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time; must be handled under inert atmosphere; catalytic activity may decrease if impure or moist solvents are used; can be safely destroyed by slowly adding isopropanol to a suspension of the reagent in hexane with good stirring.

**Catalytic Activity.**  $K/Al_2O_3$  is the most efficient among the series of alkali metals finely dispersed on alumina, although *Sodium-Alumina* (sometimes termed 'high surface sodium') essentially effects the same types of transformations. In a model system, the following order of activity for the different alkali metals supported on alumina has been established:  $K \geq Rb \gg Cs \approx Na$ .<sup>1a</sup>

$K/Al_2O_3$  readily effects both configurational as well as positional alkene isomerizations with the following three trends being observed. Firstly, alkene groups are usually shifted (with few exceptions) towards higher degrees of substitution (eq 1).<sup>2</sup> Secondly, an alkene of accentuated conformational preference will accumulate: this is evidenced, for example, by the formation of the thermodynamically more stable (*Z,Z*)-cyclodeca-1,6-diene from (*E,Z*)-cyclodeca-1,5-diene (eq 2).<sup>1</sup> as well as by the preponderance of (-)-aristolene in the equilibrium mixture obtained upon treatment of (+)-calarene with  $K/Al_2O_3$  (eq 3).<sup>2</sup> Thirdly, the double bonds in 1,*n*-(cyclo)alkadienes are shifted towards conjugation independent of their initial position in the starting material (eqs 4 and 5).<sup>1,2</sup> Similarly, 1,2,4-trivinylcyclohexane quantitatively affords 1,2,4-triethylbenzene in a highly exothermic process.<sup>3</sup> Although the mechanism responsible for such positional changes is not yet elucidated, allyl anion intermediates are likely.<sup>1</sup> This picture is supported by the observation that successive treatment of  $\gamma$ -Alumina with *Sodium Hydroxide* and Na leads to a solid superbases ( $pK_b \geq 37$ ), which effects the same types of alkene isomerizations via allyl anion species.<sup>8</sup>

## Potassium on Alumina

$K/Al_2O_3$

K

(MW 39.10)

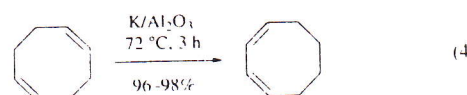
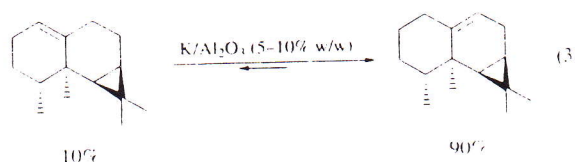
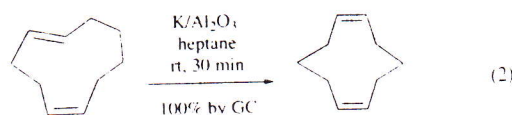
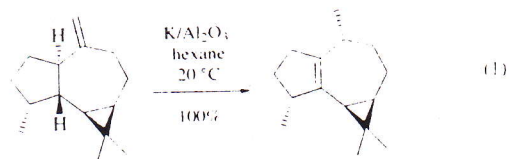
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(catalyst for hydrogenations,<sup>1,7</sup> double bond isomerizations,<sup>1-4</sup> dehydrations, and skeletal rearrangements;<sup>2-4</sup> metalating agent;<sup>5</sup> effects reductive decyanation<sup>6</sup>)

**Physical Data:** blue powder if the metal content is in the range of 2–15%; at higher loading the reagent has a gray to black appearance. The X-ray spectrum of a 14% K on  $Al_2O_3$  reagent shows no observable reflections due to potassium.<sup>6</sup> A metal content in the range of 2–15% usually leads to the highest catalytic activity.<sup>1</sup>

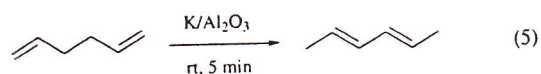
**Preparative Method:** by adding potassium to thoroughly dried basic or neutral alumina under argon with vigorous stirring at temperatures  $>100^\circ C$  until a homogeneous appearance is reached.

