and their potentiality for allowing the coupling of cation transport with the reverse flux of protons.

Calixarenes as Enzyme Mimics

Our main interest in the calixarenes focuses on their potential as enzyme mimics, and the necessary synthetic capabilities appear to now be in hand. For example, the synthesis of the conformationally semiflexible mixed calixarene 30 (R = R' = t-Bu) is feasible, and by the types of reactions shown in Scheme V it should be possible to convert 30 to 41 (Scheme VI). Derivatization of the hydroxyl groups via ethyl α-bromoacetate at an appropriate point during this sequence would, presumably, fix the system in a "partial-cone" conformation, and hydrolysis in the last stages of the sequence would yield 41 (R = CH_2CO_2H). It is postulated that 41 might serve as an aldolase model,[58] holding in its calix a molecule of metal-atom-coordinated dihydroxyacetone phosphate in such a fashion that the keto group is proximate to the amino function (leading to Schiff base formation) and the α-hydrogens of the hydroxymethylene group are proximate to a carboxylate

function (leading to proton abstraction and formation of the carbanion, shown in Scheme VI as a charge-separated enamine). Condensation with an aldehyde (glyceraldehyde phosphate in the biological reaction) can then rapidly occur at the exposed, unhindered face of the carbanion to yield the aldol product. In similar fashion, numerous other enzyme mimic systems can be envisaged in which appropriate functional groups are arrayed around the cavities provided by calixarenes either in the "cone" or "partial-cone" conformation.

The first chapters in the calixarene story, as described in this account, have dealt with the development of methods for constructing the basic frameworks, methods for controlling the conformation and contour of the calix, and methods for introducing functional groups. The chapters yet to be written must deal with the utility of the calixarenes in such applications as enzyme mimics, ion carriers, and selective complexing agents.

(58) For a brief description of the chemistry of aldolase see: Walsh, C. "Enzymatic Reaction Mechanisms"; W. H. Freeman: San Francisco, 1979; p 745. For a more extended discussion see: Horecker, B. L.; Tsolas, O.; Lai, C. Y. "The Enzymes"; Boyer, P., Ed.; Academic Press: New York, 1972; Vol. 7, p 213.

Acetylene Diethers: A Logical Entry to Oxocarbons

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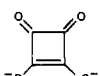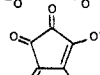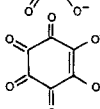
Although oxocarbons have been known for more than 150 years and several reviews[1] and even an entire book[2] have been devoted to them in the past few years, we feel that a brief account of our recent findings on the field, directed to a more general audience, is justified. Our interest in oxocarbons came through our own work on the chemistry of acetylene diethers that we developed during the past 12 years or so.[3] Acetylene diethers may be regarded as *esters* of the first member of the series of aromatic oxocarbon dianions, $C_nO_n^{2-}$, and as the common precursors of all of the other members of the series (Table I). In this context, the story of acetylene diethers is as old as the history of organic chemistry itself, and it is strongly tied to the work of the greatest chemists of the 19th century, such as Berzelius, Wöhler, Gmelin, and Liebig, who were the first to prepare croconic and rhodizonic acids from "potassium carbonyl".[4]

Over 100 years later, in 1959, Cohen, Lacher, and Park[5] synthesized the so-called squaric acid, and, soon

Table I
Aromatic Oxocarbon Dianions $C_nO_n^{2-}$

n	name	structural formula
2	acetylenediolate	$^-O-C\equiv C-O^-$
3	deltate	
4	squarate	
5	croconate	
6	rhodizonate	

afterwards in 1960, West[6] realized that rhodizonate, croconate, and squarate belong to the same oxocarbon

(1) G. Maas and P. Hegenberg, *Angew. Chem., Int. Ed. Engl.*, 5, 888 (1966); R. West and J. Niu in "Non-Benzenoid Aromatics", J. Snyder, Ed., Academic Press, New York, Vol. 1, p 311, 1969; R. West and J. Niu in "The Chemistry of the Carbonyl Group", J. Zabicky, Ed., Wiley-Interscience, New York, Vol. 2, p 241, 1970; A. H. Schmidt and W. Reid, *Synthesis*, 869 (1978); R. West, *Isr. J. Chem.*, 20, 300 (1980); A. H. Schmidt, *Chem. Unserer Zeit.*, 16, 57 (1982).
(2) "Oxocarbons", R. West, Ed., Academic Press, New York, 1980.

dianion series. The first members of this series would be the deltate, at that time unknown, and the acetylenediolate, actually the structure assigned by Büchner[7] in 1963 to the aforementioned "potassium carbonyl". Starting from this structure, it is easy to rationalize all of the earliest results obtained in this domain.

On being heated, potassium acetylenediolate cyclotrimerizes to the hexahydroxybenzene hexaanion, $C_6O_6^{6-}$, which is, in turn, the first species that can be isolated when the reaction of potassium with CO is conducted at higher temperature. The hexaanion undergoes rapid oxidation in the air, to afford rhodizonate ion, $C_6O_6^{2-}$. However, in alkaline medium, rhodizonate ion suffers a further oxidative process involving ring contraction to yield croconate ion, $C_5O_5^{2-}$, as observed for the first time by Gmelin[8] in 1825. Finally, deltic acid was prepared by West and Eggerding,[9] in 1975, by photochemical degradation of the bis(trimethylsilyl) ester of squaric acid, according to the method of Dehmlow.[10]

