The Chemistry of Vicinal Polycarbonyl Compounds

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Contents

I. Introduction

de Neufville and von Pechmann,[1] reporting in 1890 on the first synthesis of diphenyl triketone (**1a**, $R_1 =$ $R_2 =$ Ph), began in the following way: "Nachdem die Existenzfähigkeit der 1,2-Diketone nachgewiesen war, konnte man daran denken, einen Schritt weiter zu gehen und die Darstellung von Verbindungen zu versuchen, welche mehr als zwei, also zunächst drei

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Mordecai B. Rubin was born long ago in Boston, MA. Four years of military service interrupted his education. After completing his Ph.D. degree with F. Ramirez at Columbia University, he spent two years investigating the chemistry of coffee aroma at the Central Research Labs of General Foods Corporation. This was followed by a two year stint as a postdoctoral fellow with W. S. Johnson at the University of Wisconsin, culminating in the total synthesis of aldosterone. In 1958 he joined the faculty of Carnegie Mellon University (then Carnegie Institute of Technology) and moved to Haifa in 1966. He has been a visiting fireman in Rehovoth, Palo Alto, Houston, Bordeaux, Darmstadt, Canberra, Eugene, Heidelberg, and Düsseldorf. His research interests in those days were in the area of organic photochemistry with particular emphasis on α-diketones and *vic*-polyketones. Since October 1994, he has been Professor Emeritus at the Technion; retirement is like a permanent sabbatical. Current activities include teaching History of Chemistry during the fall semester and working on a History of Ozone.

Rolf Gleiter studied chemistry at the University of Stuttgart and received his Ph.D. (Dr. rer. nat.) degree in the laboratory of F. Effenberger in 1964. In 1965, he joined the group of P. von R. Schleyer at Princeton University as a postdoctoral fellow. There he was involved in solvolysis reactions and in adamantane chemistry. One year later he became aquainted with theory in the group of Roald Hoffmann at Cornell University where he carried out calculations on carbenes and tetramethylene. In 1969, he began his independent "habilitation" in the laboratory of E. Heilbronner at Basel. There he studied the electronic structures of inorganic and organic sulfur compounds by means of electronic and photoelectron spectroscopy as well as quantum chemical calculations. After an appointment as a "Dozent" in 1972 at the University of Basel, he joined in the Faculty of Chemistry at the Technical University in Darmstadt one year later as Full Professor. An offer from the University of Heidelberg in 1979 led to his present position as Professor and Director at its organic chemistry department. Professor Gleiter's research is devoted to physical organic and organic chemistry. Recent areas of research include the electronic structure of vicinal polyketones and systems with nonconjugated double and triple bonds as well as the syntheses of superphanes, cage hydrocarbons, cyclic and bicyclic alkynes, and polyketones.

benachbarte Carbonyle oder die 1,2,3-Triketogruppe −CO.CO.CO− enthalten". One year later Abenius

Chart 1

a, $R_1 = R_2 = Ph$

b, $R_1 = R_2 = 4\text{-}BrC_6H_4$

c, $R_1 = R_2 = 2,4,6\text{-}(Me)_3C_6H_2$

d, $R_1 = R_2 = 4\text{-}MeOC_6H_4$

e, $R_1 = R_2 = 4\text{-}MeC_6H_4$

f, $R_1 = R_2 = H$

g, $R_1 = R_2 = Me$

h, $R_1 = R_2 = i\text{-}Pr$

i, $R_1 = R_2 = tert\text{-}Bu$

j, $R_1 = tert\text{-}Bu, R_2 = Ph$

k. $R_1 = R_2 = 4\text{-}FC_6H_5$

and Söderbaum[2] described diphenyl tetraketone (**2a**, $R_1 = R_2 = Ph$) Chart 1. About 25 years ago one of us[3] reviewed this area of chemistry for the first time. The statement—"interest in the question of how many carbonyl groups can be juxtaposed and what will be the properties of the resulting *vicinal* polycarbonyls has continued through the years"—appears to be as valid today as it was in 1975 when the first review appeared. Interestingly, in the over 100 years since the first synthesis of a *vic*-triketone, the preparation of a pentaketone (**3a**, **3i**) was only achieved[4] in 1986 and longer polycarbonyl chains or rings still elude the synthetic chemist. These compounds remain a challenge for the future.

The present review is a summary of progress in this area of chemistry from 1975 onward and is intended as a supplement with minimal repetition of earlier work. The organization of the 1975 review will be followed as closely as possible. The "oxocarbons" have been reviewed recently[5] and will only be referred to as relevant to other discussion. Two specialized reviews on ninhydrin (**4b**) and related compounds have appeared.[6,7] The reader is referred to these for subjects of specific interest such as the Ruhemann procedure for analysis of amino acids. Improved methods of fingerprint detection[8] using **4b** and compounds of related structure have stimulated appreciable synthetic activity, and new procedures[9] have been developed which do not utilize triketones at all.

α,β-Diketoesters and amides, which were included only incidentally in the earlier review, have become of considerable interest in the past 10 years as a result of the isolation of the biologically important substances FK-506[10] and rapamycin[11] possessing masked α,β-diketoamide (**5**) moieties as key functionalities in their biological activity. Wasserman and co-workers[12] have shown that α,β-diketoesters are fabulous substrates for elegant synthesis of a wide variety of cyclic compounds.

II. Synthesis of Tricarbonyls

In addition to the considerable variety of procedures reported in the earlier review,[3] an abundance of new methods for preparation of tricarbonyl compounds have appeared since. Among the new procedures reported are a number of attractive methods for α,β-diketoesters and amides due to Wasserman and others. There is no obvious reason why many of these new methods should not be generally applicable for the synthesis of triketones also. The plethora of good synthetic methods presents one with a decision which can be dictated largely by convenience.

Schank and co-workers[40] have described five new oxidative procedures, four of which produce methylene chloride solutions of free (unhydrated) tricarbonyls containing only equimolar amounts of an innocuous second reaction product. Most of the synthetic procedures, in contrast, involve aqueous media at some stage and produce hydrates. These hydrates are *almost* always readily convertible to the free tricarbonyl compounds (see section V.A.1 on hydration).

A. From β-Dicarbonyls (Scheme 1)

The ready availability of β-dicarbonyl compounds and the enhanced reactivity at their α-position have made them the starting materials of choice for many synthetic procedures. These compounds are written here in the diketo form although they undoubtedly exist largely as enols in most cases. The major synthetic reactions are summarized in Scheme 1,

Scheme 1. Preparation of Tricarbonyls from β-Dicarbonyl Precursors

DMD = dimethyldioxirane
Ns = p-nitrobenzenesulfonyl
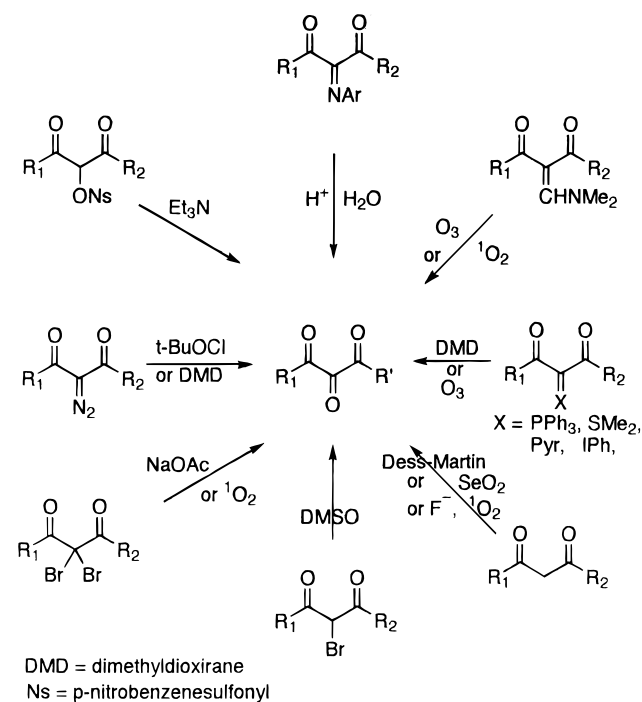
which illustrates the variety of functional group transformations which can lead to tricarbonyls; a detailed discussion follows.

Assignment of the structure of 2,2,6,6-tetramethylpiperidine-3,5-dione has been shown by Hofmann et al.[13] to be incorrect so that the product of its oxidation reactions is not 2,2,6,6-tetramethylpiperidine-3,4,5-trione.

1. The Sachs Procedure Using p-Dimethylaminonitrosobenzene (Scheme 2)

The older procedures continue to be employed. The venerable (1901) Sachs method in which a β-dicarbonyl compound is condensed with p-dimethylaminonitrosobenzene followed by acid hydrolysis of the resulting imino product has afforded good yields of diketoesters in cases where oxidation procedures (see below) could not be employed. These include the indole derivative[14] **6**, the vinylpyrrole[15] **7**, and the p-dimethylaminophenyl compound[16] **8** shown in Scheme 2.

Scheme 2
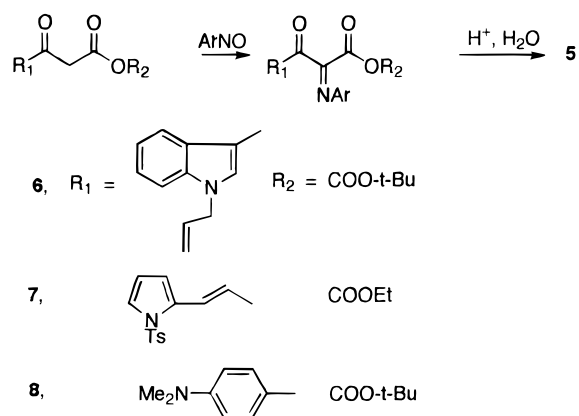
2. From α-Diazo-β-dicarbonyls (Scheme 3)

The formation of α-diazo-β-dicarbonyl compounds by the Regitz exchange procedure with tosyl azide, followed by reaction with *tert*-butyl hypochlorite in the presence of formic acid, has proved, in our hands, to be a superior synthetic method for obtaining highly pure samples of open chain triketones and has also been useful in the synthesis of pentaketones as discussed later. It has been used successfully for preparation of a number of cyclic triones including **9** and **10**,[17a] a number of 5- and 6-substituted and 5,6-disubstituted (methyl, methoxy, chloro) indanetriones,[17b] the cyclohexenetrione **11**,[18] bicyclotriones **12** (R = H, Me),[19] and a new synthesis[20] of cyclopentenetrione (**13**), all from the corresponding β-dicarbonyls. Schank and Blattner[21] have described some chemistry of the α-chloro-α-formyl intermediates in this procedure (see section V.E).

A new application of diazodiones due to Saba[22] involves reaction of diazodiketones with dimethyl dioxirane (DMD) to give high yields of triketones and of α,β-diketoesters.

In 1964 Bestmann and Klein[23] reported reaction of α-diazo-β-diketones (prepared by reaction of carboxylic acid chlorides with diazoacetic ester) with triphenylphosphine to obtain phosphazines **14**. These were then treated with nitrous acid to give α,β-diketoesters as hydrates. Kugelrohr distillation gave the free carbonyl compounds, which were characterized as quinoxalines and dinitrophenylhydrazones. The R$_1$ groups in these ethyl esters of **5** were methyl,

Scheme 3
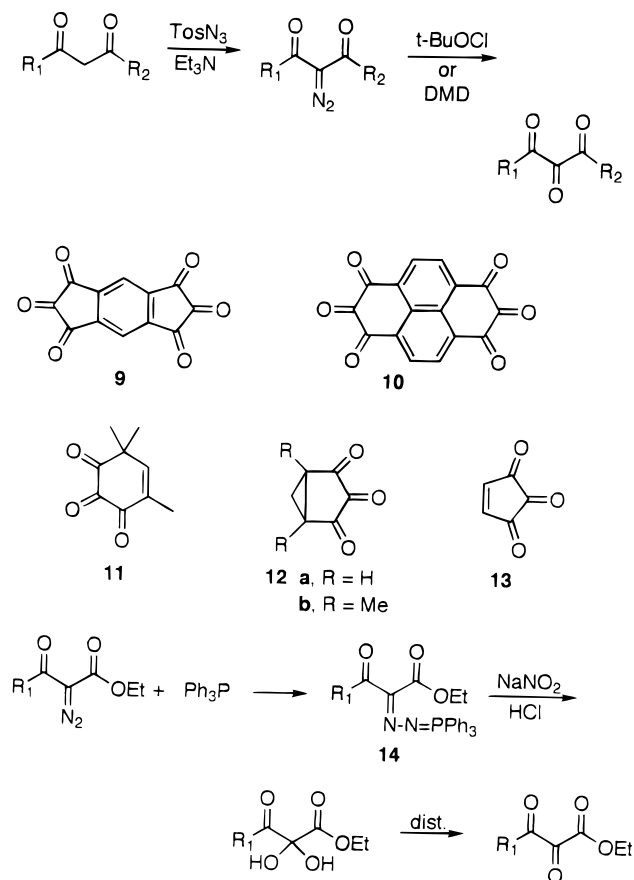
trifluoromethyl, *n*-propyl, *n*-butyl, phenyl (88% yield), and (acetoxy)(phenyl)methyl. Repetition of this procedure by Dahn and co-workers[24] for preparation of β-phenyl diketoester (**5**, R_1 = Ph, R_2 = Et) and diphenyl triketone gave very low yields. It does not seem to have been explored further.

3. From Bromodicarbonyls

a. Monobromodicarbonyls (Scheme 4). Conversion of β-dicarbonyl compounds to monobromo derivatives followed by replacement of bromine has received a new lease on life with the introduction of dimethyl sulfoxide as a mild reagent for replacing such activated bromine atoms by a carbonyl oxygen. These include 1,1-dimethyl-1,4-diphenylbutanetrione (**15**), used by Wolfe et al.[25] in their investigation of possible helical conformations of the trione chain (see section VII.B), and a variety of simple triones (R_1 =

Scheme 4
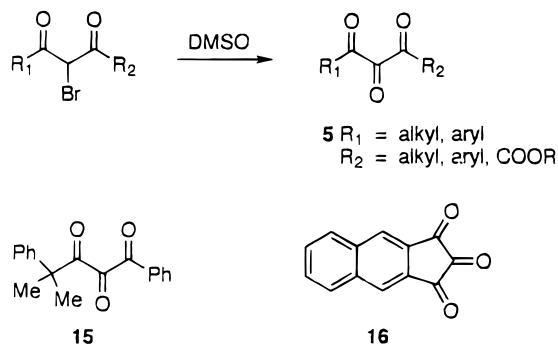
alkyl, aryl; R_2 = alkyl, aryl, ester), prepared by Dahn and co-workers[24] for studies of base-catalyzed reactions of such compounds. These workers reported that the DMSO procedure gave better yields than the old procedure using N_2O_3, which has not been employed recently.

Tatsugi and Izawa[26] have recently reported combining the bromination and DMSO oxidation steps by reaction of NBS in DMSO with 1,3-diketoindane at 80 °C under aspirator vacuum to form ninhydrin (**4b**) in high yield.

The reaction of an α-bromo-α,β-unsaturated ketone in the ninhydrin series with DMSO has been reported by Heffner and Joullié[27] to result in formation of benzo[*f*]ninhydrin (**16**).

b. Dibromodicarbonyls (Scheme 5). A new procedure was introduced by Wamhoff et al.[28] in which *gem*-dihalodiones (dibromides or dichlorides) were allowed to react with singlet oxygen (generated by methylene blue sensitized photolysis). Tricarbonyls, obtained as hydrates, were formed in 70−90% yields and included diphenyl triketone, phenyl *p*-methoxyphenyl triketone, **17b**, **4b**, and hydrates **18** (R = H, CH_3) of the quinisatins. Similar results were obtained for the two diaryl triketones above when singlet oxygen reacted with the corresponding α,β-dibromoketones.

Scheme 5
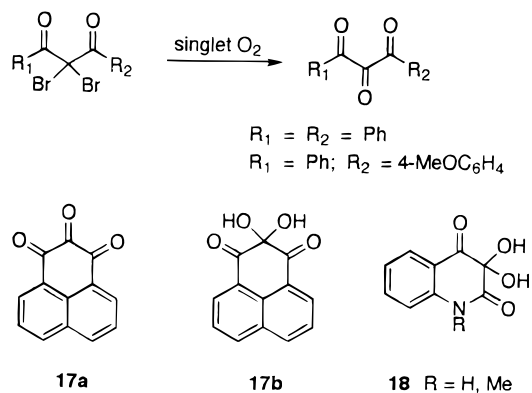
Reaction of a dibromide with DMSO has been used by Joullié et al.[29] to prepare **16**. The mechanism is not clear.

Faust and Mayer[30] reported that diethyl mesoxalate could be prepared conveniently via dibromination of malonic ester and reaction of the *crude* reaction product (*without* purification) with potassium acetate. Pardo and Salomon[31] described a similar procedure for this commercially available diester.

We note that Cannon et al.[32] reported difficulties in conversion of dibenzoylmethane to the dibromo compound and resorted to the ancient procedure of Abenius and Söderbaum[2] involving monobromination, replacement of bromine by acetoxyl, and a second bromination in order to prepare diphenyl triketone. These authors also reported difficulties in preparation of the tetrabromo product from dibenzylketone.
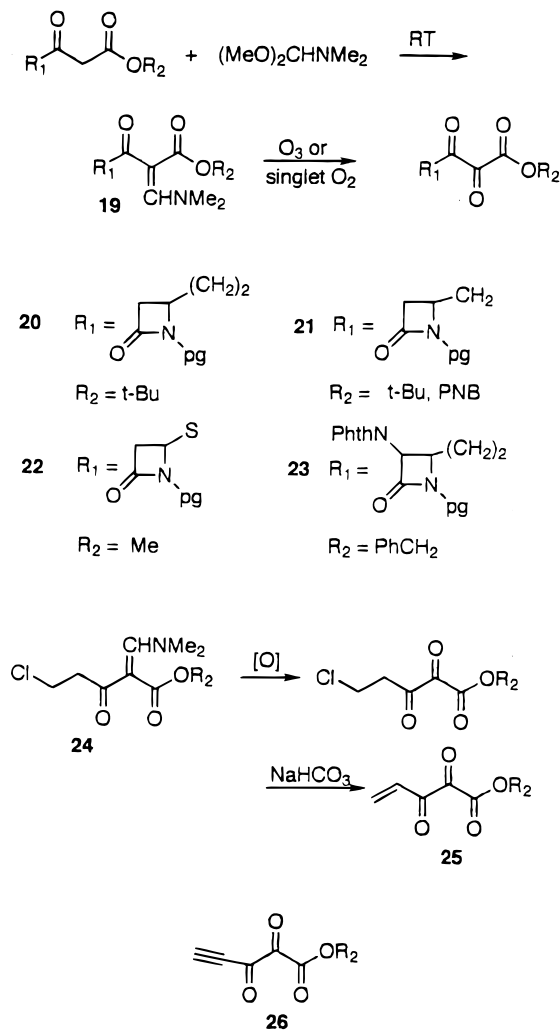
4. Oxidative Cleavage of Dimethylaminomethylene Derivatives (Scheme 6)

This is one of the methods developed by Wasserman and co-workers[12] for preparation of hydrates of diketoesters. β-Ketoesters reacted at room temperature with the dimethylacetal of dimethylformamide to give dimethylaminomethylene derivatives **19** which could be oxidatively cleaved using either singlet oxygen (dye sensitization) or ozone (dimethyl sulfide workup). The choice between the two reagents appears to be a matter of convenience. The substituted β-lactams **20**,[33] **21**,[34] **22**,[35] **23**[36] having the dimethyl-(*tert*-butyl)silyl protecting group (pg) on nitrogen were prepared by this procedure. In addition, Wasserman and Han[33] reported *tert*-butyl and benzyl diketobutyrates, diethyl mesoxalate and its mono-thioester, and monopiperidinyl amide.

This procedure was used[37] with *tert*-butyl δ-chloro-β-ketovalerate (**24**) to yield the δ-chloro-α,β-diketoester. Treatment with sodium bicarbonate then afforded the extremely useful β-vinyl-α,β-diketoester **25**. The method was also applied successfully[38] for synthesis of the β-ethynyl-α,β-diketoester **26** from the acetylenic β-ketoester.

Rao et al.[39] have used this method in model studies directed to the synthesis of FK-506. In some simple cases they also prepared benzylidene derivatives by condensation of α-dicarbonyl compounds with benzaldehyde and obtained the desired tricarbonyls by ozonolysis; comparison of the two methods was not made.

5. Oxidative Cleavage of Methoxymethylene Derivatives (Scheme 7)

A related procedure was used by Schank and Schuhknecht[40a] who reported ozonolysis of methoxymethylene derivatives of β-dicarbonyls to produce the oxo-Meldrum acids **27a**,**b** in 61% and 65% yields, respectively. Diethyl mesoxalate was obtained in 44% yield. The ozonide precursors of **27a**,**b** were isolated as crystalline solids, workup involved treatment with phosphorus trichloride.

Scheme 6

Scheme 7
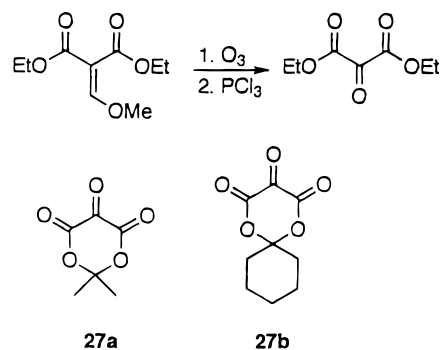
6. Oxidative Cleavage of Ylides

Three of the following procedures (b,c,d) are unique in that they produce methylene chloride solutions of free tricarbonyls containing equimolar amounts of dimethyl sulfoxide (b), pyridine (c), or iodobenzene (d). We also note that although the ylides used may, in theory, be prepared from β-dicarbonyl compounds, many were prepared by reaction of preformed ylides with carboxylic acid derivatives. These methods are included in the following discussion.

a. Phosphonium Ylides (Scheme 8). Bestmann and Kloeters[41] first showed that a triketone was obtained by ozonolysis of a phosphorus ylide in their preparation of ninhydrin (**4b**). This method has been used extensively by Wasserman and co-workers[12] for preparation of many diketoesters from phosphorus ylides (**28**), in most cases the *tert*-butyl esters were used. Both Oxone[42] (potassium peroxysulfate) and ozone were used initially as oxidizing agents; the Oxone reaction was slower than ozonolysis but more selective in complex cases. Later it was shown[43] that DMD could also be used to effect this transformation, so that three oxidation procedures are available for conversion of phosphorus ylides to tricarbonyls. A list of α,β-diketoesters prepared in this way is presented in Table 1, again products were obtained as hydrates. The triketone **29** was also prepared by this route,[44] supporting the statement made earlier that procedures for preparation of diketoesters should also be applicable for triketone synthesis. Diketoamides were prepared analogously[39] as well as peptidyl diketoesters.[45]

We note that while phosphorus ylides might be prepared starting from β-dicarbonyls, this was not
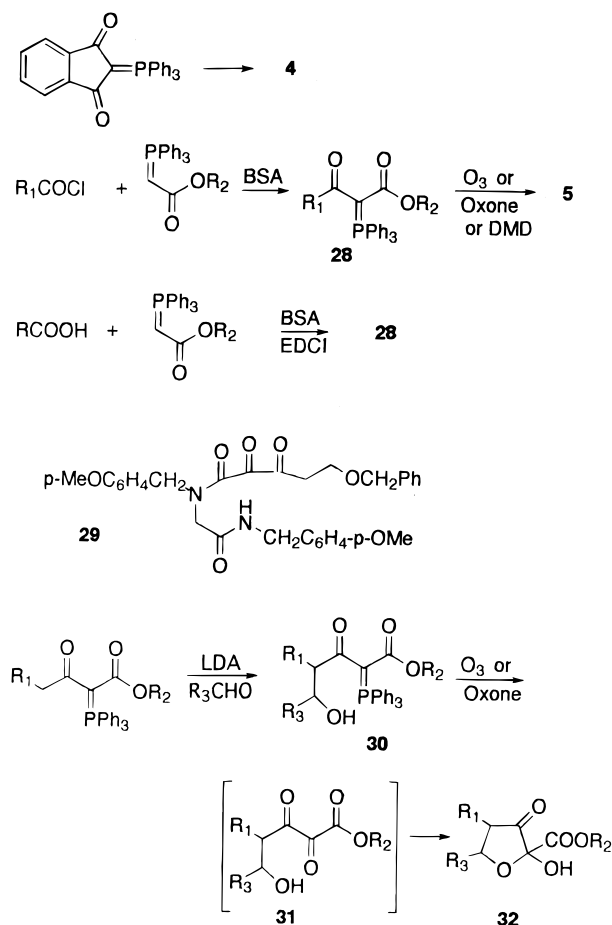
Scheme 8

Table 1. α,β-Diketoesters (R₁COCOCOO-*t*-bu, 5) Prepared by Oxidative Cleavage of Phosphorus Ylides

Table 1. α,β-Diketoesters (R$_1$COCOCOO-t-bu, 5) Prepared by Oxidative Cleavage of Phosphorus Ylides

entry	R₁	ref
a	β-chloroethyl	37, 42
b	3,4-dimethoxyphenyl	111
c	2-ethoxycarbonyl-3,4-dimethoxyphenyl	111
d	β-ethoxycarbonylethyl	42, 110, 113
e	EtOOCCH(Et)CH₂CH₂	110, 113
f	PhCH₂	110
g	PhthNCH₂CH₂CH₂	110
h	CH₂=CHCH₂CH₂	42
i	CH₃CH=CHCH=CH	42
j	(Me)₂C=CHCH₂CH₂CH(Me)CH₂	42
k	C₆H₅	116
l	*p*-MeC₆H₄	116
m	*p*-MeOC₆H₄	116
n	*o*-MeOC₆H₄CH=CH	117
o	*p*-NO₂C₆H₄	117
p	*t*-Bu	117
q	Me	43
r	Ph (R₁ = Me)	43
s	PhCH=CH	43
t	Me₂CH=CH	43
u	2-furyl	43
v	2-thienyl	43
w	MeOCH=CH	43

the case in the various diketoester preparations of the Wasserman group. Instead, carboxylic acid chlorides were reacted in the presence of the "proton sponge" BSA (*N-O*-bis(trimethylsilyl)acetamide) with the ylide obtained from α-haloacetic acid esters. This procedure allowed considerable variation of the group R₁; the ester group was almost invariably *tert*-butyl

but variation here is also possible. Later it was found that acid chlorides could be replaced by carboxylic acids using the carbodiimide EDCI (1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride) to effect reaction with ylides.

