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Review

Acetylenes and diazoketones in organic synthesis

Can a synthetic organic chemist avoid organometallic chemistry? *

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Abstract

The syntheses of patulin-oxime, oxocarbons, cyclopropanes, γ -tropolone, bullvalene, semibullvalene, and triquinacene from either acetylenes or diazoketones, all of which proceed through organotransition metal complexes of Ag^I, Co⁰, Co^I, Cu^{II}, Fe⁰, Ni⁰ and Pd^{II}, are reviewed from the point of view of organometallic chemistry.

Introduction

As an organic chemist trained in the first half of this century, to me the only really familiar element is carbon, which certainly occupies a unique position in the Periodic Table. However, I have always wondered how some of my colleagues can move so easily along the Periodic Table and become expert organometallic chemists and yet, at the end of my official career, I realise that most of the syntheses that I have carried out have involved the intermediacy of organotransition metal complexes.

Although the transition metal elements are often defined as those that have partly filled *d* or *f* shells, in this account I adopt the broader definition suggested by Cotton and Wilkinson [1] that includes also elements that in their compounds have partly filled *d* or *f* shells, such as Ag, Cu and Au, including Ag^I.

The starting materials for the syntheses described in this review are acetylenes and α -diazoketones, which are highly reactive compounds and can readily form organometallic species, whether as stable compounds or as transient species.

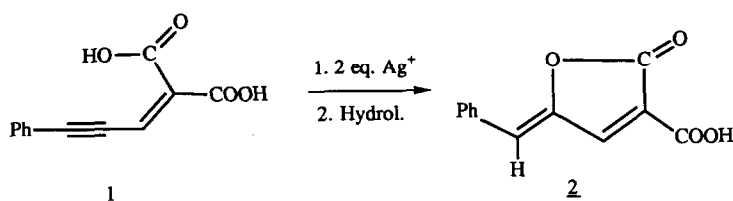
* Dedicated to Professor P.L. Pauson on the occasion of his retirement.

a. Acetylenes

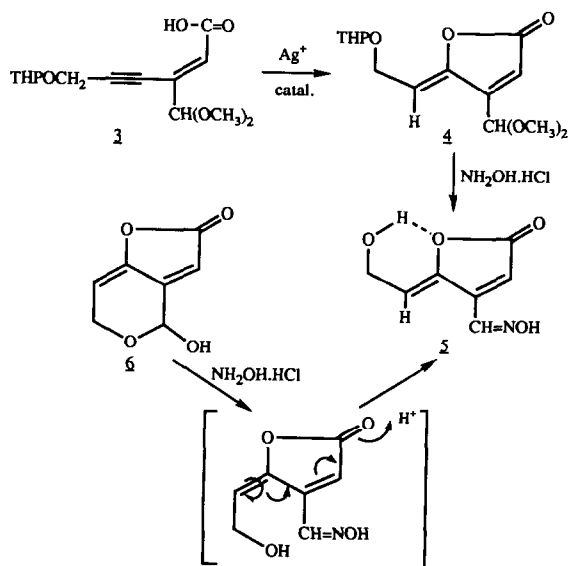
1. Propargyldenacetic acids; patulin-oxime

In 1958, Pascual and his coworkers [2] reported that attempts to prepare the silver salt of phenylpropargyldenemalonic acid (**1**) led to butenolide **2** (Scheme 1). We thus assumed that the key step of our planned synthesis of patulin (Scheme 2), which involves the cyclisation of a propargyldenacetic acid **3** to the derivative **4** of the hypothetical *trans*-patulin, would take place readily in the presence of catalytic amounts of silver(I) ion.

In practice [3], we found that the addition of two drops of 4% aqueous AgNO_3 to a methanolic solution of **3** gave rise to a highly exothermic reaction that yielded the expected compound **4** in 80% yield (almost a quantitative yield when account is taken of the fact that compound **3** is a 9:1 mixture of *E* and *Z* isomers and only the *E* isomer, in which the triple bond and the carboxyl group are in a *cis*-configuration, can undergo cyclisation). The resulting cyclisation product **4** was treated with $\text{NH}_2\text{OH} \cdot \text{HCl}$ to give an oxime **5** identical in all respects with a sample of oxime from natural patulin, **6**. The catalytic effect of silver(I) ion can be assumed to



Scheme 1



Scheme 2

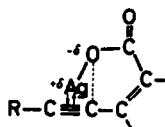


Fig. 1. Catalytic and directing effect of silver(I) ion on the intramolecular cyclisation of *cis*-propargylidenacetic acids to butenolides.

be due to its ability to bring the carboxyl group, to which it is electrostatically bound, very close to the triple bond with which it can form a coordination complex (Fig. 1).