Aromaticity of the Oxocarbon Dianions

In 1960, West et al.[6] expressed the view that monocyclic oxocarbon dianions of the general formula $C_nO_n^{2-}$ might constitute a previously unrecognized aromatic series, and their view was substantiated by pertinent theoretical calculations on delocalization energies and by the results of a study of their vibrational spectra, which showed that oxocarbon dianions have symmetric D_{nh} structures.[11] Owing to the simplicity and the high degree of symmetry exhibited by the oxocarbons, their structures are specially suited for theoretical studies. The earliest calculations were of the simple Hückel type, but, more recently, theoretical studies have been conducted by using more sophisticated methods, including EHMO, LCAO-CI, semiempirical SCF-CI, CNDO and CNDO-CI, MINDO/2 and CNDO-CI, and unrestricted Hartree–Fock.[12] Of special significance is the recent article by Aihara[13] entitled "Are the oxocarbon dianions really aromatic?", in which the graph theory of aromaticity was applied to the monocyclic oxocarbon systems. Contrary to the prediction by West et al., dianions of monocyclic oxocarbons, together with all of the neutral ones, were predicted by Aihara to have very small resonance energies. Deltate dianion alone (and only because it has the structure of a disubstituted cyclopropenone) was predicted to be aromatic, and the same conclusion was reached if the traditional magnetic criterion of aromaticity was adopted (see, however, p 6–8 of ref 2). The author concludes: "Therefore, the

Table II
Kekulé Index for Oxocarbon Dianions

Kekulé structure	HMO	π-SCF-MO
I_a	0.925	0.925
I_b	0.932	0.934
II_a	0.908	0.908
II_b	0.902	0.904
III_a	0.905	0.907
III_b	0.883	0.885
IV_a	0.904	0.911
IV_b	0.871	0.871

planarity and cyclic conjugation of the oxocarbon dianions cannot be viewed as significant evidence for the existence of aromaticity."

We have approached the problem of the aromaticity of the oxocarbon dianions from a more classical point of view by using structural elements familiar to organic chemists.[14] The Kekulé structures for oxocarbon dianions are generally written as cycloalkenone structures (I_a–IV_a). However, as had already been pointed out by
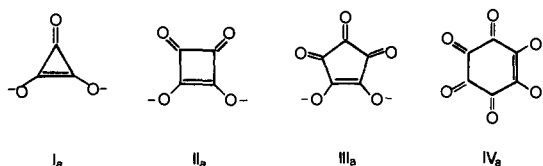
Sprenger and Ziegenbein[15] for the squarate system, it is convenient also to take into consideration the resonance forms of the cycloalkenylium type I_b–IV_b in order
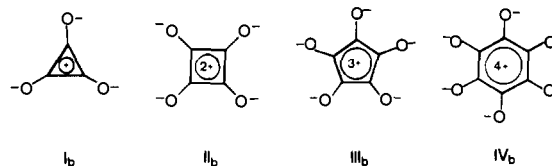
to explain the reactivity of these compounds. The so-called Kekulé Index (KI) has been proposed[16] as indicative of the relative weights of different Kekulé structures and has been defined as the arithmetical mean of the norms of the projections of bicentric orbitals corresponding to a Kekulé structure on the space spanned by the π MO's of a conjugated molecule. We have extended this definition in order to include resonance structures having lone electron pairs and have effected KI calculations on both Hückel and Dewar π SCF molecular orbitals of oxocarbons I–IV. Table II shows the values of the KI obtained for the limiting resonance forms of oxocarbon dianions.

The deltate anion is better described by the resonance structure I_b than by I_a owing to the high value of the charge localized on the oxygen atom and the small value of the CO bond order. The squarate anion is equally described by form II_a or II_b. As a general rule, the participation of resonance forms having charge separation diminishes as the ring size increases, because these forms imply the localization of $n - 2$ positive charges in a ring of n carbon atoms. The trend observed

(3) M. A. Pericàs and F. Serratosa, *Tetrahedron Lett.*, 4433, 4437 (1977); F. Sales and F. Serratosa, *ibid.*, 3329 (1979); A. Bou, M. A. Pericàs, and F. Serratosa, *Tetrahedron*, 37, 1441 (1981); M. A. Pericàs, A. Riera, and F. Serratosa, *ibid.*, 38, 1505 (1982).

(4) A brief but vivid account of the whole story is given by J. R. Partington, "A History of Chemistry", MacMillan, New York, Vol. 4, pp 794–795, 1964.

(5) S. Cohen, J. R. Lacher, and J. D. Park, *J. Am. Chem. Soc.*, 81, 3480 (1959).

(6) R. West, N. Y. Niu, D. L. Powell, and M. V. Evans, *J. Am. Chem. Soc.*, 82, 6204 (1960); R. West and D. L. Powell, *ibid.*, 85, 2577 (1963).

(7) E. Weiss and W. Büchner, *Helv. Chim. Acta*, 46, 1121 (1963); W. Büchner, *ibid.*, 46, 2111 (1963).

(8) L. Gmelin, *Ann. Phys. (Leipzig)*, 4 (2), 31 (1825); ref 2, p 3.

(9) D. Eggerding and R. West, *J. Am. Chem. Soc.*, 98, 3641 (1976).

(10) E. V. Dehmlow, *Tetrahedron Lett.*, 1271 (1972).

(11) M. Ito and R. West, *J. Am. Chem. Soc.*, 85, 2580 (1963).

(12) Reference 2, p 10.

(13) J. Aihara, *J. Am. Chem. Soc.*, 103, 1633 (1981).

(14) (a) A. Moyano, Graduation Thesis, Faculty of Chemistry, University of Barcelona, 1978; (b) A. Moyano and F. Serratosa, paper presented at ESOC II, Stresa (Italy), June 1–5, 1981; *J. Mol. Struct.* 90, 131 (1982).

(15) H. Sprenger and W. Ziegenbein, *Angew. Chem., Int. Ed. Engl.*, 7, 520 (1968).

(16) A. Graovac, I. Gutman, R. Randić, and N. Trinajstic, *J. Am. Chem. Soc.*, 95, 6267 (1973).

