Conference paper

J. Cristobal Lopez*, Fernando Lobo, Silvia Miranda, Clara Uriel and Ana M. Gomez

Ferrier–Nicholas pyranosidic cations: application to diversity-oriented synthesis

Abstract: Pyranosidic allylic (Ferrier) cations that share dicobalt hexacarbonyl propargyl (Nicholas) stabilization at *C*-1, can be easily generated by treatment of hexacarbonyldicobalt alkynyl glycals with $BF_3{\cdot}OEt_2$, and display a remarkable reactivity leading to a variety of products. The substituent at *O*-6 in these glycals plays a pivotal role in directing the outcome of the transformations. Accordingly, 6-*O*-benzyl or 6-*O*-allyl groups cause a series of transformations resulting in the stereoselective formation of oxepanes through a process that involves an initial hydride transfer step from the allyl or benzyl substituent to the Ferrier–Nicholas cation. On the contrary, 6-OH derivatives undergo an overall ring contraction to branched tetrahydrofuran derivatives. 6-*O*-Silyl derivatives, in the presence of heteroaryl nucleophiles, were transformed into *C*-3 branched bis-*C*-*C*-glycosides, containing two of such molecules.

Keywords: carbohydrates; diversity-oriented synthesis; Ferrrier reaction; glycosylation; ICS-27; Nicholas reaction; pyranosidic cations; stereocontrolled synthesis; tandem reactions.

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Introduction

In contrast to target-oriented synthesis (TOS) aimed at synthesizing discrete target molecules by way of retrosynthetic analysis [1], Schreiber introduced diversity-oriented synthesis (DOS) [2] aimed at accessing a collection of many compounds having structural diversity and complexity in order to populate chemical space broadly, and in search for new lead compounds [3]. A successful DOS algorithm must address four types of diversity: substitutional (appendage), functional group, stereochemical, and skeletal diversity [4]. In this context, carbohydrates because of their conformational rigidity and the stereo-defined display of their hydroxyl groups were early recognized as valuable substrates for the attainment of substitutional (appendage), stereochemical, and functional group diversity [5, 6]. Thus, after some seminal contributions by Smith, Nicolaou, Hirschmann and co-workers on D-glucose based peptidomimetics of somatostatin [7–9], reports appeared that focused on the use of pyranose cores for the incorporation of different functional groups. Sofia and co-workers reported the preparation of pyranose templates with three sites of diversification aiming to provide the minimal requirements needed for pharmacophoric molecular recognition [10]. In their design, they incorporated a carboxylic acid moiety, a free hydroxyl group, and a protected amino group (Fig. 1) [11].

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***Corresponding author: J. Cristobal Lopez,** Instituto de Quimica Orgánica General, CSIC, (IQOG-CSIC). Juan de la Cierva 3, 28006, Madrid, Spain, e-mail: jc.lopez@csic.es

Fernando Lobo, Silvia Miranda, Clara Uriel and Ana M. Gomez: Instituto de Quimica Orgánica General, CSIC, (IQOG-CSIC). Juan de la Cierva 3, 28006, Madrid, Spain

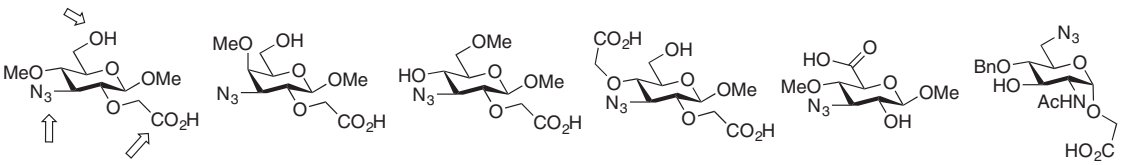


Fig. 1 Sofia's carbohydrate-based small-molecule scaffolds for a pharmacophore mapping library.

