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# 3-Nitro-5,6-dihydro-4H-pyran , a Latent -CHO Equivalent: A New Synthesis of Aldehydes[1]

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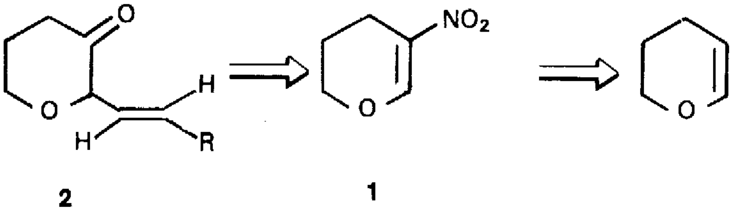
*Abstract:* 3-Nitro-5,6-dihydro-4H-pyran reacts with organoaluminum compounds and, after hydrolysis with 3 N HCl, gives aldehydes arising from a formal carbonylation of the alane.

The conjugate addition of organoalanes to $\alpha$-nitro olefins is a totally general reaction that allows the transfer of both saturated and 1-unsaturated alkyl chains to the $\beta$-carbon atom of the substrate;[2] it should be noted that the reaction produces the corresponding nitro- or carbonyl compounds, depending on the conditions of hydrolysis.[2b]

On this basis 3-nitro-5,6-dihydro-4H-pyran (**1**) appeared to be the most suitable precursor of (*E*)-2-(1'-alkenyl)-tetrahydropyran-3-ones (**2**) (Scheme 1), in turn useful intermediates in the synthesis of 3- or 4-alkylsubstituted (*E*)-2-(1'-alkenyl)-tetrahydropyrans; such compounds, at present, represent the main objective of our research.

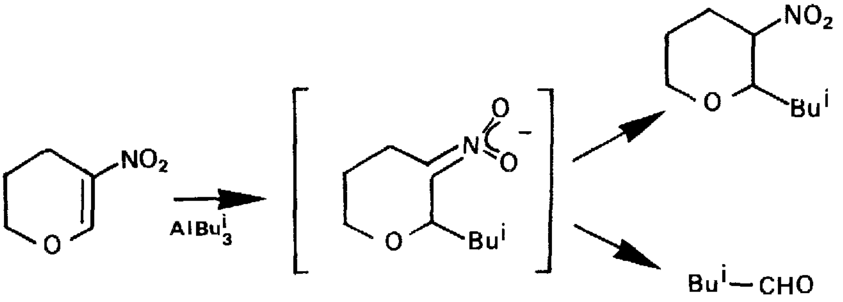
**Scheme 1**



The synthesis of **1**[3] was easily performed (85%) according to the procedure[4] described by Kogan for the preparation of 1-ethoxy-2-nitroethylene. The reaction of **1** with triisobutylaluminum was carried out as usual[2] and hydrolysis with 0.2 N HCl provided a good yield (70%) of 2-*i*.butyl-3-nitrotetrahydropyran[5] (**3**), as expected. In a further preparation, hydrolysis was carried out using 3N HCl in order to obtain, through the solvolytic Nef reaction,[2,6] the corresponding carbonyl compound.

Surprisingly, only a small amount (20%) of 2-*i*.butyltetrahydropyran-3-one[7] (4) was recovered and the main product (70%)[8] of the reaction was 3-methylbutanal (Scheme 2). Since the synthesis of aldehydes from alanes is a rather unusual process[9] and considering the fact that the reaction performed resulted in an indirect formylation of the aluminum compound, further experiments were carried out to establish the applicability of this new reaction.

**Scheme 2**



However, taking into account the self-immolative character of the reaction (only one chain of the alane is transferred)[8] and the high degree of selectivity showed by diisobutyl, 1-alkenylalanes[2a,c,d] in transferring the unsaturated chain to $\alpha$-nitroolefins, experiments were carried out using these unsaturated aluminum derivatives in order to establish whether the procedure constitutes a new approach to the synthesis of $\alpha,\beta$-unsaturated aldehydes.

The results obtained (see Table) clearly indicate that **1** is able, formally, to transfer a formyl group to the unsaturated chain of the aluminum derivative, independently of its structure, and to give the corresponding stereoisomerically (*E*) pure aldehydes (5), in satisfactory yields.

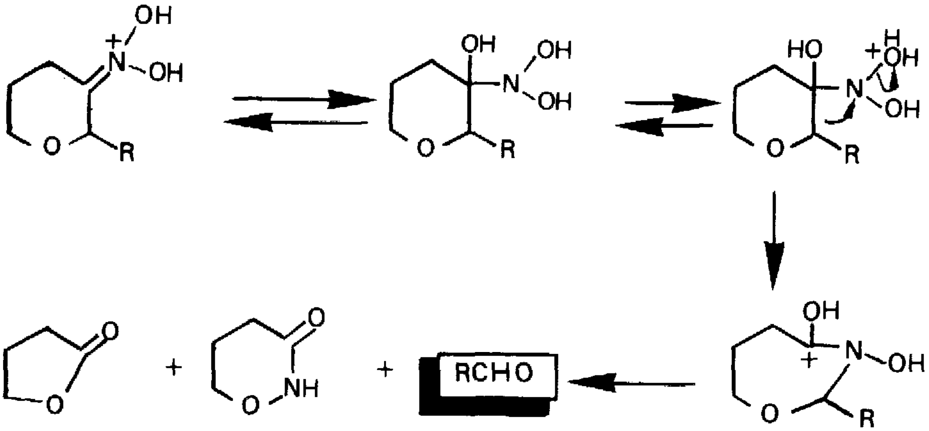
**Table**: Reaction of **1** with (E)-(*i*.Bu)$_2$ Al-CR=CHR'

| Run | R | R' | (E)-5% yield [a,b] |
|---|---|---|---|
| 1 | H | n.Bu | 71(52) |
| 2 | H | t.Bu | 80(58) |
| 3 | Et | Et | 67(43) |
| 4 | H | n.Hexyl | 90(70)[c] |
| 5 | n.Pr | n.Pr | 90(70)[c] |