Scheme I
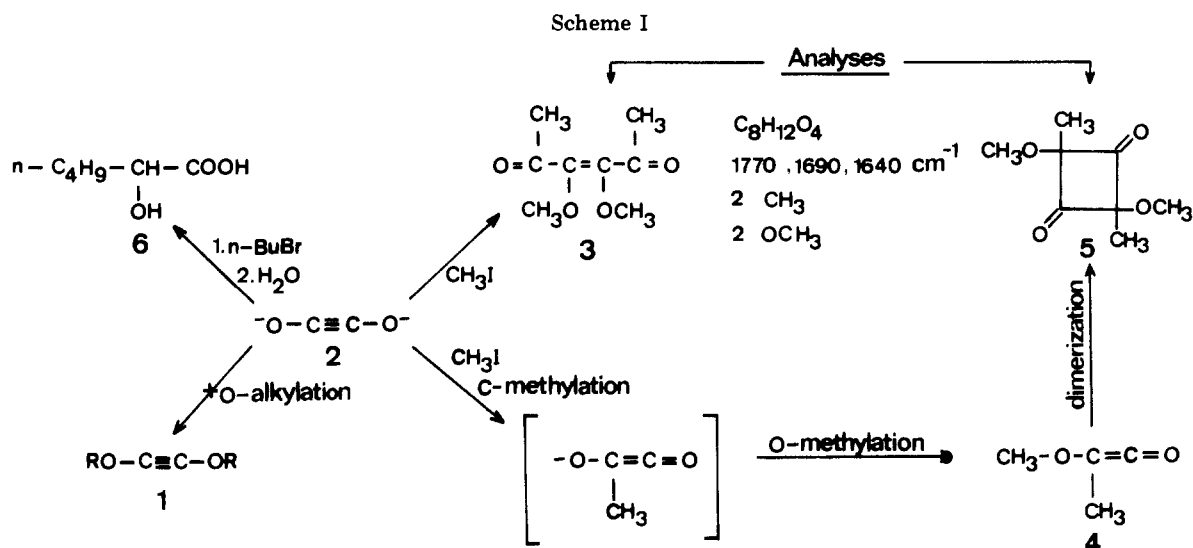
in the aromaticity of oxocarbon dianions is explained by the participation of the resonance forms with an aromatic carbocyclic nucleus (I_b–IV_b), and, in particular, is in excellent agreement with the fact that only the deltate anion presents a significant topological resonance energy.[13]

The presence in all of the oxocarbons of a cycloalkenylium nucleus of increasing formal charge $C_n^{(n-2)+}$ not only offers a direct explanation of their aromaticity,[17] but also constitutes a convenient way of rationalizing their acid strength. In the same way that, in the inorganic oxoacids of formula $(HO)_2YO_m$, the acidity increases[18] with the formal charge of the nucleus Y, the acidity of conjugated acids of the oxocarbon dianions should increase with the ring size. At least in the case of deltic and squaric acids, which are not involved in hydration equilibria, the pK_a values in aqueous solution[19] and the estimated gas-phase acidities[20] are in agreement with the foregoing statement.

Acetylene Diethers as Esters of Acetylenediolate

Although acetylene diethers (1) are formally esters of "potassium acetylenediolate" (2),[21] the actual structure assigned by Büchner[7] to the so-called "potassium carbonyl", the direct alkylation of this compound with alkyl halides fails to give the expected dialkoxyacetylenes (1). In fact, from the reaction of "potassium acetylenediolate" with methyl iodide, Sager et al.[22] isolated a compound to which they assigned the structure of a linear dimer (3) on the basis of elemental
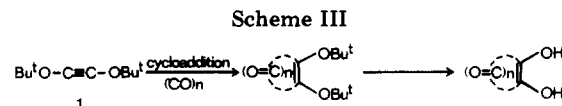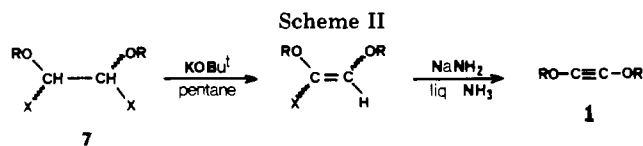
(17) However, as stated by one of the referees, "The question of the aromaticity of the oxocarbon dianions remains open for discussion and needs more work; it is also known that the aromaticity of the modern Kekulé system is still under scrutiny—and all of this makes the field more exciting. [For pertinent, recent work, see E. D. Jemmis and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **104**, 4781 (1982)|".

(18) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Interscience, New York, p 170, 1972.

(19) Reference 2, Chapter 3.

(20) L. Farnell, L. Radom, and M. A. Vincent, *J. Mol. Struct.*, **76**, 1 (1981).

(21) Acetylene diethers may be also considered as "dimers" of alkoxycarbynes [see F. Serratosa, *J. Chem. Educ.*, **50**, 402 (1973)] and we have demonstrated that thermolysis of "anthracene–dimethoxyethyne adducts" leads to methoxycarbynes rather than to dimethoxyethyne [F. Serratosa, P. Solà, L. Vilarrasa, J. Font, and J. Rivera, *Tetrahedron*, **31**, 1315 (1975)].

(22) W. F. Sager, A. Fatiadi, P. C. Parks, D. B. White, and T. Perros, *J. Inorg. Nucl. Chem.*, **25**, 187 (1963).

