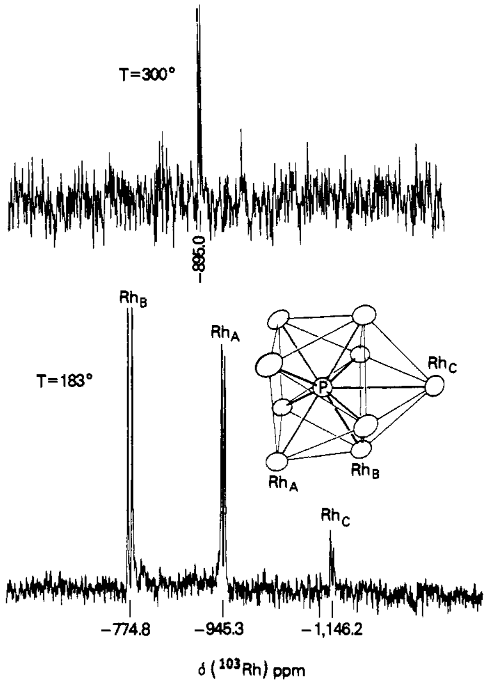

Figure 2. ^{103}Rh NMR spectra and metal atom skeletal structure of the $[Rh_9P(CO)_{21}]^{2-}$ anion.

provements now underway will hopefully make possible that research to complement earlier ^{31}P NMR work.[12]

Studies of the mechanism of exchange for the cluster anions $[Rh_7(CO)_{16}]^{3-}$, $[Rh_{12}(CO)_{30}]^{2-}$, and $[Rh_{12}(CO)_{34}]^{2-}$ are also in progress. The seven-rhodium cluster, at low temperatures, is observed to give the expected three-line pattern of intensity ratio 3:1:3 at chemical shifts near those measured by Heaton et al. using $^{13}C[^{103}Rh]$ double resonance methods.[6] However, preliminary results for the two 12-atom clusters each show only two separate spectral resonances, even at very low temperatures. Those results are not consistent[13-15] with structures proposed in the literature; so we have made the 12-atom clusters and their derivatives the focus of our current efforts.

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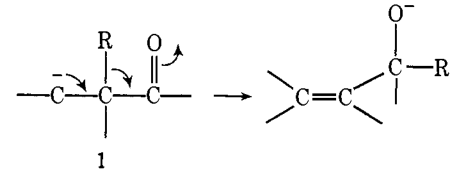
A Novel [1,2] Alkyl Shift in a Blocked Aromatic Anion

Sir:

Acid-catalyzed migrations of alkyl groups to electron-deficient centers are common reactions. In contrast, comparable base-catalyzed migrations are unknown, except for reactions such as benzilic acid rearrangements,[1] "acyloin rearrangements" of ketols,[2] "quasi-Favorskii" rearrangements of α-halo ketones,[3] and "semipinacolic" rearrangements of β-halo alcohols,[4] in which the migration origins are substituted with oxygen atoms.

In principle, migration of an alkyl group from a non-hetero-substituted carbon atom to a carbonyl carbon might occur in an anion such as **1** (eq 1). In practice, rearrangements of

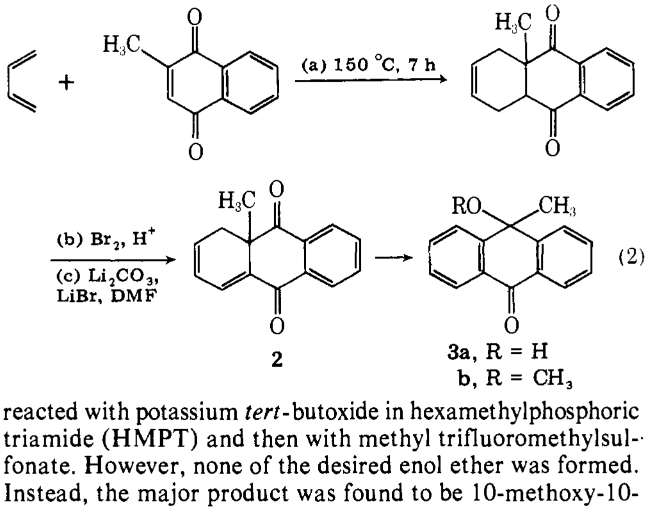


(1)

1

such homoenolate anions, when they occur, have always been observed to proceed by cyclopropanol formation and reopening, rather than by [1,2] alkyl migrations.[5] We have now observed that reaction of diketone **2** with base results in the first observed instance of base-catalyzed migration of an alkyl group from a non-hetero-substituted carbon to an adjacent carbonyl carbon.