The procedure could also be applied for synthesis of bis-α,β-diketoesters.[46] These were obtained from isophthaloyl and terephthaloyl dichlorides and 2,6-naphthalene dicarboxylic acid dichloride via reaction with phosphorus ylide followed by oxidation with either ozone or Oxone.[42] The resulting bis-tricarbonyl esters were shown to be effective interstrand DNA cross-linking agents.

Further modification[47] offering additional flexibility in synthesis was developed using β-dicarbonyl-α-ylides having a hydrogen atom on the γ-carbon. The anion generated by reaction of such species with LDA underwent further reaction, such as aldol condensation (as illustrated), to form δ-hydroxy compounds (**30**). Oxidation of the new ylides produced α,β-diketoesters **31** which were not isolated as such since they underwent rapid conversion to the more stable hemiketal ring tautomers, the furanones **32**. The compounds synthesized include methyl esters in which R₁ is hydrogen and R₃ = ethyl, isopropyl, isobutyl, *tert*-butyl, *n*-pentyl, *n*-hexyl, and phenyl as well as *tert*-butyl esters with R₃ = ethyl and phenyl and two methyl esters with R₂ = *n*-hexyl and phenyl. Further conversion to furanols was also described.[47]

b. Sulfonium Ylides (Scheme 9). Schank and Schuhknecht[40b] prepared dimethylsulfonium ylides (**33**) by reaction of β-dicarbonyl compounds with acetic anhydride and DMSO (or an alternate procedure using sulfopropanoic acid anhydride). Ozonolysis of **33** in methylene chloride at low temperature produced DMSO (no sulfone detected) and tricarbonyl compounds in good yields; no additional workup, as is usually required in ozonolysis reactions, was necessary. The additional product is presumably oxygen. Indanetrione (**4a**) could be crystallized directly from the ozonolysis mixture (81% yield); diaryl triketones were also obtained as free triones (diphenyl triketone in 88% yield, phenyl *p*-chlorophenyl triketone in 93% yield, and di-*p*-chlorophenyl triketone in 91% yield). In other cases, solutions from the ozonolysis contained free trione as evidenced by their red colors, but removal of DMSO required washing with water so that the isolated products were tricarbonyl hydrates; conceivably, the workup procedure could be modified to give other compounds directly as free tricarbonyls. In addition to the
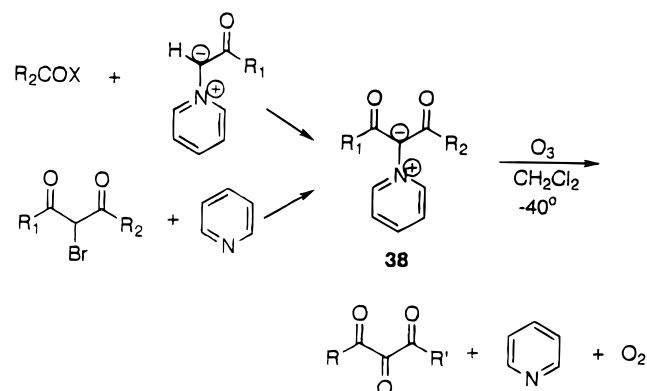
Scheme 9
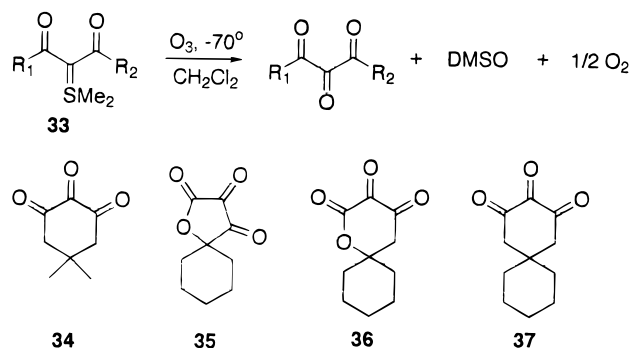
compounds mentioned above, hydrates were prepared of **27a,b**, 5,5-dimethylcyclohexane-1,2,3-trione (**34**), and the three spiro tricarbonyls **35**, **36**, and **37** shown in Scheme 9.

c. Pyridinium Ylides (Scheme 10). Schank and Lick[48] prepared pyridinium ylides **38** either by reaction of pyridine with α-bromo-β-diketones or by reaction of preformed ylides with acid chlorides (analogous to the procedure used for preparation of phosphonium ylides in section II.A.6.a). Ozonolyses at −40 °C using 1 equiv of ozone afforded products directly, again without the usual ozonolysis workup; simple evaporation of solvent gave the crude product mixture. Products, obtained as the free triketones, were di-*p*-methoxyphenyl, phenyl *p*-methoxyphenyl, phenyl *p*-chlorophenyl triketones, and phenalenetrione (**17a**). Yields were better than 70%. Again, this method is of special interest since the free triketones can be isolated directly.

Scheme 10

38

d. Iodonium Ylides (Scheme 11). In the last of the four Schank[49] procedures, phenyl iodosoacetate was reacted with β-dicarbonyls, mainly diketones, to obtain the phenyliodonium ylides **39**. These were oxidized by ozone at −40 °C to triketones plus iodobenzene and (presumably) oxygen without any further workup procedure except evaporation of solvent and purification of product. The mechanism of this ozonolysis is unclear. The method failed with
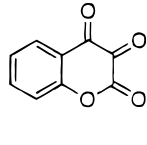
Scheme 11

39
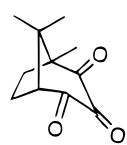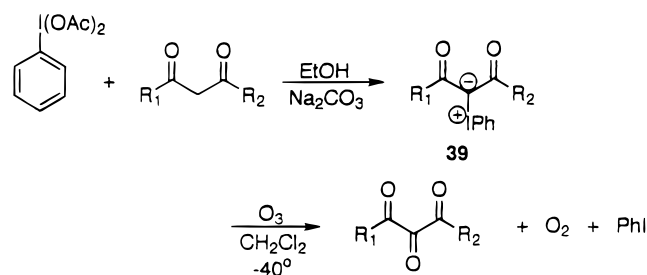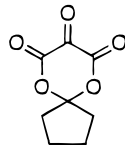
**40**   **41**   **42**

compounds containing functionality which is attacked by ozone, a cycloalkene and a cyclic sulfide, even though attempts were made to use 1 equiv of ozone. In other cases, yields ranged from 65% to 92% for the wide variety of compounds investigated. These included methyl α,β-diketovalerate and dimethyl, diphenyl, and phenyl *p*-chlorophenyl triketones. Also, cyclohexanetrione, 5-methyl, 5-phenyl, 5,5-dimethyl, 4-phenyl-5,5-dimethyl, and 4,4-diphenyl cyclohexanetriones, spiro compounds **35**, **36**, and **37**, oxo-Meldrum acids **27a,b**, and *N,N*-dimethyl alloxan (**110**, R = H) as well as compounds **40**−**42** as shown in Scheme 11.

Podolešov[50] has shown that oxidative cleavage of β-diketones occurred when they were treated with phenyl iodosoacetate under much more severe reaction conditions.

7. Direct Oxidation of β-Dicarbonyls

a. Fluoride Ion Promoted Singlet Oxygen Oxidation (Scheme 12). While enolizable β-dicarbonyls react very sluggishly with singlet oxygen (Rose Bengal photosensitized), Wasserman and Pickett[51] discovered that the presence of equimolar tetrabutylammonium fluoride resulted in rapid conversion to tricarbonyls in good yields. Compounds prepared by this procedure include dimethyl (66%), diphenyl (97%), methyl phenyl (72%), and cyclododecyl (**43**, 60%, as hydrate) triketones as well as the ethyl hemiketal of **42**. Ninhydrin (**4b**) was obtained in 75% yield. Application of the method to dimedone (**44**) allowed isolation of the corresponding trione **45** (in the bisenolic form, see section V.E) if the reaction was interrupted at an early stage. Longer reaction times afforded the product (**46**) of aldol condensation of **44** with **45** (cf. section V.A.3). It was shown separately that simple standing of a mixture of **44** and **45** resulted in formation of the same aldol product (cf. the Fremy salt reaction, part c).
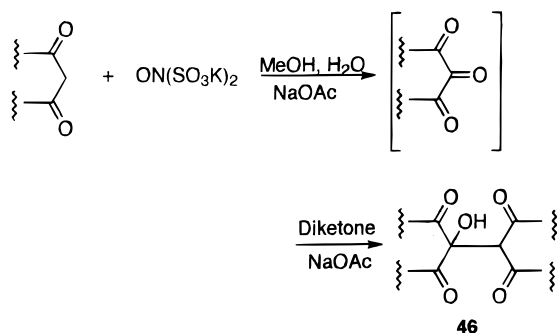
Scheme 12

$R_1 = R_2 = Ph$
$R_1 = R_2 = Me$
$R_1 = Ph, R_2 = Me$

43   **44**   **45**
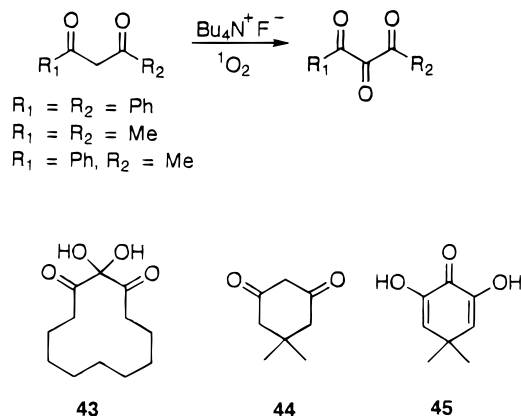
b. Selenium Dioxide Oxidation. This method has been applied in a few cases by Dahn and co-workers[24] for preparation of tricarbonyls having alkyl or ester end groups. Yields ranged from 40% to 90%. Open chain triones having one or two *p*-nitrophenyl groups could not be prepared by the DMSO reaction of monobromo-α-diketones but were obtained in good yields by the selenium dioxide

procedure. It has also been used[52] in work related to the immunosuppressant FK-506 for oxidation of a β-ketoamide to the corresponding α,β-diketoamide; the yield of a 2:1 mixture (not separated) of free carbonyl compound and its hydrate was 76%.

c. Oxidation with Fremy's Salt (Scheme 13). Reactions of the β-diketones dihydroresorcinol,[53] **44** (dimedone), 4,6-dimethylcyclohexane-1,3-dione,[54] and indane-1,2- and indane-1,3-diones[54] with Fremy's salt (potassium nitrosodisulfonate) have been shown by Teuber et al. to form triketones. In a fashion similar to the results in section II.A.7.a, these products underwent aldol reactions (sodium acetate present in the medium) to form addition products **46** with starting dione; these could be obtained separately by treating trione with dione in the presence of sodium acetate. The addition products **46** were converted into trione derivatives by reaction with phenylhydrazine or hydroxylamine. Trione products were not obtained from 5-phenylcyclohexane-1,3-dione or the dione corresponding to **37**; oxidative cleavage to dicarboxylic acids was observed with 1,2-cyclohexanedione, 2-methyl-1,3-cyclohexanedione, and dibenzylketone. Cycloheptane-1,3-dione was unreactive.
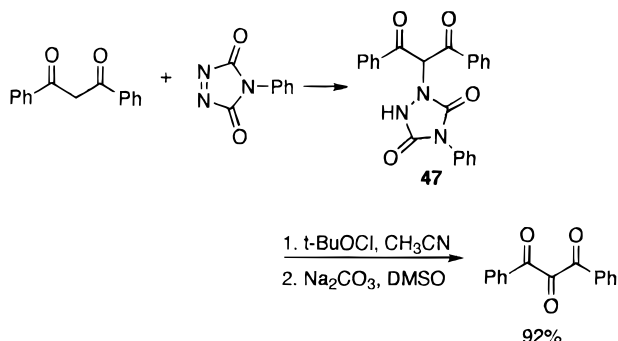
Scheme 13

46

8. From Urazoles (Scheme 14)

Wilson and Hengge described[55] the addition of β-dicarbonyl compounds to *N*-phenyltriazolinedione (PTAD) to give urazoles **47** which reacted with *tert*-butylhypochlorite in acetonitrile followed by sodium carbonate in DMSO to give high yields of tricarbonyls. This is illustrated in Scheme 14 for diphenyl triketone; the other example given was the preparation of ethyl α,β-diketobutyrate.
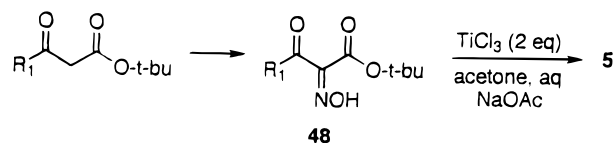
Scheme 14

47

9. From Oximes (Scheme 15)

Oximation of β-dicarbonyl compounds using nitrous acid or alkyl nitrites is a well-know reaction. At-

tempts by Miller et al.[56] to utilize the resulting oximediketones (**48**) to generate tricarbonyls using a titanium trichloride mediated reaction afforded low yields of the desired products. The method was applied to synthesis of a carbacepham.
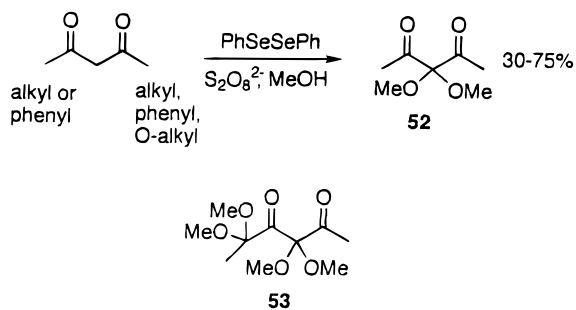
Scheme 15

48

10. From p-Nitrobenzenesulfonates (Scheme 16)

Hoffman et al.[57] have described a new method in which bis(*p*-nitrophenylsulfonyl)peroxide (**49**) reacted under mild conditions with β-dicarbonyls to form products **50** in which a hydrogen atom has been replaced by the *p*-nitrobenzenesulfonyl group (Ns). Subsequent reaction of **50** with triethylamine resulted in formation of tricarbonyls and presumably *p*-nitrobenzenesulfinate. However, these were not isolated as such but were converted, in good yields (97% for dimethyl triketone), to quinoxalines by addition of *o*-phenylenediamine to the crude reaction product. The one exception was the chloroethyl compound **24** where a low yield of vinyl tricarbonyl ester **25** was obtained by a double elimination.

Scheme 16

R_1	R_2
Me	OEt
Me	OMe
i-pr	OEt
Me	Me
ClCH$_2$CH$_2$	O-t-bu

50, R_1 = ClCH$_2$CH$_2$ + PhCH$_2$NH$_2$ →

51
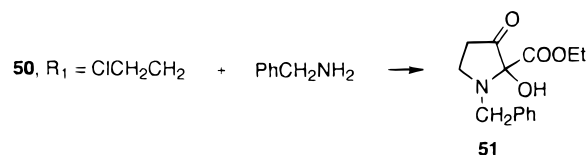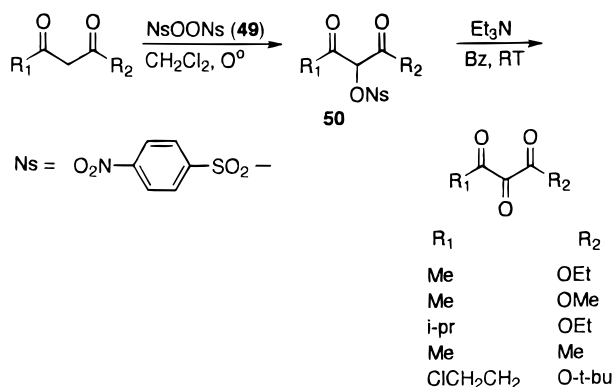
A useful modification of this procedure involved the use of benzylamine instead of triethylamine to isolate directly the pyrrole previously obtained by Wasserman (cf. section V.A.2) from reaction of **25** with benzylamine. Alternatively, the product from triethylamine could be treated with benzylamine. We are not aware of further applications of this method, although it would appear to be valuable in cases where the tricarbonyl is intended for immediate further reaction. This work also contains a reference to unpublished work using tosyl rather than nosyl groups.
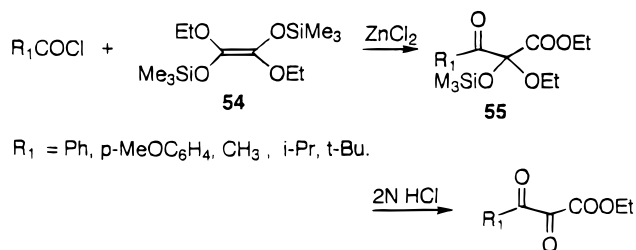
Scheme 17

11. Preparation of Monoketals of Tricarbonyls (Scheme 17)

The reaction of β-dicarbonyl compounds with diphenyl diselenide and ammonium peroxydisulfonate in methanol resulted in introduction of the *gem*-dimethoxy function at the central carbon atom as reported by Tiecco et al.[58] The resulting dimethyl-ketal dicarbonyls (**52**) are potential tricarbonyl compounds, although such a conversion was not investigated. As indicated in Scheme 17, dialkyl and diphenyl triketones as well as alkyl and phenyl diketoesters were prepared in this way in moderate to good yields. Interestingly, bisketals (**53**) were formed as minor products in yields of up to 15%, presumably from further reaction of the initially formed monoketals (cf. section III.A.1).

B. Other Methods

1. Reaction of Acid Chlorides with a Bis(trimethylsiloxyethylene) (Scheme 18)

Reetz and Kyung[59] reported the synthesis of a number of diketoesters involving the reaction of carboxylic acid chlorides with the tetrasubstituted ethylene **54** to give ketal-like products **55**. These could be hydrolyzed to diketoester hydrates in yields of over 70%. The groups attached to the β-carbon atom of the α,β-diketoesters were alkyl or aryl as indicated in Scheme 18. No further applications of this method have been recorded.

Scheme 18

### 2. Ozonolysis of p-Benzoquinones (Scheme 19)

A preliminary report of synthesis of di-*n*-dodecyl triketone by ozonolysis of a 2,6-disubstituted *p*-benzoquinone was included in our earlier review. From the full paper,[60] which appeared in 1978, it seems that this method is of limited value. The best yield of the yellow, solid trione was 40%, obtained from quinone **56** having one methoxy group in

addition to the two *n*-dodecyl substituents on the quinone. No other examples of this approach to trione synthesis have appeared.

Scheme 19
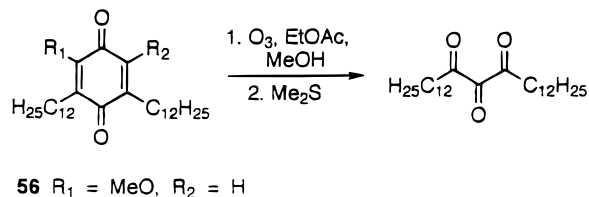
3. Oxidation with the Dess–Martin Reagent (Scheme 20)

The Dess–Martin periodinane **57** was applied to synthesis of tricarbonyls by Golec et al.[61] who showed that triketones, α,β-diketoesters, and α,β-diketoamides could be obtained in good yields by reaction of **57** with β-diketones or β-hydroxyketones under mild conditions. Apparently, hydroxyketones are oxidized to diketones which then are converted to tricarbonyls. The procedure was also applied by these workers for the synthesis of compounds related to FK-506. Interest in the latter substance also prompted Danishefsky et al.[62] to use **57** for oxidation of a number of β-(2-furyl, *n*-heptyl, or cyclohexyl)-β-hydroxy-α-phenylthio-cyclohexylamides (**58**) to the corresponding tricarbonyls in good yields and for synthesis of compounds related to FK-506. Starting materials were readily synthesized by LDA catalyzed reaction of α-thiophenylacetamide with the appropriate aldehydes.

Scheme 20
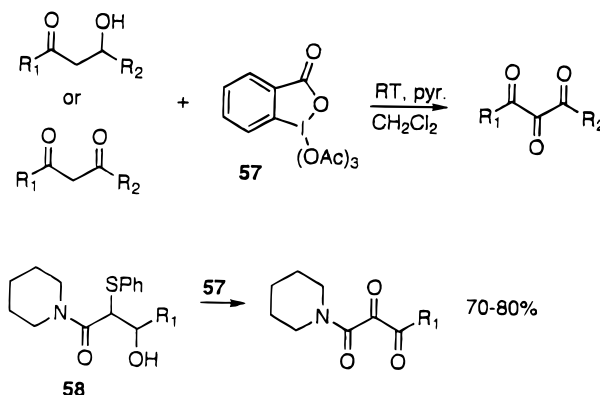
Jones et al.,[63] in their synthesis of FK-506, attempted to oxidize an α,β-dihydroxyamide with the Dess–Martin reagent and reported that glycol cleavage occurred. Successful oxidation of the diol was achieved using the Swern reagent. Schreiber et al.,[64] in another FK-506 synthesis, avoided this problem by preparing a diol with two different protecting groups. Dess–Martin oxidation after removal of one protecting group, followed by removal of the second protecting group and a second Dess–Martin oxidation afforded the desired α,β-diketoamide.

4. From Monoketones (Scheme 21)

In addition to the reaction of 1,3-indanedione with NBS in DMSO at 80 °C under aspirator vacuum

Scheme 21
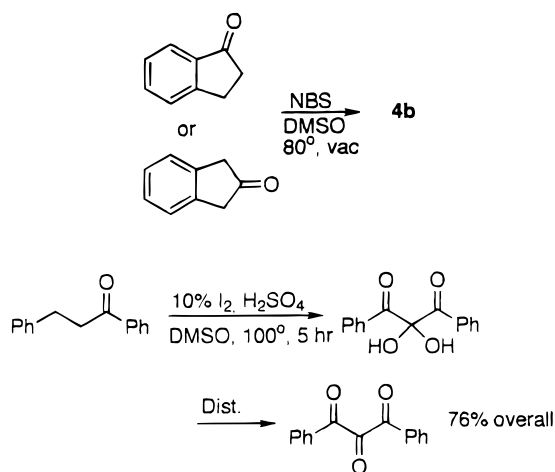

mentioned in section II.A.3, Tatsugi and Izawa[65] have recently reported using their one-pot bromination–oxidation sequence to convert 1- and 2-indanones into ninhydrin. They reported high-yield preparations of **4b** and a number of substituted ninhydrins starting from 1-indanone. The sequence of reactions was assumed to be bromination in a benzylic position and Kornblum-type oxidation to indanedione by DMSO followed by a second bromination and oxidation.