Scheme II

Scheme III

Table III
$ROC \equiv COR$

OR	ν	$t_{1/2}$, order of magnitude
OCH_3	0.38	seconds, 0 °C, in soln
OC_2H_5	0.48	seconds, 0 °C, in soln
$OCH_2C(CH_3)_3$	0.70	minutes, r.t., in soln
$OCH(CH_3)_2$	0.75	minutes, r.t., in soln
$OC(CH_3)_3$	1.22	days, r.t., neat

and functional-group analyses. However, MINDO/3 calculations[23] on the reactivity of acetylenediolate show that, most probably, the dimer has the structure of a cyclobutanedione (5), arising from a C-methylation, followed by O-methylation (or vice versa), to give methoxymethylketene (4), which would then dimerize. That C-alkylation is the predominant primary reaction is clear from the work by Büchner who isolated α-hydroxycaproic acid (6) by treating potassium acetylenediolate with one molar proportion of butyl bromide[24] (see Scheme I). On the other hand, MINDO/3 calculations also show that the conjugate acid of acetylenediolate is the hydroxyketene, not the acetylenediol.[23]

Nevertheless, acetylene diethers can now be readily prepared[25] from 1,2-dialkoxy-1,2-dihaloethanes (7) by a stepwise, double dehydrohalogenation, first with KOBu-t in pentane solution, followed by $NaNH_2$ in liquid NH_3 (see Scheme II).

Although acetylene diethers are thermodynamically stable compounds, they show a highly kinetic instability that induces polymerization, even at low temperature.[26]

(23) M. A. Pericàs, Ph.D. Thesis. University of Barcelona, 1979.

(24) In spite of the highly discriminating reactivity of trimethylsilyl derivatives vs. enolates, in which O-silylation predominates over C-silylation, the reaction of potassium acetylenediolate with Me_3SiCl did not afford the expected bis(trimethylsiloxy)acetylene (A. Messeguer, Ph.D. Thesis. University of Barcelona, 1974).

(25) 1,2-Dialkoxy-1,2-dihaloethanes are prepared either from glyoxal or 2,3-dichloro-1,4-dioxane (see ref 3).

Scheme IV

Scheme V

Scheme VI

a, X = Y = Cl

"CO" = :C<$_X^Y$> b, X = Cl , Y = F

c, X = Cl , Y = OMe

At present, different acetylene diethers have been prepared[3] by the aforementioned procedure, and their stability correlates well, in a qualitative way, with Charton's ν steric parameters[27] based on effective Van der Waals radii for the corresponding alkoxy groups (Table III).

In accordance with Table III, di-*tert*-butoxyethyne (1, R = Bu-*t*) is the only acetylene diether whose stability has allowed its use as a starting material[28] for the synthesis of oxocarbons.

Oxocarbon Synthesis: General Strategy

Besides its stability, di-*tert*-butoxyethyne offers some structural features that make it the synthon of choice for the synthesis of oxocarbons. As shown in Scheme III, di-*tert*-butoxyethyne could transfer, by pertinent cycloadditions, the protected enediol fragment in such a way that it can be actualized, at the end of the synthesis, by solvolysis under mildly acidic conditions. In this connection, it should be mentioned that the failure of Dehmlow[10] to synthesize deltic acid and deltate dianion may be attributed to the difficulty of hydrolyzing the corresponding diethyl ester at the end of the synthesis (see Scheme IV). West and Eggerding[9] circumvented this inconvenience by using the corresponding bis(trimethylsilyl) ester, which could be cleaved either by solvolysis with 1-butanol or lithium *tert*-butoxide at −78 °C.

Cyclopropanation of Di-*tert*-butoxyethyne: Deltic Acid

According to the general strategy outlined in Scheme III, deltic acid (8) could be synthesized by a [2 + 1] cycloaddition of a "CO-equivalent" to di-*tert*-butoxyethyne (see Scheme V). Dichlorocarbene is the most
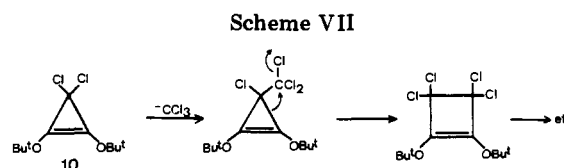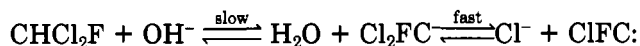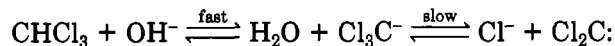
Scheme VII

Scheme VIII

Table IV
Cyclopropanation of Di-*tert*-butoxyethyne

"CO equivalent"	source	yield of deltate, %
dichlorocarbene	CHCl₃/KOBu-*t*	0
dichlorocarbene	CHCl₃/NaOH/H₂O/TEBA	12–26
chlorofluorocarbene	CHCl₂F/KOH/18-crown-6	20–35
chloromethoxy-carbene	3-chloro-3-methoxy-diazirine	40 (not isolated)

familiar "CO-equivalent" synthon and can be generated from CHCl₃ with a base such as KOBu-*t* (see Scheme VI). However, under these conditions, no trace of cyclopropanone derivative could be isolated, probably due to the reaction of the intermediate Cl₃C⁻ anion with the activated allylic chlorine atoms of cyclopropene 10[29] (see Scheme VII). For this reason, the reaction of dichlorocarbene generated under phase-transfer conditions appeared to be the method of choice, because the aqueous medium would immediately hydrolyze the highly reactive 1,2-di-*tert*-butoxy-3,3-dichlorocyclopropene to the corresponding cyclopropenone (9, di-*tert*-butyl deltate) (see Scheme VI).

In actuality, the reaction of di-*tert*-butoxyethyne with CHCl₃ in aqueous NaOH solution in the presence of TEBA gave the expected deltate, which could be isolated, either by column chromatography on alumina or by evaporative distillation under high vacuum, as colorless crystals, mp 80–82 °C, in 12–26% yield. Treatment of the ester with TFA at 6 °C leads in quantitative yield to analytically pure deltic acid (8). Better results were obtained when dichlorofluoromethane was substituted for chloroform, and the reaction was performed with KOH in the presence of 18-crown-6. In this case

$$CHCl_3 + OH^- \overset{fast}{\rightleftharpoons} H_2O + Cl_3C^- \overset{slow}{\rightleftharpoons} Cl^- + Cl_2C:$$

$$CHCl_2F + OH^- \overset{slow}{\rightleftharpoons} H_2O + Cl_2FC^- \overset{fast}{\rightleftharpoons} Cl^- + ClFC:$$

the secondary competing reactions of the Cl₃C⁻ anion were strongly inhibited because the decomposition of Cl₂FC⁻ anion is not now the rate-limiting step.[30] Under these conditions the overall yield of deltic acid increased to 35%.

