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# DIISOPROPOXY- AND DI-tert-BUTOXYETHYNE: SYNTHESIS AND REACTIVITY[1]

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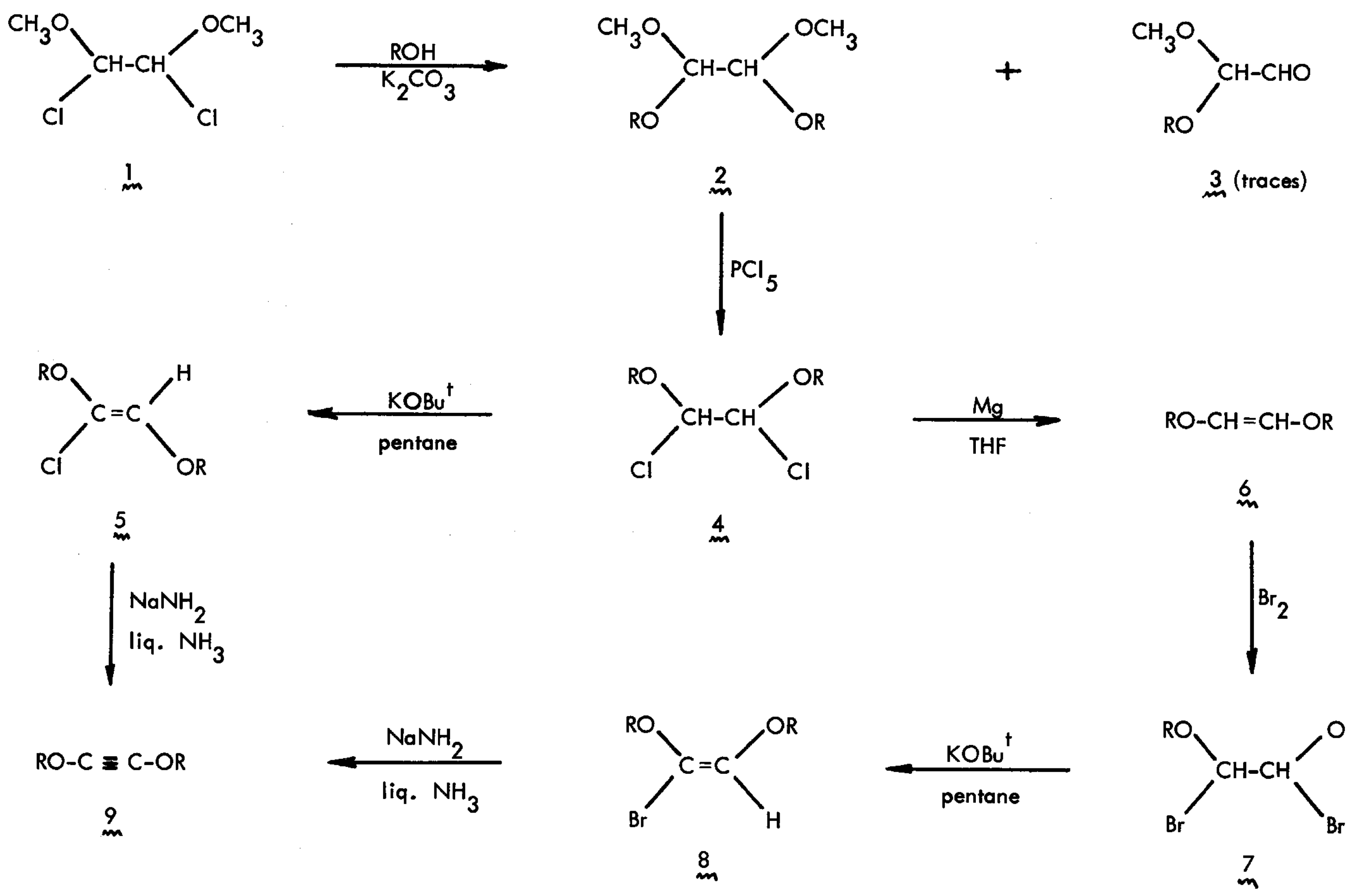
Acetylene diethers are highly unstable compounds that eluded synthesis for a number of years. Only in 1973, by the elimination method, we were able to generate dimethoxyethyne at very low temperature and to observe it by NMR spectroscopy at -40º. The compound was then isolated as the hexacarbonyldicobalt complex, m.p. 62-3º [2]. By the same procedure we have also prepared, more recently, the diethoxyethyne hexacarbonyldicobalt complex, m.p. 39-40º.