One example[66] has been reported for conversion of a monoketone to trione hydrate by reaction with iodine in DMSO containing sulfuric acid.

5. Samarium Diiodide Mediated Insertion of Isocyanides (Scheme 22)

The reaction of alkyl bromides with 2,6-xylyl isocyanide (**59**) plus esters,[67] mediated by samarium diiodide, produced diimino compounds **60** which could be hydrolyzed to tricarbonyls. The products were triketones except when dimethyl carbonate was used to give α,β-diketo methyl esters. Yields of diimines ranged from 60% to 90%. Methyl α,β-diketopentanoate, characterized as the quinoxaline, was obtained in over 70% yield from ethyl bromide, the isocyanide, and dimethyl carbonate.

Scheme 22
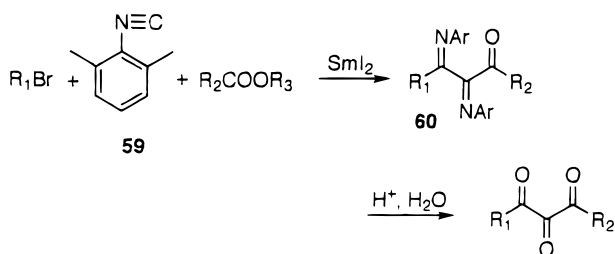
6. Oxidation of Dihydroxy Precursors

a. From α,β-Dihydroxy Carboxylic Acid Derivatives (Scheme 23). As noted above, Jones et al.[63] found that dihydroxyamides were cleaved by the Dess–Martin reagent. Successful oxidation to diketo-amide was achieved using the Swern procedure.

Appropriate conditions have been found by Inokuchi et al.[68] for oxidation of α,β-dihydroxyesters to diketoesters using 4-benzoyloxy-2,2,6,6-tetrameth-

Scheme 23
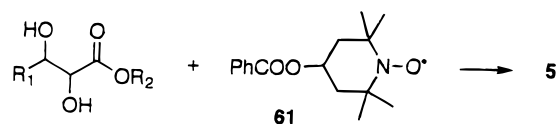
ylpiperidine-*N*-oxyl (**61**). Superior yields (80–93%) were obtained with an electrochemical procedure using sodium bromide and **61** in a buffered two-phase system as compared with the nonelectrochemical method using **61** and sodium bromite (50–66%), again in a buffered two-phase system; products were obtained as hydrates. Methyl esters were prepared with R_1 = *n*-octyl, β′-phenethyl, isopropyl, cyclohexyl, and phenyl. In addition, methyl isopropyl α,β-diketo-butyrate (R_2 = Me) was prepared.

b. From Dihydro Derivatives (Scheme 24). DDQ has proved to be a useful reagent (cf. also section III on tetraketones) for oxidation of dihydro compounds to tricarbonyls. The hydrate of *o*-tropo-quinone (**62**, a "carbonylogue" of *o*-benzoquinone) was obtained readily by Hirama and Itô[69a] via DDQ oxidation of 3-hydroxytropolone ("dihydro-*o*-tropo-quinone") in acetonitrile followed by addition of water. The hydrate proved to be resistant to dehydration until a special sublimation technique was employed.[70] Similar oxidation in methanol solution yielded the methyl hemiketal. A benzo analogue was also prepared[69b] by DDQ oxidation.

Scheme 24
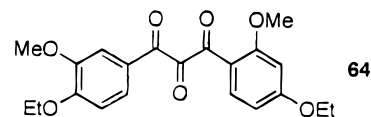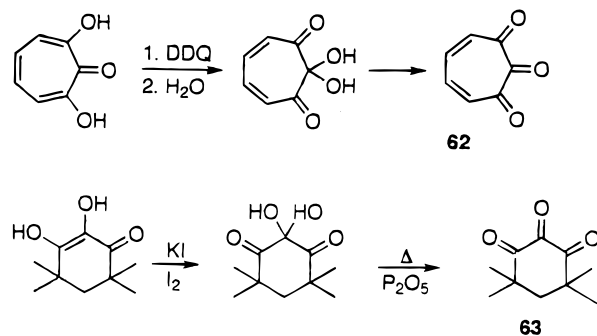
A dihydro form of 1,1,5,5-tetramethylcyclohexane-2,3,4-trione was oxidized with iodine in potassium iodide to the trione hydrate by Gill et al.[71] Free trione (**63**) was obtained by vacuum distillation over phosphorus pentoxide.

Merlini et al.[72] reported oxidation of tetra-*O*-ethyl santalin B with permanganate to give the trione **64**; the data are consistent with the hydrate.

We note that oxidation of di- or tetrahydro derivatives with nitric acid or DDQ is the usual procedure for obtaining tetraketones (see section III.A).

Triones were assumed by Frimer et al.[73] to be intermediates in the superoxide oxidation of several dihydro derivatives of triones. See section III for similar experiments with tetraketone derivatives.

Scheme 25

R$_1$ = Ph
R$_2$ = Me or Ph
R$_3$ = 4-MeOC$_6$H$_4$
4-ClC$_6$H$_4$
4-NO$_2$C$_6$H$_4$
NHC$_6$H$_{11}$
NH-t-Bu
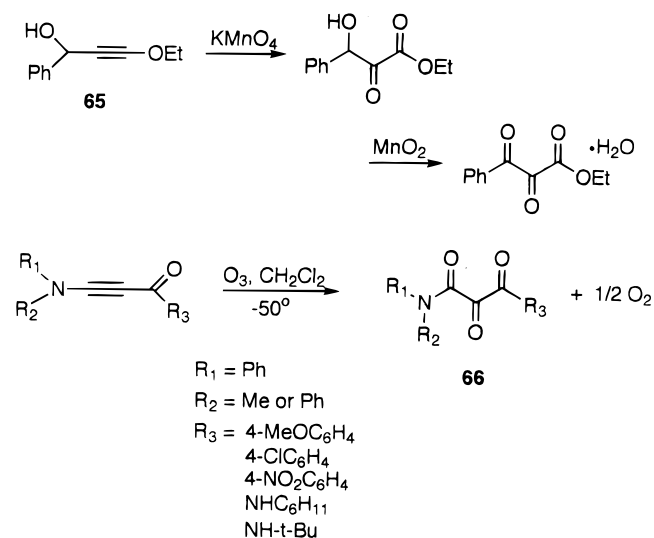
7. Oxidation of Acetylenic Precursors (Scheme 25)

Two synthetic methods based on known conversions of acetylenes to α-diketones have appeared recently. In the first of these, Tatlock[74] described the high-yield preparation of the hydrate of ethyl β-phenyl-α,β-diketopropionate (**5**, R$_1$ = Ph, R$_2$ = Et) by oxidation of 1-ethoxy-3-hydroxy-3-phenylpropyne (**65**, prepared by reaction between the lithium salt of ethoxyacetylene and benzaldehyde) with potassium permanganate to the β-hydroxy-α-diketoester followed by manganese dioxide oxidation to the diketoester.

In the second method, Schank and co-workers[75] exploited the conversion of alkynes to diketones by reaction of acylynamines with ozone for synthesis of diketoamides (**66**) or monoester−monoamides in the mesoxalate system. Neither cleavage nor peroxidic products were observed in these reactions; the other product is oxygen. With the exception of the p-nitrophenyl compound where partial loss of a nitro group was observed, free tricarbonyl compounds, pure by TLC, were obtained simply by evaporation of solvent. Application of this procedure to other systems would be of interest (see Scheme 29).

C. Sulfur Analogues of Tricarbonyls (Scheme 26)

Replacement of a carbonyl oxygen by sulfur to give a thione results in a considerable change of properties (cf. section VIII.B). The preparation of such compounds is, therefore, of considerable interest. Very limited success has been achieved to date.

Wasserman and Han[35] prepared diethyl mesoxalate with one ester oxygen replaced by sulfur from the corresponding thiamalonate using their dimethylaminomethylene method (section II.A.4).

The common procedures for conversion of a carbonyl group to a thione are reaction with tetraphosphorus decasulfide or the Lawesson reagent. Application of the decasulfide procedure by Voss et al.[76] to amides of mesoxalic acid resulted in replacement of one amide carbonyl oxygen by sulfur to give **67**; prolonged reaction produced the dithioamide. However, exhaustive reaction with decasulfide or Lawes-

Scheme 26
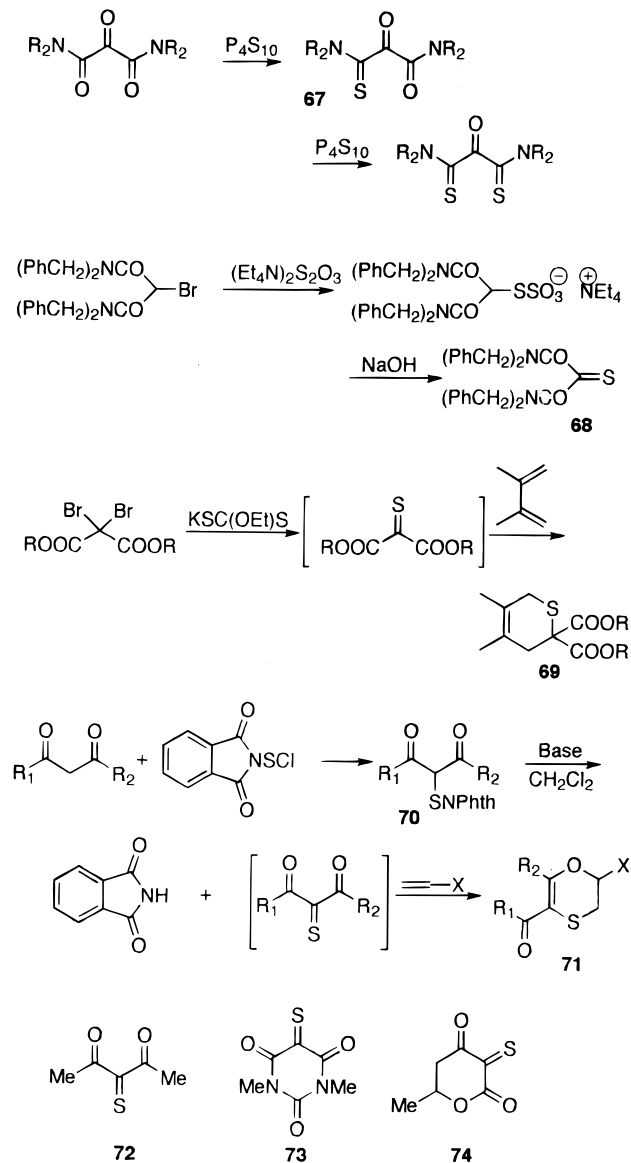
son's reagent did not afford the trithio compound. The 2-thio derivative (**68**) of mesoxalic acid N,N-bis-(dibenzyl)diamide was obtained from the bromo derivative as shown in Scheme 26. Only the specific amide shown could be obtained as a stable substance.

Praefcke and co-workers[77] appear to be the first to have obtained a thiotricarbonyl. Reaction of methyl or ethyl dibromomalonate with potassium-O-ethyl-xanthogenate (KS−CS−OEt) in the presence of 2,3-dimethylbutadiene produced in 70% yield the dihydrothiapyran **69**; this is the product of Diels−Alder addition between the diene and intermediate thiomesoxalate (cf. section V.C.1).

Franck et al.[78] prepared a number of α,α'-diketo-monothiones. Reaction of phthalimidesulfenyl chloride with β-dicarbonyl compounds to afford the sulfur derivatives **70** was followed by base-catalyzed (pyridine, lutidine) elimination of phthalimide to give thiones. Again, these were not isolated but were trapped in situ in good yields as their 1:1 cycloadducts (**71**) with electron-rich dienes, acetylenes, or allenes (cf. section V.C.1). Thiones trapped as transient intermediates in this way included α-thio-

Scheme 27
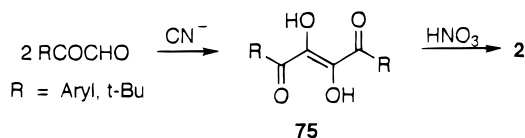
β-ketoesters, 3-thio-2,4-diketopentane (**72**), the al-loxan-derived compound **73**, and the lactone **74**. Unfortunately, no information is available on the properties of the intermediate thiodiones.

Dithia-amides of diketosuccinic acid have been prepared by Mayer et al.[79]

III. Synthesis of Tetra- and Higher Polyketones

A. Tetraketones

All of the reported methods for synthesis of tetra-ketones employed oxidation of di- or tetrahydro precursors. The following discussion is divided into separate sections on open chain and cyclic tetra-ketones. The Wolfe procedure described in the earlier review for preparing tetraketones from diacetylenes has not been used in recent years.

1. Open Chain Tetrones (Scheme 27)

Open chain diaryl and di-*tert*-butyl tetraketones continued to be synthesized by the classical procedure first reported by Abenius and Söderbaum[2] in 1891. Benzoin-like condensation of α-ketoaldehydes with cyanide ion gives "formoins" (dihydrotetraketones, **75**) which are oxidized by concentrated nitric acid to tetraketone hydrates as described in the 1975 review. The fact that concentrated nitric acid is used to obtain tetraketone hydrates from their dihydro pre-cursors is worthy of emphasis because it reiterates the fact that tetraketones are perfectly stable com-pounds under appropriate conditions. The one re-ported attempt to use this method to form a cyclic tetrone from a bis-diketoaldehyde is discussed in the section below on cyclic tetrones.

The formation of 2,4-bisketals of 1,3-dicarbonyls (**53**) as minor products of the reaction of β-ketoesters with diphenyl diselenide and ammonium peroxydis-ulfonate in methanol[58] was noted in section II.A.11. Proper choice of reaction conditions might result in preparation of such tetraketone bisketals in high yield, although their conversion to free tetraketones might well offer problems.

2. Cyclic Tetrones (Schemes 28–31, Chart 2)

Simple cyclic tetraketones such as tetralin tetrone (**76**, dihydrate) and oxocarbons continue to resist attempts to obtain free tetrones from hydrates.

Scheme 28
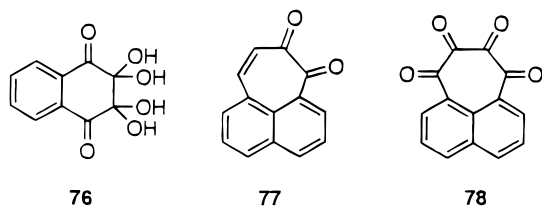
Scheme 29
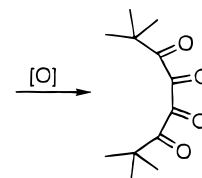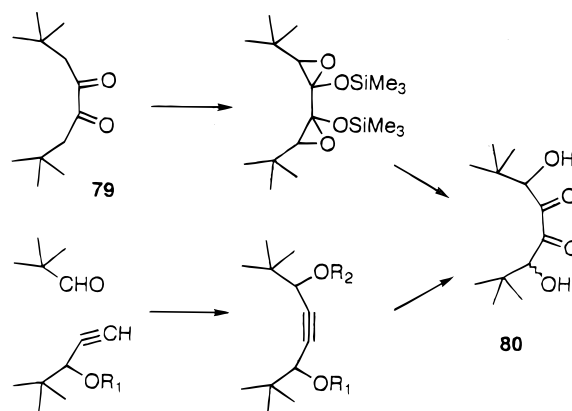
Scheme 30
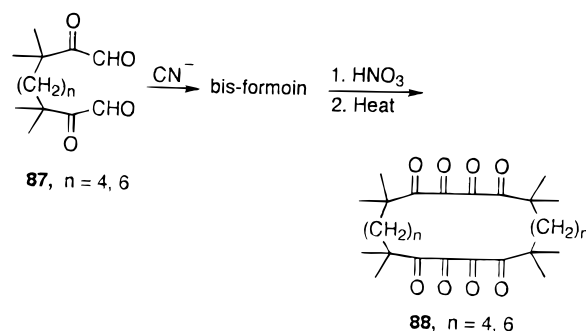
Scheme 31
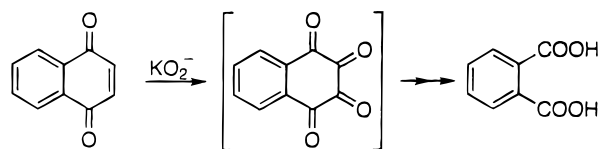
Apparently ring strain and the enforced near copla-narity of *vic*-carbonyl groups dominate here. Gleiter and Dobler[80] reported additional investigations on **76** and attempted conversion of *o*-pleiadenequinone (**77**) to the tetraketone **78**. A variety of procedures includ-ing stepwise oxidations or reaction of a diazotriketone with *tert*-butyl hypochlorite were not successful, phenalenetrione hydrate (**17b**) being obtained among other products.

However, a number of cyclic tetraketones incorpo-rated in medium-sized rings of sufficient size have been prepared by Gleiter and co-workers.[81–86] The tetraketo moiety in all of these compounds was flanked by *gem*-dimethyl groups which served the double purpose of preventing enolization and of shifting the tetrone–hydrate equilibrium in the direction of free tetrone.

Two approaches were used to construct the desired rings and introduce the tetracarbonyl moiety. One

Chart 2
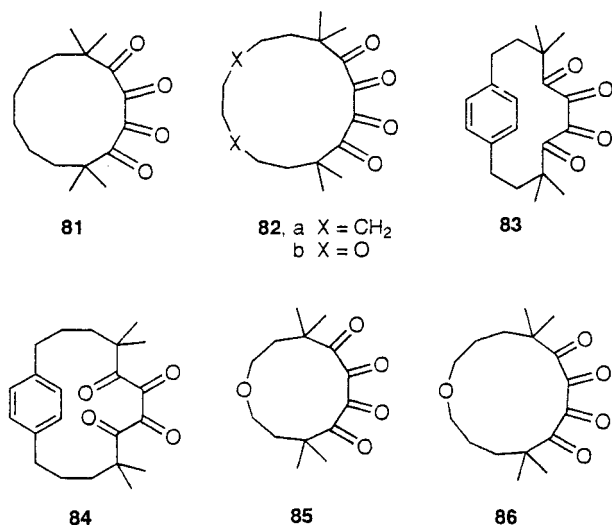
of these involved construction of the appropriate size ring by acyloin cyclization of a diester, oxidation of the acyloin to α-diketone **79**, conversion to a bis-trimethylsilyl ether, epoxidation with *m*-chloroperbenzoic acid, hydrolysis to a mixture of diastereomers (**80**) having the 1,4-dihydroxy-2,3-diketo moiety, and final oxidation to tetrone. This oxidation was achieved using *N*-bromosuccinimide except in one case noted below where benzylic bromination was a problem. Swern oxidation (DMSO/oxalyl chloride) was used successfully.

An alternative approach, used with oxacyclic compounds, involved base-catalyzed cyclization of an open chain compound having acetylenic and aldehydic terminal groups followed by subsequent manipulation to obtain the desired 1,4-dihydroxy-2,3-diketone for final oxidation to tetrone.

The compounds prepared are shown in Chart 2. Carbocycles **81** and **82a** (12- and 14-membered rings) were prepared in 1986 by the acyloin procedure;[81] the cyclophanes **83**[82] and **84**[83] were prepared by acyloin procedure. The final oxidation of the 1,4-dihydroxy-2,3-diketones **80** in the *p*-cyclophane series could not be performed with NBS because of benzylic bromination and was achieved by the Swern procedure (64% yield). The free tetrones were obtained directly. The oxacyclic compounds **85**[84] and **86**[85] and the dioxacyclic compound **82b**[86] were prepared via the acetylenic aldehyde procedure.

Formation of large rings from bis-α-ketoaldehydes (**87**) by the Abenius and Söderbaum procedure[2] did not give the desired cyclic products.[81] Instead, macrocyclic formoins (20- and 24-membered rings, yields not given), dimers of the reactant, were obtained by reaction of two molecules of diketoaldehyde. The formoins were oxidized by nitric acid to bis-tetraketone hydrates which were converted to octaketones **88** by heating in a vacuum. Compounds **88** exhibited spectroscopic properties anticipated for bis-tetraketones.

Tetrones have also been reported[87] as minor products from oxidations with potassium superoxide and 18-crown-6. 1,4-naphthoquinone and 1- and 2-tetralones afforded 56−77% of phthalic acid plus 2−7%

of **76**, while 1,4-chrysenequinone gave 84% of 1,2-phenanthrenedicarboxylic acid and 8% of the corresponding tetrone. The tetrones were suggested to be intermediates in formation of the dicarboxylic acids, as illustrated in Scheme 31 for 1,4-naphthoquinone. In separate experiments under the same conditions, tetrone (hydrate) was shown to be oxidized to the same carboxylic acids.

B. Pentaketones (Scheme 32)

The first synthesis of pentaketones was reported in 1986 by Gleiter and co-workers.[4,88] These were open chain compounds **3** with phenyl or *tert*-butyl end-groups. Starting materials were the bis-diazotriketones **90** prepared from the corresponding 1,3,5-triones by the diazo exchange reaction; the bis-diazodiphenyl compound **90a** had been reported many years ago by Regitz and Geelhaar.[89] Reaction with *tert*-butyl hypochlorite and formic acid yielded the pentaketone hydrates which were dehydrated to pentaketones.

Scheme 32

a, R₁ = R₂ = Ph
b, R₁ = R₂ = t-Bu
c, R₁ = Ph; R₂ = t-Bu
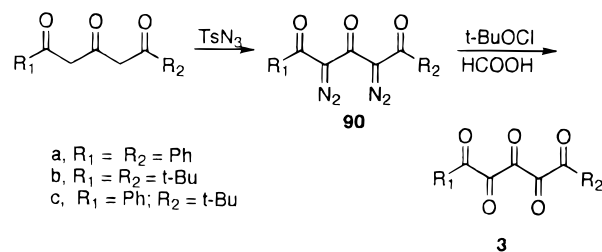
C. Hexa- and Higher Polyketones (Scheme 33)

Attempted application of the method which was successful for synthesis of pentaketones failed to yield diphenyl hexaketone in both our laboratories.[90] The bisdiazotetraketone[91] **91** did not yield identifiable products when submitted to the same reaction conditions in which compounds of type **90** afforded good yields of pentaketones. Likewise, attempts by Wolfe et al.[92] to prepare diphenyl hexaketone from diphenyltriacetylene were not successful.

Scheme 33
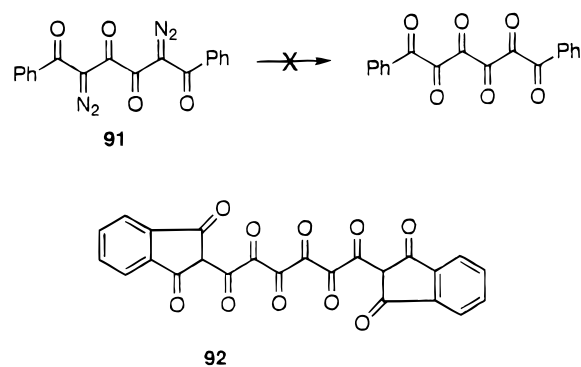
There seems to be no a priori reason hexaketones should not be stable compounds in the absence of water or protic solvent. We conjecture that hydrates in this series can undergo a variety of facile inter- and intramolecular transformations. A successful synthetic method must avoid the presence of even

traces of moisture or protic solvents to be successful; the Schank ozonolysis procedures for triones might be an interesting possibility.

The reported preparation[93] of decaketone **92** incorporating a *vic*-hexaketo moiety could not be repeated.[94] The properties reported for the substance obtained are not those which would be expected for a hexaketone. An amusing typographical error has converted oligomers of ethylene glycol[95] and sulfur-containing analogues into polycarbonyls.[96] The ether linkages −C−O−C− were inadvertently converted into COCO groups.

