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DIISOPROPOXY- AND DI-tert-BUTOXYETHYNE

STABLE ACETYLENE DIETHERS

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Abstract—The rather stable acetylene diethers diisopropoxy- and di-t-butoxyethyne are prepared either from glyoxal or dioxane. Catalytic hydrogenation, acid-catalyzed hydration and formation of the corresponding hexacarbonyl dicobalt complexes are reported.

The present paper gives full details of our work on the synthesis of stable acetylene diethers.[1] For a number of years, acetylene diethers eluded all synthetic approaches and none was known at the time we started our work on the field.[2] Although the formation of dimethoxy- and diethoxyethyne as highly reactive and unstable intermediates had been already postulated,[2,3] neigher direct observation nor compelling evidence was presented.

Several years ago, we resolved to attack the problem of the synthesis of acetylene diethers by using three different approaches: (i) the extrusion method; (ii) the alkylation and silylation of potassium acetylenediolate, and (iii) the β-elimination reactions. The results, and the failure, of the two first methods have been already reported elsewhere.[4,5]

On the other hand, we have also given some details about the synthesis of dimethoxyethyne (1, R = Me) using the elimination method. Working at low temperature we were able to generate dimethoxyethyne and to observe, for the first time, its NMR spectrum at −40°. The compound was then isolated as a stable hexacarbonyl dicobalt complex, m.p. 62–3°.[6] The method implies the preparation of a mixture of *rac* and *meso* bis-chloroacetals of glyoxal (2, R = Me), elimination of hydrogen chloride either by potassium hydroxide or potassium t-butoxide, fractional distillation of the resulting *Z* and *E* olefins (5, R = Me), and further dehydrochlorination of the *Z* isomer by $NaNH_2$ in liq ammonia.[a]

By the same method we have also prepared diethoxyethyne[7]—which is a very unstable compound too, and was isolated as the corresponding hexacarbonyl dicobalt complex, m.p. 39–40°—and, in principle, *the method is suitable for the preparation of any acetylene diether derived from a primary alcohol.* However, our next goal was the synthesis of diisopropoxy- and di-t-butoxyethyne which should be much more stable than the linear homologs, and for that we had to develop a method for the preparation of bis-chloroacetals of glyoxal from secondary and tertiary alcohols, which cannot be obtained directly from glyoxal.

General strategies

Glyoxal bis-acetals from sec and t-alcohols. As summarized in Chart 1, our first solution to the problem starts from 1,2-dichloro-1,2-dimethoxyethane (2, R = Me) and involves an "alkoxy–alkoxy interchange", a synthetic operation that proceeds in two steps; first, a "halogen–alkoxy interchange" (path 2), followed by an "alkoxy–halogen interchange" (path 3).

A 50:50 mixture of *rac* and *meso*-1,2-dichloro-1,2-dimethoxyethane (2, R = Me), in CH_2Cl_2 solution, was treated with isopropyl alcohol and dry potassium carbonate under stirring. The reaction conditions are very critical and the mixture must be continuously and efficiently stirred, otherwise isopropoxymethoxyacetaldehyde is formed in a substantial yield.[b] However, working under the proper conditions 1,2-diisopropoxy-1,2-dimethoxyethane (3, R = Me, R′ = Pr^i) was isolated in 73% yield as a 50:50 mixture of *rac* and *meso* isomers.

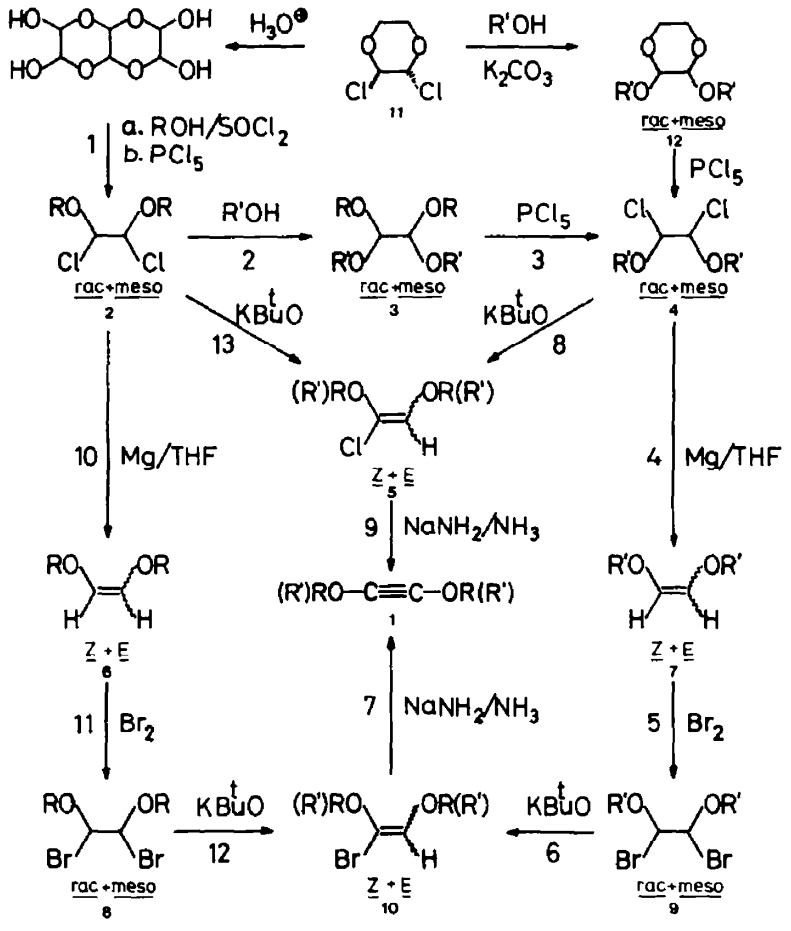
Treatment of the mixed bis-acetal with PCl_5 gives 93% yield of a 35:65 mixture of *rac* and *meso*-1,2-dichloro-1,2-diisopropoxyethane (4, R′ = Pr^i). Notice that this is a case of 100% chemoselectivity, the leaving groups being the primary alkoxy groups (more stable anions), as had been already observed by Fiesselmann and Hörndler,[8] many years ago, in the reaction of 1,2-dicyclohexyloxy-1,2-dimethoxyethane (3, R = Me, R′ = cyclo-C_6H_{11}) with PCl_5.

In a similar way, the reaction of a 75:25 mixture of *rac* and *meso*-1,2-dichloro-1,2-dimethoxyethane with t-butyl alcohol affords, in 77% yield, a 65:35 mixture of *rac* amd *meso* - 1,2 - di - t - butoxy - 1,2 - dimethoxyethane (3, R = Me, R′ = Bu^t) which, in turn, reacts with PCl_5 to give, in 97% yield, only one dichloro derivative (4, R′ = Bu^t) to which we assigned, on the bases of NMR spectroscopy and the reactivity of the corresponding olefin (see below), the *meso* configuration.

A second solution to the problem come out when we realized that 2,3 - dichloro - 1,4 - dioxane(11)—one of the industrial precursors of glyoxal[9]—is structurally related to 1,2 - dialkoxy - 1,2 - dichloroethanes (2). In fact, we have found that *trans* - 2,3 - dichloro - 1,4 - dioxane[10] reacts with both, isopropyl and t-butyl alcohol under reflux, in the presence of dry K_2CO_3, to give a mixture of *cis* and *trans* - 2,3 - di(sec- or t-)alkoxy - 1,4 - dioxane (12, R′ = Pr^i or Bu^t) (Table 1) (corresponding, respectively, to the *meso* and *rac* forms).

[a] Under the employed conditions, dehydrochlorination of the chloroolefins 5 was a stereo-specific reaction and only the (*Z*)-isomer was attacked, the (*E*)-isomer being almost quantitatively recovered unchanged.

[b] Isopropoxymethoxy and t-butoxymethoxyacetaldehyde, formed by partial hydrolysis of bis-acetals, are interesting synthons. For example, they react with dimethyl methoxycarbonylmethyl phosphonate, according to a Wittig–Horner reaction, to give the corresponding unsaturated esters.