Another approach to deltic acid involves the cyclopropanation of di-*tert*-butoxyethyne with chloromethoxycarbene,[14a] generated by thermal decomposition of 3-chloro-3-methoxydiazirine.[31] Although the IR and NMR spectra of the crude reaction mixture showed that di-*tert*-butyl deltate was formed in ∼40% yield, no

(26) The reasons for this instability have been studied theoretically by semiempirical SCF MO methods: S. Olivella, M. A. Pericàs, and F. Serratosa, paper presented at ESOC I, Cologne, August 20–22, 1979; *Real Soc. Espñ. Fís. y Quím.*, *XVIII Reunión Bienal*, Burgos, Sept. 29, 1980.

(27) M. Charton, *Prog. Phys. Org. Chem.*, 10, 81 (1973); *J. Org. Chem.*, 43, 3995 (1978).

(28) In the past few years, the synthesis of di-*tert*-butoxyethyne has been optimized by our group, and the overall yield from 2,3-dichloro-1,4-dioxane is 45–50% for quantities of 10–12 g. The procedure is ready for submission to *Organic Syntheses*.

(29) E. V. Dehmlow, *Chem. Ber.*, 100, 3829 (1967).

(30) J. Hine, "Physical Organic Chemistry", 2nd ed., McGraw-Hill-Kõgakusha Co., Ltd. Tokyo, pp 486–488, 1962.

(31) N. P. Smith and I. D. R. Stevens, *Tetrahedron Lett.*, 1931 (1978); R. A. Moss and W. Ch. Shieh, *ibid.*, 1935 (1978).
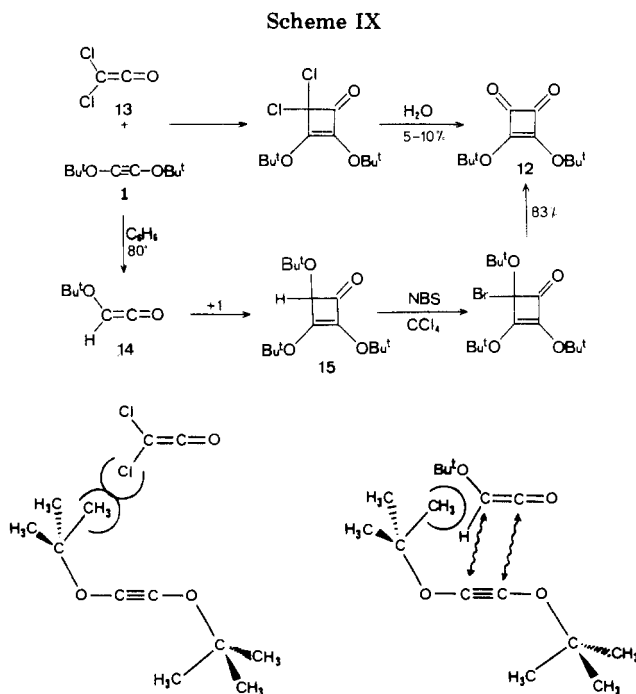
Scheme IX

Figure 1.

Figure 2.

Scheme X

Scheme XI

satisfactory purification method could be found to isolate the pure product from the reaction mixture.[32] The synthesis via chlorofluorocarbene is therefore the best one for the preparation of deltic acid in gram quantities. Table IV summarizes the experimental conditions and the results for the cyclopropanation of di-*tert*-butoxyethyne with different "CO-equivalent" synthons.

[2 + 2] Cycloadditions of Di-*tert*-butoxyethyne: Squaric and Semisquaric Acids. A logical entry to the squaric acid (11) system could be [2 + 2]-cycloaddition of di-*tert*-butoxyethyne with an "ethylenedione equivalent" (see Scheme VIII).[33] Dichloroketene (13), which has been extensively used in [2 + 2] cycloadditions,[34] might be a suitable "ethylenedione equivalent" (see Scheme IX). In actuality, however, we found that it only reacts with di-*tert*-butoxyethyne to give very low yields (5–10%) of di-*tert*-butyl squarate (12), a fact that may be explained on the basis of the high steric hindrance exhibited by the two reagents[35] (see Figure 1). By contrast, monoheterosubstituted ketenes, having a hydrogen atom as one of the substituents, might approach the triple bond in a much more efficient way, to give the corresponding adduct. In fact, the synthesis of squaric acid was much easier and more efficient than expected, *tert*-butoxyketene (14) being the reagent of choice.

Thermal "Dimerization" of Di-tert-butoxyethyne. From the chemistry of acetylene monoethers,[36] it is well-known that derivatives having at least one hydrogen atom at the β-position are thermally unstable, and split off to give an alkene and a ketene that, in turn,

reacts with the parent acetylene, to afford a cyclobutenone (see Figure 2). In a similar way, di-*tert*-butoxyethyne in boiling benzene gave 2,3,4-tri-*tert*-butoxycyclobutenone (15) in quantitative yield. Oxidation with NBS in CCl₄ gives di-*tert*-butyl squarate (12), mp 104–105 °C, in 83% yield, from which the free acid can be obtained in quantitative yield by solvolysis with TFA (see Scheme IX).

On the other hand, 3-hydroxycyclobutene-1,2-dione (16) (semisquaric acid), the parent compound of the natural mycotoxin "moniliformin" (isolated either from *Fusarium moniliform* or *Gibberella fujikuroi*),[37,38] has also been synthesized from 2,3,4-tri-*tert*-butoxycyclo-

(32) No preparative HPLC, which is probably the method of choice, was available to us at the time we did the work.