IV. Carbonyl Derivatives of Polycarbonyls (Schemes 34 and 35)

The standard derivative for characterizing polycarbonyl compounds is the quinoxaline. In a number of cases, as discussed in sections II and III on synthesis, polycarbonyls were not isolated as such but were converted directly to quinoxalines. Quinoxaline derivatives of tetraketones (**93**) and pentaketones (**94**) are formed by reaction of *o*-phenylenediamine with central carbonyl groups. The quinoxaline of the

Scheme 34
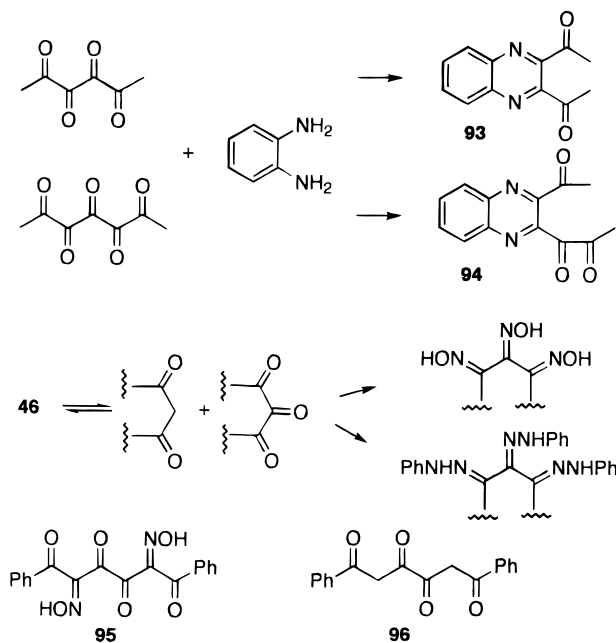
Scheme 35
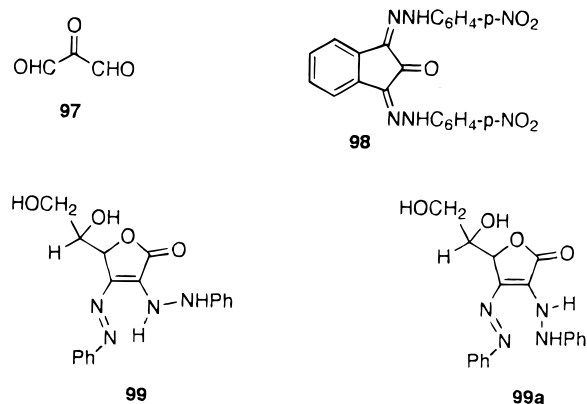
unsymmetrical *tert*-butyl phenyl tetraketone has not been reported.

Deady et al.[97] investigated the reaction of ninhydrin and 5-methylninhydrin with a number of substituted phenylenediamines. A single quinoxaline was obtained in all cases. This specificity was explained by assuming that the most basic of the two amino groups added to the central carbonyl group (reaction 1) followed by reaction of the remaining amino group with the most reactive of the two carbonyl groups in the addition product.

Teuber and Hohn,[53] in their work on oxidation of β-diketones by Fremy's salt, obtained aldol condensation products **46** of starting dione with trione formed by oxidation. These afforded bis- or trisphenylhydrazones and trisoximes as illustrated. A probable explanation is that there is some free trione in equilibrium with **46** in solution or, alternatively, that initially formed derivatives dissociate.

Many polycarbonyls are known only as their derivatives, for example diphenyl hexaketone-2,5-dioxime (**95**) which can be prepared by nitrosation of the readily available 1,3,4,6-tetrone **96**. A well-known procedure for preparing α-diketones is oximation of monoketones to α-ketooximes and subsequent conversion to diketones. Analogous syntheses of polycarbonyls have not been achieved.

Another example of a compound known only in the form of derivatives is mesoxaldehyde (**97**). Roberts[98] has reported a new derivative, the bis-*p*-nitrophenyl-osazone of **97**, obtained by periodate cleavage of glucose *p*-nitrophenylosazone. The corresponding derivative prepared from reaction of ninhydrin with *p*-nitrophenylhydrazine was assigned to the 2-keto-1,3-bishydrazono structure **98**, although no evidence was presented to support this assignment except for a combustion analysis. The same author proposed, on the basis of absorption spectra, that the phenyl osazone of dehydro-L-ascorbic acid has the phenylazo-phenylhydrazono structure **99** and that mutarotation of **99** in solution is due to tautomerism with **99a**.

Schank and Schuhknecht[40] prepared phenyl hydrazone derivatives of the triones obtained from ozonolysis of sulfur ylides.

V. Reactions of Polyketones

A. Reactions with Nucleophiles (Scheme 36)

Fuson's 1939 characterization of the reactions of *vic*-polycarbonyl compounds as "the chemistry of the highly activated carbonyl group" is as valid now as it was 60 years ago. Wasserman has written: "The central carbonyl group of a *vicinal* tricarbonyl system embodies a highly reactive electrophilic site with strong potential for bond formation in organic synthesis". In general, initial attack of nucleophiles occurs at a central carbonyl group since this relieves the maximum number of unfavorable interactions. Reactions proceed at much lower temperatures, often without the catalysis required for simpler carbonyl compounds. Cyclic polycarbonyls, where the unfavorable carbonyl−carbonyl interactions cannot be partially relieved by suitable conformational adjust-

Scheme 36
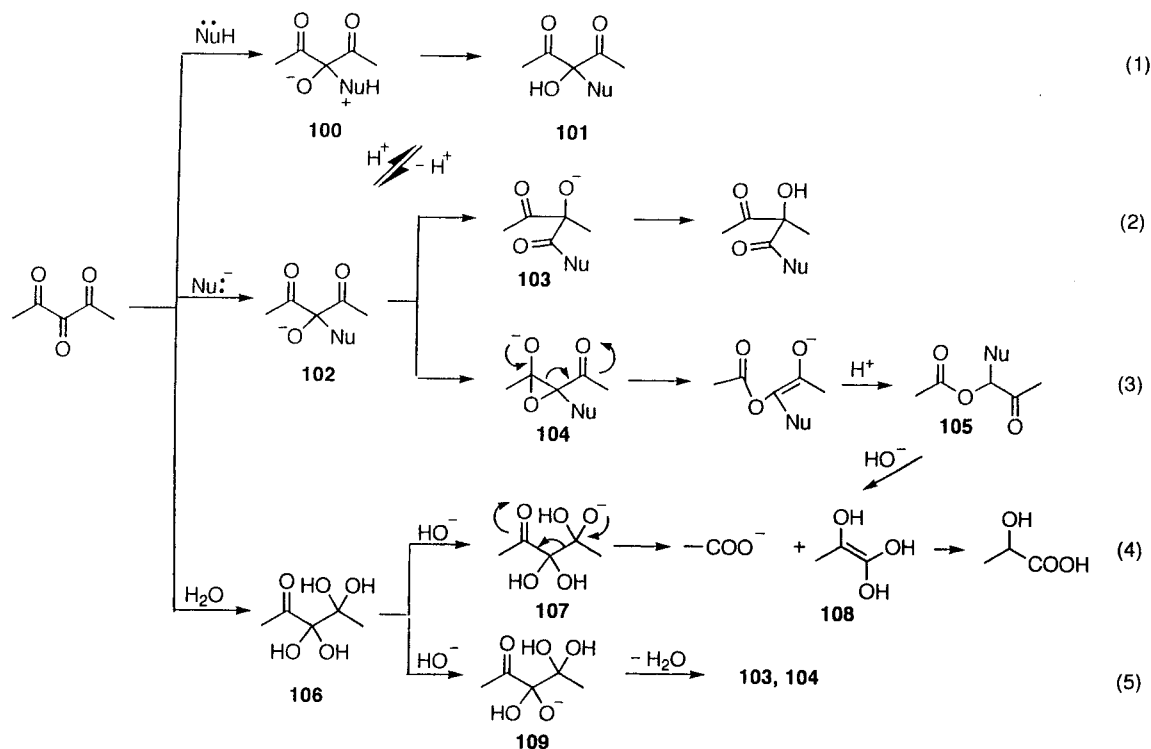
ments, tend to be even more reactive than open chain compounds.

Reactions 1−5 involving interaction of polycarbonyls with a wide range of nucleophiles are summarized in simplified form for tricarbonyls in Scheme 36. Tetracarbonyls may react similarly. Some protonation and deprotonation steps have been omitted for clarity. The scheme treats symmetrical systems; the possibilities for reaction may be multiplied when the initial tricarbonyl is unsymmetrical.

Reaction 1 is the simple reversible addition of neutral nucleophiles NuH to the central carbonyl of a tricarbonyl to give the zwitterion **100**, followed by proton transfer to give the addition product **101**; when Nu is hydroxyl, this is the classical hydration reaction.

When the attacking species is anionic, the initial (reversible) addition product is oxyanion **102**. This intermediate may protonate to **101** or react in two ways, depending on structural constraints and the steric requirements of subsequent steps. In reaction 2, migration of an acyl group produces an isomer (**103**) of the original oxyanion in which an end group and Nu have changed positions. Alternatively, when the structure of **102** permits, the oxyanion can follow reaction sequence 3 by attack on the carbon atom of an adjacent carbonyl group with formation of epoxy intermediate **104**, which rebonds with formation of ketolester anion and terminates, after proton addition, as ketolester **105**. This has been dubbed the diacyl carbinol rearrangement and has been shown by Rubin and Inbar[99] in other systems to involve a series of anionic rearrangements which result in complete scrambling of the groups attached to the initial three-carbon unit.

Reaction sequences 4 and 5 have been suggested to account for results observed with tricarbonyls in aqueous systems where dihydrate formation is possible. Two oxyanions are possible when dihydrates **106** react with strong base. In reaction 4, the oxyanion **107** at C-1 is formed and undergoes a reverse aldol-type of reaction to generate the fragmentation products, carboxylic acid and enetriol **108**; **108** is converted in turn to an α-hydroxy acid (not to an α-ketoaldehyde). We note that a similar hydrolysis of ketolester **105** would afford the same products. The alternate possibility for dihydrate **106** is reaction sequence 5 in which the oxyanion is located at the central carbon (C-2, structure **109**). This can then undergo the same type of rearrangement as described in reaction 2.

We note that a variety of compounds, including enols, phenols, certain amines, enamines, etc., undergo these reactions with the first step being formation of a carbon−carbon bond rather than a bond with a heteroatom. These are grouped together in part 3 below as Carbon Nucleophiles.

A detailed discussion of these reactions follows together with a variety of other reactions of polycarbonyls. Most of the chemistry studied has dealt with tricarbonyls; tetra- and higher polycarbonyls have received very little attention.

1. Hydration (Scheme 37)

Hydration (reaction 1, Nu = OH) is a perennial problem in working with *vic*-polycarbonyl compounds. The equilibrium (eq 6) generally lies far to the right,

$$R_1(CO)_nR_2 + H_2O \rightleftharpoons R_1(CO)_nR_2 \cdot H_2O \qquad (6)$$
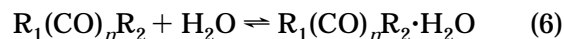
Scheme 37

110, R = cyclohexyl

111a   **111b**   **112**

113   **114**

115

116
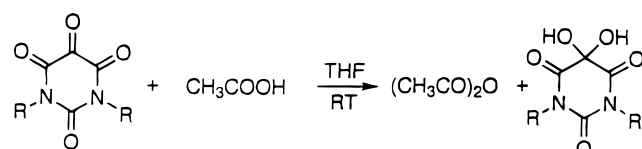
and exposure to air is often sufficient to convert highly colored polycarbonyls to their colorless or faintly colored hydrates (*gem*-diols). The simplest procedure for obtaining hydrates is addition of water to a solution of free polycarbonyl in a water-miscible solvent; immediate decoloration is usually observed. The problem of hydration is particularly acute with cyclic compounds where the carbonyl groups are constrained to near-coplanar conformations.

While probably not of practical significance, the dehydrating power of a *vicinal* tricarbonyl compound was dramatically demonstrated by Endo and Okawara,[100] who prepared acetic anhydride by reacting acetic acid with equimolar *N,N*-dicyclohexylalloxan (**110**, R = cyclohexyl) at room temperature in THF. A number of acetic acid esters were also prepared in 53−60% yields by reaction of alcohols with acetic acid under similar conditions in the presence of **110**; the product alloxan hydrate could be recycled. A colleague once stated, only partly facetiously, that diphenyl tetraketone might be superior to phosphorus pentoxide for use in a glovebox; this after abortive attempts to obtain crystals suitable for X-ray crystallography by crystallization in a glovebox. The problem was finally solved by repeated partial melting and slow cooling of purified tetraketone in a sealed capillary.

An accumulation of spectroscopic evidence has established that hydration occurs at a central car-

bonyl group of polycarbonyls. This was also established by X-ray crystallography of the hydrate of vinyl-α,β-diketoester **25**[37] and by ^{13}C NMR for the hydrate of **11**.[18] Hydration also occurs at one of the central (C-3) carbonyl groups in *vic*-pentaketones.[4] As discussed in the earlier review, steric and electronic effects play a significant role in determining the position of the hydration equilibrium. Thus, samples of di-*tert*-butyl and dimesityl triketones have been stored in ordinary vials for years in one of our laboratories[101] without undergoing appreciable hydration. We also note that the large ring cyclic tetraketones having α,α′-dimethyl groups were obtained as free tetrones without difficulty. Except for the study of diphenyl triketone reported in the earlier review, only one quantitative study of hydration rates or equilibria has been reported. Bowden and Rumpal[17b] studied rates of hydration of **1a**, **17a**, and a series of 5- and 6-substituted indanetriones as well as the parent **4a** at 25, 35, and 45 °C using NMR and UV−Vis spectroscopy. They proposed a push−pull mechanism for hydration involving two molecules of water, one acting as a nucleophile and the second as an acid. Enthalpies and entropies of activation were on the order of 5 kcal/mol and −50 cal/mol·K, respectively. A theoretical study of hydration has also appeared.[102] The value of 30 M^{-1} was given for the equilibrium constant for diphenyl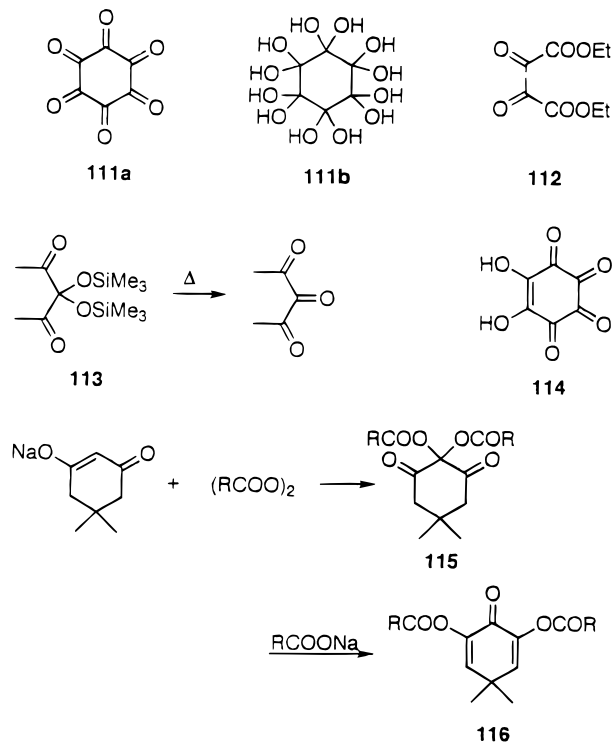 triketone in dioxane at 25 °C in the earlier review; the value for diphenyl tetraketone is on the order of 1000 M^{-1}. Di- or polyhydrates can also be formed, e.g., tetralintetrone is obtained as the dihydrate assigned structure **76**. Extreme cases are the oxocarbons such as cyclobutanetetrone or triquinoyl (**111a**) which are obtained as perhydroxy compounds (e.g., **111b**).

A variety of procedures have been used to obtain the free carbonyl compound from its hydrate. These include heating in a vacuum or sublimation, distillation, crystallization, treatment in solution with molecular sieves or chemical dehydrating agents such as phosphorus pentoxide. Azeotropic distillation with toluene or (better) chlorobenzene followed by concentration has been reported[71] to be a superior method for converting ninhydrin (**4b**) to triketoindane (**4a**), compare also ref 17b. One of the advantages of this procedure is that it leads to large crystals of **4a** which can be manipulated more readily since much less surface is exposed. The preparation of diethyl diketosuccinate (**112**) from the disodium salt of dihydroxytartaric acid by esterification and distillation has been described in a paper by Boger et al.[103]

Hydrates have been converted to bis-trimethylsilyloxy derivatives (**113**) which afforded polycarbonyls on heating.[104] Attempts to obtain rhodizonic acid (**114**) from its hydrate by this method were not successful.

Likewise, experiments designed to obtain triquinoyl (**111a**) from its hexahydrate (**111b**) were a complete failure.[101] A system designed to progressively shift the **111b** to **111a** equilibrium while allowing observation of UV−Vis absorption spectra was constructed. In the event, a yellow solution developed after a few cycles, suggesting formation of an α-diketone moiety, but further cycles resulted in decom-

position with complete disappearance of the UV spectrum.[105] It would appear that preparation of such polycarbonyls can only be achieved under extremely mild conditions in the total absence of water or protic substances.

Since there is always some concentration of free polycarbonyl present in organic solvents, hydration need not be a problem in chemical reactions. Although α,β-diketoesters have been obtained almost exclusively as hydrates, their chemistry is that of the tricarbonyl species. Also, since polycarbonyls absorb light at appreciably longer wavelengths than their hydrates, photochemical reactions can be performed using appropriate filters to ensure that only the polycarbonyl absorbs light. Thus, hydration need not be a problem in synthetic work but makes quantitative measurements, such as kinetics or quantum yield determinations, much more difficult than for compounds which are not in equilibrium with a second species. Clearly the operation of an equilibrium between polycarbonyl and its hydrate in competition with other processes can lead to much confusion. A simple apparatus has recently been described[106] for obtaining solutions of tetraketones free of traces of water for quantum yield measurements.

Diesters (**115**) of hydrates in the 5,5-disubstituted or spiro cyclohexanetrione series have been obtained by Schank et al.[107] in low yields by reaction of the sodium salts of 1,3-diones with diacyl peroxides; monoesters were obtained from the neutral diones. Reaction of **115** with the corresponding sodium acylates resulted in conversion to monoesters **116** of the enolic form of the trione. Further reaction with the appropriate acid chloride gave diesters.

Stevenson et al.[108] have investigated the exchange reaction of indanetrione radical anion with ^{17}O-labeled water.

Although a theoretical treatment[102] of diketoesters (**5**) including their hydration has appeared, the major thrust of work with these compounds has been for synthetic applications. These compounds are generally reported as yellow crystalline hydrates, although the color is suggestive of a tricarbonyl system. In any case, nothing is known about the free tricarbonyl–hydrate equilibrium, and information on other properties of unhydrated **5** is similarly lacking. One might anticipate that the equilibrium (reaction 1) is less unfavorable for diketoesters than for triones and that it should not be difficult to obtain the unhydrated substances.

We attribute the failure to isolate diphenyl hexaketone to problems relating to hydrate formation and instability of the hydrate.

2. Reactions with Alcohols, Amines, Thiols

These are all reactions of type 1 above in which NuH is alcohol, amine, or thiol. In general, rearrangements are not observed, perhaps because of rapid proton transfers to give neutral species.

a. Alcohols (Scheme 38). The rapidity of reaction of polycarbonyls with these weakly basic species is immediately evident from the instantaneous color change when a polycarbonyl is dissolved in alcoholic

Scheme 38
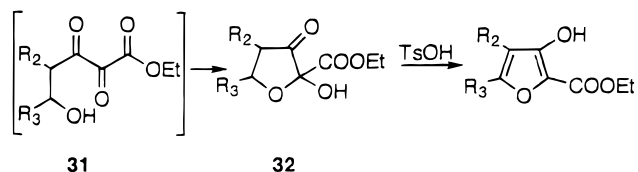
solution to give the colorless or light yellow hemiketal. A corollary is the prohibition on use of alcohol as solvents in reactions of polycarbonyls. This facile reaction was employed in the particularly favorable case of an intramolecular reaction by Wasserman and Lee[47] to synthesize substituted 3-hydroxyfurans. The δ-hydroxy-α,β-diketoesters **31a** prepared as shown in section II.A.6.a were isolated as their hemiketal ring tautomers **32**, dihydrofuranones. Treatment with p-toluenesulfonic acid then afforded substituted 3-hydroxy-2-furyl carboxylic acid esters in high overall yields.

b. Amines (Schemes 39 and 40). Addition of primary or secondary amines to the central carbonyl group of tricarbonyl compounds occurs readily at room temperature in solvents such as methylene chloride. This is reaction 1 in Scheme 36 above with Nu = R_1R_2NH. The absence of rearrangements such as reactions 2 or 3 may be due to the mild conditions or to the fact that initial addition is followed by rapid proton transfer to a neutral species (**101**, Nu = R_1R_2N).

Wasserman and co-workers have employed intramolecular reactions of tricarbonyls with amines for elegant syntheses of a wide variety of natural products. A complete survey of these achievements is beyond the scope of this review;[109] two illustrative examples are provided below, one with penicillin-

Scheme 39

Scheme 40

camine and other indole related alkaloids,[112,113] eudistomins,[114] prodigiosin,[15] carbazoles,[115] pyrrolinone derivatives,[116] and a diketopiperazine.[44]

Loss of water to form a Schiff base has been observed in the reaction of FK-506 with ethanolamine and in reactions of some aromatic amines with **4b**. Enamines and certain meta-substituted anilines undergo carbon−carbon bond forming reactions and are discussed in the subsequent section on carbon nucleophiles. Unexpected results obtained by Wasserman and co-workers[14,116,117] in the reactions of Schiff bases of primary amines are also discussed in the section on carbon nucleophiles.

The vinyltricarbonyls **25** have proved to be particularly fertile substances for synthesis. Their reaction with primary amines involves two addition reactions, Michael addition of amine to the α,β-unsaturated ketone moiety and amine addition to the central carbonyl group to form **121** which can, in turn, be converted to pyrrole derivatives **122**. A number of cases have been described in which the groups R_1 or R_3 possessed additional functionality and underwent further cyclization reactions. An elegant example is shown in Scheme 40, the synthesis of ($\pm$)-vasicine[118] via **123** in 25% overall yield in three steps from o-aminobenzylamine and **25**. Other syntheses include isoquinolines,[37] prodigiosin,[119] carbacephams and carbapenams,[120] ($\pm$)-3-demethoxy-erythratidinone,[121] indolizidines,[15,122] compounds related to pyrrolidine alkaloids,[123] 2-azadethiapenams and 3-azadethiacephams,[120,124] ($\pm$)-slaframine and ($\pm$)-6-epi-slaframine,[125] and a variety of indoles.[126]

Addition of anthranilic acid to phenalene trione **17a** as reported by Wittmann et al.[127] involved normal amine addition followed by lactonization of the intermediate hydroxyacid to give **124**. Quinisatin (**18**, R = H) behaved similarly.

The first step of the classical Ruhemann procedure for detection of amino acids involves an amine addition to ninhydrin.

In an extension of the procedure used for synthesis of imidazoles from diketones, Brackeen et al.[128] employed ethyl esters of diketoacids (R_1 = phenyl and propyl) in reaction with aldehydes (RCHO = formaldehyde, butyraldehyde, benzaldehyde) and ammonium acetate in acetic acid. Imidazoles **125** were obtained in 66−90% yields.

c. Thiols. Addition of thiols to **4a**, diphenyl triketone, and phenalenetrione (**17a**) has been shown by Mahran and Abdo[129] to proceed as expected and give the thio analogues of hemiketals (**100**, Nu = RSH). Spectroscopic behavior of **4b** and *N,N*-dimethylalloxan (**110**, R = Me) in the presence of cysteine and glutathione has been reported.[130]

3. Reactions with Carbon Nucleophiles (Scheme 41 and 42)

A considerable variety of carbon nucleophiles undergo reaction with *vic*-polycarbonyls. They include a large number of enolizable β-dicarbonyl compounds, phenols, phosphorus ylides, enamines, alkoxy- or hydroxy-substitued anilines, malonic acids, and others. These reactions, simple additions to the central carbonyl group of tricarbonyl, particularly cyclic

related compounds and one in the field of indoles. In the first example,[33] *N*-protected (pg = *tert*-butyl-(dimethylsilyl) diketoester **117a** was treated with fluoride ion to remove the protecting group; stirring the resulting **117b** with molecular sieves in methylene chloride solution at room temperature afforded carbacepham **118** in 68% yield (as a mixture of stereoisomers). In the second example,[110] the tricarbonyl **31** ($R_1 = R_3 = H$) was reacted with tryptamine to furnish the indole **119**, which underwent further cyclization to **120**; this in turn was converted into a variety of more complex indole derivatives. In addition to variations in the tricarbonyl, additional functionality could also be incorporated into the amine to allow subsequent reactions.

This approach has also been used for synthesis of the racemic form of the carbapenam antibiotic PS-5,[34] penems,[35] isoquinoline alkaloids[111] including vin-

Scheme 41

Scheme 42

appear, often performed in hot aqueous solution. Recent examples include the work of Peet et al.[131] on the reaction of ninhydrin with a number of β-ketoesters, cyclohexane-1,3-dione, dimedone and the work of Song et al.[132] with β-acylpyruvate esters. Some structures were established by X-ray crystallography.[136] These reactions produced high yields of addition products; in many cases, the presence of additional functionality resulted in subsequent reactions to form new, heterocyclic rings. Reaction between **4b** and a wide variety of monoketones was effected in refluxing acetic acid.[133] The initial addition products (reaction 1) were not isolated but treated directly with hydrazine hydrate to afford pyridazines.