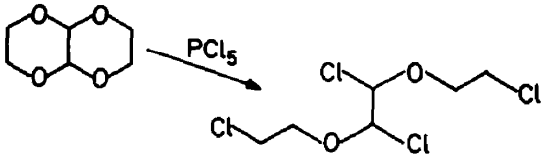
R = primary alkyl group R' = sec or tert alkyl group

path n°	synthetic operation
2	halogen-alkoxy interchange
3	alkoxy-halogen interchange
2 + 3	alkoxy-alkoxy interchange
4 + 5 10 + 11	halogen-halogen interchange

Chart 1.

The reaction of 2,3-di(sec- or t-)alkoxy-1,4-dioxanes with PCl_5 was an unexplored field.[c]

[c]The claim[11] that 1,4,5,8-tetraoxadecalin reacts with PCl_5 to give 1,2 - dichloro - 1,2 - (2 - chloroethoxy)ethane, is not relevant,



since NMR studies have recently shown that the starting product is, in fact, the bis-dioxolane of glyoxal.[12]

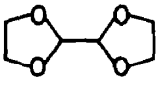


Table 1.

12, R'	%	cis:trans
Pr^i	91	60:40
Bu^t	85	25:75

We found that the reaction of *cis* and *trans* - 2,3 - di(sec- or t-)alkoxy - 1,4 - dioxanes (12) with PCl_5, in CH_2Cl_2 solution, may occur according to two different pathways, either (i) by a double intermolecular attack to give $POCl_3$, 1,2 - dichloroethane and a mixture of *rac* and/or *meso* - 1,2 - di(sec- or t-)alkoxy - 1,2 - dichloroethane (4, R' = Pr^i or Bu^t), or (ii) by an intermolecular attack followed by an intramolecular one to afford the bis-chloroacetals 4 and 2-chloroethyl di-

chlorophosphate (**14**). In both cases, however, the *primary* alkoxy groups are selectively displaced by the chloride ion, as observed in the reaction of PCl_5 with the acyclic mixed acetals **3** (Chart 2). 2-Chloroethyl dichlorophosphate (**14**) is probably formed via 2,2,2 - trichloro - 1,3,2 - dioxaphosphole (**13**).[13]

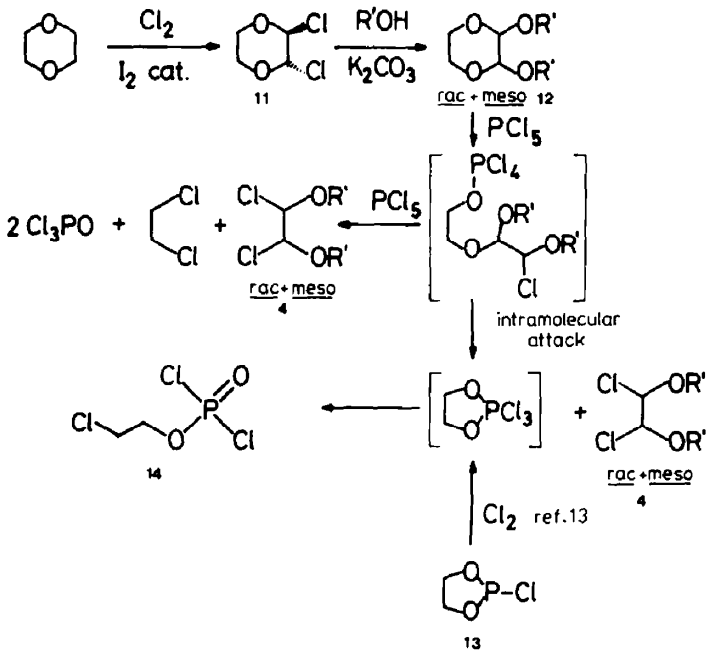


Chart 2.

NMR spectroscopic analyses of the crude reaction mixtures allowed to conclude that, with the diisopropoxy derivative (**12**, $R' = Pr^i$), the intramolecular attack accounts for nearly 75% of the observed reaction. The resulting mixture of *rac* and *meso* - 1,2 - dichloro - 1,2 - diisopropoxyethane (**4**, $R' = Pr^i$) could be separated from the reaction mixture by fractional distillation, in 88% yield.

On the other hand, the cleavage of 2,3 - di - t - butoxy - 1,4 - dioxane (**12**, $R' = Bu^t$) by PCl_5 occurs exclusively by the intramolecular attack and affords a mixture of *meso* - 1,2 - di - t - butoxy - 1,2 - dichloroethane (**4**, $R' = Bu^t$) (only one isomer!) and 2-chloroethyl dichlorophosphate (**14**), which resulted rather difficult to separate. In order to destroy dichlorophosphate **14**, the crude reaction mixture was dissolved in pentane, cooled at 0°, and treated with powdered NaOH for 24 hr. After filtration and evaporation of the solvent *in vacuo*, crude *meso* - 1,2 - di - t - butoxy - 1,2 - dichloroethane, contaminated with some dichlorophosphate, was obtained in 80% yield. Although the crude product was suitable for the next operation, more recently we have developed an alternative procedure in which 2,2 - dihydro - 2,2,2 - trichloro - 1,3,2 - benzodioxaphosphole (**15**)[14] is substituted for PCl_5. The crude reaction mixture is then treated with several portions of hexane, the chlorophosphate **16** remaining almost insoluble, as the residue. The hexane solution of *meso* - 1,2 - di - t - butoxy - 1,2 - dichloroethane, eventually contaminated with traces of phosphate **16** is suitable for the next steps (Experimental).

Diisopropoxyethyne via chloroolefin **5** ($R' = Pr^i$). The mixture of *rac* and *meso* - 1,2 - dichloro - 1,2 - diisopropoxyethane (**4**, $R' = Pr^i$), when treated with $KOBu^t$ in pentane solution at 0°, affords the corresponding chloroolefin **5** ($R' = Pr^i$), the ratio of *Z*:*E* isomers (33:66) being independent of the original ratio of *rac* and *meso* derivatives.[4]

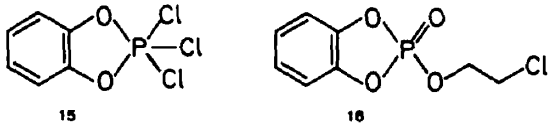


Fig. 1.

Dehydrochlorination of the mixture of (*Z*) and (*E*) - 1 - chloro - 1,2 - diisopropoxyethene (**5**, $R' = Pr^i$) by $NaNH_2$ in liq NH_3 led to diisopropoxyethyne (**1**, $R' = Pr^i$), characterized by the presence of a new isopropyl system in the NMR spectrum of the crude reaction mixture. However, even in the presence of a large excess of $NaNH_2$, only the *Z* isomer was attacked, and the acetylene diether was always contaminated with the *E* isomer, which cannot be eliminated by distillation or chromatographic methods.

On the other hand, the larger the excess of $NaNH_2$ and the larger the reaction time, the poorer the recovery of organic material and the lower the yields of diisopropoxyethyne, indicating that a competitive nucleophilic attack of the base to the triple bond of the resulting acetylene takes place.

For these reasons, we developed an alternative and more sophisticated sequence based on the fact that the corresponding bromoolefins (**10**) do not show such a

[4] The assignments of NMR signals to (*Z*) and (*E*) olefins could be done by analogy with the methoxy series and by stereospecific attack of the (*Z*) isomer by $NaNH_2$ in liq NH_3 (see text, below).

degree of stereospecificity. This strategy, that involves a "halogen–halogen interchange", is summarized in Chart 1, path 4 + 5 (and 10 + 11).

Diisopropoxyethyne via bromoolefin **10** (R' = Pr^i). A mixture of *rac* and *meso* - 1,2 - dichloro - 1,2 - diisopropoxyethane (**4**, R' = Pr^i) was dechlorinated by magnesium in THF[15] to give a mixture of (*Z*) and (*E*) - 1,2 - diisopropoxyethene (**6**, R' = Pr^i), in 82% yield. Bromination and dehydrobromination with KOBu^t gives only one isomer to which we assigned the *E* configuration (**10**, R' = Pr^i) on the basis of the chemical shift of the olefinic proton (δ 5.71). However, the product undergoes thermal isomerization, and after distillation[e] and standing at room temperature for 72 hr a mixture of (*E*) and (*Z*)-isomers was obtained (*Z* isomer, δ 6.16), in which the latter is the predominant one (*Z*:*E* = 57:43). The isomerization is, however, inhibited at −13°. Photochemical isomerization was also observed when a pentane solution was irradiated at 254 nm for 3 hr, a 1:1 mixture of isomers being formed.

