

**ADSORPTION EFFECTS ON THE EFFICIENCY OF COBALT-MEDIATED
CYCLIZATIONS OF ALLYLPROPARGYL ETHERS INTO DERIVATIVES OF
3-OXABICYCLO[3.3.0]OCT-5-EN-7-ONE**

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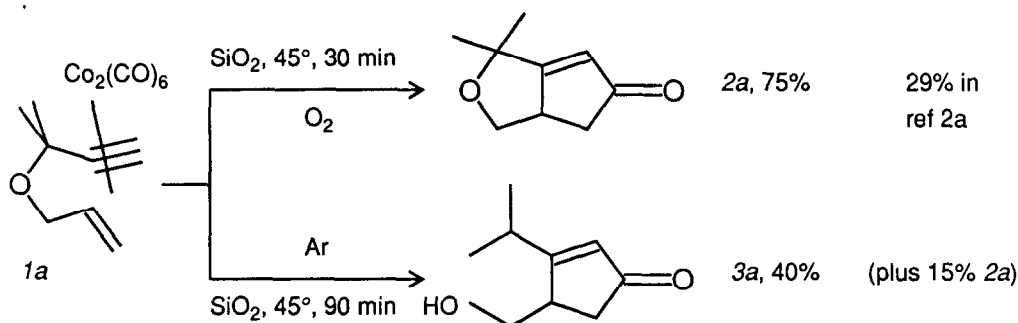
ABSTRACT. Thermolysis in an adsorbed state under oxygen is shown to be a mild and general method for promoting a Khand-Pauson cyclization of dicobalt hexacarbonyl complexes of allylpropargyl ethers into derivatives of 3-oxabicyclo[3.3.0]oct-5-en-7-one.

Cyclization of dicobalt hexacarbonyl (DCHC) complexes of substituted allylpropargyl ethers (1) into derivatives of 3-oxabicyclo[3.3.0]oct-5-en-7-one (2)¹ has been recently suggested as a new and prospective route for the synthesis of various cyclopentanoid compounds^{2a,b}. However under typical conditions, thermolysis in a hydrocarbon solvent, this reaction proceeds rather slowly and produces target compounds in low to moderate yields (11-41%)^{2a,b}.

In the preceding communication³ we have described an isolated example showing the rather unusual effect of adsorption on the efficiency of the Co-mediated conversion of an enyne substrate into the corresponding bicyclo[3.3.0]octenone. This accidental finding prompted us to start a more detailed investigation of the preparative potential of such *surface promoted* Khand-Pauson cyclizations and here we present the results of the studies on the adsorption effects for the transformation 1 → 2⁴.

Trial experiments have shown that adsorption causes a dramatic acceleration of this reaction. Thus, the complete conversion of 3-allyloxy-3-methylbutyne (1a) under conventional conditions^{2a} (thermolysis in

Scheme 1



isooctane at 60°C) is achieved only after prolonged heating (24h) and by this procedure 4,4-dimethyl-3-oxabicyclo[3.3.0]oct-5-en-7-one (2a) was prepared in only a 29% yield (see Scheme 1). At the same time the cyclization of 1a adsorbed on silicagel for tlc (LX 5/40 μ , Chemapol, CSSR) proceeded smoothly even at 45°C and was complete within 30 min⁵. Quite unexpectedly it turned out that the yield of the bicyclic product 2a depends on the presence of oxygen. Thus 2a could be obtained as the sole product (yield 75%)⁶ if the thermolysis of 1a on SiO₂ was carried out in an oxygen atmosphere. Under essentially the same conditions, but in an argon atmosphere, 1a was converted into the monocyclic product 3-isopropyl-4-hydroxymethylcyclopent-2-enone, (3a, yield 40%)^{6,7}.