In terms of the Chatt–Dewar–Duncanson model [4] for the ethyne-transition metal coordination complex (in the triple bond there are two π -orbitals (π_x and π_y) and the corresponding π^* -antibonding orbitals, which are arbitrarily oriented but always orthogonal to each other) the overlap between Ag^+ and the triple bond is always optimum whatever the direction of the attack of silver(I) ion to the triple bond (Fig. 2). This would account for the catalytic ability of silver (I) ion in this type of reaction, as well as for the observed directing effect, which favors formation of butenolides rather than α -pyrones [5].

2. Dialkoxyethynes; oxocarbons

Although monoalkoxyacetylenes had been extensively studied [6] at the time my coworkers and I undertook our work on acetylene ethers, almost nothing was known about dialkoxyacetylenes (**9**). However, dialkoxyacetylenes appeared to be the starting material of choice for the synthesis of deltic acid and, eventually, for all other members of the oxocarbon series.

For the synthesis of dialkoxyacetylenes two different approaches were explored: (i) the thermal extrusion of barrelenes [7], and (ii) the double dehydrohalogenation of 1,2-dihalo-1,2-dialkoxyethanes **7** [8]. Only the second approach gave the desired results.

The first direct evidence that dimethoxyethyne was formed when an ether solution of (*Z*)-1-chloro-2-methoxyethene (**8**, $\text{R} = \text{CH}_3$, $\text{X} = \text{Cl}$, prepared from 1,2-dichloro-1,2-dimethoxyethane (**7**) by dehydrochlorination with KO^tBu) was treated with NaNH_2 in liquid NH_3 , was obtained by NMR spectroscopy at -45°C [9]. This compound, as well as its higher homologs, showed a highly kinetic instability that leads to polymerisation even at 0°C . However, dimethoxyethyne (**9**, $\text{R} = \text{CH}_3$) was trapped as the corresponding hexacarbonyldicobalt complex **10**, m.p. $62\text{--}63^\circ\text{C}$ (Scheme 3).

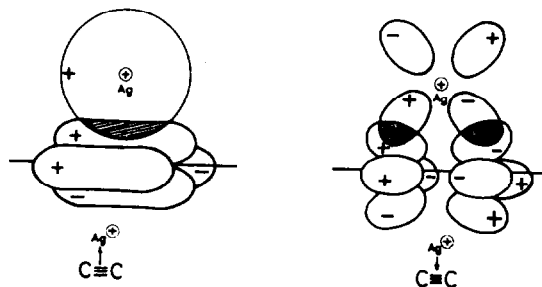
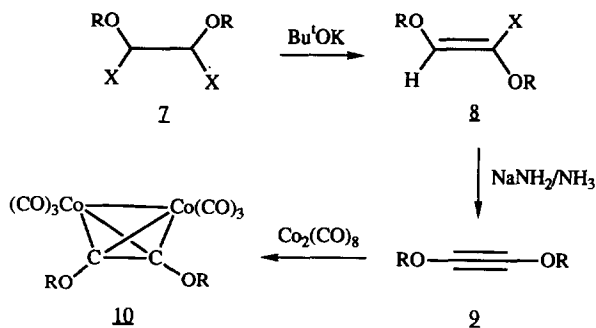


Fig. 2. The Chatt–Dewar–Duncanson model for the ethyne-silver(I) ion coordination complex.



Scheme 3

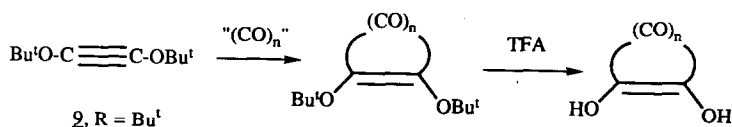
Later on, various acetylene diethers derived from secondary and tertiary alcohols were prepared by a modification of the above procedure [8] and their stabilities found to correlate qualitatively with Charton's ν steric parameters based on effective Van der Waals radii for the corresponding alkoxy groups [10]. In practice, di-tert-butoxyethyne is the only acetylene diether whose stability allowed it to be handled at room temperature.

Besides its stability, di-tert-butoxyethyne (**9**, R = ^tBu) offers some structural features that make it the synthon of choice for the synthesis of all the members of oxocarbons [11]. As shown in Scheme 4, di-tert-butoxyethyne can, by appropriate cycloadditions, transfer the protected endiol fragment in such a way that it can be liberated at the end of the synthesis by solvolysis under mildly acidic conditions.