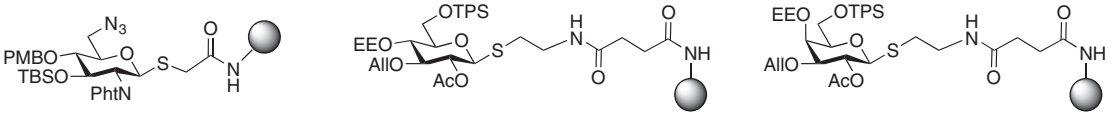
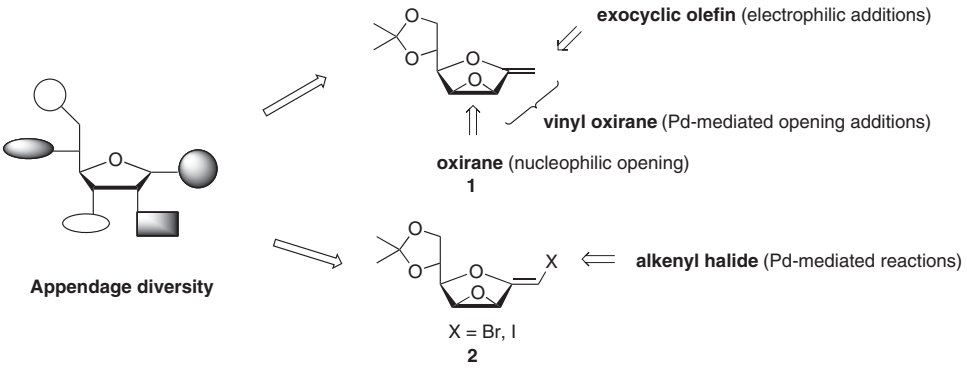


Fig. 2 Kunz's orthogonally protected carbohydrate scaffolds for combinatorial chemistry.



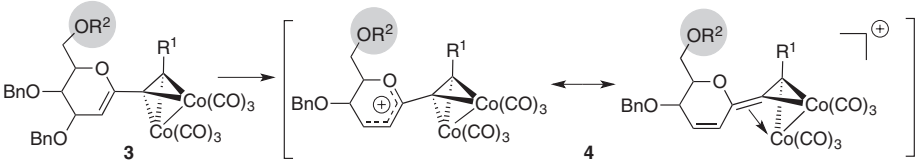
Scheme 1 Gomez, Lopez, and co-workers approach to appendage diversity in furanoses from epoxy exo-glycals.

Kunz and co-workers, on the other hand, developed some pyranose templates with orthogonal protecting groups that allowed selective deprotection at all-four positions of the carbohydrate regardless of the synthetic sequence [12, 13]; they also managed to prepare pyranosidic cores with five points of diversity with application in solid phase synthesis [14, 15] (Fig. 2).

In these strategies, the substitutional diversity had been achieved by modification of the carbohydrate hydroxy-groups. On the other hand, our research group focused in an approach to appendage diversity consisting on "decorating" the carbohydrate moiety with additional functionalities that could be exploited in synthetic transfomations aimed at the formation of C–C, C–N, and C–O bonds [16, 17]. In this context, we designed a furanose epoxy *exo*-glycal endowed with an exocyclic (enol-ether type) olefin and an oxirane moiety, i.e., **1** (Scheme 1). Such derivative was engaged in diverse types of reactions including electrophilic addition to the double bond, nucleophilic opening of the oxirane, and Pd-mediated reactions of the vinyl oxirane moiety. The additional presence of a halogen in the olefin, i.e., **2**, permitted us to engage these derivatives in Sonogashira [18, 19], Stille [20], and Suzuki cross-coupling reactions [21] leading to a variety of furanose-based templates [22].

Ferrier–Nicholas cations and skeletal diversity

More recently, we have drawn our attention to the more elusive task of developing an approach to skeletal diversity from glycal derivatives. Skeletal diversity [23] can be achieved mainly by two strategies: "reagent-based approach", which involves exposition of one common starting material to different reagents [24], or "substrate-based approach" where different starting materials, containing pre-encoded information [25], are subjected to a common set of reaction conditions resulting in different skeletal outcomes [26].



Scheme 2 Ferrier–Nicholas cation **4**, a combination of a Ferrier allylic cation and a hexacarbonyl dicobalt Nicholas cation.