(33) Cf. D. Belluš, ref 2, Chapter 9.

(34) I. Fleming, "Frontier Orbitals and Organic Chemical Reactions", Wiley, New York, p 143, 1976 and references cited therein.

(35) The same steric effect explains the great stability of di-*tert*-butoxyethyne towards polymerization.

(36) L. Bradsma, H. J. T. Bos, and J. F. Arens, in "Chemistry of Acetylenes", H. G. Viehe, Ed., Marcel Dekker, New York, pp 808–809, 1969 and references cited therein.
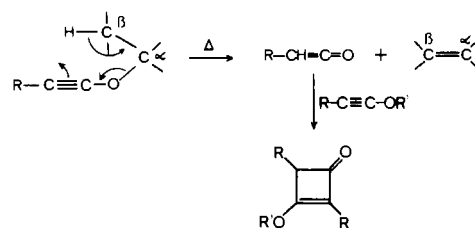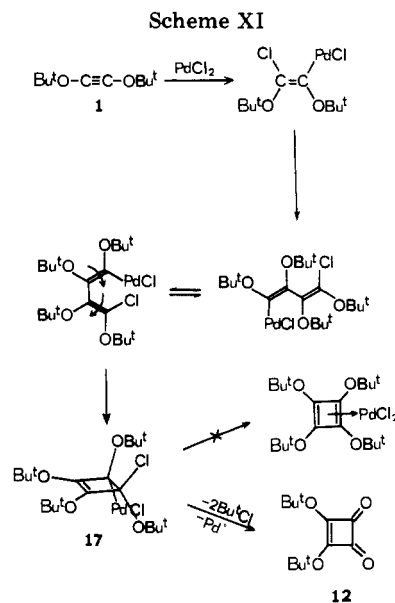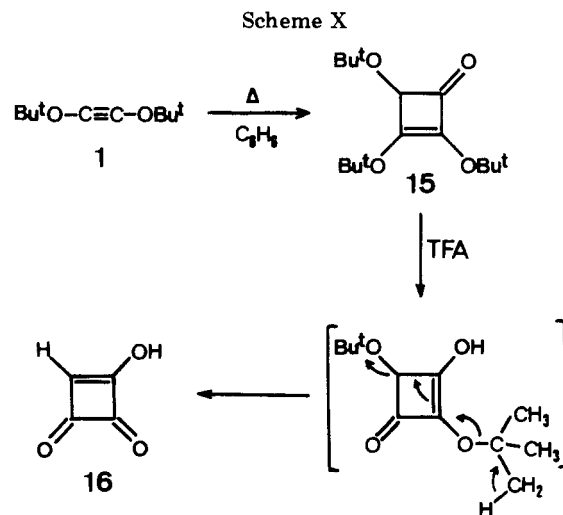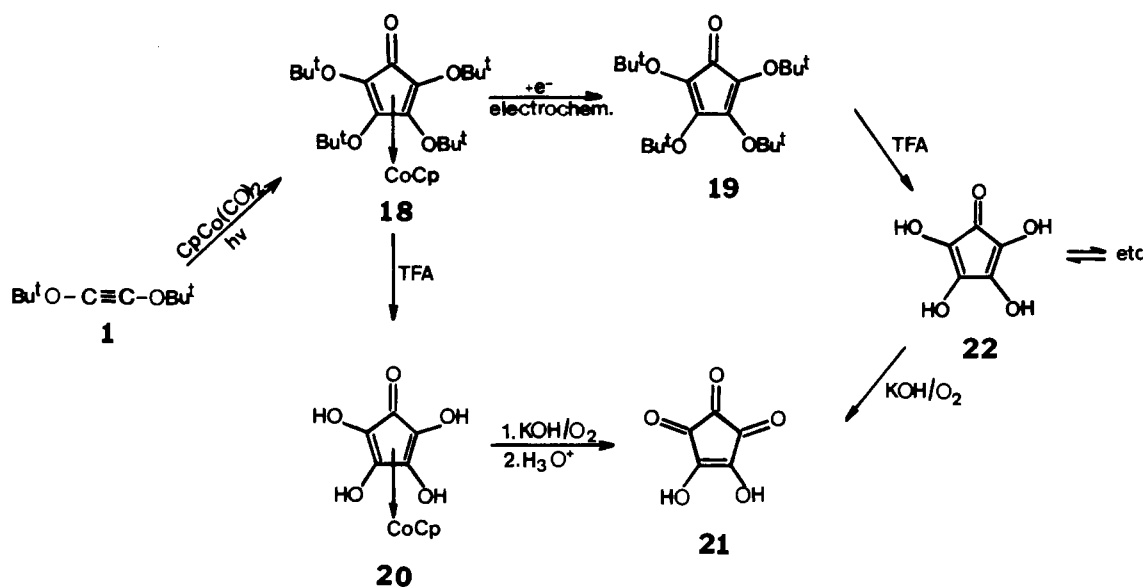
(37) R. J. Cole, J. W. Kirksey, H. G. Cutler, B. L. Doupnik, and J. C. Peckham, *Science (Washington D.C.)*, **179**, 1324 (1973).

(38) H.-D. Scharf and H. Frauenrath, ref 2, pp 101–119.

Scheme XII

butenone (15). In fact, both compounds have the same oxidation level so that a single deprotection/elimination process on 15 was expected to lead to 16. In actuality, solvolysis of 15 with TFA in pentane solution at 6 °C for 18 h afforded, in one step, the semisquaric acid (16) in quantitative yield, as white crystals, mp 163 °C (dec.)[39] (see Scheme X).