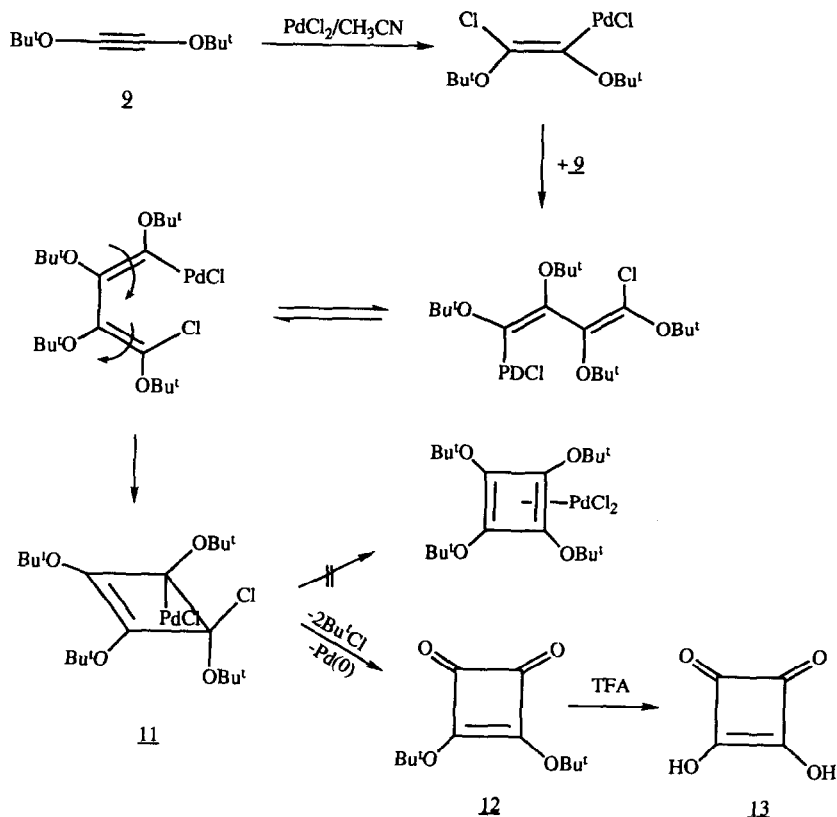
Although deltic acid could be synthesised by this general strategy, the intermediate "CO-equivalents" (dichloro-, chlorofluoro- or chloromethylcarbene) [11b] were not organotransition metal species. The higher members of the series were, however, synthesised through organotransition metal intermediates, involving Pd^{II}, Co⁰, Co^I, Ni⁰ and Fe⁰ species.

(i) *Squaric acid*: One of the procedures leading to squaric acid involved dimerisation of di-tert-butoxyethyne induced by the PdCl₂/CH₃CN complex. In terms of Maitlis's mechanism for the dimerisation of acetylenes [12], the probable sequence of reactions is shown in Scheme 5 [11b]. Since the elimination of Pd⁰, involved in the oxidation step (**11** → **12**), makes the purification of the product mixture rather difficult, the route to squaric acid (**13**) by thermal dimerisation of di-tert-butoxyethyne, followed by oxidation with NBS [11b], provides a far superior procedure.

(ii) *Croconic and hydrocroconic acids*: These were synthesised by photochemical dimerisation–Co insertion of di-tert-butoxyethyne induced by (η -cyclopentadienyl) dicarbonylcobalt [11b,13], which gave a 58% yield of (η -tetra-tert-butoxycyclopentadienone)(η -cyclopentadienyl)cobalt (**14**, ML_n = CoCp) as orange crystals, m.p. 152–153°C, or much better, by treatment of the acetylene diether with Fe₂(CO)₉ at