Examples of acid-catalyzed addition were provided by Schank and Schuhknecht[40] who treated methylene chloride solutions of **34** and a variety of related 5,5-disubstituted cyclohexanetriones with their dione precursors (dimedone in the case of **34**) at room temperature in the presence of catalytic amounts of p-toluenesulfonic acid; condensation products **46** were formed in good yields.

Analogous behavior has also been reported for phenols[134] with C–C bond formation *ortho* to a hydroxyl group followed by equilibrium between phenols (**128**) and cyclic hemiketals (**129**).

Reaction of vinyltricarbonyl **25** with active methylene compounds including pentane-2,4-dione, dimedone, and ethyl nitroacetate in the presence of silica gel in methylene chloride at room temperature afforded high yields of **130**, **131**, and **132**, respectively. These reactions are reminiscent of amine additions to **25** in that they involve sequential Michael addition and aldol condensation. Under similar conditions, the trimethylsilyl ether of pentanedione gave **130** in 87% yield. Triethylamine catalysis in methylene chloride gave similar results.

compounds, occur under the mildest of conditions, sometimes simply by mixing the reactants at room temperature in an appropriate solvent. They have presented problems when triones are prepared directly from diones as was indicated in section II.A.7 where it was noted that the Wasserman fluoride ion promoted singlet oxygen oxidation[51] procedure for conversion of dimedone to trione **34** could lead to the condensation product of starting dione with **34**. The same result could be achieved by allowing a solution of dimedone and **34** to stand at room temperature. The aldol-type product, **46**, was obtained in high yield. What could be simpler.

A second example of the same type was shown in Teuber's work[53,54] on the reaction of Fremy's salt with a variety of cyclic 1,3-diones in the presence of sodium acetate. The products **46** obtained resulted from reaction of newly formed trione with unreacted dione. The same products could be obtained when dione and separately prepared trione were allowed to react in the presence of sodium acetate.

Additional examples of reactions of enolizable β-dicarbonyl compounds with ninhydrin continue to

These reactions of **25** provide entry to a variety of substituted cyclopentane derivatives.

A new type of reaction involving successive carbon–carbon bond formations was provided by Wasserman et al.[135] who observed that simply mixing the phosphorane shown with vinyltricarbonyl **25** in ethyl acetate at 0 °C afforded 65% of the cyclopentenone **133** after a reaction time of 0.5 h. This reaction involves Michael-type addition plus Wittig reaction.

Aniline and *para*-substituted anilines reacted in the expected manner with ninhydrin (reaction 1) by addition of the amine to a central carbonyl group (**101**, Nu = ArNH) followed by loss of water to give (unstable) imines. The situation is more complicated with anilines bearing *meta*-hydroxyl or alkoxyl substituents. A number of earlier structural assignments have recently been corrected by application of NMR[136] and X-ray crystallographic[137] methods. *m*-Hydroxy- or *m*-methoxy-substituted anilines were finally shown to react as carbon nucleophiles with formation of a carbon–carbon bond between a position *ortho* or *para* to the amino group and the central carbon of ninhydrin. A simple example is the reaction of *m*-methoxyaniline to form addition product **134** as shown in Scheme 42.

Medium effects were pronounced; failure to reproduce earlier results may be due to considerable sensitivity to reaction conditions as well as to the fact that reactions are reversible. Solubility effects may play a key role in product determination in aqueous solutions. The results with 3,5-dimethoxy aniline illustrate the importance of solvent effects. In benzene solution, a 55% yield of indeno[1,2-*b*]indole **136** was obtained. This resulted from initial reaction at the C-atom *ortho* to both an amino and a methoxyl group to give **135** (not isolated) with an amino group suitably placed to interact with a carbonyl group of the original tricarbonyl. In aqueous solution, a 1:3 mixture containing **136** and **137**, the product of reaction at the position *ortho* to two methoxyl groups, was obtained. Further reaction of **137** gave **136**. The differing behavior in the two solvents was attributed to an equilibrium between starting materials and **136** and **137**; solubilities in water may also play a role.

Enamines also reacted by carbon–carbon bond formation as shown in Scheme 43. The simplest case involved β-aminocrotonic ester which afforded **138** as reported by Huffman.[138] Wasserman and co-workers[14,16,120] investigated the reactions of Schiff bases of primary amines with a variety of *tert*-butyl diketoesters (**5**, R₁ = phenyl, *p*-tolyl, *p*-methoxyphenyl, *p*-dimethylaminophenyl, *o*-methoxycinnamyl, *tert*-butyl, 2-*N*-methylpyrrolyl, *N*-allyl-3-indolyl, and *p*-nitrophenyl, R₂ = *tert*-butyl). The Schiff base **139** from isovaleraldehyde and benzylamine was used in almost all cases. Since the only Schiff bases which were reactive were those derived from primary amines, it was assumed that the enamine tautomer **140** was the reactive species.

X-ray crystallographic analysis established that the products did not have the expected structure **141** but that a rearrangement occurred involving migration of a carboalkoxy group and loss of water to give **142**. This was explained by assuming that **140** reacted at

Scheme 43
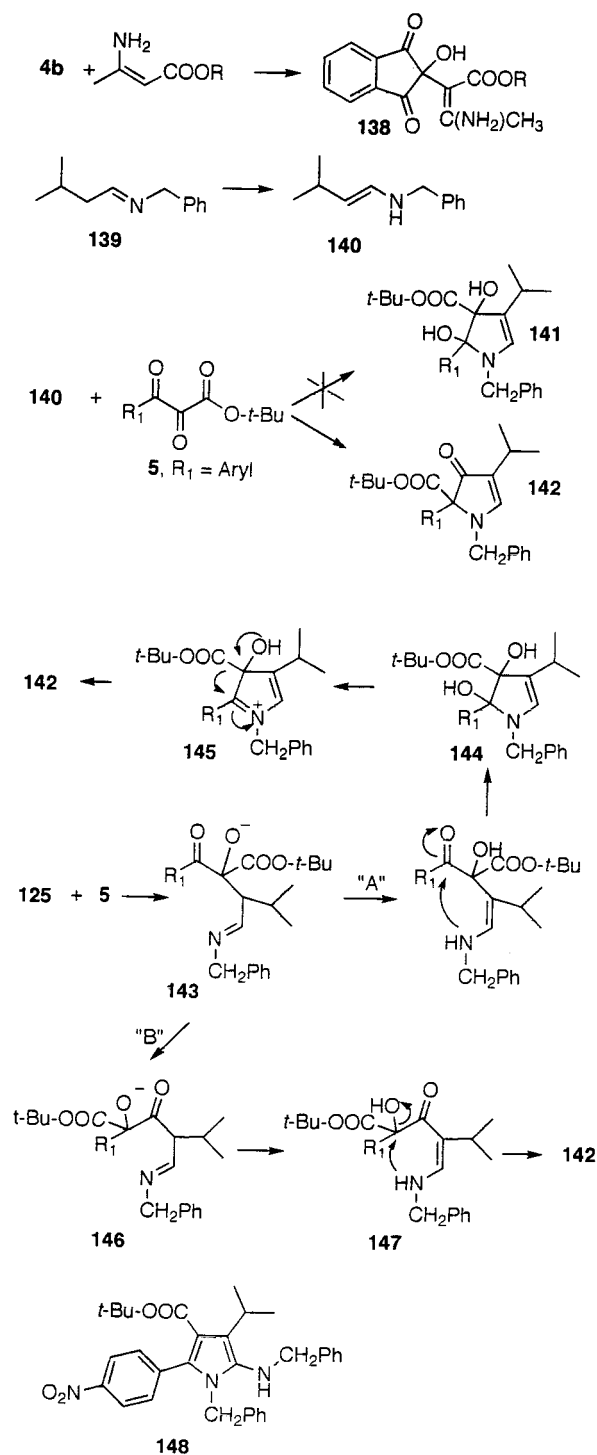
the central carbonyl group of **5** in a carbon–carbon bond forming reaction to give intermediate **143**. Wasserman proposed a series of reactions involving intermediates **144** and **145** followed by rearrangement to **142** as shown in Scheme 43. However, an alternative can be proposed in which initially formed **143** undergoes the benzilic acid type rearrangement (reaction 2, cf. following section V.A.4) **146**. Subsequent conversion to **147** and cyclization would give **142**. If the latter mechanism is correct, these would be the first examples of benzilic acid rearrangements with amines. However, the situation in addition of enamines differs in that stabilization of zwitterion

100 by proton transfer might be much slower than for amine addition.

The β-(p-nitrophenyl)diketoester (**5**, R_1 = p-nitrophenyl) behaved anomalously to give the pyrrole **148** (X-ray structure); the reader is referred to ref 120b for a mechanistic proposal.

4. Rearrangement Reactions

Both the benzilic acid (reaction 2) and diacyl carbinol (reaction 3) rearrangements proceed from the same oxy anion intermediate **102**. Preference for one or the other pathway appears to depend on the steric requirements for migration of acyl groups vs formation of an epoxy anion intermediate **104**, the diacyl carbinol sequence has not been observed with cyclic triones. Competition between the two is only evident in open chain compounds where all necessary conformations can be achieved easily. The benzilic acid rearrangement will be discussed first.

a. Benzilic Acid Type Rearrangement (Scheme 44; Reaction 2, Nu = OH). The classical benzilic acid rearrangement is initiated by attack of hydroxide ion on one of the carbonyl groups of benzil

Scheme 44

102

81, n = 6

82, n = 8 ⟶ n = 8 monohydrate

149

150

151

152
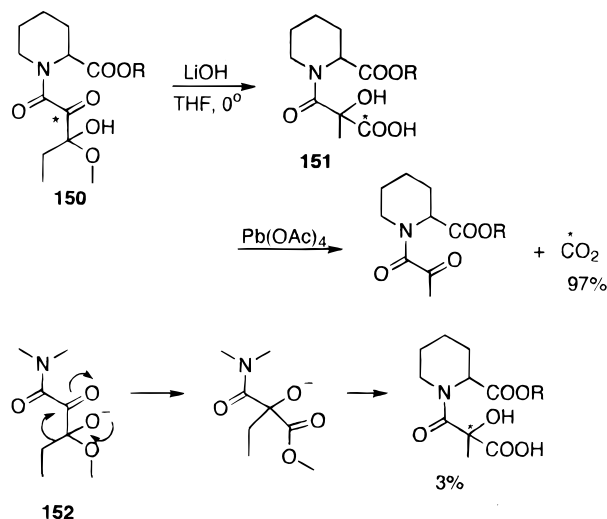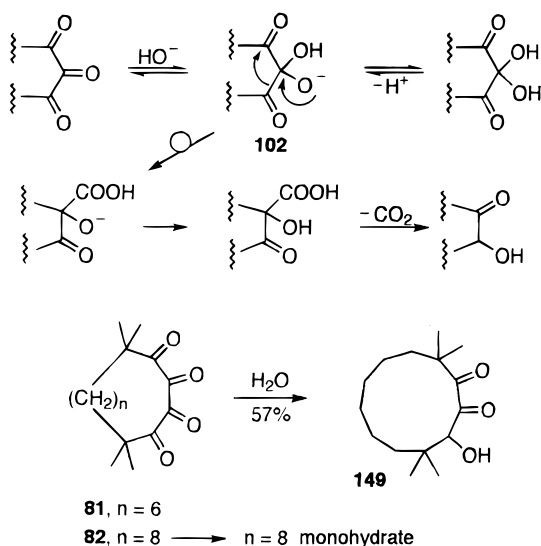
followed by migration of a phenyl group to the carbon atom of the second carbonyl. Similar attack of hydroxide on a polycarbonyl compound would be expected to occur at a central carbonyl group to give intermediate **102**. Formation of **102** can also be achieved by ionization of the weakly acidic hydrates of polycarbonyls and occur in solution without addition of any reagent. In either case, migration of an acyl group as shown in reaction 2 in the general scheme produces an isomer of **102** in which one of the end groups of the tricarbonyl has become Nu. In unsymmetrical cases, all of the groups attached to the tricarbonyl system can exchange positions. The products, after protonation, are β-ketoacids; these have been isolated in a few cases as discussed in the earlier review. In most cases, however, decarboxylation occurs to form an α-hydroxyketone which may be oxidized to dione (or trione when starting from a tetraketone).

A striking example of the ease with which this reaction may occur in appropriate systems is the reaction of cyclododecanetetrone **81** in "wet" organic solvents[81] to give a good yield of the dihydro derivative **149** of ring-contracted cycloundecanetrione (shown as one possible tautomer). The corresponding 14-membered ring tetraketone **82** was converted to its hydrate without rearrangement under similar conditions.

Since hydrates are nicely crystalline compounds in many cases, it is tempting to store polycarbonyls as their hydrates, but this may not be a trouble-free procedure.

An interesting example of the benzilic acid type of rearrangement was observed[139] when immunosuppressant FK-506 (masked α,β-diketoamide, partial structure **150**) was treated with 1 equiv of aqueous lithium hydroxide in THF at 0 °C. The product was shown to include the rearranged moiety **151**. Similar rearrangement of FK-506 to a methyl ester, simply by refluxing in methanol, was reported by Danishefsky et al.[140] (82% yield after 3 h reflux); the products from the two procedures were interrelated. Experiments on the lithium hydroxide reaction using ^{13}C-labeled starting material showed[141] that 97% of the label was incorporated in the carboxyl group of the rearranged product by analysis of the decarboxylation product from reaction with lead tetraacetate. The remaining 3% of the label, found in the rearranged product after decarboxylation, was attributed to rearrangement via oxy-anion **152**; no cleavage products resulting from a reverse aldol reaction (see below) were reported.

In agreement with earlier work on triketones (ref 3), labeling experiments by Dahn et al.[142] showed that the migrating group in the benzilic acid rearrangement of an α,β-diketoester is the carboalkoxy group.

b. Diacylcarbinol Rearrangement (Scheme 45). This rearrangement[143] is reaction 3 in the general scheme and has only been observed with compounds where the diacyl carbinol moiety is not entirely incorporated in a single ring. In the mechanism proposed, the initial oxyanion **102** attacks a neighboring carbonyl group with formation of an epoxide intermediate **104** which undergoes rebonding

Scheme 45
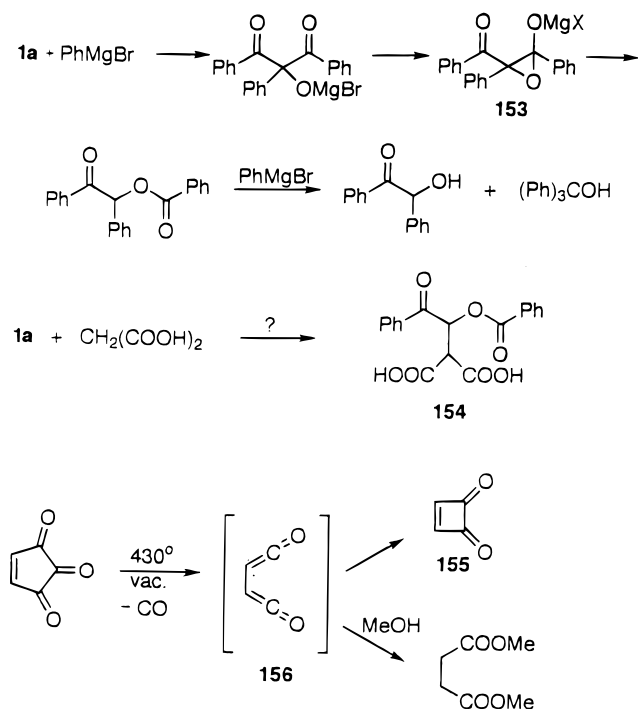
and eventual protonation to form esters. It explains early results observed in reactions of diphenyl triketone with phenylmagnesium bromide and malonic acid (cf. ref 3).

The products obtained in the Grignard reaction were benzoin benzoate from inverse addition of the reagent and benzoin plus triphenyl carbinol from normal addition. The diacyl carbinol mechanism accounts nicely for these products. Initial addition of reagent can be followed by formation of the epoxide intermediate **153** followed by rebonding and eventual protonation (Scheme 45). The cleavage observed with normal addition of reactant to the Grignard reagent is simply the result of further reaction of reagent with the ester product. Similarly, the product from reaction with malonic acid was tentatively assigned to structure **154** on the basis of combustion analysis. However, it was noted in section V.A.4 that benzilic acid rearrangements can result in scrambling of the groups attached to a diacyl carbinol. If this were to occur in the malonic acid reaction, isomeric ketol esters would be formed; no evidence on this point is available. Reaction with sodio malonic ester resulted in unspecified cleavage of trione.

The base-catalyzed cleavage reactions reported by Dahn[144,145] could proceed via diacyl carbinol rearrangement followed by hydrolysis of the product esters in the strong (aqueous) base used. This will be discussed in detail in the following section.

Ester and amide derivatives gave almost exclusive cleavage with the exception of ethyl β-mesityl-α,β-dioxopropionic acid where 90% of the product was derived from the benzilic acid rearrangement pathway. It was shown by ^{14}C labeling in this case that the carboxylate group had migrated.[147]

The possibility of a benzilic acid rearrangement in the reaction of Schiff bases with tricarbonyls[118] was discussed in section V.A.2.b.

5. Cleavage Reactions

Dahn and co-workers have investigated the reaction of a considerable variety of open chain triketones[144a] (alkyl and aryl substituted) and β-aryl-substituted α,β-diketo ethyl esters[145] and one amide[145] in 1−2 N aqueous or aqueous methanolic sodium or potassium hydroxide. Competing benzilic acid rearrangement and cleavage to carboxylic acid plus α-hydroxyacid were observed. With triketones, benzilic acid rearrangement was relatively insensitive to substitution and accounted for about 20% of the product; the major reaction was cleavage. It was suggested that in the aqueous media employed, the tricarbonyls exist as their dihydrates. Reversible reaction with hydroxide ion then generated either oxyanion **107** or **109**. The two competing reactions were considered to arise from the two different oxyanions formed: cleavage from a terminal oxyanion (reaction 4, reverse aldol) and benzilic acid rearrangement from the oxy-anion on the central carbon of the triketo system (reaction 5). The initial cleavage products would be a carboxylic acid and the anion of enetriol **108**. Protonation of **108** was suggested to give the neutral enetriol when ketonized to α-hydroxy acid (and not α-ketoaldehyde). The intermediacy of protonated **108** was supported by iodine trapping experiments, although it has not been observed directly.[145]

We note, however, that it is not necessary to postulate two different oxyanions to explain the observed results. Both types of reaction can be explained via the single oxyanion **102** formed by hydroxide attack at the central carbonyl group of the tricarbonyl system, as shown in reactions 4 and 5 in the general scheme. Such an anion can react either via benzilic acid rearrangement or via the diacyl carbinol pathway. In the latter case, the product ketolester **105** would undergo hydrolysis in the strongly basic medium to produce the observed fragmentation products.

A similar situation is found in the base-catalyzed cleavage of indanetrione (**4a**) and 5- and 6-substituted derivatives of **4a** (cf. ref 17b) which gave o-carboxymandelic acids upon cleavage by hydroxide ion.[144b] The authors considered both reactions 2 and 3 as mechanistic possibilities but did not refer to reaction 4. Rate constants were measured at 25, 35, and 45 °C using UV−Vis spectroscopy to monitor changes in concentration of **4a**.

B. Thermolysis (Scheme 45)

Flash vacuum thermolysis of cyclopentenetrione at 430 °C produced a 10% yield of cyclobutenedione (**155**).[146] The bisketene **156** was suggested to be an intermediate since it is a reasonable precursor of **155**, and trapping with methanol gave a good yield of dimethyl succinate. These results are reminiscent of the photolysis of **4a** discussed in section VI.

Thermal stability of polycarbonyls has not been examined in a systematic manner. It might be noted that techniques such as sublimation, crystallization from solvents such as toluene, and heating in vacuo are frequently used without difficulty for purification

of tri- and tetracarbonyls. However, in their study of thermal ene reactions, Gill and Kirollos[147] noted that 4,4,6,6-tetramethylcyclohexane-1,2,3-trione could not be used at 80 °C because of rapid (unspecified) decomposition and that 4,4,5,5-tetramethylcyclopentanetrione underwent slow decomposition at that temperature.

C. Cycloaddition Reactions

1. Diels–Alder Reactions (Scheme 46)

The function of the central carbonyl of a tricarbonyl as a heterodienophile was described in the earlier review. More recently, vinyl and ethynyl tricarbonyls have been shown to act as normal dienophiles and to a minor extent as heterodienes, and tricarbonyls incorporating a central thione group show heterodiene reactivity.

a. Tricarbonyls as Heterodienophiles. Ruden and Bonjouklian[148] have repeated earlier reactions of diethyl mesoxalate with butadiene, piperylene, and 2,3-dimethylbutadiene. In all cases, the keto function played the role of dienophile and products had the general structure **157**. The malonate moiety in the resulting adducts was converted to a carbonyl group by a series of reactions so that the overall result was equivalent to reaction of a diene with carbon dioxide as dienophile. Reaction of diethyl mesoxalate with 1,4-bis(ethoxycarbonylamino)-1,3-butadiene has also been reported.[149]

Schmidt and Vogt[150] have shown that **4a**, **27a**, and alloxan (**110**) also behave as heterodienophiles in reactions with 1-methoxycarbonyl-, 1,4-bis(methoxycarbonyl)-, and 1,4-bis(trimethylsilyloxy)-1,3-butadienes, yields ranged from 32% to 87%. Similar heterodiene behavior was shown much later by Gill
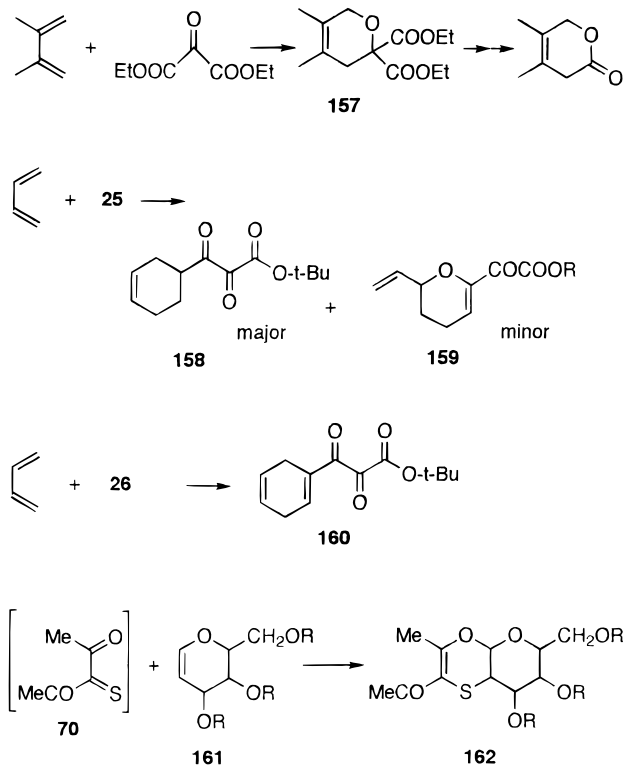
and co-workers[71,154,155] in reactions of **4a** and **110** with isoprene and 2,4-dimethyl-penta-1,3-diene as discussed in section V.D on ene reactions.

Trapping of 2-thiomesoxalates by 2,3-dimethyl-butadiene was mentioned in section II.C in connection with the preparation of thiomesoxalates. The carbon–sulfur double bond behaves as dienophile in these cases.

b. Unsaturated Triones as Normal Dienophiles. Diels–Alder reactions of tricarbonyls having a vinyl or ethynyl group adjacent to the tricarbonyl system with a variety of dienes have been investigated by Wasserman and Blum.[126] The major products from reaction of **25** with dienes were adducts **158** in which the unsaturated ketone moiety in **25** behaved as a normal dienophile. Minor products in these reactions (on the order of 10%) were dihydropyrans **159** formed by reaction of the unsaturated ketone function as a heterodiene. Reaction of acetylenic **26** produced 1,4-cyclohexadienyl tricarbonyls **160** which reacted with primary amines in the same way as the unsubstituted vinyltricarbonyl **25** to yield products which could be converted to substituted indoles. Additional flexibility could be introduced by use of dienes having remote functionality.

c. 2-Thione-1,3-diones as Heterodienes. As noted in section II.C, 2-thio-1,3-dicarbonyls were prepared in solution by Franck[78] et al. but were not isolated as such. Instead, the (presumably) unstable compounds were reacted in situ with a variety of activated dienophiles including enol ethers, silyl enol ethers, vinyl sulfides, vinyl amides, styrenes, electron-rich alkynes and allenes. In all cases the regiospecificity was as indicated in the Scheme. Reactions of the monothione **70** were performed with a variety of glycals **161** by the same group[78] and proceeded with yields of 54–80%; application of the adducts (**162**) for further synthesis was under investigation. Similar results were obtained with five-membered ring compounds. Thiodiones such as **72** reacted in a similar fashion. Reactivity was correlated with the HOMO–LUMO gap of the reactants.

