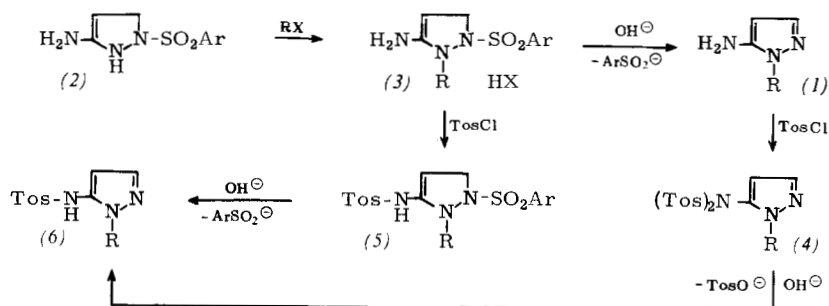


1-Methyl-5-aminopyrazole can be tosylated to give (4),  $R = \text{CH}_3$ , m. p. 188–190 °C, the structure of which has been substantiated by the characteristic position of its sulfonyl absorption [5] in the infrared and by the synthesis [4] of analogous derivatives of (1) with two different arenesulfonyl residues. The salts (3) react with *p*-toluenesulfonyl chloride to give very good yields of 1-alkyl-2-arenesulfonyl-5-(*p*-toluenesulfonamido)- $\Delta^4$ -pyrazolines (5),  $\text{Ar} = p\text{-H}_3\text{C-C}_6\text{H}_4$ ,



$R = \text{CH}_3$ , m. p. 189–190 °C, which like (3) can also lose 1 mole of sulfinate. The structures of (2) and (3) are certified by the fact that alkaline cleavage of (4),  $R = \text{CH}_3$ , and (5),  $R = \text{CH}_3$ , leads to the same compound, viz. 1-methyl-5-(*p*-toluenesulfamido)pyrazole (6),  $R = \text{CH}_3$ , m. p. 151.5 to 152.5 °C.

Received, August 31st, 1964 [Z 835/659 IE]  
German version: Angew. Chem. 76, 921 (1964)

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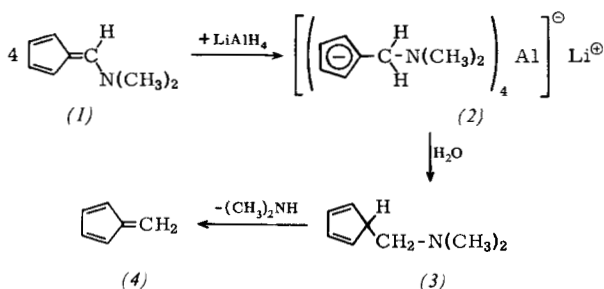
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### A Simple Synthesis of Fulvene and Its 6-Alkyl Derivatives

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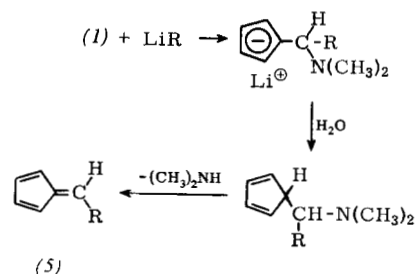
The base-catalysed condensation of cyclopentadiene with formaldehyde or a homologue affords fulvene (4) or its 6-alkyl derivative (5) respectively, but only in yields of less than 5% [1]. We have found that (4) is obtained in ca. 60% yield from the "reductive deamination" of the readily accessible 6-dimethylaminofulvene (1) [2] with lithium aluminium hydride in ether.



The cyclopentadiene-metal compound first formed, which can be isolated, is converted on hydrolysis at 0 °C into the Mannich base (3), which rapidly loses dimethylamine above 100 °C in high vacuum or during chromatography on alumina

(neutral, activity grade II) with ether or *n*-pentane. On reaction with methyl iodide at 0 °C, (3) yields a quaternary salt which immediately splits out trimethylammonium iodide to give (4) which is isolated by distillation (b. p. –5 °C/15 mm) as a pale yellow oil and is very sensitive to heat and oxygen. Its ultraviolet spectrum agrees with that given in the literature [1]. The NMR spectrum of (4) in  $\text{CCl}_4$  shows a multiplet between 3.6 and 4.1  $\tau$ .

Compound (1) reacts similarly with organolithium compounds to form fulvenes of type (5) in yields of 80–90%.



For example, 6-methylfulvene (5),  $R = \text{CH}_3$ , is obtained in 81% yield from (1) and methyl-lithium as a yellow oil, b. p. 19–21 °C/12 mm; ultraviolet spectrum in ethanol:  $\lambda_{\text{max}} = 255 \text{ m}\mu$  ( $\log \epsilon = 4.24$ ), 357 (2.50); NMR spectrum in  $\text{CCl}_4$ : multiplet between 3.7 and 4.1  $\tau$  (5), doublet at 8.0  $\tau$  (3). Numerous 6-arylfulvenes can be readily prepared in the same manner.

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### Synthesis of 2,3-Diphenyl-1,1,4-trioxo-1,2,3-thiadiazolidines

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When *N*'-chloroacetylhydrazobenzene (1),  $R = \text{H}$ ,  $X = \text{Cl}$  [1], and potassium sulfite are boiled in ethanol/water (2:1) for 3 h under reflux, the potassium salt of sulfoacetylhydrazobenzene (2),  $R = \text{H}$ , is formed with 95% yield (colorless crystals, m. p. 245 °C, from aqueous ethanol). This salt was readily cyclized by phosphorus oxychloride to (3),  $R = \text{H}$ , m. p. 150 °C, in about 50% yield [2].

Similarly,  $\alpha$ -bromobutyryl hydrazobenzene (1),  $R = \text{C}_2\text{H}_5$ ,  $X = \text{Br}$  [3], yielded 5-ethyl-2,3-diphenyl-1,1,4-trioxo-1,2,3-thiadiazolidine (3),  $R = \text{C}_2\text{H}_5$ , m. p. 109 °C.