Palladium-Induced Dimerization of Di-tert-butoxyethyne. Another entry from di-*tert*-butoxyethyne, to the squaric acid system, came from the analysis of Maitlis's mechanism for palladium-induced cyclodimerization of alkynes.[40] The possibility of an intramolecular *t*-BuCl elimination in the postulated intermediate 17 (see Scheme XI) could cause the ordinary course of the reaction to deviate in an oxidative way, as depicted in Scheme XI. Accordingly, when a solution of di-*tert*-butoxyethyne in CH_2Cl_2 was treated with $PdCl_2$–CH_3CN complex for 3 h under reflux, the formation of di-*tert*-butyl squarate (12) was observed. However, probably owing to slow Pd^0 elimination in the latter stage of the process, purification of the di-*tert*-butyl ester was rather difficult. The problem was finally circumvented by treatment of the crude reaction mixture with TFA for 2 h under reflux, the free acid 11 being isolated in 52% overall yield from 1.

Photochemical, Cobalt-Induced Dimerization–CO Insertion of Di-*tert*-butoxyethyne: Croconic and Hydrocroconic Acids. The interaction of cobalt carbonyl complexes with alkynes gives a large number of products depending on the experimental conditions and on the nature of the acetylene derivatives involved. Although cyclic dimers and trimers (see next section) are the usual products, Markby et al.[41] were the first to report the formation of substituted cyclopentadienone complexes from the reaction of (η-cyclopentadienyl)dicarbonylcobalt with either dimethyl- or

diphenylacetylene in sun-light. Later, Lee and Brintzinger[42] demonstrated that the primary photochemical reaction involves the formation of the mixed mononuclear species $(C_5H_5)Co(CO)(RC\equiv CR)$, which is then thermally converted either into the cyclobutadiene or into the cyclopentadienone complex, depending on the partial pressure of CO in the reaction system.

We have found that low-temperature irradiation of di-*tert*-butoxyethyne in the presence of $(C_5H_5)Co(CO)_2$ affords, in 58% yield, (η-tetra-*tert*-butoxycyclopentadienone)(η-cyclopentadienyl)cobalt (18) as orange crystals, mp 152–153 °C, which appears to be a suitable starting material for a direct synthesis of croconic (21) and hydrocroconic acid (22). However, all efforts that we have made to liberate tetra-*tert*-butoxycyclopentadienone (19) from the complex by standard methods[43] were unsuccessful. Accordingly, an alternative route to croconic acid was devised.

Treatment of the complex 18 with TFA for 2 h at room temperature afforded, in quantitative yield, (η-tetrahydroxycyclopentadienone)(η-cyclopentadienyl)-cobalt[44] (20), which was converted into croconate by oxygen oxidation in basic medium. Croconic acid (21) was characterized as the corresponding dimethyl ester by precipitation of the silver salt and methylation with methyl iodide: orange crystals, mp 109–110 °C; UV max (MeOH) 294 nm (cf. ref 45) (see Scheme XII).

More recently, demetallation of complex 18 has been successfully accomplished by electrochemical means, working with Pt electrodes in a four-compartment cell separated by sintered glass disks, and using TBAP (0.05 M) as the supporting electrolyte.[46] Tetra-*tert*-butoxycyclopentadienone (19) was isolated in ~80% yield

(39) Cf. J. P. Springer, J. Clardy, R. J. Cole, J. W. Kirksey, R. K. Hill, R. M. Carlson, and J. L. Isidor, *J. Am. Chem. Soc.*, **96**, 2267 (1974); H.-D. Scharf, H. Frauenrath, and W. Pinske, *Chem. Ber.*, **111**, 168 (1978); D. Belluš, P. Martin, H. Sauter, and T. Winkler, *Helv. Chim. Acta*, **63**, 1130 (1980); W. T. Brady and K. Saidi, *J. Org. Chem.*, **45**, 727 (1980); W. T. Brady and R. D. Watts, *ibid.*, **45**, 3525 (1980); R. W. Hoffmann, U. Bressel, J. Gehlhaus, and H. Häuser, *Chem. Ber.*, **104**, 873 (1971).

(40) P. M. Maitlis, *Acc. Chem. Res.*, **9**, 93 (1976).

(41) R. Markby, H. W. Sternberg, and I. Wender, *Chem. Ind. (London)*, 1381 (1959).

(42) W. S. Lee and H. H. Brintzinger, *J. Organometal. Chem.*, **127**, 93 (1977).

(43) E. D. Sternberg and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, **102**, 4839 (1980); Ch.-A. Chang, J. A. King, Jr., and K. P. C. Vollhardt, *J. Chem. Soc., Chem. Commun.*, 53 (1981).

(44) Notice that complex 20 is a stabilized form of the enolic tautomer of hydrocroconic acid (22). For stabilization of enols as transition-metal complexes, see, for example, C. H. DePuy, R. N. Greene, and T. E. Schroer, *J. Chem. Soc., Chem. Commun.*, 1225 (1968).

(45) J. P. Phillips and F. C. Nachod, "Organic Electronic Spectral Data", Interscience, New York, Vol. IV, p 109, 1958–1959.