Glycals, i.e., $\Delta^{1,2}$-unsaturated carbohydrate derivatives, have already shown its usefulness in DOS. For instance, Schreiber and co-workers reported the combination of Ferrier [27, 28] and Pauson–Khand [29, 30] reactions to gain access to a library of tricyclic compounds [31], whereas Porco and co-workers employed a glycal-derived scaffold to produce a collection of highly substituted tetrahydrofurans [32]. In line with our previous approach to appendage diversity based in polyfunctionalized carbohydrate derivatives, we have studied the behavior of, previously unknown, Ferrier–Nicholas cations, e.g., **4** [33]. These species were generated by $BF_3{\cdot}OEt_2$ treatment of differently-(*O*-6)-substituted dicobalt hexacarbonyl (*C*-1)-alkynyl glycals, i.e., **3**, (Scheme 2), the latter, in their turn, obtained by incorporation of the dicobalt hexacarbonyl group by treatment of the corresponding C-1 alkynyl glycals with $Co_2(CO)_8$.

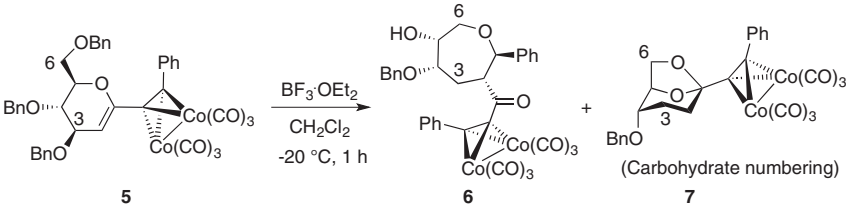
Results and discussion

6-*O*-Benzyl and 6-*O*-allyl derivatives

The reaction of 6-*O*-benzyl dicobalt hexacarbonyl derivative **5**, with $BF_3{\cdot}OEt_2$ in CH_2Cl_2 at –20 °C took place smoothly to give a mixture of oxepane **6** and 1,6-anhydro derivative **7**. The composition of this mixture proved to be highly dependent on the presence (or absence) of H_2O in the reaction media, as detailed in Table 1. Thus in the presence of H_2O, 1,6-anhydro derivative **7** became the major product of the reaction (entry *iv*, Table 1), whereas gradual exclusion of H_2O from the reaction mixture resulted in an increased yield of oxepane **6** (compare entries *i*, *ii*, and *iii*, Table 1).

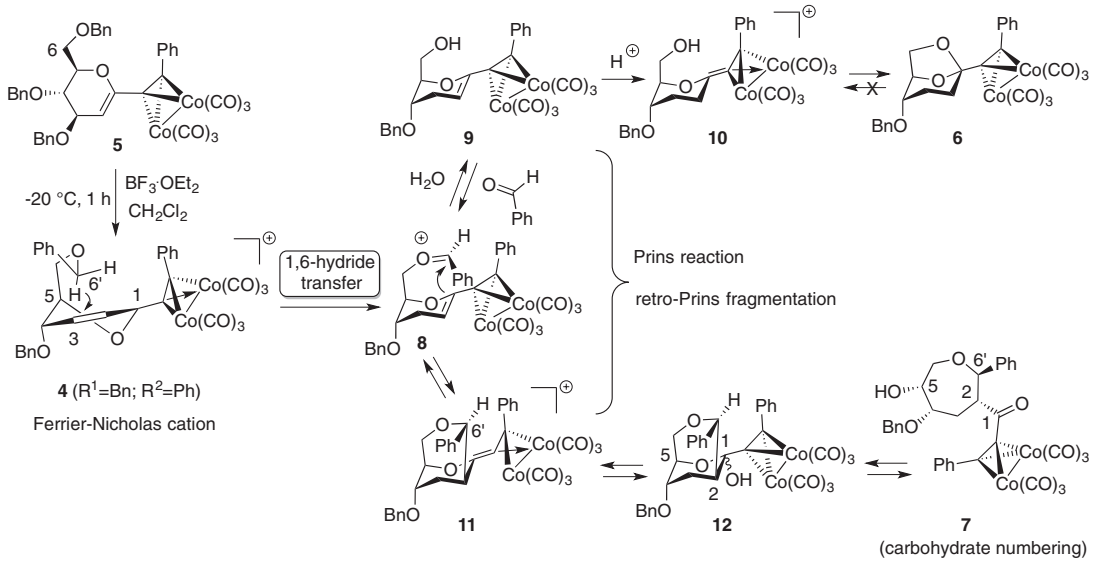
From these data we were able to postulate the reaction pathway outlined in Scheme 3. The transformation is initiated by a 1,6-hydride transfer from the 6-*O*-benzyl group to *C*-3 of cation **4** (R^1 = Bn, R^2 = Ph) [34, 35], which generates an oxocarbenium ion **8**. The latter might evolve by two different routes: i) hydrolysis and loss of benzaldehyde to give 6-hydroxy derivative **9**, which by protonation would generate a pyranosidic Nicholas-oxocarbenium ion **10** [36] whose cyclization will lead to 1,6-anhydro derivative **6**; ii) a Prins-type cyclization [37–39] leading to bicyclic Nicholas-oxocarbenium ion **11**, and thence hemiketal **12**, whose ring opening will lead to oxepane hydroxy-ketone **7**.