2. Reactions with Aroyloxyketenes (Scheme 47)

Investigation of the photochemistry (section VI.B) of *vic*-tetraketones[106] prompted study of the reactions of such tetraketones (**2**, Ar = phenyl, *p*-tolyl, *p*-anisyl, mesityl, *tert*-butyl) with (benzoyloxy)phenyl ketene (**163**). This ketene was generated, in the presence of tetraketone, by reaction of triethylamine and the appropriate α-(aroyloxy)-α-arylcarboxylic acid chloride. The formation of β-lactones **164** was supported in some cases by isolation of unstable substances having infrared maxima at about 1840 cm^{-1}. These were assumed to be formed by cycloaddition of **163** to a central carbonyl group of tetraketone; two stereoisomers, **164a** and **164b**, are possible in such cases. Subsequent rearrangement of these β-lactones produced the tricyclic lactone **165a** (from **164a**) and, in some cases, minor amounts of the isomeric **165b**. The products from reaction of **163** with diphenyl tetraketone and of (*p*-anisoyloxy)*p*-anisylketene with di-*p*-anisyl tetraketone were identical with the products of photoreaction of these tetraketones. No reac-

Scheme 46
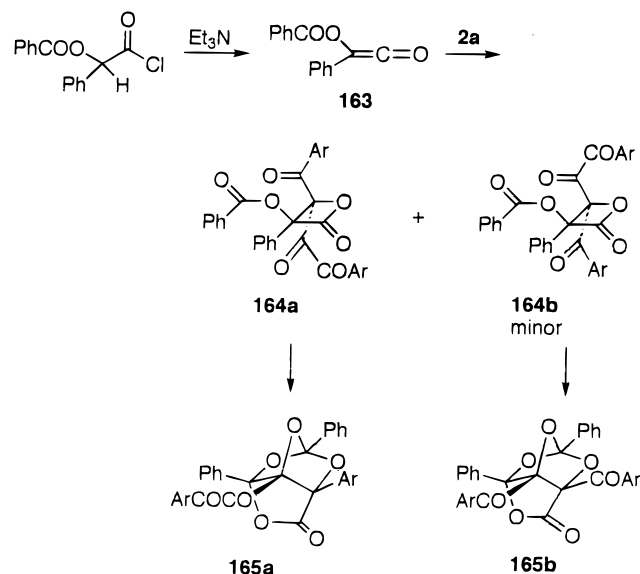
Scheme 47

tion was observed between diphenylketene and diphenyl tetraketone.

3. Reactions with Sulfenes (Scheme 48)

Hanefeld and co-workers[151] have investigated the reactions of a number of tricarbonyls (presumably as their hydrates) with sulfenes **166** generated in situ by the reaction of trimethyl- or triethylamine on sulfonyl chlorides having a hydrogen atom α to the sulfonyl chloride group. All of these reactions were assumed to involve [2 + 2] cycloaddition between the sulfene and the central carbonyl group of the tricarbonyl. Intermediate **167** then reacted further to form products. Chlorosulfonates **168a** were obtained in high yields with diphenyl triketone, **1a**, and quinisatin (**18**, R = H). Alloxan (**110**, R = H) afforded **168b** in which chlorine was replaced by hydroxyl, assumed to be formed by reaction with water present in the

Scheme 48
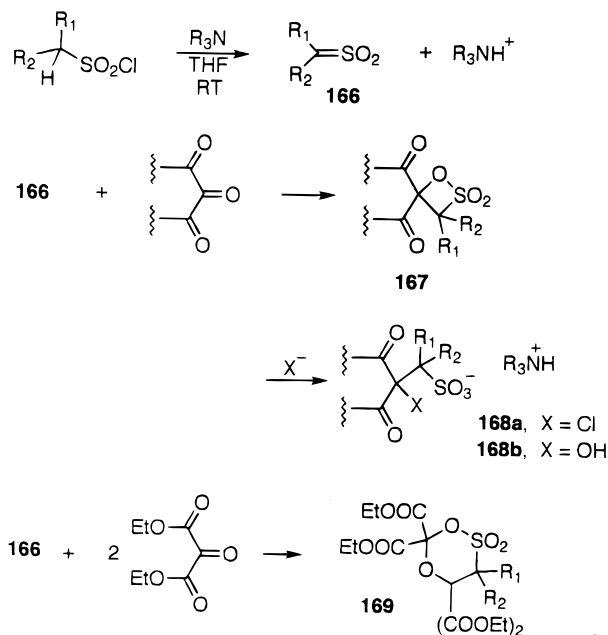
workup. Diethyl mesoxalate gave a different result in which two molecules of mesoxalate reacted to give the cyclic six-membered product **169**.

4. Reactions with Diaryldiazomethanes (Scheme 49)

Schönberg et al.[152] continued their investigations of the reaction of diaryldiazomethanes with tricarbonyls. Both phenalenetrione hydrate (**17b**) and quinisatin (**18**, R = H) reacted with phenyl-(*p*-nitrophenyl)diazomethane to give dioxolanes **170** and **171** in high yields. Other possible products, such as epoxides, were not detected.

Scheme 49
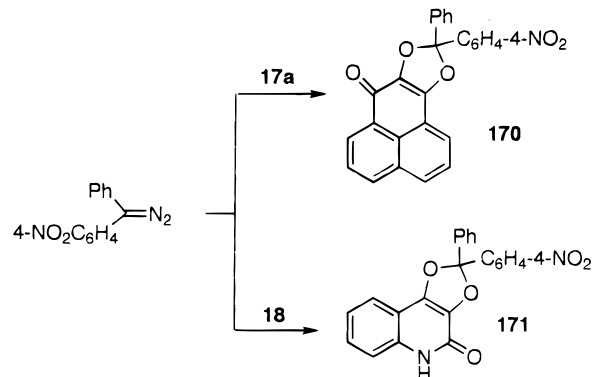
D. Ene Reactions (Scheme 50)

Salomon and co-workers[153] reported a series of thermal ene reactions with diethyl mesoxalate in which an alkene having an allylic hydrogen atom added to the central carbonyl group of the tricarbonyl with migration of the olefinic double bond to give 1:1 adducts **172**. This work was confirmed by Gill and Kirollos[154] who also investigated reactions of 4,4,5,5-tetramethylcyclopentanetrione and triketoindane (**4a**) with a considerable variety of open chain and cyclic mono-, di-, and trisubstituted olefins in the temperature range 80−180 °C. Mixtures of *E*- and *Z*-isomers resulted. Preferential reaction occurred at a terminal double bond in compounds having two nonconjugated double bonds. Terminal acetylenes were also reactive, producing allenes **173**. Later work[155] described similar results using alloxan (**110**, R = H) and *N,N*-dimethylalloxan (**110**, R = Me). The fact that 4,4,6,6-tetramethylcyclohexane-1,2,3-trione could not be used because of thermal instability at 80 °C has been noted above. The order of reactivity at 80 °C was indanetrione > tetramethylcyclopentanetrione > mesoxalate. In fact, Gill et al.[71] have given indanetrione the complimentary title of "super enophile". Generally, yields were high in all of the above reactions. The observation that 1,3-dienes gave cycloaddition products with **4a** and **110** in which the central carbonyl group functioned as a heterodiene has been mentioned in section V.C.1 on Diels−Alder reactions.

Oxidation of the resulting addition products (ceric ammonium nitrate in acetonitrile at room temperature[159] or periodic acid in dry ether[71,151]) afforded good yields of allylic **174** or allenic **175** carboxylic acids containing one carbon more than the original olefin (one stereoisomer shown), so that the tricarbonyls

Scheme 50

Scheme 51
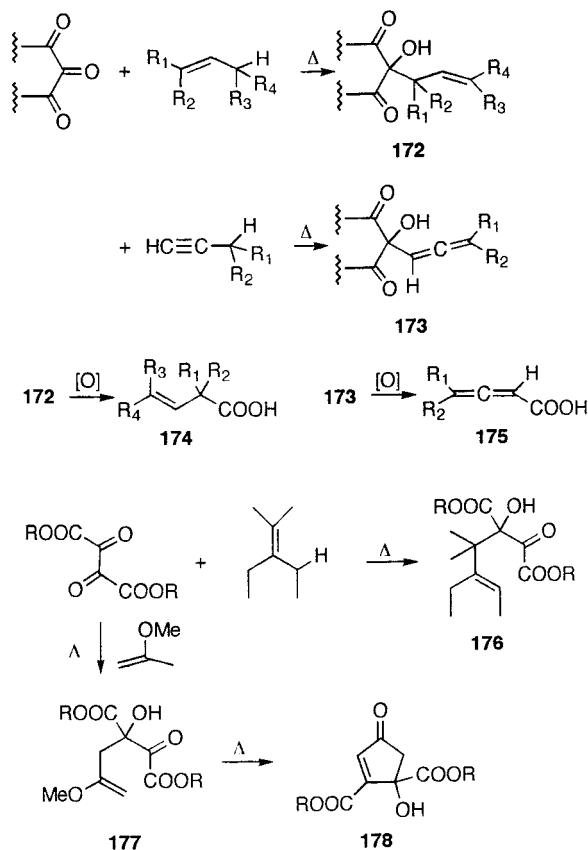
have been likened to a "masked carbon dioxide equivalent". The other product was phthalic acid.

Similar reactions of alkenes to give adducts **176** have been reported[156] with dimethyl and diethyl diketosuccinates, also with high yields. These required 24−72 h at 120 °C, indicating that diketosuccinates are less reactive than indanetrione. Heating methoxyalkenes with diketosuccinate resulted in a double ene reaction, first to give intermediates **177** which underwent a second ene reaction to cyclopentenones **178** in moderate yield; the reaction with 2-methoxypropene illustrated below gave 41% of cyclopentenone. Ene reactions have not been investigated for other tetracarbonyls.

E. Keto–Enol Tautomerism (Scheme 51)

Polycarbonyls having suitably disposed hydrogen atoms might undergo keto−enol tautomerism. The enol tautomer contains a conjugated carbonyl group plus the possibility of hydrogen bonding with a carbonyl oxygen and might be expected to have considerable stabilization. A second such enolization is possible if a hydrogen atom is available on the other side of the polycarbonyl moiety. Such behavior has not been reported with any open chain triketones, reminiscent of the behavior of α-diketones. Likewise, enolic forms have not been reported with diketoesters, although it should be noted that these have almost invariably been obtained as hydrates.

On the other hand, cyclohexane-1,2,3-triones undergo a facile conversion to bisenolic forms **179**. Red solutions in methylene chloride containing such triones (plus an equimolar amount of DMSO) can be
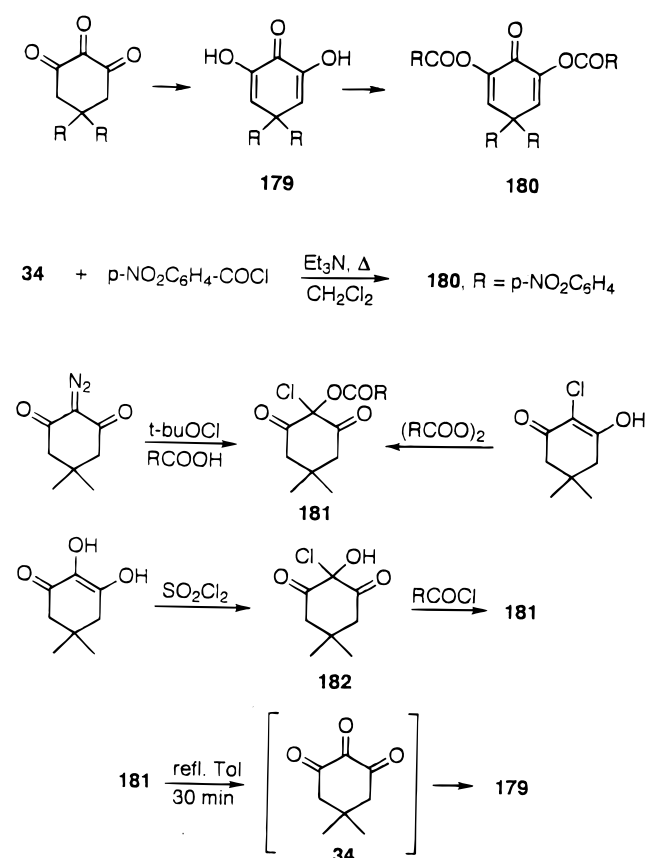
obtained by low-temperature ozonolysis of sulfonium ylides (cf. section II.A.6.c). Schank and Schuhknecht[40] showed that the red solution containing trione **34** yielded 75% of the bisenol diester **180** after 0.5 h reflux with *p*-nitrobenzoyl chloride and triethylamine in methylene chloride. Related 5,5-disubstituted cyclohexanetriones (e.g., **37**) behaved in the same way.

Similarly, Schank et al.[157] showed that the usual procedure of heating *gem*-chloroesters (**181**) in toluene, a useful preparative procedure for tricarbonyls (cf. section II.A.2), could not be applied to cyclohexanetriones. Heating **181** briefly in toluene solution afforded a transient red color (triketone) which rapidly faded; the product isolated was bisenol **179**. **181** could also be prepared by the reaction of diacyl peroxides with 2-chloro-1,3-cyclohexanediones or by the reaction of sulfuryl chloride with dihydrodiones to give chlorohydrin **182** followed by esterification with acid chlorides. The chlorohydrin **182** also gave **179** upon heating. In the latter two examples, hydrogen chloride is produced so that a catalyst for enolization is formed together with the expected trione. These results are in accord with general observations that cyclic triones, particularly when incorporated in relatively small rings, are appreciably less stabilized than open chain analogues. These methods might be applicable to synthesis of tricarbonyls which are not plagued by enolization problems. Systematic studies of keto−enol equilibria in other systems have not been performed.

All of the tetraketones reported to date have been flanked by quaternary carbon atoms or by aryl groups

so that there is no possibility of enolization. Discretion may be the better part of valor; at present no information is available.

F. Reductions (Scheme 52)

Reduction of tri- and tetracarbonyls can lead to mixtures of polyhydroxy compounds as discussed in the earlier review and have hardly been investigated except for the two examples below on compounds related to 5,5-disubstituted cyclohexanetrione. The two recent examples of trione reduction, discussed below, involved cyclic compounds.

Scheme 52
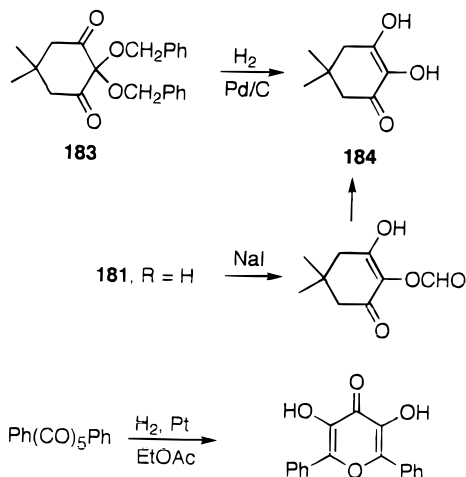
Schank et al.[107] reduced bis-dibenzyl ethers (**183**) of 5,5-dimethyl and 5,5- spirocyclohexanetrione hydrates (from reaction of bisbenzyloxycarbonyl peroxide with the sodio derivative of dimedone) catalytically over Pd/C in methanol−ethyl acetate to obtain the dihydrotriones **184** (reductones). Schank and Blattner[21] showed that the *gem*-chloroformates **181** (R = H) were reduced by sodium iodide to formate esters of **184**; hydrolysis gave **184**.

In addition Gleiter and co-workers[88] have reported some reductions of pentaketones. Catalytic hydrogenation of diphenyl pentaketone (**3**, $R_1 = R_2 = Ph$) afforded the γ-pyrone shown. The same result was obtained using a solution of ascorbic acid in aqueous ethanol.[158]

VI. Photochemical Reactions of Polyketones

The active interest in diketoesters and related compounds has been confined to applications of these compounds for synthesis. Little attention has been paid to other aspects of the chemistry or physical properties of these compounds, most of which have only been obtained as their hydrates. This section on photochemistry is, therefore, wholly concerned with polyketones.

A. Triketones (Schemes 53 and 54)

Photochemical reactions of open chain triketones have proved to be very sluggish and to result in mixtures of products.[159] Quantum yields for disappearance of diaryl and di-*tert*-butyltriketones (**1**) in

Scheme 53
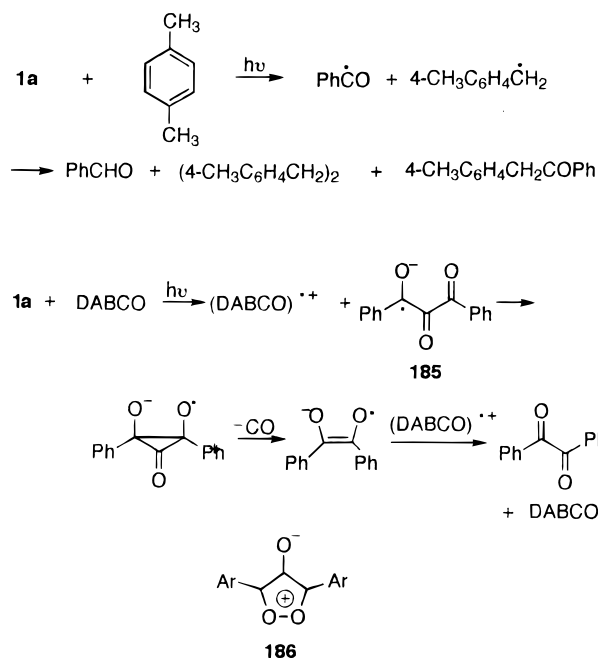
Scheme 54
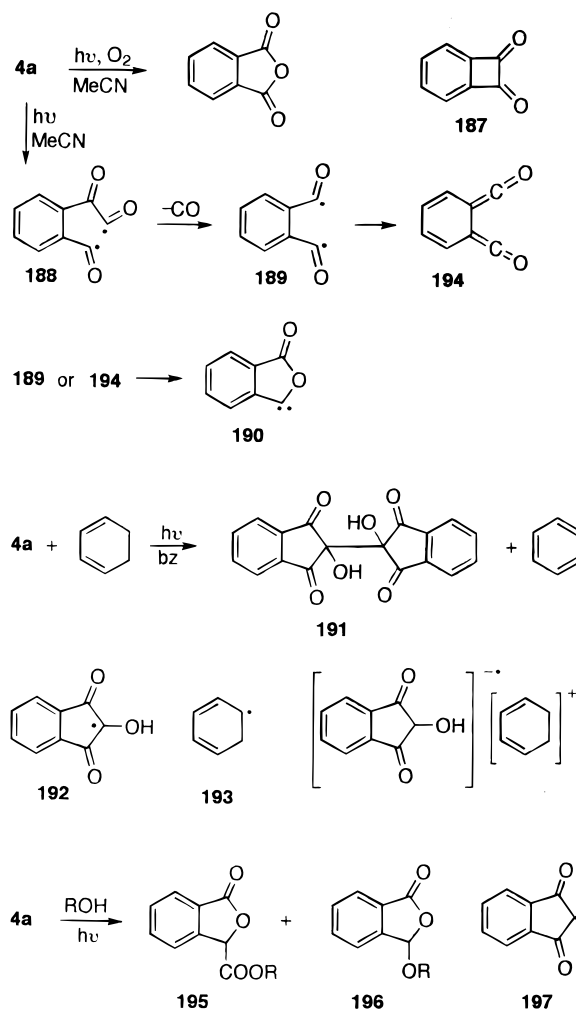
degassed benzene or *p*-xylene solutions at 436 nm were on the order of 0.001−0.0001; qualitatively similar results were obtained in toluene and cyclohexane solutions. Major products from prolonged

preparative irradiation (full spectrum of a mercury vapor lamp through Pyrex, 19 h irradiation for 90% conversion of 0.25 g of compound) of diphenyl triketone in *p*-xylene solution were *p*-methylbenzyl phenyl ketone, *p,p′*-dimethylbibenzyl, and benzaldehyde; in addition, smaller amounts of oxidation products such as *p*-methylbenzyl benzoate were identified. The products appear to be formed from intermediate benzoyl and *p*-methylbenzyl radicals which might have resulted from very inefficient (or reversible) initial H-atom abstraction or α-cleavage mechanisms. Distinction between these possibilities has not been possible. The very minor products appear to derive from reactions of intermediate radicals with traces of oxygen present.

Similar products were obtained with other open chain triketones and bicyclic trione **40**.

Interestingly, photolysis proceeded very differently in the presence of an electron donor such as DABCO.[159] Reaction of diphenyl triketone proceeded with significantly higher quantum yield and produced a single product, benzil. The photochemical step is assumed to involve single electron transfer (SET) from DABCO to trione to give radical anion **185** followed by subsequent radical ion chemistry as illustrated in the scheme.

Low-temperature (down to 77 K) irradiation of **1** (R = Ph) provided no evidence for formation of the mesoionic form **186**. The absorption spectrum was essentially unchanged except for the usual effects of cooling and was not affected by irradiation using the full spectrum of a mercury vapor lamp through Pyrex. X-ray crystallographic evidence that **186** is not important in the electronic ground state of **1** has been provided by Cannon et al.[32]

Three reports on the photochemistry of triketoindane (**4a**, λ_{max} 610 nm), the dehydration product of ninhydrin, have appeared. Netto-Ferreira and Scaiano[160] carried out steady state and laser flash photolysis investigations. They determined the triplet energy to be 42 kcal/mol from phosphorescence emission (λ_{em} 682 nm). A value of 47 kcal/mol was reported earlier[3] for cyclic trione **34**. **4a** sensitized the formation of singlet oxygen with a quantum yield of 0.65. The photochemical efficiency showed a considerable similarity to that obtained with open chain triones summarized above. While quantum yields were not determined, the photochemical inertness of **4a** is clear from the fact that 250 h irradiation of a degassed solution in dry acetonitrile with a moderately powerful light source resulted in only 5% conversion! The products were the dimeric lactones which have been shown to be products of the irradiation of benzocyclobutenedione (**187**) under similar conditions. This was rationalized by assuming α-cleavage of **4a** to biradical **188**, which decarbonylated to **189** and was converted to carbene **190**, the precursor of the isolated dimeric lactones. Irradiation in the presence of oxygen resulted in exclusive formation of phthalic anhydride, a result reminiscent of α-diketone photochemistry.

Interestingly, photolysis in the presence of 1,3-cyclohexadiene resulted in a more efficient reaction with formation of a single product, hydrindantin

(**191**). Presumably intermediates are the ketyl radical (**192**) of **4a** together with the cyclohexadienyl radical **193**, which could then lose a second hydrogen atom to give benzene. The authors suggested that adjacent carbonyl groups participate in the hydrogen-atom transfer process. This effect, which may require appropriate conformations of the polycarbonyl system in the excited state, was not observed with diphenyl or other triketones in hydrogen-atom-donating solvents such as toluene, *p*-xylene, or cyclohexane (see above). An attractive alternative is a SET mechanism such as that observed with diphenyl triketone in the presence of DABCO. The initial products would be the radical anion of **4a** and the radical cation of cyclohexadiene with proton transfer following the electron transfer step.

In a later report on indanetrione, Adam and Patterson[161] confirmed the results reported for **4a** by Netto-Ferreira and Scaiano.[160] They also described high-intensity ("laser-jet") irradiations of **4a**. Under the high-intensity conditions, an additional product, benzocyclobutenedione (**187**), shown separately to be stable under the irradiation conditions, constituted about 10% of the product. This was suggested to arise by an electrocyclic photoreaction of intermediate bisketene **194** in a process involving two successive excited-state reactions. It was proposed that the short lifetime of **194** precluded any significant light absorption and subsequent photochemistry under conventional irradiation conditions in contrast to the high-intensity experiments.

