

CRYSTALLINE PENTADIENYL AND CYCLOOCTADIENYL POTASSIUM
 PREPARATION BY DIRECT METALLATION WITH METALLIC POTASSIUM

Hajime Yasuda, Toshihito Narita, and Hisaya Tani

Department of Polymer Science, Faculty of Science, Osaka University

Toyonak, Osaka 560, Japan

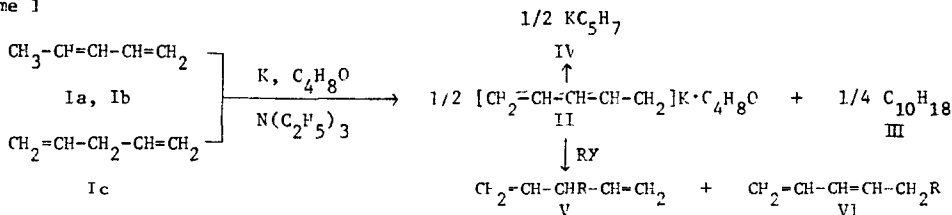
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This paper describes the syntheses by direct metallations and reactions with some alkyl halides of novel crystalline dienyl alkali metal compounds, except lithium ones, derived from isomeric pentadienes and cyclooctadienes

A general procedure for the preparation of these compounds is as follows: a diene(1.5 mol) is reacted with dispersed potassium(1.0 mol) in an argon atmosphere in tetrahydrofuran (THF) (20 mol) in the presence of triethylamine(10 mol) to give an orange-red solution, without any gas evolution. The crystalline dienyl potassium is obtained by the addition of excess of n-hexane to the solution, and the dimer(s) of the diene is obtained from the n-hexane soluble fraction. The corresponding pentadienyl sodium, rubidium, and cesium compounds were also obtained in crystalline forms.

Cis-1,3- (Ia), trans-1,3- (Ib), and 1,4-pentadiene (Ic) gave an identical pentadienyl potassium tetrahydrofuranate $KC_5H_7 \cdot THF$ (II) as yellow needles or prisms. The vacuum distillation and preparative glpc of the filtrate gave a mixture of reduced dimers $C_{10}H_{18}$ (III), which is composed of 4-methyl-2,5- (IIIa), 4-methyl-2,6-nonadiene (IIIb), and 4,5-dimethyl-2,6-octadiene (IIIc) in a molar ratio of 7/7/5.¹ The yields of II and III calculated by the equation shown in scheme 1 were both 95%.

Scheme 1



Similar results were obtained in the reaction of isomeric n-hexadienes (2,4-, 1,4-, and 1,5-hexadienes) and 1,7-octadiene with alkali metals. In the case of 1,7-octadiene, a reduced monomer, trans-3-octene, was obtained instead of reduced dimers.

Recently, Bates, et al., reported the preparation of pentadienyl lithium by the reaction of 1,4-pentadiene with n-butyl lithium². Nevertheless, the reaction of isomeric pentadienes with metallic lithium in the existence of triethylamine and THF gave only poly(pentadiene), but not pentadienyl lithium.

The presence of a suitable tertiary amine is required for the successful occurrence of this type of reaction. Triethylamine, triethylenediamine, and N,N,N',N'-tetramethylethylenediamine are the most effective, and pyridine and dipyridyl are less effective (yield of II, 15%) in suppressing the polymerization of 1,3-pentadiene; in the absence of a tertiary amine, the yield of II was only 2%. The nature of solvent is another important factor: no reaction was observed in diethyl ether at 30°C for 20 hr.

The complex II liberates its coordinated THF at 50°C/1 mm in an argon atmosphere to give a yellow powdery substance (IV), which is less stable than II. This instability is proved by its transformation into a polymeric substance in the solid state when it is allowed to stand at 35°C for 1 week. The crystalline tetrahydrofuranate of NaC₅H₇ is stable even under a vacuum. The reason for this good stability of NaC₅H₇·THF will be clarified in future.

The reaction of II with an alkyl halide (RX) in THF gave quantitatively a mixture of mono-alkyl derivatives composed of 3-alkyl-1,4- (V) and 5-alkyl-1,3-pentadiene (VI) in a ratio which depends on the nature of the alkyl group (Table 1). Thus, a bulky alkyl group favors the 3-alkylated derivative.

Table 1. Reaction between C₅H₇K and Alkyl Halides in THF at 0°C for 15 hr.