Dehydrobromination of bromoolefin **10** (R' = Pr^i) depends mainly on the proportion of $NaNH_2$ used, rather than the isomeric composition of the starting material. However, even with the bromoderivatives some degree of stereoselectivity was observed. Thus, using 200% excess of $NaNH_2$, mixtures in which the (*Z*)-isomer accounted, at least, for 50% of the mixture, were completely dehydrobrominated in 30 min, diisopropoxyethyne being obtained in good yields (82–87%). But larger reaction times (up to 50 min) were necessary to accomplish the reaction either with mixtures in which the (*E*)-isomer was the predominant one (*Z*:*E* = 15:85) or with pure (*E*)-isomer, the yields of diisopropoxyethyne being slightly lower (70–72%).

Diisopropoxyethyne was, in fact, the first acetylene diether obtained so far as a pure compound. The product may be handled at room temperature for a few min, mainly as a pentane solution. Although its stability allowed a first approximation to the chemistry of acetylene diethers (see below), it was not stable enough to fulfil our expectations and the synthesis of di-t-butoxyethyne from the corresponding dichloro derivative was undertaken.

Di-t-butoxyethyne (**1**, R' = Bu^t). Since only one isomer—to which we assigned the *meso* configuration on the bases of NMR spectroscopy—was obtained for 1,2 - di - t - butoxy - 1,2 - dichloroethane (**4**, R' = Bu^t), either from glyoxal or 2,3 - dichloro - 1,4 - dioxane (see above), dehydrochlorination with KOBu^t leads to an isomerically pure (*E*) - 1,2 - di - t - butoxy - 1 - chloroethene (**5**, R' = Bu^t), the (*E*)-configuration being supported by its rather slow reaction with $NaNH_2$ in liq NH_3. Again, we had to resort to the alternative route via bromoderivatives, an "halogen–halogen interchange" synthetic operation (path 4 + 5) being performed.

meso - 1,2 - Di - t - butoxy - 1,2 - dichloroethane (**4**, R' = Bu^t) was dechlorinated by Mg in THF solution, to give a 47:53 mixture of (*Z*)- and (*E*) - 1,2 - di - t - butoxyethene (**7**, R' = Bu^t). Bromination of this olefin afforded a 44:56 mixture of *rac* and *meso* - 1,2 - dibromo - 1,2 - di - t - butoxyethane (**9**, R' = Bu^t)[f] which was immediately dehydrobrominated with KOBu^t to give an isomerically pure 1 - bromo - 1,2 - di - t - butoxyethene (**10**, R' = Bu^t), to which the *E* configuration was assigned (δ 5.96). In contrast to other bromoolefins **10** with smaller substituents, (*E*) - 1 - bromo - 1,2 - di - t - butoxyethene neither isomerizes nor oxidizes in the presence of atmospheric oxygen.[16] Dehydrobromination with 5-fold excess of $NaNH_2$, in liq NH_3, and a reaction time of 10 min, afforded di - t - butoxyethyne (**1**, R' = Bu^t) in 92% yield, which was spectroscopically identical with the analytical sample prepared as a crystalline solid, m.p. 8.5°, after evaporative distillation at 34–5°/0.3 Torr. Di - t - butoxyethyne is stable at room temperature for some hours and remains unchanged for months when stored as a solid at −13°.

Later on, owing to the stability of di-t-butoxyethyne, and in contrast with all the other acetylene diethers, we found that it can be prepared directly from (*E*) - 1,2 - di - t - butoxy - 1 - chloroethene (**5**, R' = Bu^t) by using 5-fold excess of $NaNH_2$ and a very large reaction time (90 min). Although the yields are lower (50–60%) and the product must be distilled from the reaction mixture, presently it is the method of choice for the preparation of di-t-butoxyethyne in large scale. The whole sequence, starting from dioxane, involves five steps, the overall yield being about 20%.

Reactivity of acetylene diethers

Acetylene diethers, as many other alkynes do, exhibit a kinetic unstability that induces polymerization.[17] However, diisopropoxy- and di-t-butoxyethyne are, for steric reasons, rather stable acetylene diethers, mainly the last one.

In any case, whereas the inhibitation of polymerization for steric reasons should increase exponentially with the volume of the substituents—since these are present in both, the "substrate" and the "reagent"—, the evolution of the reactivity in front of a given external reagent must change in a linear manner and one should expect that the stable acetylene diethers will react "normally" with some nucleophiles and, specially, some electrophiles.

Acid catalyzed hydration of the triple bond. As summarized in Chart 3, diisopropoxyethyne reacts with 2 N H_2SO_4, at 0°, to give, after 45 min, quantitative yields of isopropyl isopropoxyacetate.[18] Under the same conditions, di-t-butoxyethyne does not react at all and it is quantitatively recovered unchanged. However, under more severe conditions, such as 6 N H_2SO_4, in the presence of mercury sulfate, at room temperature for 165 min, t-butoxyacetic acid was isolated in 59% yield.[19] In this case, owing to the sensitivity of t-butoxy groups to acids, the formation of t-butoxyacetic acid might be explained as the result of the protonation of the etheral O-atom, rather than protonation of the triple bond C-atoms.

Catalytic hydrogenation. Catalytic hydrogenation of diisopropoxyethyne in pentane solution, previously cooled at −78°, either in the presence of PtO_2 or 5% Pd-on-C, gave 1,2-diisopropoxyethane,[20] which was isolated in 89% yield, after evaporative distillation. The product was identical with that obtained by catalytic hydrogenation of a mixture of (*Z*)- and (*E*) - 1,2 - diisopropoxyethene (**6**, R' = Pr^i). With Adams' catalyst some hydrogenolysis was observed.

[e] On the other hand, like the corresponding methoxy and ethoxy derivatives (**10**, R = Me and Et), (*E*) - 1 - bromo - 1,2 - diisopropoxyethene shows great sensitivity to atmospheric oxygen to give isopropyl bromoisopropoxyacetate.[16]

[f] It is worthwhile to mention that chlorination of 1,2 - di - t - butoxyethene reverts to *meso* - 1,2 - di - t - butoxy - 1,2 - dichloroethane, a fact that may be explained in terms of the relative stabilities of the intermediate "halogenonium ions" vs the corresponding "carbenium ions".

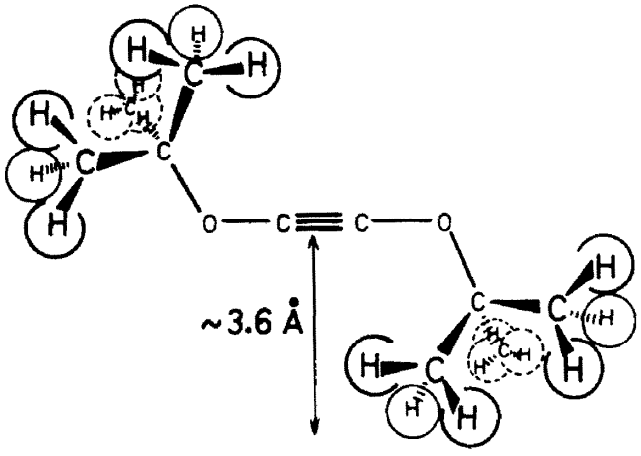


Fig. 2.

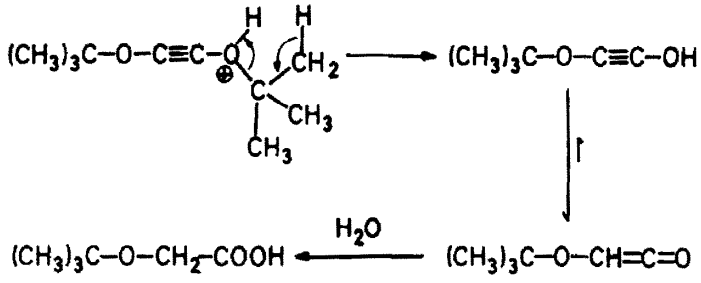


Fig. 3.