Table 1 Reaction of *C*-1 alkynyl glycal **5** in CH_2Cl_2 the presence of $BF_3{\cdot}OEt_2$ with variable H_2O content.



5 **6** **7**

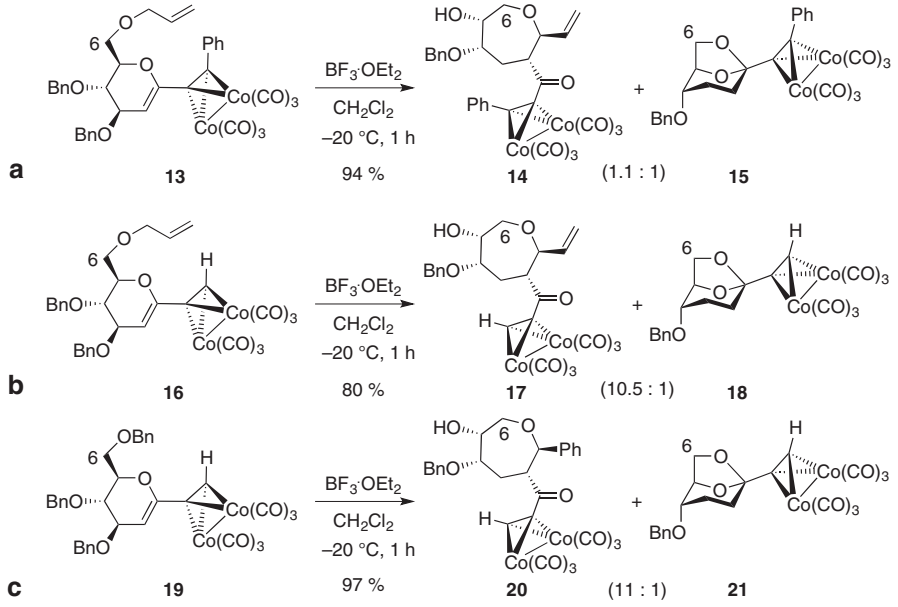
Entry	Reaction conditions	6 (%)	7 (%)
i	CH_2Cl_2	34	63
ii	CH_2Cl_2/4 Å MS (pellets)	45	34
iii	CH_2Cl_2/4 Å MS (powder)	61	23
iv	CH_2Cl_2/H_2O (2 equiv)	18	67



Scheme 3 Proposed reaction pathway leading to oxepane **7** and 1,6-anhydro derivative **6.**