An additional investigation of triketoindane, this time in methyl, ethyl, or isopropyl alcohol solutions, was reported by Tatsugi et al.[162] to give the lactones **195** and **196** shown. In these solvents, the trione is converted nearly quantitatively to hemiketal **197**. Since the full spectrum of a high-pressure mercury lamp was used for irradiation, **197** would also absorb incident light and the observed photochemistry is most probably due to **197** and not to **4a**. The products can be rationalized readily by α-cleavage of **197** and subsequent radical reactions. Similar cases, where triketone photochemistry was claimed when hydrates or ketals were actually involved, were reported in the earlier review. It was emphasized that photochemistry in the presence of protic solvents will not be due to the trione system unless the appropriate range of irradiating light is employed.

Otsuji et al.[163] have reported an investigation of the photolysis of the diethylketal of phenalenetrione (**17a**) which proceeded via an α-cleavage mechanism. Differences in behavior between this compound and ninhydrin were discussed.

The reasons for the photochemical inertness of triketones are not understood, but it is clear that radiationless deactivation is the (almost) exclusive process. While this might be attributed to the low singlet and triplet energies of such molecules, analogous tetraketones, which must have even lower excited-state energies, showed reasonable photochemical reactivity.

B. Tetraketones (Scheme 55)

Photoirradiation of open chain tetraketones[106] provided a delightful contrast to the reactions of tri-

Scheme 55
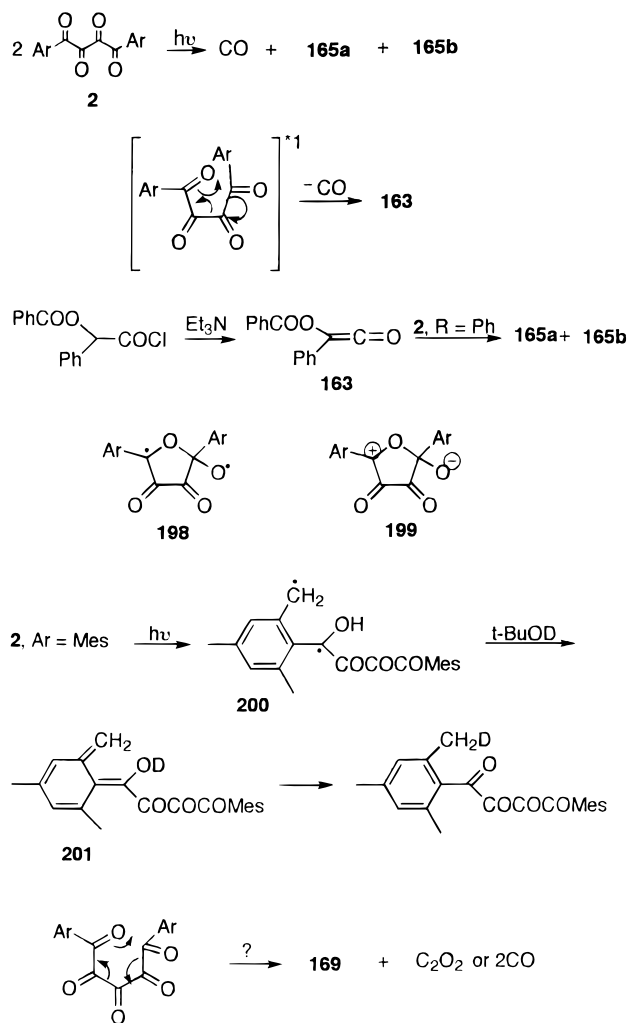
ketones. Although quantum yields at 546 nm were low (ca 0.02), interesting products were obtained from **2** (R = phenyl, *p*-tolyl, *p*-anisyl, and *p*-bromophenyl) in high chemical yields. The highly flexible molecules **2** were converted into rigid tricyclic ortho ester lactones as illustrated; isomer **165a** was the major or exclusive product in all cases with a low yield of **165b** in the case of diphenyl tetraketone. These reactions were shown, by matrix isolation photolysis at 10 K and by other methods, to proceed via intermediate acyloxyketenes **163**. These ketenes, prepared by conventional treatment of appropriate carboxylic acid chlorides with triethylamine, reacted in the dark with tetraketones to produce the same products as the photochemical reactions (cf. section V.C.2). Limited evidence supported a singlet-state reaction. If this is correct, a cyclic mechanism such as that shown in the scheme could be involved in conversion of tetraketone to ketene; a triplet-state reaction would require cyclic biradical (**198**) or zwitterionic (**199**) intermediate(s).

Exceptions to this behavior were dimesityl and di-*tert*-butyl tetraketones and the cyclophane tetrone **84**, all having bulky groups flanking the tetraketone moiety. Steric effects may be responsible for retarding ketene formation in these molecules. In the case of dimesityl tetraketone, a competing reaction, hydrogen-atom abstraction from *ortho*-methyl groups was

shown to occur. This produces biradical **200** which is converted to the enol **201**; ketonization regenerates the starting tetraketone. Irradiation in the presence of *tert*-butylOD, which reacts extremely slow with tetraketones, resulted in incorporation of deuterium, via such an enol, into *ortho*-methyl groups. This proposal, analogous to that observed for *ortho*-substituted benzophenones and *ortho*-substituted phenyl-α-diketones, is shown in the scheme. Similar reactions could be involved in the cases of the other unreactive tetraketones, although steric effects could also be important.

An analogous cyclic mechanism for triketones would also produce **191** without elimination of carbon monoxide. However, this would require a four-membered ring in the transition state.

C. Pentaketones (Scheme 55)

Analogy with the photoreaction of diaryl tetraketones suggested that pentaketones might form the same ketene **163** by elimination of C_2O_2 (ethylenedione) or 2 CO in a cyclic process. Unfortunately, it has not been possible to isolate any pure product(s) from irradiations of diphenyl pentaketone under a variety of conditions in either of our laboratories.[90]

VII. Structures of Polyketones. Theory and Experiment (Figure 1)

The juxtaposition of carbonyl groups raises a number of interesting questions concerning the structures of the resulting polycarbonyls. Both bond lengths and bond angles could be modified as compared with simple carbonyl compounds. In addition, the justifiable assumption[25] (see below) that rotational barriers about the intercarbonyl single bonds will be small means that chains of carbonyl groups can adopt a variety of conformations. Of particular interest is the possibility of helical (ergo chiral) conformations.

In the following discussion, we use the notation for a string of carbonyl groups starting from C-1, O-1; C-2, O-2, and so on, the torsion angles between adjacent carbonyl groups are designated α_1, α_2, etc.,
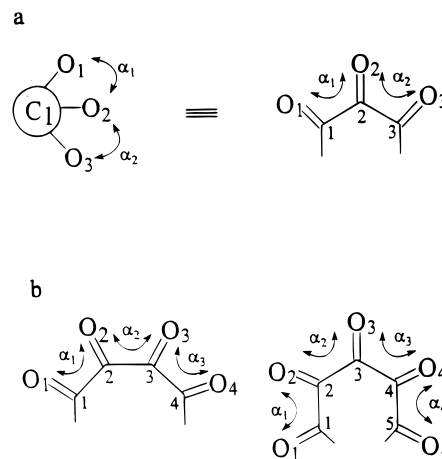
Figure 1. (a) Atom numbering and torsion angles of a *vicinal* triketone unit. (b) Atom numbering and torsion angles of a *vicinal* tetraketone and a *vicinal* pentaketone unit.

Chart 3

202 203 204 205 206 207 208

209 210

211a, X = S   211b   211c
212a, X = O   212b   212c

213 214 215

216a ⇌ 216b
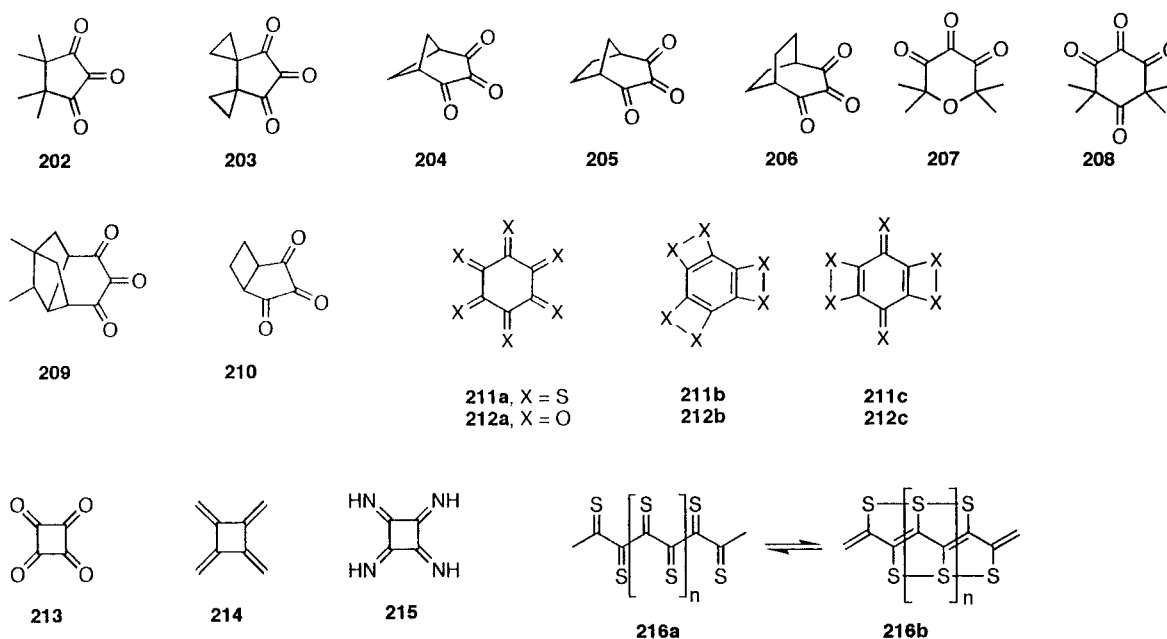
Table 2. Selected Bond Lengths (Å) and Torsion Angles (deg) of Diphenyltriketone (1a), Dimesityltriketone (1c), Di(p-bromophenyl)triketone (1b), Indanetrione (4a), 1,5-Dimethylbicyclo[3.1.0]hexane-2,3,4-trione (12b), Cyclopentenetrione (13), o-Tropoquinone (62), 4,4,6,6-Tetramethylcyclohexane-1,2,3-trione (63), Tetramethylcyclopentane-1,2,3-trione (202), Dispiro[2.0.2.3]pentane-7,8,9-trione (203), Bicyclo[3.1.1]heptane-2,3,4-trione (204), Bicyclo[3.2.1]octane-2,3,4-trione (205), Bicyclo[3.2.2]nonane-2,3,4-trione (206), Tetrahydro-2,2,6,6-tetramethyl-2H-pyran-3,4,5-trione (207), 4,4,6,6-Tetramethylcyclohexane-1,2,3,5-tetrone (208), and 7,8-Dimethyltricyclo[5.2.1.1^{5,8}]undecane-2,3,4-trione (209)[a]

compound	α_1	α_2	C_1-C_2	C_2-C_3	C_1-O_1	C_2-O_2	C_3-O_3	ref
1a[b]	125	110	1.523(4)	1.522(5)	1.216(1)	1.213(4)	1.209(3)	164
1a[c]	129	107	1.556(5)	1.556(5)	1.212(5)	1.212(3)	1.212(3)	170
1c	154	127	1.525	1.529	1.213	1.207	1.213	165
1b	130.9	130.9	1.540	1.540	1.220	1.221	1.220	165
4a	0	0	1.526	1.526	1.227	1.189	1.227	168
12b[d]	17	−18						169
13	0	0	1.521(5)	1.521(5)	1.208(5)	1.199(3)	1.208(5)	166
62	9.9	−21.2	1.562	1.519	1.216	1.200	1.222	70
63	20	23	1.539(7)	1.531(6)	1.214(6)	1.209(5)	1.214(6)	169
202[d]	0	0						169
203[d]	0	0						169
204	0	−11	1.553(2)	1.545(2)	1.206(2)	1.199(2)	1.207(2)	169
205[d]	7	−9						169
206[d]	12	12						169
207[d]	51	8						169
208[d]	27	17						169
209[d]	51	8						169

[a] For the definition of α_1, α_2, and the numbering of the atoms, see Figure 1a. [b] X-ray study. [c] Electron diffraction in gas phase. [d] Bond lengths were not available.

as illustrated in Figure 1. Experimental evidence is largely confined to single crystals studied by X-ray diffraction and limited to polyketones.

A. X-ray Crystallography

1. Triketones (Table 2, Chart 3)

X-ray structures of a considerable number of triketones have been reported[32,70,164−168] since the earlier review when only indanetrione (**4a**)[168] and alloxan (**110**, R = H)[167] had been determined. The compounds which have been investigated in this way are shown in Charts 1 and 3. The torsion angles α_1 and α_2 (as defined above) and selected bond lengths are listed in Table 2.

The torsion angles between CO groups in the open chain triketones, diphenyl triketone (**1a**),[164,170] dimesityl triketone (**1c**),[165] and di-p-bromophenyl triketone (**1b**)[32] varied between 110° and 154°. A further point of interest with these compounds is the torsion angles between the aromatic end groups and their neighboring carbonyl groups. For **1a** and **1b**, these angles were small (ca. 15°), in agreement with the UV absorption spectra, but were relatively large for **1c** (27°, 40°; the comparable torsion angle in dimesityl diketone[165] was close to 90°).

The cyclic triketones which have been investigated include the conjugated triones cyclopentenetrione (**13**),[166] indanetrione (**4a**),[168] and cyclohepta-4,6-diene-1,2,3-trione (**62**)[70] as well as the variety of saturated

Table 3. Selected Bond Lengths (Å) and Torsion Angles (deg) of Diphenyltetraketone (2a), Dimesityltetraketone (2c), 4,4,9,9-Tetramethyl[12]paracyclophane-5,6,7,8-tetrone (84), and 4,4,9,9-Tetramethyl-1-oxacycloundeca-5,6,7,8-tetrone (85)[a]

compound	α_1	α_2	α_3	C_1-C_2	C_2-C_3	C_3-C_4	C_1-O_1	C_2-O_2	C_3-O_3	C_4-O_4	ref
2a	144.6	−24.2	128.4	1.522(4)	1.552(4)	1.512(4)	1.221(3)	1.194(3)	1.200(4)	1.220(3)	164
2c	144.1	128.5	144.1	1.541	1.523	1.541	1.218	1.196	1.196	1.218	165
84	141.2(4)	−52.7(4)	−145.4(4)	1.541(6)	1.541(6)	1.543(6)	1.203(5)	1.208(5)	1.201(5)	1.206(5)	83
85	130.2(2)	−107.1(2)	−130.2(2)	1.529(2)	1.534(2)	1.529(2)	1.210(2)	1.202(2)	1.202(2)	1.210(2)	84

[a] For the definition of $\alpha_1-\alpha_3$, see Figure 1b.

cyclic compounds shown in Chart 3. The torsion angles are zero for those triketones in which the ring size is five: **4a**, **13**, tetramethylcyclopentane-1,2,3-trione (**202**),[169] and dispiro[2.0.2.3]pentane-7,8,9-trione (**203**).[169] As anticipated, larger angles were found with triones of increasing ring size. It seems that at least one torsion angle is small in the cisoid configuration of a triketone unit. This could be between adjacent CO groups such as in **62**, bicyclo[3.1.1]-heptane-2,3,4-trione (**204**), 2,2,6,6-tetramethyl-2,3,5,6-tetrahydro-γ-pyran-3,4,5-trione (**207**), 4,4,6,6-tetra-methyl-cyclohexan-1,2,3,5-tetrone (**208**), and 7,8-dimethyltricyclo[5.2.1.1^{5,8}]undecane-2,3,4-trione (**209**) or in the outer ones such as in 1,5-dimethylbicyclo-[3.1.0]hexane-2,3,4-trione (**12b**), bicyclo[3.2.1]octane-2,3,4-trione (**205**), and 4,4,6,6-tetramethylcyclohexane-1,2,3-trione (**63**). It is interesting to note that even in **209**, where the possibility of a torsion angle of 90° exists, two adjacent CO groups are nearly coplanar.

Comparison of the listed bond lengths shows a minimal variation of the intercarbonyl C−C bond lengths from 1.52 to 1.53 Å with the exception of o-tropoquinone (**62**) in which the variation is larger (1.52−1.56 Å). In the case of the C−O bond length, the bond of the central CO unit is usually shorter than the outer two.

Comparison of the X-ray data obtained on single crystals of diphenyl triketone (**1a**)[164] with the results of an electron diffraction study[170] showed a remarkable similarity in bond lengths and torsion angles between the single crystal and molecules in the gas phase. This study of **1a** is the only report of its kind for polycarbonyls in the gas phase.

2. Tetraketones (Table 3, Figure 2)

Four X-ray structures of tetraketones have been reported (see Charts 1 and 2) to date: diphenyl tetraketone (**2a**),[164] dimesityl tetraketone (**2c**),[165] 4,4,9,9-tetramethyl[12]paracyclophane-5,6,7,8-tetrone (**84**),[83] and 4,4,9,9-tetramethyl-1-oxacycloundecane-5,6,7,8-tetrone (**85**).[84] The most relevant structural data are listed in Table 3. As with *vicinal* triketones, we compare the torsion angles between the CO groups ($\alpha_1-\alpha_3$) and the C−C and C−O bond lengths within the tetraketone unit. The molecular structure of **85** is shown in Figure 2.

The data in Table 3 reveal a small torsion angle α_2 for diphenyltetraketone (**2a**) but a large one for dimesityltetraketone (**2c**) and two cyclic derivatives **84** and **85**. In the latter three compounds, the four CO groups show a helical arrangement (see Figure 2). We also note that the central CO−CO bond length (C(2)−C(3)) varies with the torsion angle α_2. In the case of **2a** in which α_2 is small (−24.2°), the C(2)−
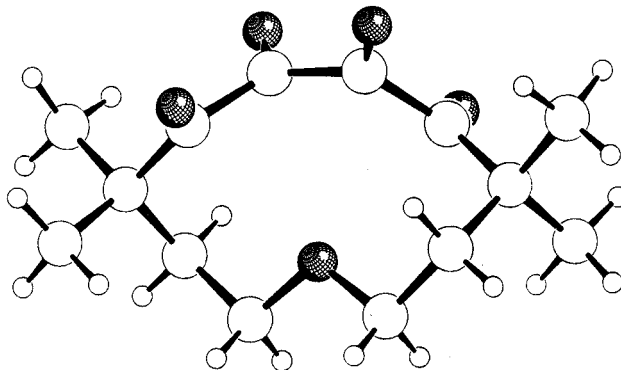
Figure 2. Molecular structure of 4,4,9,9-tetramethyl-1-oxacycloundecane-5,6,7,8-tetrone (**85**). Oxygen atoms are cross-hatched.

C(3) distance equals 1.552(4) Å. In **2c**, **84**, and **85**, where α_2 is large, the C(2)−C(3) distances varied between 1.52 and 1.54 Å. The somewhat larger distance in the case of **84** was ascribed to additional strain of the [12]cyclophane moiety.

Turning to C−O bond lengths, a slight shortening of the central CO distances in the diaryl-substituted species **1a** and **1c** (1.19 Å) was observed as compared with the terminal C−O distances (1.22 Å). A similar trend was observed in the 11-membered ring of **85**. In the latter case, there were short contacts of 2.703(2) Å and 2.794(2) Å between the ether oxygen and the C_4O_4 moiety.

3. Pentaketones (Table 4, Figure 3)

X-ray structures are available for two penta-ketones, *tert*-butylphenyl pentaketone (**3j**) and diphenyl pentaketone (**3a**).[88,94] Bond distances and torsion angles $\alpha_1-\alpha_4$ are summarized in Table 4, and the molecular structure of **3a** is shown in Figure 3. Comparison of the structures of **3j** and **3a** shows that, in both, the three central CO groups are arranged approximately cisoid to each other while the outer ones show a transoid conformation. As a result, a helical conformation is observed in which the distances between O(5) and C(1) and C(2), respectively, are relatively short (cf. Table 4, Figure 3). This interaction leads to a slight pyramidalization of the keto groups at C(1) and C(2). These results are reminiscent of those observed for packing of indane-trione in the crystal where the molecules are arranged so that the oxygen atom of a central carbonyl group lies over the carbon atom of the central carbonyl of a second molecule.

A comparison of the structures of the open chain tri-, tetra-, and pentaketones shows no significant changes in the bond lengths. There is a broad

Table 4. Most Relevant Bond Lengths (Å), Torsion Angles (deg), and Nonbonding Atom Distances (Å) of *tert*-Butylphenylpentaketone (3j) and Diphenylpentaketone (3a)[a]

Torsion Angles

compound	α_1	α_2	α_3	α_4
3j	158.4	−52.1	−11.4	172.9
3a	155.8	−55.4	30.7	−151.0

Bond Lengths

compound	C(1)−C(2)	C(2)−C(3)	C(3)−C(4)	C(4)−C(5)
3j	1.524(3)	1.533(2)	1.553(2)	1.545(3)
3a	1.529(4)	1.522(3)	1.530(3)	1.533(3)

	C(1)−O(1)	C(2)−O(2)	C(3)−O(5)	C(4)−O(4)
3j	1.203(2)	1.199(2)	1.189(2)	1.207(2)
3a	1.215(2)	1.204(2)	1.196(3)	1.195(2)

Distances between O(1) and O(5) and Carbon Centers

compound	O(5)−C(1)	O(5)−C(2)	O(1)−C(4)	O(1)−C(5)
3j	2.738(2)	2.578(2)	2.953(2)	3.195(2)
3a	2.775(3)	2.519(3)	3.036(3)	3.589(5)

[a] For the definition of $\alpha_1 - \alpha_4$ and the numbering of the atoms, see Figure 1b, data from ref 88.
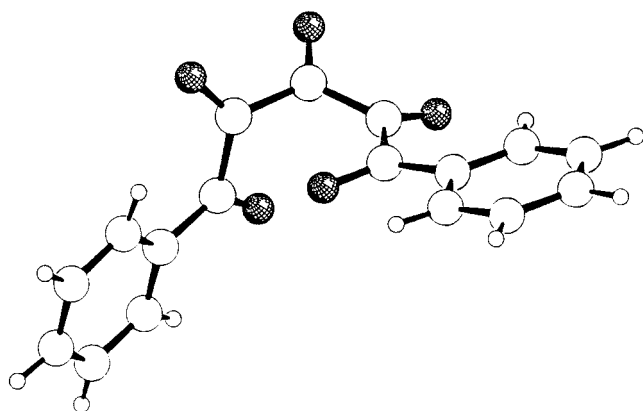
Figure 3. Molecular structure of diphenylpentaketone (**3a**). Oxygen atoms are cross-hatched.

variation of the torsion angles of the CO groups, indicating a flat potential for the rotation around the C−C bond. As anticipated in the case of systems with a five-membered ring or in bicyclic systems with small bridges, the torsion angles adopt values close to zero. The most surprising result is the helical arrangement observed for crystalline pentaketones.

B. Calculations and Conformations of Polyketones

Speculation on conformations of polyketones goes back to at least 1940 when Calvin and Wood[171] discussed the structure of dimethyl triketone (see section VIII.B). To the best of our knowledge, however, only one experimental attempt has been made to observe a helical conformation of a triketone. This was reported in 1976 by Wolfe et al.[25] who described results of a low-temperature NMR study on **15** in which the trione moiety is flanked on one side by a phenyl group and on the other by a trisubstituted carbon bearing phenyl and *gem*-dimethyl groups. It was anticipated that if the tricarbonyl indeed had a

helical conformation, the signals of the two methyl groups would be different at temperatures sufficiently low to prevent interconversion of the two enantiomeric helices. In the event, at the lowest temperature achieved (173 K) only a broadening of the methyl singlet of **15** was observed. Further, it was shown that the corresponding monoketone exhibited analogous behavior. The conclusion was that the barrier for conformational change in **15** was appreciably less than 7 kcal/mol.

The alternative approach to conformational study has been application of theoretical calculations to polycarbonyl systems. As early as 1972 Kroner and Strack[172] reported MNDO/2 calculations on conformations of triketones in connection with PE-spectroscopic investigations (cf. section VIII.A). They concluded that a helical structure of the triketone should be more favored than the all *s-trans* conformer. The torsion angles between the CO groups were predicted to be 90°, a result inconsistent with the X-ray data described above. Similar results were obtained with the CNDO/2,[25] MINDO/3,[173] and MNDO[173] procedures. The semiempirical procedures did well in prediction of the bond lengths but failed to predict the global minimum correctly. The CNDO/2 calculations of Wolfe[25] were undertaken in connection with ^{1}H NMR experiments described above.