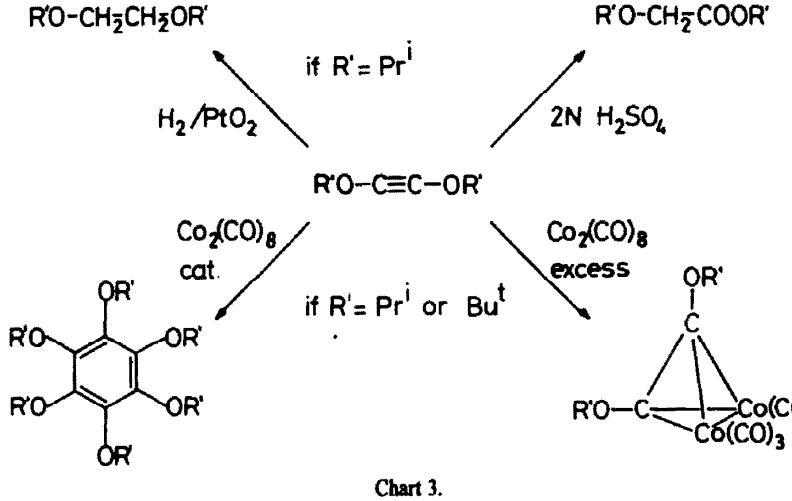


Chart 3.

Under similar conditions, at room temperature, di-t-butoxyethyne was not hydrogenated at all, which is a good evidence of the steric differential protection of the triple bond by isopropoxy and t-butoxy groups.

Reaction with octacarbonyl dicobalt. As reported for the "unstable acetylene diethers", such as dimethoxy and diethoxyethyne,[b] the reaction of diisopropoxy and di-t-butoxyethyne with excess $Co_2(CO)_8$, in pentane, give the corresponding hexacarbonyl dicobalt complexes, m.p. 61° and 58–9°, in 5% and 35% yield, respectively, which were characterized by IR, NMR and MS.[g]

Cycloadditions. Di-t-butoxyethyne fails to undergo a 4+2 cycloaddition with hexachlorocyclopentadiene—a Diels–Alder reaction with reverse electronic demand—, at room temperature. Under more severe conditions, a 2+2 cycloaddition is observed, which will be reported in a separated paper (see footnote g).

[g] On the other hand, the reaction of the stable acetylene diethers with catalytic amounts of $Co_2(CO)_8$ leads to the corresponding aromatic cyclic trimers, a reaction that will be reported in a separated paper dealing with some synthetic applications of di-t-butoxyethyne.

The starting material: rac *and* meso - 1,2 - *dichloro* - 1,2 - *dimethoxyethane* (2, R = Me)

1,2 - Dichloro - 1,2 - dimethoxyethane (2, R = Me) is directly prepared from glyoxal trimer by reaction with methanol and thionyl chloride, according to the method of Baganz and Domasche.[21] The crude reaction is, in fact, a ternary mixture of *rac* and *meso* - 1,2 - dichloro - 1,2 - dimethoxyethane (2, R = Me), 2 - chloro - 1,1,2 - trimethoxyethane (CTME) and 1,1,2,2 - tetramethoxyethane (TME)(Table 2), which can be converted to a 70:30 mixture of pure *rac* and *meso* - 1,2 - dichloro - 1,2 - dimethoxyethane by treatment with PCl_5 at 0°, followed by distillation at 77–8°/17 Torr.

Equilibration to the thermodynamically more stable *meso* form is observed,[22] either in solution or as a net liquid (36:64 mixture of *rac*:*meso* in cyclohexane, ΔG°_{293} 0.74 ± 0.03 kcal · mol^{-1}), which can be separated by crystallization at low temperature, as a solid m.p. 68–70°.

The *rac* and *meso* configuration were assigned assuming an *anti* stereospecific elimination of hydrogen chloride, induced by KOBu^t, to (*Z*) and (*E*) - 1 - chloro - 1,2 - dimethoxyethene (5, R = Me), respectively, which configuration was, in turn, corroborated from the preferential attack of the (*Z*)-isomer by $NaNH_2$ in liq NH_3 to form dimethoxyethyne.

EXPERIMENTAL

M.ps are uncorrected, and were determined on a Kofler microscope. IR spectra were recorded with Perkin–Elmer spectrophotometers, models 457 and 257, and NMR spectra with a Perkin–Elmer spectrometer, model R-12B (the values are given in ppm, δ scale, using TMS as internal reference). MS were recorded with an AEI apparatus, model MS 902 S, working at 70 eV.

All stereochemical assignments reported in this paper are made on the bases of NMR spectra: (i) dialkoxyhalogenoethenes (5), by comparison with the methoxy series[6] and assuming a preferential attack of $NaNH_2$ in liq NH_3 to (*Z*)-isomers; (ii) glyoxal bis-halogenoacetals (4), by comparison with *rac* and *meso* - 1,2 - dichloro - 1,2 - dimethoxyethane;[6] (iii) 1,2 - di(sec - or t -) alkoxyethenes (7) by comparison with the Me and Et derivatives;[15] (iv) glyoxal mixed acetals (3), and 2,3 - di(sec - or t-)alkoxy - 1,4 - dioxanes (12) on the basis of conformational analysis.

1,2 - *Dichloro* - 1,2 - *dimethoxyethane* (2, R = Me)

A soln of glyoxal in MeOH (prepared from 96.0 g of glyoxal trimer—equivalent to 1.37 mole anh glyoxal—, 128 ml anhyd MeOH and 1 ml $SOCl_2$, and heating the mixture for a while) and 240 ml CCl_4 were introduced into a 1 l, 3-necked round-bottomed flask, equipped with a mechanical stirrer, a pressure-equalized dropping funnel fitted with an inlet tube for N_2, an immersion termometer and a condenser with a $CaCl_2$-tube. The flask was cooled with an ice-salt bath and, when the inside temp was 0°, 240 ml (3.34 mole) $SOCl_2$ was added dropwise so that the temp did not exceed 5°. After 25–30% $SOCl_2$ had been added, a vigorous gaseous evolution took place and the reaction became endothermic. In this moment, the cooling bath was substituted by a water bath, the $SOCl_2$ was added faster than before and the mixture was heated to keep the inside temp at 20–25°. The addition took 5–6 hr, and the mixture was then stirred overnight at room temp. The solvent and excess $SOCl_2$ were evaporated under vacuum, and the residue distilled at 19 Torr, collecting a single fraction b.p. up to 100°, the NMR spectrum showed that it had a 13:11:3 mixture of *rac* and *meso* - 1,2 - dichloro - 1,2 - dimethoxyethane (5.50 and 5.42 s), 1 - chloro - 1,2,2 - trimethoxyethane (5.24 d, J = 6 Hz and 4.28 d, J = 6 Hz) and 1,1,2,2 - tetramethoxyethane (4.09 s).

In a 250 ml Erlenmeyer flask, equipped with magnetic stirring and a pressure-equalized dropping funnel, an amount of PCl_5 equivalent to the moles of monochloro derivative plus twice the moles of tetramethoxyethane was added, the flask was cooled with an ice-water bath and the ternary mixture was added dropwise (the reaction is controlled by NMR, adding more PCl_5 if necessary). The $POCl_3$ was distilled off at 50–5°/18–20 Torr, and the residue (154–165 g) distilled at 77–78°/17–18 Torr (71–76% yield).

The ratio *rac*:*meso* is 70:30, and the *meso* form could be separated by crystallization at low temp, m.p. 69–70°.

NMR (CCl_4): 5.50(s)(1H) *rac* and 5.42(s)(1H) *meso*; 3.52(s)(3H *rac* + 3H *meso*).