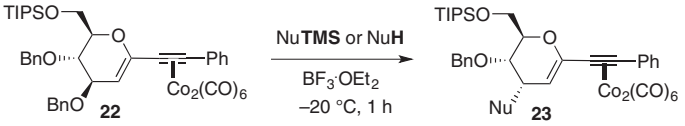
We have also shown that some of these transformations are reversible, e.g., oxepane **7** evolved to 1,6-anhydro derivative **6** upon treatment with $BF_3{\cdot}OEt_2$ (CH_2Cl_2, –20 °C, 8 h), thus implying reversibility in the steps **7** → **12** → **11** → **8**, the latter step being a retro-Prins fragmentation [40]. Likewise, treatment of 6-hydroxy derivative **9** with benzaldehyde in the presence of $BF_3{\cdot}OEt_2$ led to compounds **7** and **6**, then demonstrating the reversibility in the transformation **8** → **9**. Finally, we have observed that treatment of **6** with benzaldehyde in the presence of $BF_3{\cdot}OEt_2$ did not result in any transformation, leaving the 1,6-anhydro derivative unchanged [41].

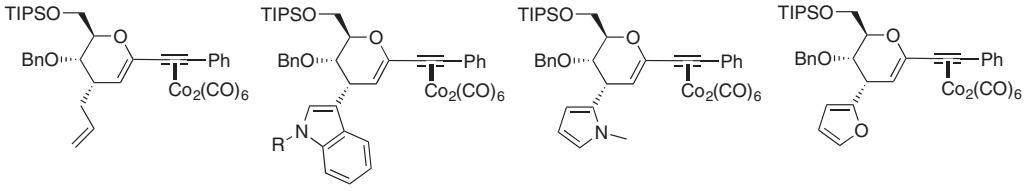
We have also found that vinyl oxepanes, e.g., **14**, **17**, can be obtained by reaction of related 6-*O*-allyl glycals, e.g., **13**, **16**, with $BF_3{\cdot}OEt_2$ (Schemes 4a,b) [41]. Thus implying that 1,6-hydride transfer from 6-*O*-allyl substituents is also possible. On the other hand, we have shown that oxepane formation can be optimized in



Scheme 4 Improving the oxepane yield and the ratio oxepane/1,6-anhydro derivative.

Table 2 Reaction of 6-*O*-triisopropylsilyl *C*-1 alkynyl glycal **22** in the presence of allyltrimethyl silane and some heteroaryl derivatives mediated by $BF_3{\cdot}OEt_2$ in CH_2Cl_2 at –20 °C.





23a (70 %) **23b, R = H** (65 %) **23c, R = CH_3** (59 %) **23d** (93 %) **23e** (57 %)

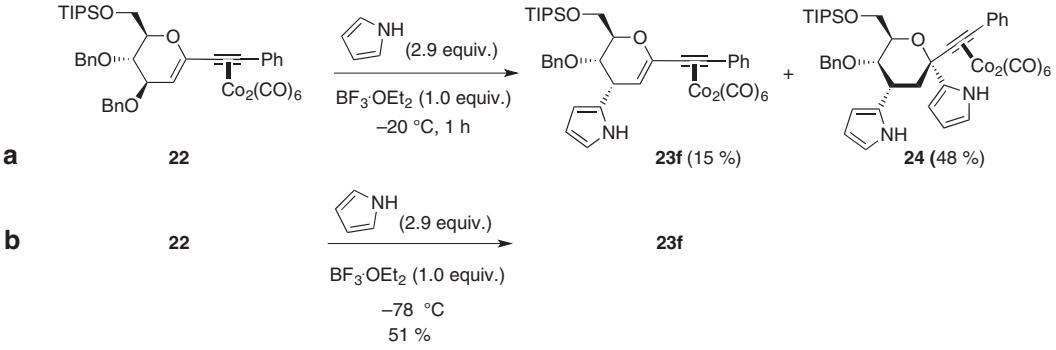
terms of yield and ratio oxepane/1,6-anhydro derivative by use of unsubstituted terminal alkynes (Schemes 4b,c, also compare Scheme 4a with Scheme 4b). We have ascribed this behavior to the higher electrophilicity of the Nicholas cation arising from the unsubstituted alkyne compared to the cation from the alkyne with the terminal phenyl substituent [42]. We believe that the higher electrophilicity of the corresponding intermediate Nicholas cation would render the ionization of hemiketal, leading back to the Nicholas cation, more difficult, e.g., **12** → **11** (Scheme 3).