*[a]Glc evaluation (<5% unknown products were rejected), the numbers in brackets are isolated yields of chemically pure products; [b]Spectral data (IR, NMR, Mass) confirmed the structure of the compounds recovered; [c]THF (200ml) was added to 3N HCl (see Experimental).*

At present no mechanistic study of the reaction has yet been carried out; however, in our opinion, the formation of aldehydes from aluminum nitronates probably occurs through an acid catalyzed rearrangement of the *aci*-nitro intermediates (Scheme 3) which has not yet been reported; the presence of butyrolactone[10] and 2H-tetrahydro-1,2-oxazin-3-one,[10] in the reaction mixture, supports this hypothesis. Further studies are in progress.

**Scheme 3**



*Typical procedure*

A hexane solution of DIBAH (20 mmol) was reacted with the suitable alkyne (20 mmol) according to reported procedures;[11] the solution was cooled at ca. -25°C and **1** (20 mmol), dissolved in $CH_2Cl_2$, was added dropwise. After 10 min., the cooling bath was removed and the reaction mixture was stirred at room temperature for a further 30 min and then poured into a flask containing a stirred cold (0°C) solution of 3N HCl (ca. 300 ml). After 20 min the pale yellow mixture was extracted into pentane. After drying and evaporating the solvent, an almost colorless liquid residue was recovered and it was purified by flash chromatography.

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**References and Notes**

1. Dedicated to Professor Luciano Lardicci of the University of Pisa, on the occasion of his 65th birthday.

2. a) A. Pecunioso, R. Menicagli, *Tetrahedron*, 1987, 43, 5411; b) Idem, *J. Org. Chem.*, 1988, 53, 46; c) Idem, *ibid*, **1988**, *53*, 2614; d) Idem, *ibid*, **1989**, *54*, 2391.

3. Compound **1** showed: m/e (I%), 129($M^+$, 25.0); $^1$H NMR ($CDCl_3$, 8.20 (s, 1H), 4.14 (t, 2H, J=5.3 Hz), 2.66 (dt, 2H, J=6.30, 0.50 Hz), 2.20-1.90 (m, 2H) $\delta$ ppm; $^{13}$C NMR ($CDCl_3$), 154.84, 112.40, 67.32, 20.06, 19.92 $\delta$ ppm; IR, 3089, 2953, 2892, 2861, 1723, 1641, 1554, 1495, 1469, 1390, 1341, 1271, 1230, 1186, 1124, 1079, 1048, 992, 860, 761 $\bar{\nu}$ cm$^{-1}$.

4. T. P. Kogan, F. C. A. Gaeta, *Synthesis*, **1988**, 706.

5. Compound **3** showed: m/e (I%), 141($M^+$ -46, 15);

6. M. Yamashaita, M. Nomoto, H. Imoto, *Synthesis*, 1987, 176 and ref. cited therein.

7. Compound **4** showed: m/e (I%), 113($M^+$ -43, 2.1); $^1$H NMR ($CDCl_3$), 4.07 (dtd, 1H, J=11.7, 4.6, 1.2 Hz), 3.86 (dd, 1H, J=8.8, 4.4), 3.73 (ddd, 1H, J=11.7, 9.2, 4.3 Hz), 2.70-2.35 (m, 2H), 2.30-2.00 (m, 2H), 1.90-1.75 (m, 1H) 1.59 (ddd, 2H, J=8.0, 5.8, 5.7 Hz), 0.94, 0.90 (2d, 6H, J=6.7, 6.7 Hz) $\delta$ ppm; $^{13}$C NMR ($CDCl_3$), 209.90, 81.69, 64.96, 37.97, 37.08, 25.78, 23.98, 23.10, 21.30 $\delta$ ppm; IR, 2957, 2870, 2723, 1724, 1642, 1547, 1499, 1468, 1448, 1433, 1422, 1386, 1369, 1341, 1309, 1278, 1252, 1230, 1194, 1170, 1100, 1049, 1024, 993, 860, 752 $\bar{\nu}$ cm$^{-1}$.

8. Glc evaluation (toluene internal standard); the yield is referred to the reacted **1**.

9. H. Yasuda, T. Araki, H. Tani, *J. Organomet. Chem.*, **1973**, *49*, 103.

10. Identified by $^1$H NMR and Mass spectral data.

11. a) J. J. Eisch, W. C. Kaska, *J. Am. Chem. Soc.*, **1966**, *88*, 2213; b) G. Wilke, H. Muller, *Justus Liebigs Ann. Chem.*, **1960**, *629*, 222.

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