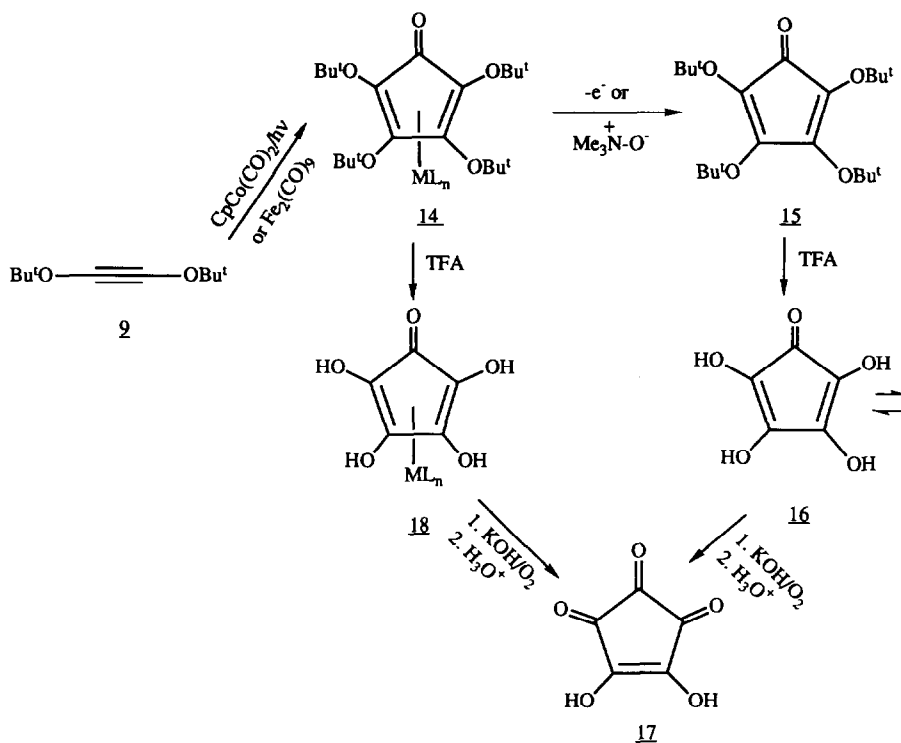
Scheme 4



Scheme 5

room temperature [14], which gave a 77% yield of (tetra-tert-butoxycyclopentadienone)tricarbonyliron [14, $\text{ML}_n = \text{Fe}(\text{CO})_3$] as orange-yellow crystals, m.p. 130°C , the structure of which was confirmed by X ray analysis. Whereas the demetallation of the cobalt complex could only be achieved by electrochemical means (80% yield), that of the corresponding iron complex could be brought about by standard procedures (99% yield with trimethylamine oxide). In both cases, tetra-tert-butoxycyclopentadienone (15) was obtained as red crystals, m.p. 44°C , and was converted into hydrocroconic acid and croconate anion as shown in Scheme 6. An alternative route, involving (tetrahydroxycyclopentadienone)tricarbonylmetal(0) complexes (18), which are stabilised forms of the enolic tautomer of hydrocroconic acid, is also shown in Scheme 6. It is noteworthy that the reported syntheses were the first direct syntheses of these cyclopentanoid systems reported because previously they were only accessible through ring contraction of the 6-membered ring of the rhodizonate system [15].

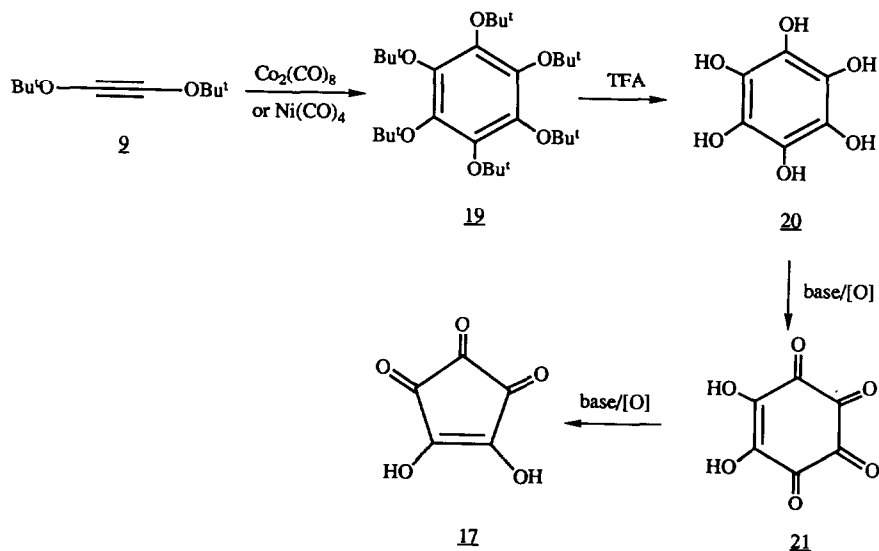
(iii) *Rhodizonic acid*: Di-tert-butoxyethyne reacts, like dimethoxyethyne and its higher homologs (see above), in pentane solution at room temperature with an excess of $\text{Co}_2(\text{CO})_8$ to give the corresponding hexacarbonyldicobalt complex, m.p. $58\text{--}59^\circ\text{C}$. However, in the presence of catalytic amounts of octacarbonyldicobalt cyclotrimerisation takes place and hexa-tert-butoxybenzene (19), m.p. $223\text{--}224^\circ\text{C}$,



Scheme 6

was isolated in a rather poor yield (5%) [11b]. The yield was substantially improved to 60% when $\text{Ni}(\text{CO})_4$ was substituted for $\text{Co}_2(\text{CO})_8$ [16].

Acid solvolysis of hexa-tert-butoxybenzene with TFA under reflux for 3.5 h



Scheme 7

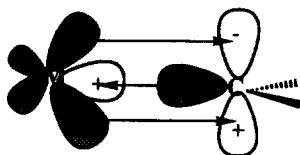


Fig. 3. HOMO-LUMO interactions showing the bonding and back-bonding of complexes of carbene species with transition metals (cf. Fig. 2).