This method of synthesis -that involves, as the first step, the formation of the corresponding bis-chloroacetal of glyoxal- is, in principle, suitable for the preparation of <u>any acetylene diether derived from a primary alcohol</u>. However, in order to proceed to the synthesis of diisopropoxy- and di-*tert*-butoxyethyne a method for the preparation of bis-chloroacetals from secondary and tertiary alcohols was needed. The problem was solved in the following manner (Chart I).

A mixture of *meso*- and *d,l*-1,2-dichloro-1,2-dimethoxyethane[2] (**1**) was treated with isopropyl alcohol and dry potassium carbonate under stirring to give *meso*- and *d,l*-1,2-diisopropoxy-1,2-dimethoxyethane (**2**) in 73% yield. The reaction conditions are very critical and the mixture must be continously and efficiently stirred, otherwise the monoaldehyde **3** is formed in a substantial yield. Treatment of the mixed acetal **2** with $PCl_5$ gives a mixture of *meso*- and *d,l*-1,2-dichloro-1,2-diisopropoxyethane (**4**) in 93% yield, the more stable alkoxide anion ($CH_3O^-$) being selectively displaced by the chloride ion. Reaction of the bis-chloroacetal **4** with potassium *tert*-butoxide in pentane solution gives a mixture of *(E)- and (Z)-1-chloro-1,2-diisopropoxyethene* (**5**), *in 65% yield. Further dehydrochlorination with sodium* amide in liquid ammonia affords diisopropoxyethyne (**9**); however, since only the *Z* isomer is attacked, the acetylene diether is always contaminated with the *E* isomer, which cannot be eliminated by distillation. For this reason, we developed an alternative and more sophisticated sequence.

CHART I (R = isopropyl or *tert*-butyl)



1,2-Dichloro-1,2-diisopropoxyethane (**4**) was dechlorinated by magnesium in THF to yield a mixture of (*E*)- and (*Z*)-1,2-diisopropoxyethene (**6**), in 80% yield. Bromination and dehydrobromination lead to (*E*)-1-bromo-1,2-diisopropoxyethene (**8**) (80% yield from 6), which reacts with excess of sodium amide in liquid ammonia to give diisopropoxyethyne (**9**) (75% yield). The product could be distilled at low temperature and high vacuum as a low melting point solid (25-30% yield). Diisopropoxyethyne is only moderately stable and it can be handled at room temperature only for a few minutes.

By the same procedure, and using *tert*-butyl alcohol instead of isopropyl alcohol, di-*tert*-butoxyethyne has been also synthesized[4], in 92% yield (72% after distillation), as a colorless solid m.p. 8.5º. The compound is a fairly stable acetylene diether and it can be handled at room temperature for hours, and even for some days.