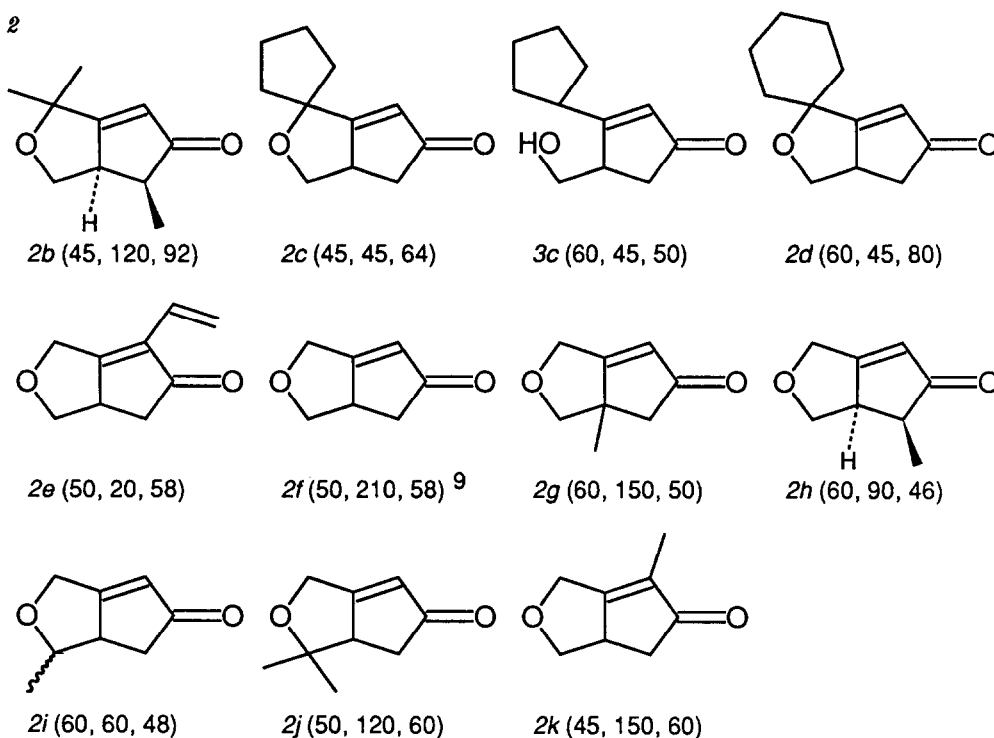
Typical experimental procedure: 1a (0.5g) in hexane (15ml) was mixed with SiO₂ (Silicagel LS 5/40 μ Chemapol, 15ml) and the solvent was removed on a rotovap at 20°C (30mm Hg). The system then was flushed with oxygen and the pink powder of the adsorbent with 1a was heated for 30 min. at 45°C in a rotating bulb under a slow stream of oxygen. Extraction of the SiO₂ with ether and subsequent removal of the solvent gave 0.17g of a yellow oil containing 2a as the major product. Chromatography on SiO₂ (Silpearl, CSSR) gave pure 2a (0.14g yield 75%), *R_f* 0.41 (ether-hexane 20:1). PMR (250 MHz, σ , TMS): 1.43(S,3H), 1.49(S,3H), 2.18 and 2.65 (AB part of ABX system, *J*=17.0, 6.1 and 3.5 cps, 2H), 3.68 and 4.30 (AB part of ABX system, *J*=11.5, 7.5 and 7.4 cps, 2H), 3.42 (m,1H), 5.81(d, *J*=2.5 cps, 2H); CMR 62.89 MHz, σ , TMS): 26.3(CH₃), 27.4(CH₃), 40.2(CH₂ CO), 45.1(CH), 70.4(CH₂ O), 96.3(-CO), 129.8 and 191.4(C=C), 208.9(C=O).

The same procedure was used to convert 1a into 3a, the only difference being the use of argon instead of oxygen. 3a (yield 40%), *R_f* 0.22 (ether-hexane 20:1). PMR (250 MHz, σ TMS): 1.19 and 1.21 (d,*J*=7 cps, 6H), 2.37 and 2.51 (AB part of ABX system, *J*=18.5, 6.5 and 2.5 cps), 3.77 and 3.88 (AB part of ABX system, *J*=11.0, 5.5 and 4.5 cps), 2.70(m, 1H), 3.17(m,1H), 6.0 (dd, *J*=5 and 1.2 cps, 1H). CMR (62.89 MHz, σ , TMS): 20.6 (CH₃), 21.5(CH₃), 29.7 (CH (CH₂)₃), 39.4 (CH₂ CO), 44.4 (CH), 63.1(CH₂ OH), 129.4 and 187.7 (C=C), 208.6(C=O).

In order to evaluate the scope of the elaborated procedure several representative substituted allylpropargyl ethers 1 have been prepared and their DCHC complexes were subjected to the treatment described for 1a. The structures of the resulting cyclic products 2b-k are shown in Scheme 2^{6,8}.

These results demonstrate the applicability of the procedure to an entire series of allylpropargyl ethers containing substituents in various positions in both the allyl and propargyl moieties. With the convenient conditions elaborated one may claim that the conversions of the type 1 \rightarrow 2 now can be recognized as a general and reliable preparative method for the synthesis of various cyclopentanoids from accessible

Scheme 2



precursors.

The observed influence of SiO_2 on the rate of the reaction merits special comments. Qualitative comparison of the efficiency of $1a \rightarrow 2a$ conversion (in an oxygen atmosphere) revealed that: (i) various silicagels produce comparable rate enhancement effects (Silpearl 0.2-0.4/ μ , CSSR; Kieselgel Woelm, 100-200 μ or <30 μ , BRD; Kieselgel G Stahl, 10-40 μ , BRD); (ii) alumina may also be used as an active support in this reaction, the effect being insensitive to the pH of the adsorbent (Aluminoxid Woelm, <30 μ , basic, pH 9; neutral, pH 7; acid, pH 4.5, BRD or Al_2O_3 , Reanal, pH 9-10, Hungary); (iii) silicagels containing about 30% water or dried up to 5% are rather inactive as media for the reaction and the optimum water content lies between 10-20%.