6-*O*-Silyl derivatives

In line with these findings reaction of 6-*O*-triisopropylsilyl derivative **22** (where the above-mentioned 1,6-hydride transfer is not possible) with nucleophiles in the presence of $BF_3{\cdot}OEt_2$ provided regio- and stereocontrolled access to *C*-3 branched glycals **23a**–**e** (Table 2).

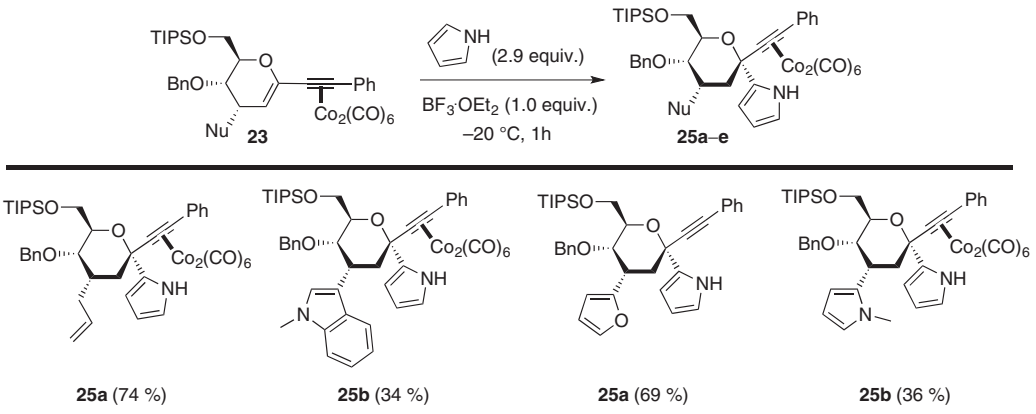
Analogous reaction of **22** with pyrrole in CH_2Cl_2 at –20 °C provided a mixture of *C*-3 branched glycal **23f** (15 %), and *C*-3 branched bis-*C*,*C*-glycoside **24** (48 %) [41]; where incorporation of two pyrrole molecules had taken place, thence indicating a higher reactivity of pyrrole compared to the rest of heteroaryl derivatives employed (Scheme 5a). On the other hand, exclusive access to **23f** (51 %) was accomplished when the reaction was performed at –78 °C (Scheme 5b).

Based on these discoveries, a sequential two-nucleophile incorporation leading to tri-substituted derivatives **25**, was developed by reaction of *C*-3 branched glycals **23** with pyrrole at –20 °C in the presence



Scheme 5 Reaction of hexacarbonyl dicobalt alkynyl glycal **22** with pyrrole at –20 and –78 °C.

Table 3 Reaction of *C*-3 branched glycals **23,** with pyrrole in the presence $BF_3{\cdot}OEt_2$ in CH_2Cl_2 at −20 °C.



of $BF_3{\cdot}OEt_2$ (Table 3). A variety of trisubstituted derivatives were obtained by this approach in modest to good yields.

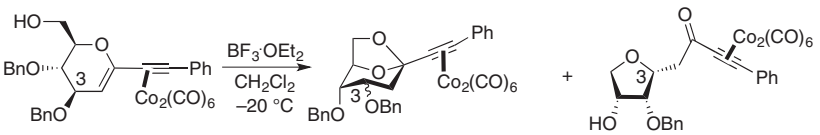
6-OH derivatives

Intramolecular trapping of hydroxyl groups by Nicholas cations has been extensively used to gain access to oxacycles of different sizes [43]. Accordingly, we treated hydroxy-derivative **26** with $BF_3{\cdot}OEt_2$ in the absence of an external nucleophile and observed the formation of three compounds: C-3 epimeric-1,6-anhydro, derivatives **27**, and ring contraction product **28**, whose relative ratios changed with the reaction time (Scheme 6). Prolonged reaction times favored formation of larger amounts of tetrahydrofuran **28** (45 min, 70 % yield compared to 15 min, 36 % yield) over **27**, whereas short reaction times led to a more uniform distribution of reaction products **27**, **28** (Scheme 6).