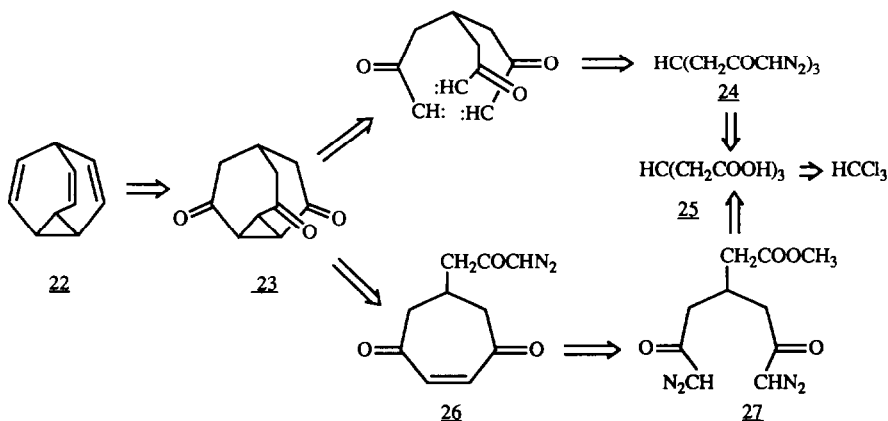
afforded a quantitative yield of hexahydroxybenzene (**20**), which is, as shown by the classic work of Nietzki [15], the precursor of rhodizonic (**21**) and croconic acid (**17**) (see Scheme 7).

b. α -Diazoketones

The view that the transient intermediates from the catalytic decomposition of α -diazoketones induced by transition metals are carbene-metal complexes is supported by recent studies [17]. In view of the stereospecificity observed in their reactions they must be electrophilic, stabilised species in the singlet state. In terms of molecular orbitals the carbene-metal complexes can be represented in the same way as the acetylenic triple bond-metal complexes (see above), in which there is also stabilising back-bonding from the highest occupied orbital of the metal to the unoccupied π -orbital of the carbene (Fig. 3).

The first catalysts used in the decomposition of α -diazoketones were copper-bronze and copper(II) sulphate. Latter on, soluble chelates such as $\text{Cu}(\text{acac})_2$ or $\text{CuCl} \cdot \text{P}(\text{OR})_3$ were used, and nowadays the most used catalysts are rhodium acetate [18], copper(II) triflate [19], and palladium acetate [20].

The starting point of our work on α -diazoketones was a new synthesis of bullvalene (**22**) (an unusual fluxional molecule that undergoes pandegeneration [21,22]), which could be expected to involve very few steps from methane(tri- α -diazooacetone), as shown in Scheme 8 (or, alternatively, from the closely related bis- α -diazoketone **27**). Methane(tri- α -diazooacetone) (**24**) had been previously described by Stetter [23], and it can be reduced retrosynthetically to chloroform. The



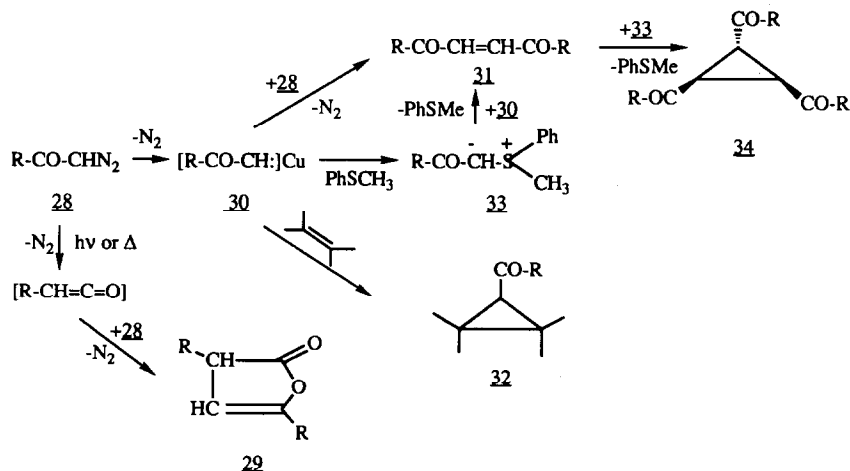
Scheme 8

presence of a C_3 axis of symmetry, which would be preserved all along the synthetic sequence, would confer a great simplicity and intrinsic elegance on the synthesis. However, the need to use some special techniques, such as high dilution, in the cyclisation step, and only moderate-to-low yields could be expected owing to the fact that all the synthetic intermediates require modification of three identical functional groups.