Diketone **2** was prepared in 23% overall yield as shown in eq 2.[6] In an attempt to convert **2** into its enol ether,[7] **2** was



(2)

2

3a, R = H
b, R = CH_3

reacted with potassium *tert*-butoxide in hexamethylphosphoric triamide (HMPT) and then with methyl trifluoromethylsulfonate. However, none of the desired enol ether was formed. Instead, the major product was found to be 10-methoxy-10-methylanthrone (**3b**),[8] accompanied by smaller amounts of 10-hydroxy-10-methylanthrone (**3a**).[9] When **2** was reacted with potassium *tert*-butoxide in either HMPT or THF at −10 °C, the sole product obtained was **3a**, which could be converted into **3b** by reaction with methyl iodide in base.

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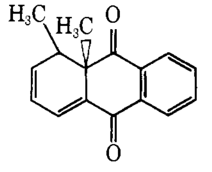
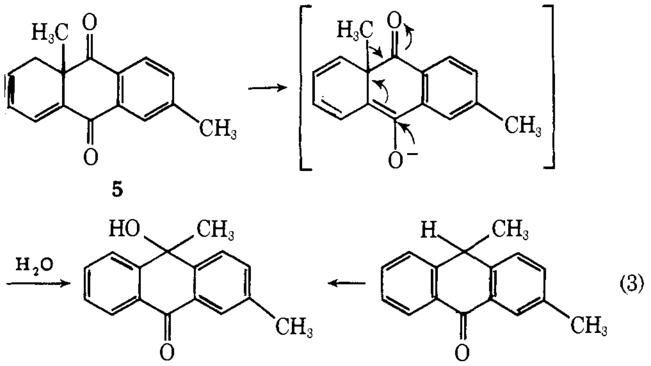
Formation of anthrone **3a** from reaction of **2** with base might proceed by either a [1,2] or a [1,3] shift of a methyl group to a carbonyl carbon.[10] To distinguish between these two mechanisms, it was necessary to carry out the rearrangement with a starting material which would yield a less symmetrical product. For this purpose diketone **4** was synthesized starting with a Diels-Alder reaction between 2-methyl-1,4-naphthoquinone and *trans*-piperylene. Surprisingly, however, no reaction was observed with **4** under conditions in which **2** was completely converted into **3a.** Use of stronger base or higher temperatures gave an inseparable mixture of products which did not appear to contain significant amounts of the desired analogue of **3a.**

Diketone **5** was therefore prepared in a manner similar to that used to synthesize **2**, starting with 2,6-dimethyl-1,4-naphthoquinone.[12] Rearrangement of **5**, catalyzed by potassium *tert*-butoxide in HMPT, yielded a single product, which was identified as **6** (eq 3). Hydroxyanthrone **6** was independently prepared by oxidation of anthrone **7**[13] with hydrogen peroxide in base.



4



5 **6** **7**

Thus, rearrangement of **5** (and undoubtedly of **2**) proceeds by a [1,2] shift of the methyl group.[14] The occurrence of this novel type of rearrangement is clearly due to the fact that a new aromatic ring is formed in the reaction. The anions of **2** and **5** can thus be considered to be novel members of the class of "blocked aromatic molecules", which can become aromatic by migration of a single ring substituent.[16]

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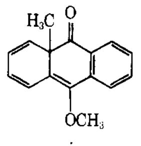

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Pyridine-Containing Polymers: New Matrices for Protein Immobilization

Sir:

Owing to the increased use of polymers in chemistry and biology, a considerable interest in immobilization of entities such as enzymes, cells and small ligands has developed.[1] Such preparations are used for practical applications such as purification of compounds by affinity chromatography[2] and for fundamental studies such as mechanisms of chemical[3] and enzymatic reactions.[1] The advantage of using immobilized species are numerous and include reuse, ease of separation from the reaction mixture and increased stability against heat, autolysis, and chemical effects.

The formation of a Schiff base between an aldehyde-containing matrix and free amino groups of proteins provides mild and simple reaction conditions for coupling. Polymeric aldehydes are usually prepared by reaction of an excess of glutaraldehyde with polymeric amines[4] or hydrazides[5] or by oxidation of polysaccharides with sodium periodate.[6] The excess of glutaraldehyde is used to block all the amino groups and to prevent cross-linking of the polymer.

The reaction of the nucleophilic pyridine nitrogen with strong electrophiles such as cyanogen bromide, fluorodinitrobenzene, and *p*-toluenesulfonyl chloride to yield glutaconic aldehyde is well known.[7] This reaction is the basis for a quantitative method for the determination of cyanides[8] and was recently used for determining the extent of activation of polysaccharides with cyanogen bromide.[9]

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