been investigating the photochemistry of cyclooctatetraene. Although cyclooctatetraene (**1**) has been obtained photochemically from barrelene and semibullvalene (**2**), and similar behavior has been found for the benzo derivatives,[2] such transformations have not been found to be photochemically reversible. Thus, benzene and acetylene[3] and the valence tautomer bicyclo[4.2.0]-octa-2,4,7-triene (**3**)[4] have been reported as being formed on photolysis of cyclooctatetraene, but no semibullvalene (**2**) has been noted. We now wish to report the formation of semibullvalene from cyclooctatetraene as the major product at low temperature from sensitized photolysis. The reaction is of both preparative and theoretical value.

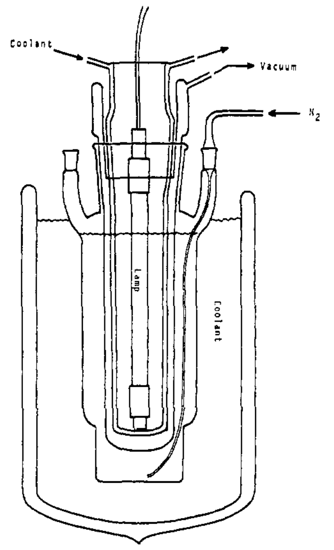

Figure 1.

In initial semimicro scale runs in a low-temperature infrared cell at −78°, irradiation of a 0.387 *M* solution of cyclooctatetraene in THF–*n*-propyl ether (2:1 v/v) led to a decrease of the 12.4- and 14.7-μ bands of reactant **1** and the appearance of peaks at 6.82, 12.68, and 14.6 μ which are characteristic of semibullvalene (**2**). Furthermore, this absorption remained upon warming the sample to room temperature. Preparative irradiation of cyclooctatetraene at low temperature was carried out in the apparatus depicted in Figure 1. Irradiation of 11.4 g of cyclooctatetraene in 500 ml of isopentane and 16.6 g of acetone at −60° with a 450-W medium-pressure lamp with a Vycor filter for 50 hr afforded a mixture which was shown by nmr and vpc to contain 9.27 g of cyclooctatetraene, 0.845 g of semibullvalene (**2**), and 0.340 g of benzene. Semibullvalene was separated from cyclooctatetraene (**1**) by crystallization of **1** from the mixture followed by aqueous silver nitrate–ether liquid–liquid partition chromatography. Final isolation was by preparative vpc. Separate experiments, including some in sealed quartz tubing attached to the medium-pressure lamp, showed: (1) that in the absence of acetone the reaction proceeded slowly, (2) that a stationary state of ~88% cyclooctatetraene and 12% semibullvalene could be reached by extended photolysis, and (3) that benzophenone and acetophenone were ineffective as sensitizers.

Prior to concerning ourselves with molecular details of the reaction mechanism, two points are of interest. First, the reaction clearly proceeds *via* the triplet, since without acetone the conversion is inefficient. Second,

(1) For paper XXXVI see H. E. Zimmerman and D. S. Crumrine, *J. Am. Chem. Soc.*, in press.
(2) (a) H. E. Zimmerman and G. L. Grunewald, *ibid.*, **88**, 183 (1966); (b) H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *ibid.*, **89**, 3932 (1967); (c) H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *ibid.*, **90**, 4191 (1968).
(3) (a) I. Tanaka, S. Miyakawa, and S. Shida, *Bull. Chem. Soc. Japan*, **24**, 119 (1951); (b) I. Tanaka and M. Okuda, *J. Chem. Phys.*, **22**, 1780 (1954).
(4) (a) E. Migirdicyan and S. Leach, *Bull. Soc. Chim. Belges*, **71**, 845 (1962); (b) G. J. Fonken, *Chem. Ind.* (London), 1625 (1963).