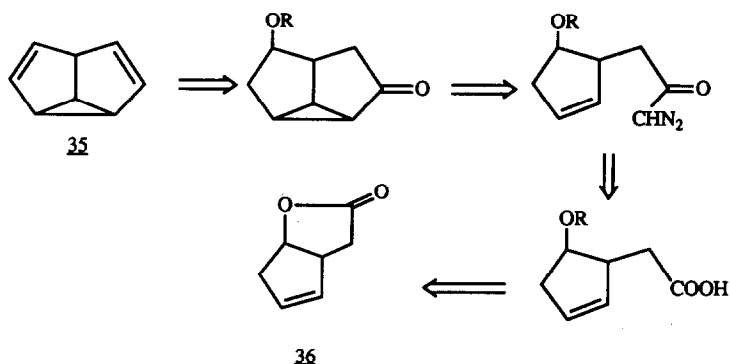
The idea behind our synthetic approach was that the cyclisation step leading to the cyclopropane ring of bullvalene would take place very easily since, according to some reviews [24], "purely thermal decomposition of diazoketones leads to cyclopropane derivatives; in the presence of copper compounds symmetrical diacylethylenes are formed". However, we could not find any experimental evidence confirming cyclopropane formation in purely thermal decomposition of diazoketones. Only a few references [25] could be found in the chemical literature reporting such a formal trimerisation of "ketocarbenes", and the yields given were not higher than 1.4%. Since we found that butenolides (**29**) rather than cyclopropanes are the predominant products from purely thermal decomposition of diazoketones [24], prior to our planned synthesis of bullvalene, an exhaustive study on the decomposition of mono- α -diazoketones and bis- α -diazoketones, under a variety of conditions, was undertaken in order to determine the optimal conditions for the formation of 3- and 7-membered rings respectively, which are the ones present in the bullvalene molecule. Diazomethyl-tert-butylketone (**28**, R = t Bu) and 1,7-bisdiazoheptane-2,6-dione (**37**, $n = 3$) were used as the appropriate models for our studies.

1. Mono- α -diazoketones; triacylcyclopropanes; semibullvalene

In agreement with previous reports [25a,26] we found that copper(II) acetylacetonate-induced decomposition of diazomethyl-tert-butylketone (**28**, R = t Bu) in benzene solution, at room temperature, gave an 85% yield of a 3 : 1 mixture of *trans*- and *cis*-1,2-dipivaloyl ethylene (**31**, R = t Bu) (Scheme 9) [27]. Although the *cis*-isomer readily isomerises to the more stable *trans*-isomer, it could be characterised by NMR spectroscopy since the olefinic protons appear at δ 6.7 instead of the δ 7.4



Scheme 9



Scheme 10

observed for the *trans*-isomer. In the presence of copper-bronze or copper(II) sulphate decomposition took place in boiling benzene, and the *trans*-isomer was the only reaction product, isolated in 80% yield.

The copper-induced decomposition of diazomethyl-*tert*-butylketone in the presence of 2,3-dimethyl-2-butene leads to 1,1,2,2-tetramethyl-3-pivaloylcyclopropane (**32**) in 43% yield, together with 57% yield of the dipivaloylethylene. However, the intramolecular cyclopropanation of double bonds proceeds to give very high yields, as shown by Stork and Ficini [28], an observation that provided us with a direct route to the semibullvalene tricyclic structure (**35**) from lactone **36** (Scheme 10) [29]. On the other hand, when diazomethyl-*tert*-butylketone was decomposed under nitrogen in the presence of either copper-bronze or copper(II) sulphate in thioanisole solution at 70 °C, *trans*-1,2,3-tripivaloylcyclopropane (**34**, R = *t*Bu) was formed in high yield (80–90%) (Scheme 9).

The results obtained from these preliminary experiments demonstrated that the nature of the products formed in the decomposition of diazoketones depends upon the relative nucleophilicities of the species present in the reaction mixture, as well as on the reaction conditions. In inert solvents, the catalytic decomposition of diazoketones gives a ketocarbene-copper(II) complex (Fig. 3), which is intercepted by the unreacted nucleophilic diazoketone to give an intermediate betaine, nitrogen being then lost to yield 1,2-diacylethylene (formally a “dimer”). In the presence of a nucleophilic olefin, a competitive reaction of the electrophilic ketocarbene-copper complex takes place, and a cyclopropylketone, together with the dimer, is formed. In intramolecular reactions, the reaction with the double bond is highly favoured and the cyclopropane derivative is practically the only product observed (Scheme 10).

Notice that neither the diazoketone nor the ketocarbene-copper complex react with electrophilic 1,2-diacylethylenes. However, in the presence of thioanisole and copper catalyst, the thioether is a strong enough nucleophile to compete effectively for the ketocarbene-copper complex and a β -ketosulphonium ylid (**33**) is formed *in situ* [27,30]. The sulphonium ylid is a stronger nucleophile, which reacts with the electron-poor double bond of 1,2-diacylethylenes to give, finally, *trans*-1,2,3-triacylcyclopropane (**34**). It is noteworthy that thioanisole acts as an “inversion operator”, in such a manner that the electrophilic ketocarbene-metal complex becomes temporarily a nucleophilic species, such as a sulphonium ylid. Moreover,

the whole process involves, starting from the weak nucleophilic diazoketone, a "double reactivity inversion".