These data suggest that the observed rate enhancement of cyclization could not be ascribed to some specific acid or base properties of the SiO_2 or Al_2O_3 surface. A tentative explanation of this phenomena may be advanced if one considers the possible influence of the adsorption on the conformation of the precursor 1. It seems obvious that the adsorption of the latter on the SiO_2 (or Al_2O_3) surface is mainly governed by the interaction of the hydrophilic adsorbent centers with the ether center of 1. One may assume that this effect, together with the repulsive interaction of the surface with the hydrophobic ends of 1, would assist in the creation of the preferred coiled conformation of the substrate thus decreasing the entropy barrier for the formation of the cyclic transition state leading to 2 (or 3)¹⁰.

There is a plethora of data referring to reactions on adsorbents¹¹. However, the vast majority of studies in this field deal with some specific modifications in the nature of the reagents due to its immobilization on the surface. To the best of our knowledge little information is available on the alternative approach based on the use of adsorption as a factor controlling the conformation of the reacting substrate¹². The results of

this study suggest that the concept of adsorption promoted conformational changes seems to have promising ramifications for various entropy controlled reactions (e. g., intramolecular [2+4] and [2+2] cycloadditions, oxy-Cope or Claisen type rearrangements, etc.). One might also consider the use of this adsorption technique with chiral adsorbents as a tool to achieve asymmetric induction in these reactions.

LITERATURE AND NOTES

1. This cyclization follows the general pattern of Khand-Pauson reaction reviewed in P. L. Pauson, I. U. Khand, *Ann. N.Y. Acad. Sci.*, **295.2** (1977).
2. a) D. C. Billington, D. Willison, *Tetrahedron Lett.*, **25**, 4041 (1984); b) G. S. Mikaelian, W. A. Smit, *Izvestia Acad. Nauk. SSSR, ser. chim.*, 1984, 2562.
3. W. A. Smit, A. S. Gybin, A. S. Shashkov, U. T. Struchkov, L. G. Kuzmina, G. S. Mikaelian, R. Caple, E. P. Swanson, *Tetrahedron Lett.*, **1986**, 000.
4. For a preliminary communication, see: W. A. Schmidt, A. S. Gybin, S. O. Simonian, A. S. Shashkov, V. A. Tarasov, I. I. Ibragimov, *Izvestia Acad. Nauk SSSR*, **1985**, 2642.
5. The progress of the reaction was followed by the disappearance of the pink color of the starting Co-complex and is additionally monitored by tlc.
6. All yields refer to purified products. Homogeneity and structures were ascertained by spectral (MS, PMR 250 MHz) data and elemental analysis.
7. The rate of **1a** conversion seems to be insensitive to variations in the atmospheric composition (air, O₂, H₂, Ar, CO). Control experiments have shown that **2a** is not an intermediate product in the formation of **3a** (hydrogenolysis of **2a** does not occur even in the presence of hydrogen). The mechanism of **3a** formation is not clear. The structure of the product **3a** suggests the intermediate formation of some hydridocobalt complex (c.f. date in S. G. Davies *Organotransition Metal Chemistry: Application in Organic Synthesis*, 1982, Pergamon, N.Y., p. 367) and in fact tlc data clearly indicated that at the initial step of the process, **1a** is converted to some Co-containing compound.
8. In brackets are given: reaction temperature (°C) time (min) and yield (%): in all cases (except **3c**) the reaction was carried out under O₂.
9. This product was obtained earlier by thermolysis in solution in 14% yield^{2a}.
10. Similar effects also should be operative for other enyne sybstrates in the Khand-Pauson reaction containing polar groups in the middle part of the molecule and we are currently studying these possibilities.
11. For a review, see: G. H. Posner, *Agnew, Chem. Int. Ed.*, **1978**, 487; A. McKillop, D. W. Koung, *Synthesis*, **1979**, 401, 481.
12. See, for example: Fries rearrangement on SiO₂, D. Avnir, V. de Mayo, I. Ono, *J. Chem. Soc., Chem. Comm.*, **1978**, 1109; Diels-Alder reaction: on modified clays, P. Laszlo, J. Lucchetti, *Tetrahedron Lett.*, **25**, 1567, 2147, 4387 (1984) or on SiO₂, M. Hudlicky, *J. Org. Chem.*, **39**, 3460 (1974). Conceptually similar approach was used in studies on Diels-Alder reaction in water media (e.g., R. Breslow, U. Mait, *Tetrahedron Lett.*, **25**, 1239 (1984); P. A. Grieco, K. Yoshida, Zhen Min He, *ibid.*, **25**, 5715 (1984) or in microemulsions (e.g, Gonzales, S. L. Holt, *J. Org. Chem.*, **47**, 3186 (1982).

(Received in USA 6 November 1985)