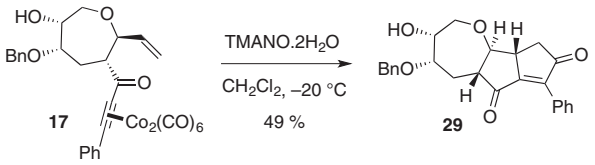
In addition, the formation of branched tetrahydrofuran **28** proved to be irreversible, since it remained unchanged upon treatment with $BF_3{\cdot}OEt_2$. However, bicyclic derivative **27-**α evolved, under related reaction conditions, to give a mixture of **27-**β, **27-**α and **28,** analogous to that obtained by reaction of glycal **26** [44].

Unmasking of alkynes from hexacarbonyl dicobalt derivatives

Even though there have been reports of cytotoxic activity associated to some hexacarbonyl dicobalt complexes [45, 46], the compounds described in this study have not yet been submitted to biological evaluation. However, decobaltation of these derivatives was straightforward and several methods were used to that end: tetrabutylamonnium fluoride (TBAF) in THF [47], trimethylamine *N*-oxide (TMANO) [48], and iodine/THF [49]. In our hands, TBAF/THF proved to work better for the decobaltation of these derivatives.



Scheme 6 Intramolecular Nicholas reaction of **26** leading to 1,6-anhydro derivatives **27** and branched tetrahydrofuran **28**, and variation in the final-products ratio with the reaction time.



Scheme 7 Pauson–Khand reaction of hexacarbonyl dicobalt derivative **17**.

Tandem Ferrier–Nicholas/Pauson–Khand: Access to tricyclic derivatives

Besides transformations based in decobaltation of hexacarbonyl dicobalt derivatives to alkynes or alkenes [50] these complexes have proven useful in a series of reactions in which the dicobalt complex played a key role, such as the Pauson–Khand cyclization [51]. In this context, vinyl oxepane **17** was a particularly well-suited intermediate to test this possibility. In fact, we found that upon treatment with TMANO·$2H_2O$ oxepane **17** was transformed, in a completely stereoselective manner, to tricyclic derivative **29** in 49 % yield (Scheme 7) [52].

Conclusion

Ferrier-Nicholas cations, a singular type of vinilogous Nicholas cations [53] that arise from dicobalt hexacarbonyl (*C*-1)-alkynyl glycals, can be used to generate skeletal diversity in a substrate-based approach to diversity-oriented synthesis (DOS). In transformations of 6-*O*-benzyl or 6-*O*-allyl glycal derivatives treatment with BF_3·OEt_2 induced a series of processes including: 1,6-hydride transfer, Prins cyclization, and retroketalization of the ensuing hemiketal, to give a polyfunctionalized oxepane in a completely stereocontrolled manner, in a ring-expansion process. In reactions of 6-*O*-TIPS derivatives the 1,6-hydride transfer is avoided and, in the presence of a nucleophile, a "normal" Ferrier rearrangement takes place to generate *C*-3 branched pyranose glycals. Furthermore, *C*-3 branched pyranose glycals reacted in the presence of pyrrole under the agency of BF_3·OEt_2 to give C-3 branched, bis-*C*-*C*-glycosides where the pyrrole moiety occupies the anomeric center with an exclusive α-orientation. Finally, from 6-OH derivatives a ring contraction process generating a branched tetrahydrofuran structure can be observed, the tetrahydrofuran being the thermodynamic product of an equilibrium that involves initial formation of functionalized 1,6-anhydro pyranoses. When a 6-*O*-allyl group is present in the ensuing dicobalt hexacarbonyl alkynyl oxepane, an intramolecular Pauson-Khand cyclization can take place by treatment with TMANO·$2H_2O$, leading to a single tricyclic derivative.

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