2. Bis- α -diazoketones; cycloalk-2-ene-1,4-diones; γ -tropolone

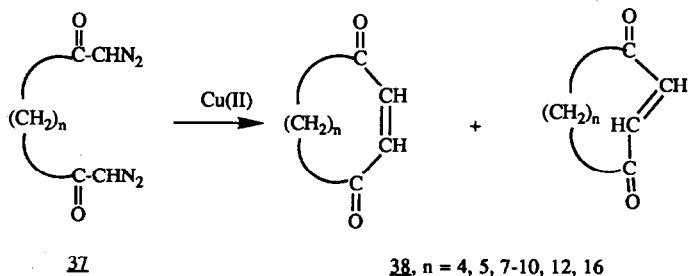
Under the conditions in which mono- α -diazoketones give *trans*-1,2-diacylethylenes, bis- α -diazoketones could be expected to give cycloalk-2-ene-1,4-diones by an intramolecular cyclisation. In terms of ring strain and of the possibility of enolisation–aromatisation of the resulting cycloalk-2-ene-1,4-diones to hydroxy derivatives, which would interfere with the cyclisation, bis- α -diazoketones derived from glutaric acid and the higher homologs (**37**, $n > 3$) appeared to be the most suitable (Scheme 11). Whereas we studied the cyclisation leading to seven-membered rings [31], which are the rings present in the bullvalene molecule, Kulkowit and McKervery [32] applied the procedure to the synthesis of some medium- and large-ring cycloalk-2-ene-1,4-diones as mixtures of *cis* and *trans* isomers (**38**, $n = 4, 5, 7-10, 12, 16$).

The decomposition of 1,7-bis-diazoheptane-2,6-dione (**37**, $n = 3$) in boiling toluene with a soluble copper catalyst, under Ruggli–Ziegler high dilution conditions, afforded 32.5% of cyclohept-2-ene-1,4-dione (**38**, $n = 3$). The cyclisation of the corresponding 4-chloro derivative (**39**, R = Cl) in benzene led to 6-chloro-cyclohept-2-ene-1,4-dione (**40**, R = Cl), which is only moderately stable but was isolated in about 15% yield by column chromatography on silica gel. Elimination of HCl either spontaneously, induced by careful concentration of the benzene eluates *in vacuo*, or promoted by weak bases (Et₃N), gives 4-hydroxytropone (**41**) (γ -tropolone) in 70–75% yield. The conditions for the former procedure are very critical, otherwise complex mixtures of hydroxy and aromatic aldehydes are formed.

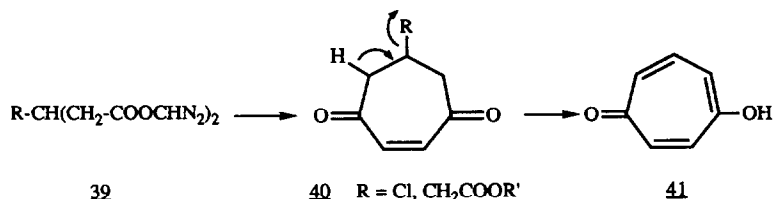
On the other hand, the cyclisation of 4-methoxycarbonylmethyl-1,7-bis-diazoheptane-2,6-dione (**39**, R = CH₂COOCH₃) (prepared from the 3-carboxymethylglutaric anhydride) gives 6-methoxycarbonylmethyl-cyclohept-2-ene-1,4-dione (**40**, R = CH₂COOCH₃) in 26.6% yield, and this in alkali medium easily undergoes elimination of the acetic acid side chain to give 4-hydroxytropone once again (Scheme 12) [31b].

3. Tris- α -diazoketones; bullvalene

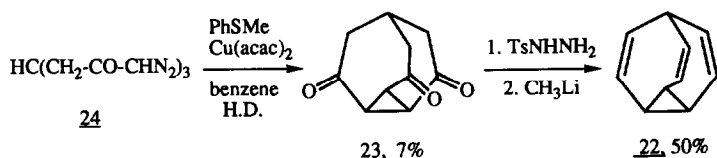
The decomposition of methane(tris- α -diazoacetone) (**24**) in benzene solution in the presence of a soluble copper(II) catalyst and thioanisole under the high dilution conditions should give the triketone **23**, which has the basic tricyclic structure of bullvalene. In practice [33], the high dilution was achieved by slow dropwise



Scheme 11



Scheme 12



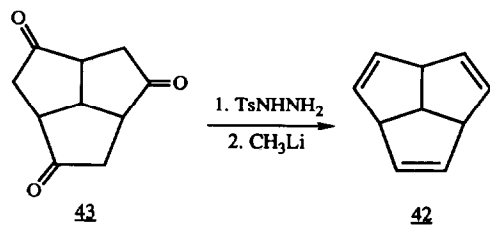
Scheme 13

addition, by use of a peristaltic pump (Variperpex LKB, Model 12000) adjusted at 4 ml/h, of a $10 \times 10^{-3} M$ solution of tris- α -diazoketone in benzene to a vigorously stirred, boiling solution of copper(II) acetylacetonate containing thioanisole. Under these conditions, the yield of pure isolated triketone **23** was 7%, which was quite satisfactory and allowed the preparation of ca. 150 mg of bullvalene-trione (**23**) from each batch, using a standard 2 litre, three-necked, round-bottomed flask. Bullvalene-trione (**23**) was converted into bullvalene (**22**) in 51% yield via tritosylhydrazine [34] (Scheme 13).