1,2 - *Di* - *t* - *butoxy* - 1,2 - *dimethoxyethane* (3, R = Me, R' = Bu^t)

To a 1 l, 3-necked round-bottomed flask, equipped with a mechanical stirrer, a pressure-equalized dropping funnel fitted with an inlet tube for N_2, and a condenser with a $CaCl_2$-tube, 150 g of recently activated K_2CO_3 (at 250–300° for 3 hr) and 600 ml dry t-BuOH were added. Working under dry N_2 and vigorous stirring,[k] 28.72 g (0.18 mole) of a 75:25 mixture of *rac* and *meso* - 1,2 - dichloro - 1,2 - dimethoxyethane were added rapidly. After washing the dropping funnel with a little CH_2Cl_2,[l] the funnel was removed, the mixture stirred for 48 hr,[l] and then poured into a stirred mixture of 500 ml CH_2Cl_2 and 300 ml H_2O. The organic layer was separated and the aqueous one extracted with 100 ml CH_2Cl_2. The combined organic extracts were washed with 100 ml H_2O and then dried with $NaSO_4$. The solvents were removed *in vacuo* and 2 - methoxy - 2 - t - butoxyacetaldehyde distilled off at 65–70°/11 Torr. The remaining product was distilled at 44–6°/0.45 Torr, to give 31.55 g (76.5% yield) of a 65:35 mixture of *rac* and *meso* - 1,2 - di - t - butoxy - 1,2 - dimethoxyethane.

NMR (CCl_4): 4.49(s)(1H) *rac* and 4.21(s)(1H) *meso*; 3.28(s)(3H) *meso* and 3.23(s)(3H) *rac*; 1.21(s)(9H) *meso* and 1.19(s)(9H) *rac*.

IR (CCl_4): 2970, 2820, 1470, 1450, 1385, 1360, 1250, 1230, 1190,

[k] An efficient and continuous stirring is necessary, otherwise neutralization does not take place effectively and decomposition of the products is observed.

[l] In case of using a mixture of bis-chloroacetals containing large amounts of the highly crystalline *meso* isomer, it should be added as a solution with a small amount of CH_2Cl_2.

[l] The progress of the reaction may be controlled introducing a glass rod into the reaction mixture and then putting it in contact with a wet pH paper: after the initial blue color owing to the presence of particles of K_2CO_3, a red color spreads over the paper after a few seconds if bis-chloroacetal is still present. However, it is very convenient to confirm the end of the reaction by NMR spectroscopy. Larger reaction times have deleterious effects on the final yields.

Table 2.

product	yield	rac:meso	acetalic protons (δ, ppm)
2, R = Me	48%	40:60	5.50 (rac), 5.42 (meso)
CTME	41%	-	5.24 and 4.28
TME	11%	-	4.09

1110, 1090, 1055, 1020, 950, 938 and 868 cm^{-1}. (Found: C, 61.49; H, 11.45. Calc. for $C_{12}H_{26}O_4$: C, 61.51; H, 11.18%).

1,2 - *Diisopropoxy* - 1,2 - *dimethoxyethane* (3, R = Me, R' = Pr^i)

Using i-PrOH, and operating as described for the di-t-butoxy derivative, a 50:50 mixture of *rac* and *meso* - 1,2 - diisopropoxy - 1,2 - dimethoxyethane, b.p. 88–91°/21 Torr, was obtained in 73% yield.

NMR(CCl_4): 4.20(s)(1H) *rac* and 4.15(s)(1H) *meso*; 3.80(m, J = 6 Hz)(1H, *rac* + 1H, *meso*); 3.30(s)(3H) *meso* and 3.27(s)(3H) *rac*; 1.16 (d, J = 6 Hz) and 1.13 (d, J = 6 Hz)(6H, *rac* + 6H, *meso*).

IR (CCl_4): 2970, 2930, 2827, 1465, 1450, 1380, 1370, 1330, 1290, 1210, 1192, 1178, 1120, 1090, 1060, 978, 950, 928 and 862 cm^{-1}. (Found: C, 58.17; H, 10.72. Calc. for $C_{10}H_{22}O_4$: C, 58.31, H, 10.76).

2,3 - *Di - t - butoxy* - 1,4 - *dioxane* (12, R' = Bu^t)

To a 2 l, 3-necked flask, equipped with mechanical stirring and condenser with $CaCl_2$-tube, 157 g (1 mole) *trans* - 2,3 - dichloro - 1,4 - dioxane, 750 g (10 mole) anhyd t-BuOH and 552 g (4 mole) K_2CO_3 freshly activated at 250° for 3 hr were added. The mixture was stirred and heated under reflux for 30 hr. The mixture was treated, at room temp, with 800 ml CH_2Cl_2 and a few ml H_2O (just to dissolve all the inorganic salts). The organic layer was separated, dried with Na_2SO_4 and the solvents removed under vacuum. The residue crystallized partially on standing: the crystals were filtered off and recrystallized from pentane at −78°, to give 70 g *trans* - 2,3 - di - t - butoxy - 1,4 - dioxane. The remaining product was distilled at 60–61°/0.3 Torr, to afford 127 g of a 25:75 mixture of *cis* and *trans* isomers (overall yield: 85%).

Trans, m.p. 64–65°: NMR(CCl_4): 4.30(s)(2H); 4.20–3.05(m, AA'BB')(4H) and 1.19(s)(18H). IR(CCl_4): 2975, 2930, 1390, 1367, 1190, 1145, 1100, 1060, 1040 and 857 cm^{-1}. MS: 232(M^+) (< 1%), 73(13.8), 59 (6.5), 58 (5.4), 57 (100), 41 (5.4).

Mixture of *cis* and *trans*: liquid b.p. 60–61°/0.3 Torr: NMR(CCl_4): 4.43(s)(2H) *cis* and 4.30(s)(2H) *trans*; 4.20–3.05(m)(4H) *cis* + (4H) *trans*; 1.19(s)(9H) *cis* + (9H) *trans*: IR(CCl_4): 2975, 2930, 1390, 1367, 1190, 1170, 1145, 1130, 1120, 1100, 1080, 1067, 1045, 1020, 1000, 960 and 879 cm^{-1}. (Found: C, 62.00; H, 10.60. Calc. for $C_{12}H_{24}O_4$: C, 62.04; H, 10.41%).

2,3 - *Diisopropoxy* - 1,4 - *dioxane* (12, R' = Pr^i)

Using i-PrOH, and operating as described for di-t-butoxy derivative, a 60:40 mixture of *cis* and *trans* - 2,3 - diisopropoxy - 1,4 - dioxane was prepared in 91% yield, b.p. 49–50°/0.2 Torr: NMR(CCl_4): 4.37(s)(1H) *cis* and 4.29(s)(1H) *trans*; 4.15–3.15(m)(3H) *cis* + (3H) *trans*; 1.18 (ψt, J = 5.5 Hz)(6H) *cis* + (6H) *trans*: IR(CCl_4): 2970, 2930, 1380, 1368, 1180, 1120, 1085, 1069, 1045 and 910 cm^{-1}. MS: 204(M^+)(0.5%), 145(12.9), 119(7.6), 116(31.9), 103(24.3), 89(6.2), 74(71.4), 73(100), 70(7.1), 60(5.7), 47(5.0), 45(34.3), 43(44.8), 42(15.2), 41(13.3). (Found: C, 58.51; H, 10.18. Calc. for $C_{10}H_{20}O_4$: C, 58.80, H. 9.87%).