**Handling, Storage, and Precautions:** nonpyrophoric solid which can be stored under argon for extended periods of



Macrocyclic 1,3-cycloalkadienes produced by isomerization of 1,*n*-cycloalkadienes are slowly reduced to cycloalkenes even

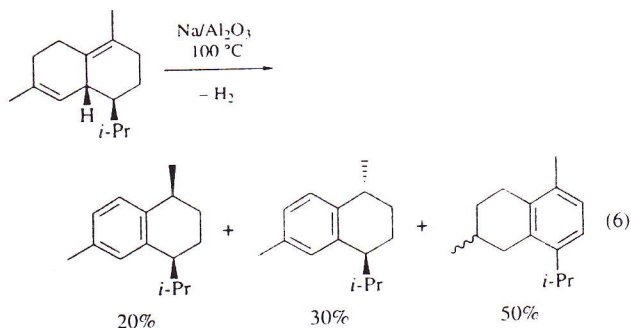




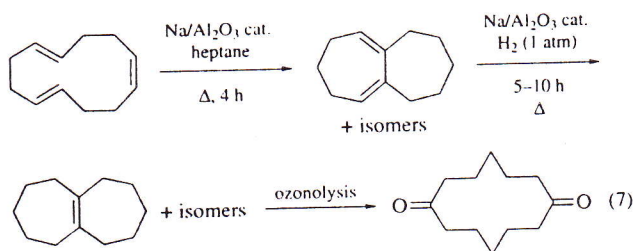
in the absence of external hydrogen.<sup>1</sup> Residual water or -OH groups on the alumina in combination with the adsorbed potassium may serve as the hydrogen source in this process. Under a hydrogen atmosphere (1 atm), however, this selective hydrogenation of conjugated dienes by  $M/Al_2O_3$  ( $M = Na, K$ ) is considerably accelerated, with no overreduction to the respective cycloalkane being observed.<sup>1</sup>

$K/Al_2O_3$  exhibits a distinct propensity to catalyze transannular reactions of unsaturated macrocyclic systems as well as skeletal rearrangements leading to ring contraction, as shown with (+)-longifolene as substrate.<sup>2</sup>

**Catalytic Cascades.** Six-membered rings bearing two alkene and/or cyclopropyl groups in the vicinity are smoothly aromatized when exposed to  $M/Al_2O_3$  ( $M = Na, K$ ) as catalyst by a sequence of double-bond isomerizations followed by dehydrogenation (eq 6).<sup>2,3</sup>

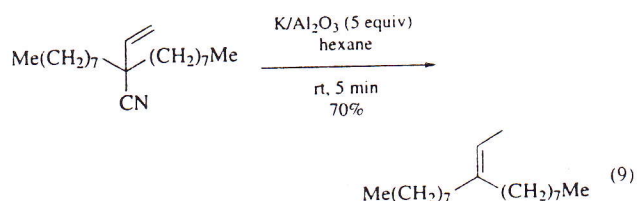
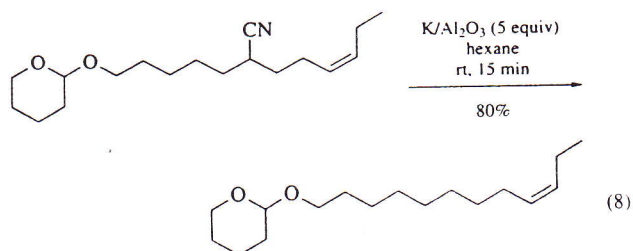


In a one-pot procedure (*Z,E,E*)-cyclododeca-1,5,9-triene as substrate runs through a cascade of catalytic processes induced by  $Na/Al_2O_3$ . This sequence comprises a transannular reaction, double bond isomerizations, and selective hydrogenation of the conjugated diene produced in the presence of hydrogen. Final ozonolysis of the crude reaction mixture afforded cyclododeca-1,7-dione in good yield (eq 7).<sup>4</sup>



**Organometallic Synthesis.**  $K/Al_2O_3$  has been used as base to metalate ketones, ethyl phenylacetate, alkyl nitriles, aldehyde-*N,N*-dimethylhydrazones, or *N*-cyclohexylketimines.<sup>5</sup> However, an excess of the reagent was necessary and the yields reported for alkylation of the intermediate potassium carbanions were moderate. In the case of alkyl nitriles as starting materials, the choice of solvent turned out to be decisive for the reaction path:

while deprotonation of these substrates predominates in THF, they are readily decyanated when treated with  $K/Al_2O_3$  in hexane as the reaction medium.<sup>6</sup> Residual -OH groups on the alumina may be the proton sources in this reductive C-C bond cleavage. While the reaction leaves acetal groups and disubstituted alkene moieties in the substrates unaffected (eq 8), terminal double bonds are rearranged to internal ones during the decyanation process (eq 9).<sup>6</sup> Recently,  $Na/Al_2O_3$  has been used as reducing agent for ketones, esters, and oximes.<sup>9</sup> It also serves as a catalyst for the Tischenko coupling of benzaldehyde to benzyl benzoate,<sup>10</sup> and may be employed for preparing activated zinc and titanium samples.<sup>11</sup>



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