(46) A. Bou, M. A. Pericàs, and F. Serratosa, *Tetrahedron Lett.*, 361 (1982); A. Bou, M. A. Pericàs, F. Serratosa, J. Claret, J. M. Feliu, and C. Muller, *J. Chem. Soc., Chem. Commun.* 1305 (1982).
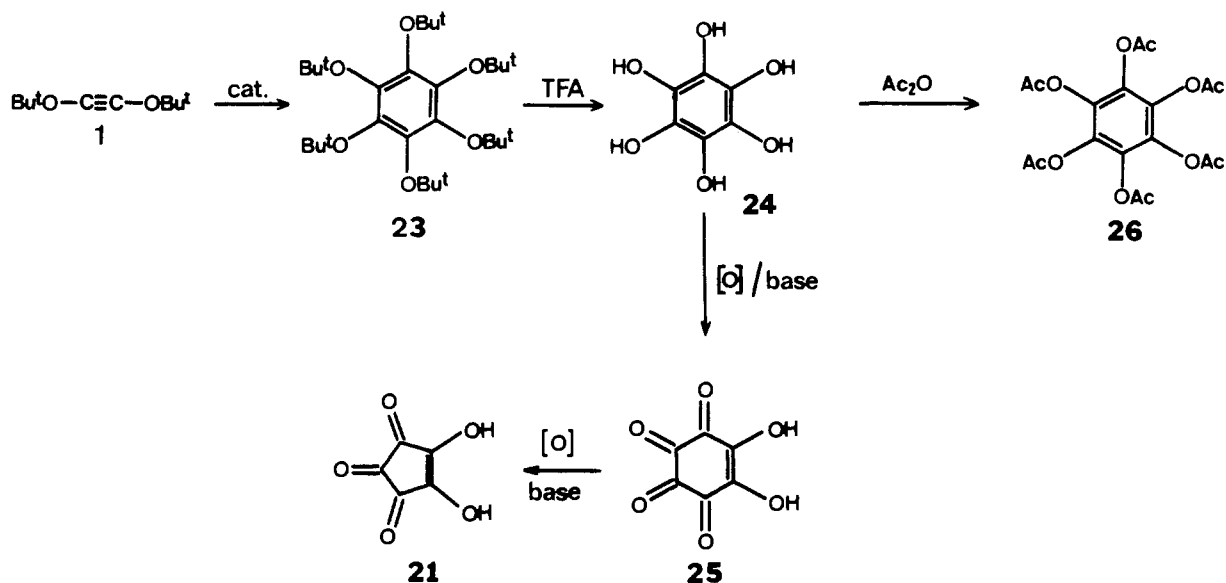
Scheme XIII

Table V
Cyclotrimerization of Disubstituted
Acetylenes with Metal Carbonyls[49]

RC≡CR,R	metal carbonyl	temp, °C	yields of hexa-substituted benzene, %
Ph	Co₂(CO)₈	280	60
Ph	Ni(CO)₄	260	5
OBu-*t*	Co₂(CO)₈	rt	5
OBu-*t*	Ni(CO)₄	rt	60

as an orange-red, crystalline compound, mp 44 °C, UV max (pentane) 234 and 455 nm. Treatment of the cyclopentadienone 19 with TFA afforded in 89% yield the so-called hydrocroconic acid (22), UV max (dioxane) 227 and 288 nm; (H₂O) 250 and 337 nm, which was readily oxidized to croconic acid (21) in alkaline medium (UV max (0.1 N NaOH) 364 nm).[47]

It is worthwhile to emphasize here that the reported syntheses of croconic and hydrocroconic acids are the first, direct syntheses of these cyclopentanoid systems reported so far because, until now, they were only accessible by ring contraction of the 6-membered ring of the rhodizonate system.

Cobalt- and Nickel-Induced Cyclotrimerization of Di-*tert*-butoxyethyne: Rhodizonic Acid. Di-*tert*-butoxyethyne, like other acetylene diethers, reacts in pentane solution at room temperature with an excess of Co₂(CO)₈, to give the corresponding hexacarbonyldicobalt complex, mp 58–59 °C, in 35% yield.[3] However, in the presence of catalytic amounts of Co₂(CO)₈, cyclotrimerization takes place,[48] and hexa-*tert*-butoxy-

benzene (23), mp 223–224 °C, can be isolated in ~5% yield.

Although it has been reported that Ni(CO)₄ is a poorer catalyst for the cyclotrimerization of diphenylacetylene[49] than Co₂(CO)₈ (Table V), in the case of di-*tert*-butoxyethyne, the situation is reversed, and Ni(CO)₄ gave hexa-*tert*-butoxybenzene (23) in yields as high as 60%.

Acid solvolysis of hexa-*tert*-butoxybenzene (23) with TFA under reflux for 3.5 h afforded hexahydroxybenzene (24) in quantitative yield, which is, according to the classical work of Nietzki,[50] the precursor of rhodizonic (25) and croconic acid (21).[51] Hexahydroxybenzene (24) was characterized as the corresponding hexaacetate (26), mp[52] 220–221 °C (see Scheme XIII).

Concluding Remarks

The uniqueness of di-*tert*-butoxyethyne for the synthesis of oxocarbons has been shown; it has no equal in transferring the protected *enediol* fragment in such a way that it can be actualized at the end of the synthesis under mildly acidic conditions. Starting from di-*tert*-butoxyethyne, which may be regarded as the di-*tert*-butyl ester of the first member of the aromatic oxocarbon series, successful syntheses of deltic, squaric, semisquaric, croconic, hydrocroconic and rhodizonic acids have been achieved.

(47) R. Nietzki and T. Benckinser, *Chem. Ber.*, **19**, 293 (1886); J. M. Carpentier, *Bull. Soc. Chim. France*, 2209 (1973) and references cited therein.

(48) Cyclotrimerization of acetylenes is a stepwise process and different mechanisms are probably operating: see J. P. Collman and L. S. Hegedus, "Principles and Applications of Organotransition Metal Chemistry", University Science Books, Mill Valley, California, pp 525–527, 640–649, 1980.

(49) N. Huebel and C. Hoogzand, *Chem. Ber.*, **93**, 103 (1960).

(50) R. Nietzki and T. Benckinser, *Chem. Ber.*, **18**, 499 (1885); **19**, 293 (1886).

(51) See also, K. Yamada and Y. Hirata, *Bull. Chem. Soc. Jpn.*, **31**, 551 (1958); B. Homolka, *Chem. Ber.*, **54**, 1393 (1921).

(52) H. J. Backen and S. Van der Baan, *Recl. Trav. Chim. Pays-Bas*, **56**, 1161 (1937).