1,2 - *Di - t - butoxy* - 1,2 - *dichloroethane* (4, R' = Bu^t)

(a) *From* 1,2 - *di - t - butoxy* - 1,2 - *dimethoxyethane*. To a 100 ml flask, equipped with a pressure-equalized dropping funnel and magnetic stirring, 17.75 g (8.50×10^{-2} mole) PCl_5 and 30 ml of CCl_4 were added, and the flask cooled with an ice-salt bath. Under stirring, a soln of 10.0 g (4.27×10^{-2} mole) 1,2 - di - t - butoxy - 1,2-dimethoxyethane in 10 ml CCl_4 was added dropwise. After the addition, the mixture was stirred for 90 min at −12°, almost all the PCl_5 being consumed. The methyl chloride formed as a by-product was evaporated *in vacuo* (15–20 Torr) at −12° (traces of moisture must be avoided) and, if necessary, the soln was filtered to remove traces of PCl_5 through a sintered filter of fine porosity. The filtered soln was evaporated at 0.3 Torr and −12°, the CCl_4 and $POCl_3$ being collected at −78°. The semicrystalline residue was dissolved in 20 ml CCl_4 and evaporated again in order to remove all traces of $POCl_3$. The remaining product was dissolved in CH_2Cl_2 and stirred with 4 g of anhyd K_2CO_3 at room temp. The soln was filtered, the solid washed with 10 ml CH_2Cl_2, and the solvents evaporated *in vacuo* to give 10.10 g of crystalline *meso* - 1,2 - di - t - butoxy - 1,2 - dichloroethane (97% yield). The product could be sublimed at 40°/0.05 Torr to give colorless crystals, m.p. 77–78° (dec). NMR(CCl_4): 5.62(s)(1H) and 1.32(s)(9H): IR(CCl_4): 2975, 2925, 1470, 1458, 1390, 1368, 1310, 1250, 1180, 1130, 1025, 850 and 650 cm^{-1}. (Found. C, 49.37; H, 8.48; Cl, 29.02. Calc. for $C_{10}H_{20}Cl_2O_2$: C, 49.39; H, 8.28; Cl, 29.15%).

(b) *From* 2,3 - *di - t - butoxy* - 1,4 - *dioxane*. To a 250 ml flask, equipped with magnetic stirring and a pressure-equalized dropping funnel, 11.7 g (5.6×10^{-2} mole) PCl_5 and 20 ml CH_2Cl_2 were added. The mixture was cooled at 0° with a water-ice bath, and a soln of 9.28 g (4×10^{-2} mole) *trans* - 2,3 - di - t - butoxy - 1,4 - dioxane in 50 ml CH_2Cl_2 was added dropwise. The mixture was stirred for 30 min at room temp, the solvents removed under vacuum, the residue dissolved in hexane and the impurities filtered off. After elimination of the solvent, 14.5 g of crude mixture was obtained.

In a 250 ml flask, equipped with a pressurequalized dropping funnel and a magnetic stirrer, 16 g (0.4 mole) finely powdered NaOH and 60 ml pentane was introduced. The mixture was cooled at 0° and the above crude mixture, dissolved in 50 ml pentane, was added dropwise. The mixture was then stirred for 24 hr at room temp, filtered and the solvent removed under vacuum to give 7.8 g crude crystalline *meso* - 1,2 - di - t - butoxy - 1,2 - dichloroethane, which was suitable for the next operation. However, since the product was contaminated with 2-chloroethyl dichlorophosphate (peaks at 4.7–3.3 region), a great excess of KOBu^t was needed to covert it to the chloroolefin (see below).

(c) *From* 2,3 - *di - t - butoxy* - 1,4 - *dioxane* (improved method). To a 250 ml flask, equipped with magnetic stirring and a pressure-equalized dropping funnel, 36 g (14.6×10^{-2} mole) 2,2 - dihydro - 2,2,2 - trichloro - 1,3,2 - benzodioxaphosphole[14] and 75 ml CH_2Cl_2 were introduced, the soln cooled with chilly water, and a soln of 20.3 g (8.76×10^{-2} mole) 2,3 - di - t - butoxy - 1,4 - dioxane in 75 ml CH_2Cl_2 was added dropwise in a 90 min period. The mixture was stirred then at room temp for 5 hr, and the solvent removed under vacuum.

The *meso* - 1,2 - di - t - butoxy - 1,2 - dichloroethane was taken up by treating the crude mixture with several portions cold hexane (4 × 50 ml).[k] The NMR spectrum of a sample showed that the product contained about 15% 2 - chloroethyl 2,2 - dihydro - 1,3,2 - benzodioxaphosphate, but it was eliminated in the following steps (see below).

1,2 - *Dichloro* - 1,2 - *diisopropoxyethane* (4, R' = Pr^i)

(a) *From* 1,2 - *diisopropoxy* - 1,2 - *dimethoxyethane*. Operating as described for the di-t-butoxy derivative, a 35:65 mixture of *rac* and *meso* - 1,2 - dichloro - 1,2 - diisopropoxyethane, b.p. 42–44°/0.25 Torr, was obtained in 93% yield. NMR(CCl_4): 5.56(s)(1H) *rac* and 5.48(s)(1H) *meso*; 4.02(m, J = 6 Hz)(1H *rac* + 1H *meso*); 1.25(d, J = 6 Hz)(6H *rac* + 6H *meso*): IR(CCl_4): 2980, 2938, 1465, 1452, 1385, 1377, 1331, 1298, 1200, 1183, 1155, 1138, 1110, 950, 915 and 664 cm^{-1}. (Found: C, 44.33; H, 7.55; Cl, 32.93. Calc. for $C_8H_{16}Cl_2O_2$: 44.66; H, 7.50; Cl, 32.96%).

(b) *From* 2,3 - *diisopropoxy* - 1,4 - *dioxane*. Operating as described for the di-t-butoxy derivative, but followed by vacuum distillation after the treatment with PCl_5, a 38:62 mixture of *rac* and *meso* - 1,2 - dichloro - 1,2 - diisopropoxyethane, b.p. 97–98°/18 Torr, was obtained in 88% yield (the product was contaminated by ~3% of 2-chloroethyl dichlorophosphate).

1,2 - *Di - t - butoxy* - 1 - *chloroethene* (5, R' = Bu^t)

To a 100 ml flask, equipped with magnetic stirring and a Liebig condenser, with a $CaCl_2$-tube, 5.63 g (2.32×10^{-2} mole) *meso* - 1,2 - di - t - butoxy - 1,2 - dichloroethane, in 30 ml pentane, was introduced. The soln was cooled at 0°, with a water-ice bath, and 4.55 g (4.06×10^{-2} mole) of KOBu^t was added slowly through the condenser. The mixture was stirred at room temp for 90–120 min (control by NMR), and then 10% K_2CO_3 aq was added to dissolve all the inorganic salts. The organic layer was separated, dried over K_2CO_3 and the solvent removed *in vacuo*. The residue

[k] In fact, using this procedure a mixture of *rac* and *meso* is observed in the control samples. However, the final product is always the more stable *meso* isomer.

was distilled at 40°/0.1 Torr (collector at −78°) to give 3.6–4.3 g of (*E*) - 1,2 - di - t - butoxy - 1 - chloroethene (75–90% yield). NMR(CCl_4): 5.91(s)(1H); 1.33(s)(9H) and 1.26(s)(9H): IR(CCl_4): 2972, 1670, 1470, 1390, 1366, 1290, 1260, 1240, 1180, 1140, 1070, 1025 and 935 cm^{-1}. (Found: C, 58.22; H, 9.63; Cl, 16.96. Calc. for $C_{10}H_{19}ClO_2$: C, 58.10; H, 9.26; Cl, 17.14%).

When using crude *meso* - 1,2 - di - t - butoxy - 1,2 - dichloroethane prepared from 2,3 - di - t - butoxy - 1,4 - dioxane (improved method, see above) the following procedure gave the best results: In a 250 ml flask, equipped with magnetic stirring and a Liebig condenser, fitted with a $CaCl_2$-tube, was introduced the hexane soln of *meso* - 1,2 - di - t - butoxy - 1,2 - dichloroethane (200 ml, see above "improved method") and 24.57 g (2.19×10^{-1} mole) of KOBu^t (Merck) was added slowly in small portions through the condenser. The addition was done slowly (1 hr), in order to control the temp of the mixture. The mixture was stirred at room temp for 90 min, and then treated with enough H_2O to dissolve all the inorganic salts. The organic layer was separated, dried over Na_2SO_4 and the solvent removed under vacuum. The residue was distilled at 40–42°/0.1 Torr (collector at −78°) to give 9.7 g (*E*) - 1,2 - di - t - butoxy - 1 - chloroethene. The overall yield of the two steps is about 50%. The NMR spectrum showed, eventually, the presence of weak peaks at 3.5–4.5, corresponding to traces of **16**, which was eliminated in the next step, after treatment with $NaNH_2$ in liq NH_3 (see below).