Alkyl halide	3-alkyl-1,4-pentadiene (%)	5-alkyl-1,3-pentadiene (%)
CH ₃ I ³	35	65
C ₂ H ₅ Br	53	47
n-C ₄ H ₉ Br	71	29
tert-C ₄ H ₉ Br	84	16

Crystalline etherates which were obtained by the addition of n-hexane to the ether solution of C₅H₇K were hydrolyzed to give a mixture of cis- (Ia) and trans-1,3-pentadiene (Ib) in a ratio

Table 2. Hydrolysis of Solid Etherates, C_5H_7K ether, with Water.

Coordinated ether	Cis isomer (%)	Trans isomer (%)
None (IV)	2	98
THF (II)	38	62
Monoglyme	37	63
Triglyme	40	60
Diglyme	78	22
1,3-Dioxane	89	11

which depends on the nature of coordinated ether (Table 2) Thus, a strongly coordinated ether favors the cis isomer

Three different structures, cis,cis (U-shaped), cis,trans (Sickel-shaped), and trans, trans (W-shaped), are conceivable for $C_5H_7K \cdot THF^{4-6}$. Although nmr and ir data suggest the coexistence of three forms in solution, the correct structure of C_5H_7K THF must await an X-ray analysis⁷

Cis,cis-1,3- (VIIa) and cis,cis-1,5-cyclooctadiene (VIIb) gave an analogous potassium compound (VIII) as needles (yield, 90%) and a reduced dimer $C_{16}H_{26}$ (IX)⁸ (yield, 96%). Crystalline VIII liberates its coordinated THF at 50°C/1 mm to give cyclooctadienyl potassium (X) as a yellow powdery substance.

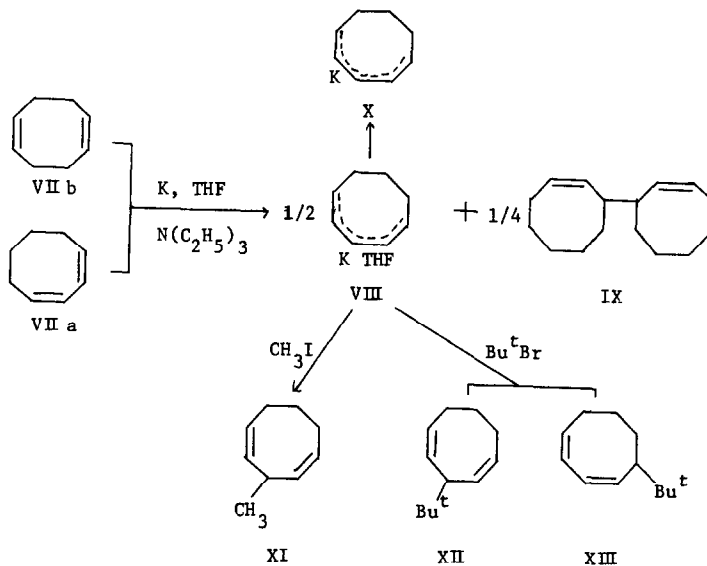
The cis,cis structure can be assigned to VIII on the basis of its nmr and ir spectra. The examination of a molecular model supports this interpretation.

The reaction of VIII (1.0 mol) with methyl iodide (1.0 mol) in THF gave almost exclusively 3-methyl-1,4-cyclooctadiene (XI) (yield, 95%), together with a small amount of 5-methyl-1,3-cyclooctadiene³. The reaction with tert-butyl bromide, however, gave similar amounts of 3-tert-butyl-1,4- (XII) and 5-tert-butyl-1,3-cyclooctadiene (XIII). Thus, a bulky alkyl group favors the 5-alkyl derivative, in sharp contrast with the case of the pentadiene compound. The reason for this contrast as well as the reaction mechanism remains to be solved.

The reaction condition required for the successful occurrence of this type of reaction depends on the structure of pentadiene (0°C/3 hr for Ia and Ib, and 30°C/15 hr for Ic) or of cyclooctadiene (0°C/3 hr for VIIa and 40°C/20 hr for VIIb). This result suggests that unconjugated dienes must be isomerized to conjugated ones prior to the initiation of the reaction.

The reaction of an alkali metal except lithium with a diene compound mentioned above seems to be applicable quite generally to both aliphatic and cyclic dienes.

Scheme 2



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