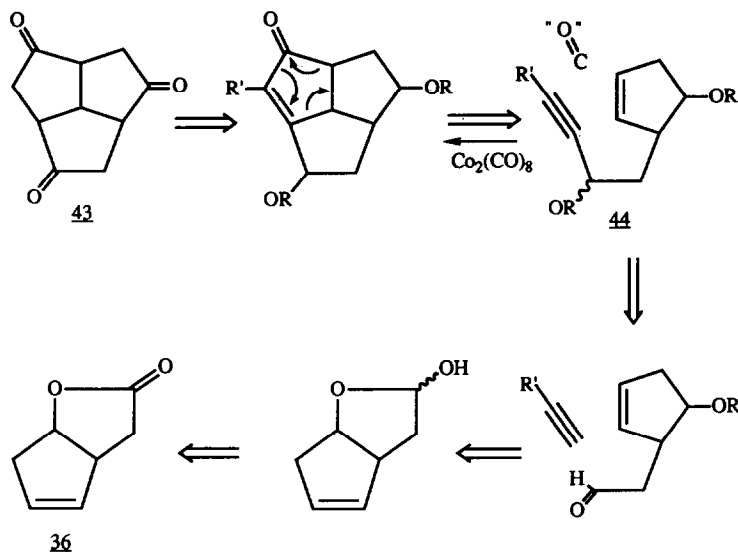
c. Intramolecular Pauson–Khand bis-annulation; triquinacene

Triquinacene (**42**), like bullvalene (**22**), belongs to the $C_{10}H_{10}$ class of polycyclic hydrocarbons, a group of theoretically important compounds that have been exhaustively investigated in the last 25 years. Triquinacene may be regarded as a homoaromatic neutral molecule [35] as well as the building block for a convergent synthesis of dodecahedrane [36].

After our successful synthesis of bullvalene an obvious synthetic objective was the synthesis of triquinacene, following a similar sequence of reactions (Scheme 14), in which the key intermediate would be the perhydrotriquinacene-1,4,7-trione (**43**). In the meantime, a rational synthetic analysis of dodecahedrane let us to realise that the racemic form of perhydrotriquinacene-1,4,7-trione (**43**) would be the ideal synthon for the long-sought convergent synthesis of this highly symmetrical mole-



Scheme 14



Scheme 15

cule [37]. With this new synthetic objective in mind, various syntheses of the triketone **43** were developed. However, since most of the routes started either from triquinacene itself, or from some of its simple derivatives or synthetic intermediates [38], the synthesis of triquinacene turned out to be somewhat pointless and so all our efforts were directed to the synthesis of dodecahedrane.

Later on, in a memorable brain-storming session, at which A.E. Greene from Grenoble was also present, the Pauson–Khand reaction [39] (which involves the hexacarbonyldicobalt complexes of acetylenes, so useful and familiar to us in connection with our work on acetylene diethers and oxocarbons) was considered as a possible approach to synthesis of the triketone **43**. Since the superiority of intramolecular Pauson–Khand cyclisations over the intermolecular ones had been well established by Schore [40] and Magnus [41], the next morning my former coworkers M.A. Pericàs and A. Moyano came to me and suggested the synthetic sequence outlined in Scheme 15, which emerged from rational and iterative retrosynthetic analysis.

The idea was acted upon experimentally as soon as possible, and the triketone **43** was isolated, for the first time, in substantial amounts [42]. However, scale-up of the original procedure, in which trialkylsilyl groups ($R = {}^t\text{Bu}_2\text{MeSi}$; $R' = \text{Me}_3\text{Si}$) were used as the protecting groups, presented some difficulties. The synthetic sequence was finally optimised replacing the trialkylsilyl ethers by the corresponding benzyl ethers and using acetylene ($R' = \text{H}$) instead of its trimethylsilyl derivative ($R' = \text{Me}_3\text{Si}$) [42]. The overall yields of triketone **43** were 31–36% from diol **44**. Triquinacene (**42**) was then synthesised from the triketone **43** by the procedure we had used many years before in the synthesis of bullvalene [44].

The optically active triketone **43** was also prepared, starting from the commercially available optically active form of lactone **36** [45].

On the other hand, the “narcissistic coupling” [37] of the racemic triketone, under a variety of experimental conditions, did not give the expected hexahydro-

xydodecahedrane, although it was detected in some experiments by $\text{Cl}(\text{NH}_3)/\text{MS}$ spectrometry. But this is another story, which does not involve an organometallic intermediate.

Acknowledgements

My efforts in these areas could not have succeeded without the dedicated and skillful work of my students and coworkers, whose names appear in the references listed. My deepest gratitude to all of them.

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