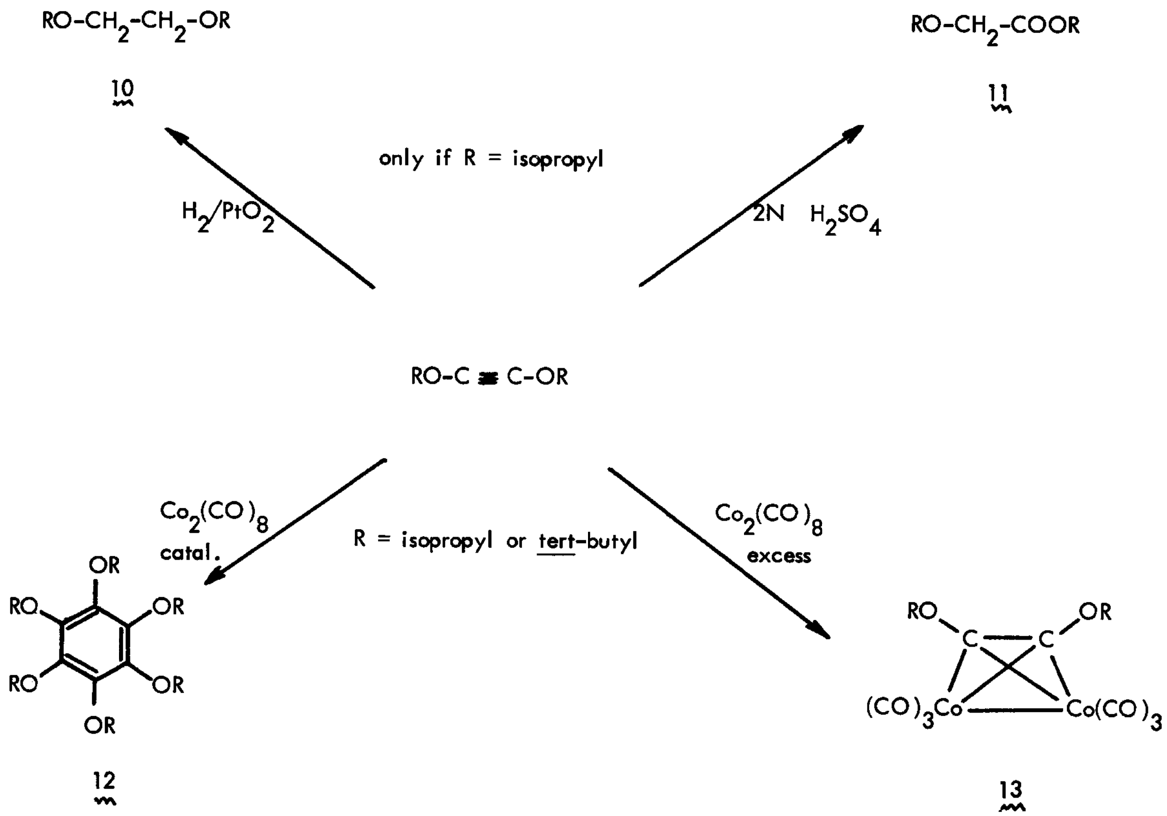
As shown in Chart II, the triple bond of diisopropoxyethyne is both hydrogenated and hydrated, under acid-catalysis, to give 1,2-diisopropoxyethane (**10**) and isopropyl isopropoxyacetate (**11**), respectively; on the other hand, whereas catalytic amounts of $Co_2(CO)_8$ induces trimerization to hexaisopropoxybenzene (**12**) (41.5%; m.p. 136-7º), excess of the reagent leads to the hexacarbonyldicobalt complex **13** (5% yield; m.p. 61º).

By contrast, the triple bond of di-*tert*-butoxyethyne is neither hydrogenated nor hydrated under the same conditions that diisopropoxyethyne is, and trimerization to hexa-*tert*-butoxybenzene (m.p. 223-4%) takes place only in low yields (5%). However, the corresponding hexacarbonyldicobalt complex (m.p. 58-9º) could be isolated in 35% yield. Some synthetic applications of di-*tert*-butoxyethyne are described in the following communication.

## References and Notes

1. Taken, in part, from a communication presented at the Second International Symposium on Acetylenes, Allenes and Cumulenes, held in Nottingham, 5-8 September 1977, by The Chemical Society (London).
2. A. Messeguer, F. Serratosa and J. Rivera, *Tetrahedron Letters*, 1973, 2895.
3. All compounds gave satisfactory analysis, except the rather unstable diisopropoxyethyne.
4. The stereochemistry of the intermediates is, however, slightly different from that of the corresponding isopropoxy derivatives.

CHART II


RO-CH$_2$-CH$_2$-OR
10
RO-CH$_2$-COOR
11
only if R = isopropyl
H$_2$/PtO$_2$
2N H$_2$SO$_4$
RO-C ≡ C-OR
Co$_2$(CO)$_8$
catal.
R = isopropyl or tert-butyl
Co$_2$(CO)$_8$
excess
OR
RO
OR
RO
OR
OR
12
RO
OR
C
C
(CO)$_3$Co
Co(CO)$_3$
13