1-*Chloro*-1,2-*diisopropoxyethene* (**5**, R′ = Pr^i)

Starting from a mixture of *rac* and *meso* - 1,2 - dichloro - 1,2 - diisopropoxyethane, and operating as described above for the di-t-butoxy derivative, a 33:67 mixture of (*Z*)- and (*E*) - 1 - chloro - 1,2 - diisopropoxyethene, b.p. 31°/0.3 Torr (or 77–79°/18 Torr) was obtained in 82% yield. NMR(CCl_4): 6.05(s)(1H) *Z* and 5.70(s)(1H) *E*; 4.50–3.50(m)(2H, *Z* + 2H, *E*) and 1.28–1.14(m)(6H, *Z* + 6H, *E*): IR(CCl_4): 2980, 2940, 2890, 1680, 1468, 1452, 1385, 1375, 1340, 1318, 1285, 1190, 1168, 1137, 1120, 1108, 1070, 955 and 908 cm^{-1}. MS: 178(M^+)(6.2), 138(5.0), 136(14.4), 100(5.9), 96(32.7), 94(100), 89(5.0), 73(15.2), 59(6.8), 58(29.8) and 57(6.8). (Found: C, 53,92; H, 8.67; Cl, 19.72. Calc. for $C_8H_{15}ClO_2$: C, 53.78; H, 8.46; Cl, 19.84%).

1,2-*Di-t-butoxyethene* (**7**, R′ = Bu^t)

A 250 ml, 3-necked flask, equipped with magnetic stirring, a condenser, a pressure-equalized dropping funnel, an inlet tube for N_2 and an immersion thermometer, was dried with an IR lamp under dry N_2, and 3.0 g (1.25×10^{-1} mole) Mg and 10 ml anhyd THF were added. The mixture was heated at 50° by means of the IR lamp, and 0.1–0.2 ml 1,2 - dibromoethane was added under stirring. Once the reaction had started, a soln of 12.81 g (5.27×10^{-2} mole) 1,2 - di - t - butoxy - 1,2 - dichloroethane in 50 ml anhyd THF was added dropwise in a 45 min period, the inside temp being controlled at about 40° by a water bath. After the total addition, the resulting greenish-yellow soln was heated at 40° for a further 30 min, the bath was then removed and stirring continued until the reaction reached the room temp. 40 ml ether was added and then a soln of 20 g NH_4Cl in 80 ml H_2O. The mixture was stirred for a few min and filtered through a sintered filter; 40 ml hexane was added in order to facilitate the separation of the two layers. The organic layer was washed with 50 ml Na_2CO_3 aq and dried with Na_2SO_4.

The solvents were removed *in vacuo* at room temp and the residue distilled at 30°/0.05 Torr, collecting the product at −78°, to give 5.4–6.8 g of a 50:50 mixture of (*E*)- and (*Z*) - 1,2 - di - t - butoxyethene (60–75% yield). NMR(CCl_4): 6.08(s)(1H) *E* and 5.30(s)(1H) *Z*; 1.20(s)(9H) *Z* and 1.16(s)(9H) *E*: IR(CCl_4): 3040, 2972, 2928, 1691, 1665, 1470, 1400, 1390, 1365, 1275, 1255, 1235, 1190, 1150, 1115, 1030 and 860. (Found: C, 69.87; H, 11.65. Calc. for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70%).

1,2-*Diisopropoxyethene* (**7**, R′ = Pr^i)

Starting from 1,2 - dichloro - 1,2 - diisopropoxyethane, and operating as described for di-t-butoxy derivative, a 44:56 mixture of (*Z*)- and (*E*) - 1,2 - diisopropoxyethene, b.p. 50–51°/14 Torr, was prepared in 82% yield. NMR(CCl_4): 5.99(s)(1H) *E* and 5.11(s)(1H) *Z*; 3.83(m, J = 6 Hz)(1H) *Z* and 3.69(m, J = 6 Hz)(1H) *E*; 1.19(d, J = 6 Hz)(6H) *Z* and 1.14(d, J = 6 Hz)(6H) *E*: IR(CCl_4): 3035, 2970, 2930, 2870, 1687, 1662, 1460, 1448, 1400, 1380, 1368, 1328, 1275, 1176, 1158, 1132, 1110, 960 and 912 cm^{-1}. (Found: C, 66.95; H, 11.54. Calc. for $C_8H_{16}O_2$: C, 66.63; H, 11.20%).

1-*Bromo*-1,2-*di-t-butoxyethene* (**10**, R′ = Bu^t)

(a) *Bromination.* In a 100 ml flask, equipped with magnetic stirring, a pressure-equalized dropping funnel and a $CaCl_2$-tube was added, a soln of 4.70 g (2.73×10^{-2} mole) 1,2-di-t-butoxyethene in 40 ml pentane. The soln was cooled at −15° and Br_2 added until the color persisted (*ca* 1.45 ml = 2.73×10^{-2} mole).

An aliquot was evaporated to give a crystalline dibromo derivative, which thermally decomposed even in soln at 30–40° to give a carbonyl compound ($\nu_{C=O}$ 1740), probably 2-bromo-2-t-butoxyacetaldehyde. NMR(CCl_4): 6.22(s) and 6.13(s)(1H); 1.38(s) and 1.36(s)(9H): IR(CCl_4): 2975, 1470, 1392, 1370, 1260, 1158, 1115, 1080, 1029, 928, 910, 840 cm^{-1}.

(b) *Dehydrobromination.* To the above soln at −15°, under stirring, 4.10 g (3.63×10^{-2} mole) KOBu^t was added in small portions in a 5 min period. The mixture was stirred for 120 min, while the temperature was allowed to rise 0°; it was then treated with 20 ml iced H_2O and the layers separated. The organic soln was dried with Na_2SO_4, solvent removed *in vacuo* and the residue distilled at 40°/0.1 Torr to give 5.60 g of (*E*) - 1 - bromo - 1,2 - di - t - butoxyethene (83% yield). NMR(CCl_4): 5.96(s)(1H); 1.32(s)(9H) and 1.22(s)(9H): IR(CCl_4): 2970, 1660, 1470, 1390, 1367, 1260, 1240, 1180, 1135, 1065, 1022, 930 and 915 cm^{-1}. (Found: C, 47.58; H, 7.96; Br, 32.11. Calc. for $C_{10}H_{19}BrO_2$: C, 47.80; H, 7.62; Br, 31.80%).

1-*Bromo*-1,2-*diisopropoxyethene* (**10**, R′ = Pr^i)

Starting from a mixture of (*Z*)- and (*E*)-diisopropoxyethene, (*E*) - 1 - bromo - 1,2 - diisopropoxyethene, b.p. 40–45°/0.1–0.05 Torr (evaporative distillation), was prepared in 72–86% yield. The bromoolefin isomerized thermally and it was sensitive to atmospheric oxidation to isopropyl bromoisopropoxyacetate.[16] NMR(CCl_4): 5.71(s)(1H): 4.14(m, J = 6 Hz)(1H): 3.83(m)(J = 6 Hz)(1H); 1.23(d, J = 6 Hz)(6H) and 1.20 (d, J = 6 Hz)(6H): IR(CCl_4): 3055, 2973, 2926, 2880, 1672, 1465, 1450, 1384, 1372, 1340, 1315, 1183, 1160, 1130, 1115, 1100, 1057, 942, 900 and 860 cm^{-1}. (Found: C, 43.04; H, 7.00; Br, 36.27. Calc. for $C_8H_{15}BrO_2$: C, 43.07; H, 6.78; Br, 35.80%).

Di-t-butoxyethyne (**1**, R′ = Bu^t)

(a) *From* (E) - 1,2 - *di* - *t* - *butoxy* - 1 - *chloroethene.* In a 500 ml 3-necked flask, equipped with magnetic stirring, an acetone-dry ice condenser, stopped with a KOH-tube, and a pressure-equalized dropping funnel, a suspension of $NaNH_2$ in liq NH_3 was prepared from 5.4 g (2.39×10^{-1} mole) Na and 250 ml liq NH_3. To the stirred suspension, a soln of 9.7 g (4.3×10^{-2} mole) (*E*) - 1,2 - di - t - butoxy - 1 - chloroethene in 40 ml anhyd ether was added dropwise, the mixture was then stirred for 90 min, diluted with 60 ml pentane (cooled at −50°), and hydrolyzed with 100 ml iced H_2O. The organic layer was separated, washed with 50 ml buffered 0.1 M phosphate soln (NaH_2PO_4/Na_2PO_4) and dried with a mixture of K_2CO_3 and Na_2SO_4 at −6°. Elimination of the solvents under vacuum and distillation at 34–5°/0.3 Torr (collector at −78°), afforded 4.38 g pure di-t-butoxyethyne (59% yield).

(b) *From* (E) - 1 - *bromo* - 1,2 - *di* - *t* - *butoxyethene.* In a 500 ml 3-necked flask, equipped with magnetic stirring, an acetone-dry ice condenser, stopped with a KOH-tube, and a pressure-equalized dropping funnel, a suspension of $NaNH_2$ in liq NH_3 was prepared from 2.3 g (0.1 mole) Na and 100 ml liq NH_3. To the stirred suspension, a soln of 5.50 g (2.18×10^{-2} mole) (*E*) - 1 - bromo - 1,2 - di - t - butoxyethene in 30 ml anhyd ether was added dropwise, the mixture stirred for 18 min, 60 ml pentane (cooled at −50°) added and then hydrolyzed with 100 ml iced H_2O. The layers were separated and the organic one washed with 50 ml buffered 0.1 M phosphate soln (NaH_2PO_4/Na_2PO_4) and dried with a mixture of K_2CO_3 and Na_2SO_4 at −6°. Evaporation of the solvents under vacuum afforded 3.43 g of di-t-

butoxyethyne (92% yield). Distillation at 26–32°/0.09–0.05 Torr (collector at −78°) yielded 2.64 g analytically pure compound as colorless crystalls, m.p. 8.5°. NMR(CCl_4): 1.31(s): IR(CCl_4): 2972, 2922, 1470, 1450, 1390, 1367, 1301, 1263, 1245, 1150 and 825 cm^{-1}. (Found: C, 70.20; H, 10.61. Calc. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.61%).

Diisopropoxyethyne (1, R' = Pr^i)

Starting from (*E*)- and/or (*Z*) - 1 - bromo - 1,2 - diisopropoxyethene, and using 200% excess of $NaNH_2$ and a reaction time of 30 min, diisopropoxyethyne was obtained in 82–87%, which could be distilled at 0.001 Torr (collector at −78°) in 20–25% yield. Diisopropoxyethyne was an unstable liq at room temp. NMR(CCl_4): 3.97 (m, J = 6 Hz)(1H) and 1.25(d, J = 6 Hz)(6H).

Catalytic hydrogenation of diisopropoxyethyne: 1,2-diisopropoxyethane

A soln of 0.532 g (3.75×10^{-3} mole) diisopropoxyethyne in 15 ml pentane, containing 0.052 g of PtO_2, was cooled at −78° and hydrogenated at atmospheric pressure until stequiometric uptake of H_2 was observed (5% excess). Glc analysis (SE 52; 60°) showed the presence of only one product. Elimination of solvent *in vacuo* afforded 0.485 g pure 1,2-diisopropoxyethane[20] (89% yield), characterized by comparison with an authentical sample prepared by catalytic hydrogenation of 1,2-diisopropoxyethene. NMR(CCl_4): 3.52(m, J = 6 Hz)(1H); 3.40(s)(2H) and 1.08(d, J = 6 Hz)(6H): IR(CCl_4): 2980, 2930, 2865, 1468, 1455, 1382, 1370, 1332, 1312, 1245, 1173, 1150, 1130, 1090, 985, 910 and 860 cm^{-1}.

Under the same conditions, at room temp, di-t-butoxyethyne was not hydrogenated.

Acid catalyzed hydration of acetylene diethers

(a) *Diisopropoxyethyne: isopropyl isopropoxyacetate.* To a 100 ml flask, equipped with magnetic stirring and a pressure-equalized dropping funnel, 0.46 g (3.24×10^{-3} mole) diisopropoxethyne dissolved in a mixture of 15 ml pentane and 15 ml ether was added. Under an atmosphere of N_2, and cooling the soln at 0°, 20 ml of 2 N H_2SO_4 were added dropwise, and the mixture stirred for 45 min at 0°. Glc analysis of a sample showed that practically only one product was present (>96%). Evaporation of the solvents and evaporative distillation of the residue at 120–125°/760 Torr, gave 0.445 g (86% yield) of isopropyl isoproxyacetate (lit.[18] 170°/742 Torr). NMR(CCl_4): 5.00(m, J = 6 Hz)(1H); 3.90(s)(2H); 3.61(m, J = 6 Hz)(1H) and 1.19 (ψt, J = 6 Hz)(12H): IR(CCl_4): 2980, 2935, 2875, 1753, 1730, 1468, 1455, 1385, 1376, 1281, 1273, 1205, 1180, 1130, 1108 cm^{-1}.

(b) *Di-t-butoxyethyne: t-butoxyacetic acid.* (i) With 2 N H_2SO_4: Di-t-butoxyethyne was recovered unchanged by treatment with 2 N H_2SO_4, at room temp.

(ii) With 6 N H_2SO_4 + $HgSO_4$. To a 100 ml flask, equipped with magnetic stirring and a pressure-equalized dropping funnel, 441 mg (2.60×10^{-3} mole) di-t-butoxyethyne dissolved in a mixture of 15 ml pentane and 15 ml ether was added, and then 105 mg $HgSO_4$ was added. After cooling at 0°, 25 ml 6 N H_2SO_4 was added dropwise, and the mixture stirred at room temp for 165 min. The organic layer was separated, the aqueous layer extracted twice with 15 ml ether, and combined ether extracts washed with H_2O and then with 15 ml $NaHCO_3$ aq. Drying the soln and evaporation of the solvents gave 256 mg of di-t-butoxyethyne (52% recovery).

The combined aqueous solns (pH strongly acid) were extracted with CH_2Cl_2 (10 × 10 ml), the soln dried and evaporated under vacuum to give 85 mg (59% yield of reacted acetylene) of an oily compound that crystallized on standing, and characterized as t-butoxyacetic acid.[19] NMR(CCl_4): 8.05(s, broad)(1H); 4.03(s)(2H) and 1.26(s)(9H): IR(CCl_4): 3520, 3450, 3100, 1785, 1760, 1735, 1368, 1260, 1240, 1190, 1123 and 1100 cm^{-1}.

Reaction of acetylene diethers with $Co_2(CO)_8$

(a) *Di - t - butoxyethyne: hexacarbonyl - μ - η - (di - t - butoxyethyne) - dicobalt* (Co–Co). To a 50 ml flask, equipped with magnetic stirring and atmosphere of dry N_2, 500 mg (2.94×10^{-3} mole) di-t-butoxyethyne, 1.21 g (3.52×10^{-3} mole) $Co_2(CO)_8$ and 25 ml pentane were added and the mixture stirred at room temp for 21 hr. Evaporation of the solvent under vacuum and chromatographic pruification on alumina, using pentane as eluent, gave 465 mg (35% yield) hexacarbonyl dicobalt complex, m.p. 58–9° (dec). NMR(CCl_4): 1.42(s): IR(CCl_4): 2972, 2925, 2080, 2040, 2020, 1540, 1500, 1388, 1367, 1260, 1210, 1165, 1130, 935 and 910 cm^{-1}. MS: (Found: 455.9599. Calc. for $C_{16}H_{18}Co_2O_8$: 455.9665).

(b) *Diisopropoxyethyne: hexacarbonyl - μ - η - (diisopropoxyethyne) - dicobalt* (Co–Co). Starting from diisopropoxyethyne, the corresponding hexacarbonyl dicobalt complex, m.p. 61°, was isolated in 5.1% yield. NMR(CCl_4): 4.05(m, J = 6 Hz)(1H) and 1.47(d, J = 6 Hz)(6H): IR(CCl_4): 2970, 2920, 2080, 2040, 2010, 1575, 1455, 1385, 1372, 1328, 1215, 1135, 1100 and 1060 cm^{-1}. MS: (Found: 427.9293. Calc. for $C_{14}H_{14}Co_2O_8$: 427.9352).

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