A number of MO calculations[173] on *vicinal* polyketones revealed that there is a flat potential surface with respect to rotation of the CO groups. This picture was confirmed by force field calculations.[88,94] However, with the following restrictions: (1) neglect of torsion and van der Waals forces, and (2) assuming that the dipole moment of each CO group is 2.30 D, that the bond distances between adjacent carbon atoms are fixed at 1.54 Å and those between C and O at 1.20 Å as well as bond angles of 120°, the torsion angles between CO groups of *vicinal* polyketones could be reproduced in contrast to the semiempirical methods discussed above. The minima found on the corresponding hypersurface showed remarkable agreement with experimental data. For 1,2-diketones a torsion angle of 180° resulted; for 1,2,3-triketones both predicted torsion angles were 127°. For *vicinal* tetraketones one broad minimum was found with two *trans*-1,2-diketone units ($\alpha_1 = 180°$, $\alpha_2 = 90°$, $\alpha_3 \approx 180°$). A helical structure with $\alpha_1 = \alpha_2 = \alpha_3 = 130°$ also fits well into this broad minimum. For *vicinal* pentaketones, three almost equal minima were predicted[88,94] at $\alpha_2 = \alpha_3 = 25°$, $\alpha_1 = \alpha_4 = 190°$ (**A**) at 20.9 kcal/mol; at $\alpha_2 = \alpha_3 = 129°$, $\alpha_1 = \alpha_4 = 140°$ (**B**) at 20.0 kcal/mol; and $\alpha_1 = \alpha_4 = 170°$, $\alpha_2 = 0°$, $\alpha_3 = 90°$ at 21.2 kcal/mol (**C**). Minimum **A** corresponds to the X-ray structures of *tert*-butylphenylpentaketone (**3j**) and diphenylpentaketone (**3a**).

Ab initio calculations (RHF/6-31G*) were performed on 1,2,3-propanetrione.[102] In some cases, MP2/6-31G* geometry optimizations were carried out. Four conformations (see Figure 4) were examined. The helical conformer with the *s-trans*, *s-trans* conformation with torsion angles of 149° (**A**) was found to be the global minimum. The planar species with *s-trans*, *s-trans* conformation (**B**) was found to be a transition state for the interconversion of the

Figure 4. Four possible conformations of 1,2,3-propane-trione.

chiral conformers **A**. The *s-cis*, *s-trans* and *s-cis*, *s-cis* conformers **C** and **D**, respectively ,were local minima on the potential surface.

Ab initio and DFT calculations on polyketones at the HF, MP2, and B3LYP levels using a 6-31G** basis set have been reported.[174] For pentane-1,2,3,4,5-pentone, the conformation of the lowest energy corresponds to the helical conformation found for **3j** and **3a**. The second lowest energy predicted corresponds to the all-trans conformation.

There have been several calculations on cyclic polyketones, thioketones, and related systems (Chart 3). Frenking[175] investigated the C_6S_6 (**211**) and C_6O_6 (**212**) systems in connection with mass spectrometric investigations on C_6S_6. Explicitly, he calculated the energy difference of the valence isomers **a**, **b**, and **c** by using ab initio methods. It is found that **211b** represents the global minimum by using the HF/6-31G* approach with **211a** (chair conformation) and **211c** as a local minima. A perturbational approach (MP2/3-21G*) favors **211c** over **211b** by 10 kcal/mol. For the oxo congeners, a planar structure was predicted favoring **212a**. In all cases it was assumed that **211** and **212** exist in a singlet ground state while a possible triplet state was disregarded.

A theoretical investigation[176] of tetraoxocyclobutane (**213**), [4]radialene (**214**), and tetraiminocyclo-butane (**215**) using ab initio MO calculations of the second-order Møller Plessett (MP2) level of theory predict that in the singlet ground state of **213** only three out of four σ MOs describing the C–C σ bonds of the cyclobutane ring are occupied while in the case of **214** and **215** all four C–C σ MOs are occupied. As a consequence of this difference it was found that four CO molecules are more stable by 33 kcal/mol than the tetramer **213**.

A hypothetical sulfur analogue of polyketone has been scrutinized by Gemin and Hoffmann[177] using the extended Hückel method. It was shown that its planar structure is best described by resonance structure **216b** with an extended multicenter electron-rich S–S bonding. The most stable conformation predicted was one with Peierls distortions in both sulfur and carbon sublattices. The possibility for a helical conformation has also been investigated, and it was found that this is a local minimum only.

The calculations performed on various *vic*-poly-ketones show that semiempirical methods are not reliable to predict the geometry of these molecules. Especially poor is the performance on the conformations. Ab initio and DFT calculations with extended basis sets (6-31G* and higher) at the HF/ MP2 and B3LYP levels perform quite well with respect to geometrical parameters and orbital sequences.

C. Related Systems (Chart 4)

Electronic systems isovalent to *vic*-polyketones are the dendralenes (**217**), their cyclic congeners the radialenes (**218**), the polyiminomethylenes ("polyiso-cyanides", **219**), and polythiones (**216**). The first in this series of acyclic cross-conjugated polyolefins has been named dendralenes, a review has appeared.[178] Although several examples have been synthesized, not much is known about their structures and spectroscopic properties. More structural details are known about the radialenes.[179] There are several reports on the structure and bonding properties of these species,[179] indicating the anticipated planarity for [3]radialenes and nonplanar structures for the higher congeners.

The polyisocyanides **219** are well-known sub-stances which have been prepared by polymerization of isocyanides using acid or transition metal catalysis and investigated intensively by Drenth, Nolte, and colleagues[180] and by Millich and co-workers.[181] These

Chart 4

Chart 5

225 226 227 228 229

230a,b 231a,b 232a,b 233b

a, R = Me
b, R = PhCH2

234b 235a,b 236a,b 237a,b

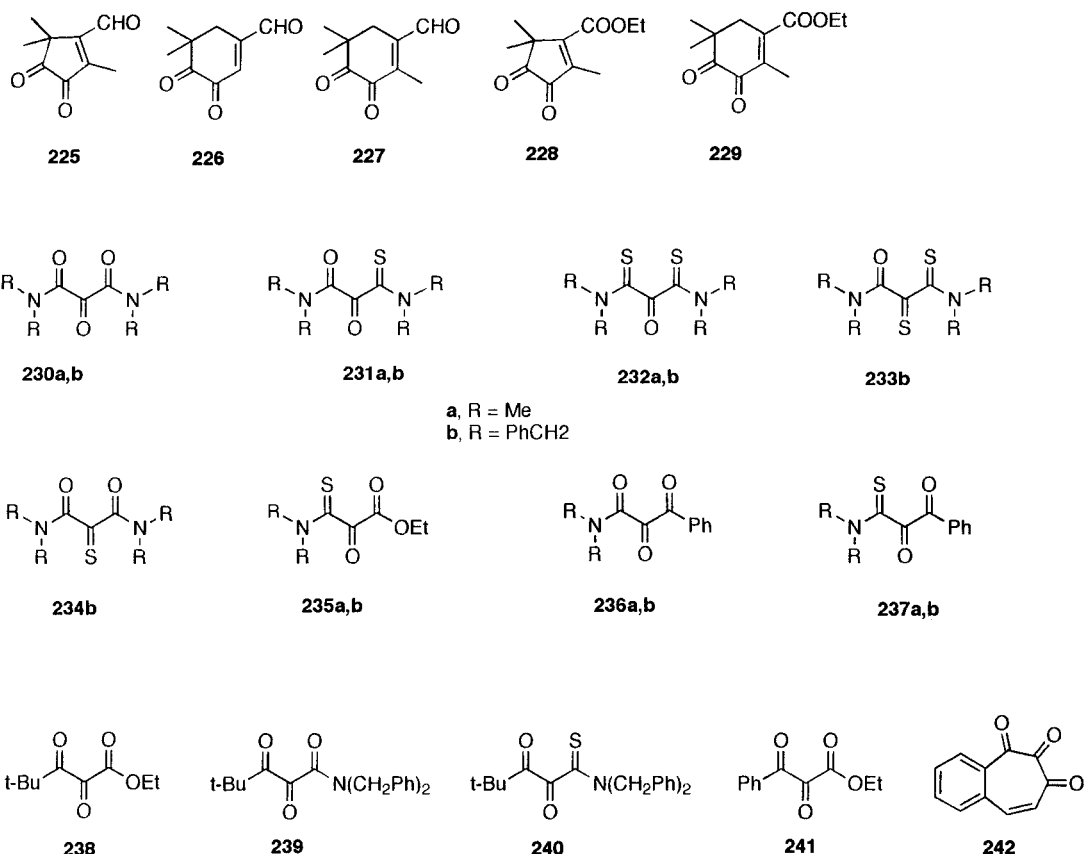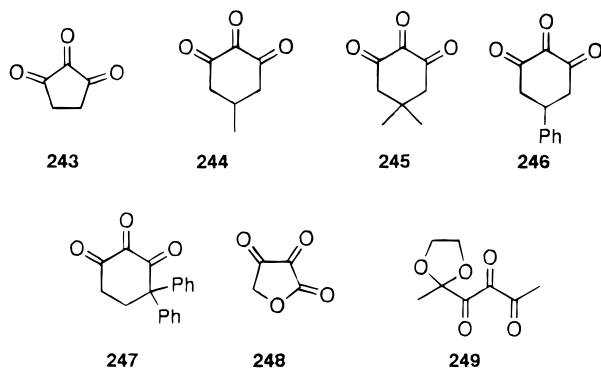238 239 240 241 242

Chart 6

243 244 245 246

247 248 249

compounds have been conclusively shown to possess helical conformations, and optically active forms have been isolated. The presence of the R substituent on the imino nitrogen obviously results in a marked increase in the barrier to conformational change in these systems. Molecular orbital calculations of the electronic structure of polyisocyanides[182] point to a balance of π-delocalization and N lone pair repulsion as important structure-determining factors.

In 1969 Schönberg and Frese[183] reported the preparation of 1,3-diphenyl-1,3-dithiooxo-2-propanone (**220**), which was later shown by X-ray analysis to exist in the mesoionic form **221**.[32] 1,3-Dioxo-2-thiones **222** have been trapped by Diels−Alder reactions.[78] In the case of **222a**, ab initio calculations (HF/3-21G*) reveal that the torsion angle between CO and CS groups amounts to 100°. For **222b**, a torsion angle of 160° between the keto and thioketone groups was calculated, while the ester carbonyl and the thio-

ketone group have a torsion angle of 55.3°.[78] Further congeners of the cyclic *vic*-polyketones are the aminoboranes (**223**, **224**) for which alkyl derivatives of the tetramer[184] and hexamer have been reported.[185]

In the blue-colored tetrakis(diisopropylamino)cyclotetraborane (**223**), the four-membered ring is folded. For the orange-colored hexakis(dimethylamino)cyclohexaborane (**224**),[185] a chair conformation was found in the solid state. The B−N distances are shorter than expected for a B−N single bond in both molecules.

VIII. Spectroscopic Properties of Polyketones (Chart 5)

A. Photoelectron Spectra (Tables 5−9; Figures 5−8)

Photoelectron spectroscopy is a valuable method for studying the sequence and sometimes the symmetry of the highest occupied valence orbitals of organic compounds.[186] A number of papers on He(I) photoelectron (PE) spectra of *vicinal* polyketones have appeared[19,172,186−190] since the earlier review on *vic*-polyketones.

1. Vicinal Triketones

The highest occupied molecular orbitals (MOs) of 1,2,3-triketopropane (**1f**) can be constructed from the three symmetry adapted linear combinations of the 2p lone pairs centered at the oxygen atoms (Figure 5, left) and the C−C σ bonds (Figure 5, right). It is found that the through-space interaction of the 2p
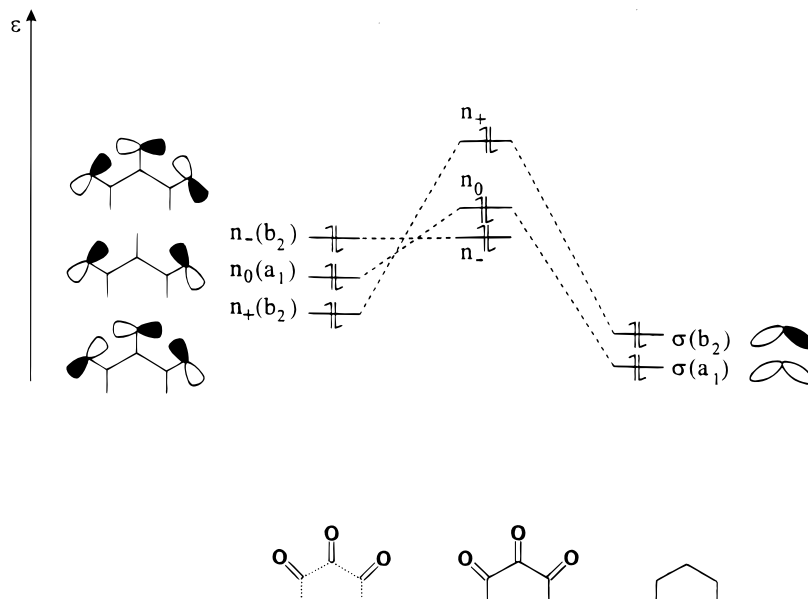
Figure 5. Interaction diagram between the three symmetry adapted linear combinations of the 2p lone pairs of a *vicinal* triketone unit (left) and the C−C σ bonds (right) to yield the highest occupied MOs of 1,2,3-triketopropane (center).

lone pairs at the oxygen atoms is relatively small. However, molecular orbital calculations suggest that the through-bond interaction between the C−C σ bonds and the lone pairs is fairly strong.

As a result of the dominance of the through-bond interactions, the n_+ linear combination is the HOMO of a triketone unit. The three highest occupied molecular orbitals of a triketone unit are shown schematically in Figure 6.
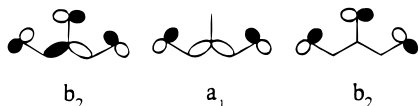

Figure 6. Schematic drawing of the highest occupied MOs of a *vicinal* tetraketone.

In Tables 5−7 we have listed the three lowest ionization energies of a number of triketones. In addition to results for the triketones shown in Chart 3, results are presented for 1,8,8-trimethylbicyclo-[3.2.1]octane-2,3,4-trione (**40**),[188] dimethyl triketone (**1g**),[172] diisopropyl triketone (**1h**),[172] di(*tert*-butyl)-triketone (**1i**),[172] and 4,6,6-trimethyl-4-cyclohexene-1,2,3-trione (**11**).[18] An extensive study on PE and UV−vis spectra of vinylogous tricarbonyl compounds incorporated in five- and six-membered rings should be mentioned here.[191]

A comparison between the ionization energies of n_+ to n_- in the saturated mono-, bi-, and tricyclic systems shows that there is little variation with structure even though the dihedral angles vary considerably. This is in line with the results of MO calculations predicting that the through-space inter-actions of the 2p lone pairs are small. As a result, the through-bond interaction dominates. Thus, the splitting of the n-bands should not depend very much on the dihedral angles between the CO groups.

2. Tetraketones and Pentaketones

By analogy to *vicinal* triketones, the 2p orbitals at the oxygen centers of tetraketones interact weakly

Table 5. Vertical Ionization Energies, $I_{v,j}$, of Cyclic Saturated *vicinal* Triketones: Bicyclo[3.1.0]hexane-2,3,4-trione (12a), Its 1,5-Dimethyl Derivative (12b), 1,8,8-Trimethylbicyclo[3.2.1]octa-2,3,4-trione (40), 4,4,6,6-Tetramethylcyclohexane-1,2,3-trione (63), Tetramethylcyclopentane-1,2,3-trione (202), Dispiro-[2.0.2.3]pentane-7,8,9-trione (203), Bicyclo[3.1.1]-heptane-2,3,4-trione (204), Bicyclo[3.2.1]octane-2,3,4-trione (205), Bicyclo[3.2.2]nonane-2,3,4-trione (206), Tetrahydro-2,2,6,6-tetramethyl-2H-pyran-3,4,5-trione (207), 4,4,6,6-Tetramethylcyclohexane-1,2,3,5-tetrone (208), and 7,8-Dimethyltricyclo[5.2.1.1^{5,8}]undecane-2,3,4-trione (209) (All values in eV)

compound	$I_{v,j}$	assignment	ref
12a	9.36	$b_2(n)$	19
	11.0	$a_1(n)$	
	11.8	σ	
12b	9.1	$b_2(n)$	19
	10.5	$a_1(n)$	
	11.2	σ	
40	9.1	n	188
	10.20	n	
63	9.10	$b(n)$	186
	10.38	$a(n)$	
	11.35	σ	
202	9.00	$b_2(n)$	186
	10.55	$a_1(n)$	
	11.58	σ	
203	8.9	$b_2(n)$	187
	10.0	σ	
	10.7	$a_1(n)$	
204	9.42	$b_2(n)$	187
	10.63	$a_1(n)$	
	11.37	σ	
205	9.49	$a''(n)$	186
	10.60	$a'(n)$	
	11.47	$a''(n)$	
206	9.14	n	186
	10.3	n	
	10.6	σ	
207	9.0	$b_2(n_+)$	187
	9.8	$a_1(n_0)$	
	10.6	$b_2(n_{-1})$	
208	9.2	$a''(n)$	187
	9.94	$a'(n)$	
	10.77	$a'(n)$	
	11.8	$a''(n)$	
209	8.9	$b_2(n_+)$	169
	10.2	$a_1(n_-)$	

through space but strongly through bonds. A quantitative analysis of these interactions reveals[190] matrix elements for the through-space interaction of

Table 6. Vertical Ionization Energies, $I_{v,j}$, of Open Chain Triketones: Diphenyltriketone (1a), Dimethyl-2,3,4-triketone (1g), Diisopropyltriketone (1h), and Di(*tert*-butyl)triketone (1i) (All values in eV)

compound	$I_{v,j}$	assignment	ref
1a	8.8	n	4, 173b
	9.56	$\pi_1-\pi_4$	
	10.2	n	
1g	9.53	$b_2(n_+)$	172
	10.97	$a_1(n_0)$	
	12.30	$b_2(n_-)$	
1h	9.04	$b_2(n_+)$	172
	10.48	$a_0(n_0)$	
	11.82	$b_2(n_-)$	
1i	9.00	$b_2(n_+)$	172
	10.28	$a_1(n_0)$	
	11.59	$b_2(n_-)$	

Table 7. Vertical Ionization Energies, $I_{v,j}$, of Unsaturated Cyclic Triketones: Indanetrione (4a), 4,6,6-Trimethyl-4-cyclohexene-1,2,3-trione (11), Cyclopentene-1,2,3-trione (13), Cyclohepta-4,6-diene-1,2,3-trione (62) (All values in eV)

compound	$I_{v,j}$	assignment	ref
4a	9.1	$b_2(n)$	186
	10.32	$a_2(\pi)$	
	10.72	$b_1(\pi)$	
	10.72	$a_1(n)$	
	11.87	$b_2(n)$	
11	9.16	$b_2(n)$	18
	10.18	$b_1(\pi)$	
	10.51	$a_2(n)$	
	11.56	$b_2(n)$	
13	9.56	$b_2(n)$	189
	11.32	$a_1(n)$	
	11.66	$b_1(\pi)$	
	12.32	$b_2(n)$	
62	9.21	$b_2(n)$	189
	10.07	$a_2(\pi)$	
	10.67	$a_1(n)$	
	11.59	$b_2(n)$	
	12.4	$b_1(\pi)$	

0.2−0.3 eV but values for the through-bond interaction up to 2.5 eV. To demonstrate the strong interaction with the σ-frame, we show in Figure 7 the contour diagrams of the four highest occupied MOs of butane-1,2,3,4-tetrone. The results of PE spectroscopic investigations on diphenyltetraketone (**2a**),[190] dimesityltetraketone (**2c**),[190] di(*tert*-butyl)tetraketone (**2i**),[190] di(*p*-tolyl)tetraketone (**2e**),[190] and di(*p*-fluorophenyl)-tetraketone (**2k**)[190] are summarized in Table 8. From these data it can be seen that the split between n_1 and n_2 (1.3 eV) is only slightly larger than between n_2 and n_3 (1.0−1.1 eV) while the difference between n_3 and n_4 (0.6−0.8 eV) is considerably smaller than the other two differences. The PE data of the pentaketones di-*tert*-butylpentaketone (**3i**),[173a] diphenylpentaketone (**3a**),[4] and di(*p*-tolyl)pentaketone (**3e**)[173a] are listed in Table 9.

To conclude the chapter on the PE spectra on *vic*-polyketones, we have compared in Figure 8 the first PE bands of diphenyl ketones $C_6H_5-(CO)_n-C_6H_5$ with $n = 1-5$. This comparison shows that the energy difference between $n = 1$ and 5 converges to a value of about 3 eV. As a consequence, the arithmetic mean of the ionization energies of the n-bands also approaches a value of about 10.5 eV and the first ionization energy adopts a value of 8.9 eV. A comparison between the results of the calculated orbital energies with the measured ionization energies shows
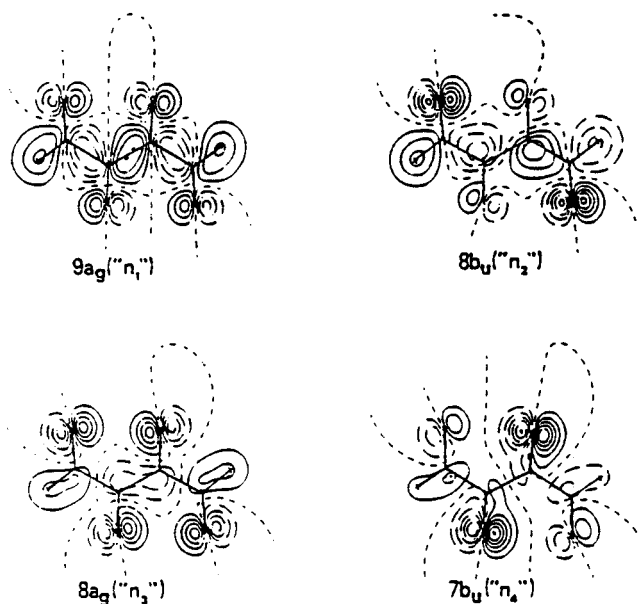
Figure 7. Contour diagram of the four highest occupied molecular orbitals of butane-1,2,3,4-tetrone.

Table 8. Vertical Ionization Energies, $I_{v,j}$, of *vicinal* Tetraketones: Diphenyltetraketone (2a), Dimesityltetraketone (2c), Di(*p*-tolyl)tetraketone (2e), Di(*tert*-butyl)tetraketone (2h), 5,5-Dimethyl-1-phenylhexane-1,2,3,4-tetrone (2j), Di(*p*-fluorophenyl)tetraketone (2k), 5,5,12,12-Tetramethylcyclododeca-1,2,3,4-tetrone (81), 5,5,14,14-Tetramethylcyclotetradeca-1,2,3,4-tetrone (82a), 1,4-Dioxa-7,7,12,12-tetramethylcyclotetradeca-8,9,10,11-tetrone (82b), and 1-Oxa-4,4,9,9-tetramethylcycloundeca-5,6,7,8-tetrone (85) (All values in eV)

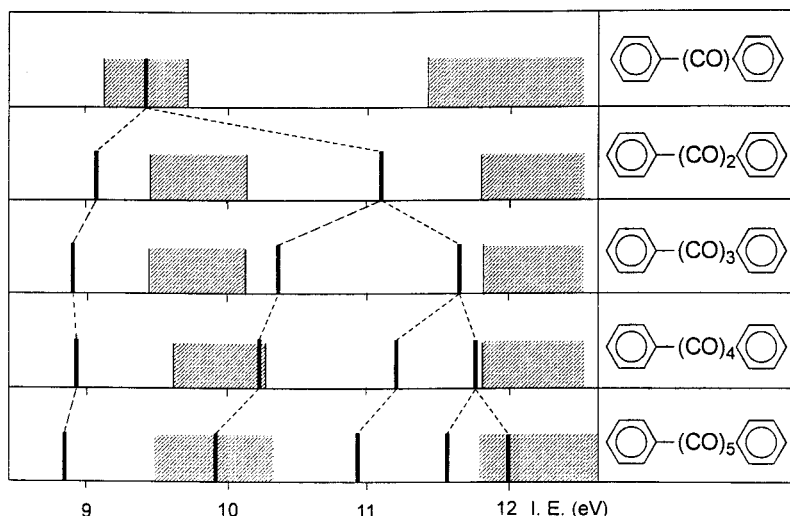| compound	$I_{v,j}$	assignment	ref
2a	8.9	n_1	190
	9.6−10.0	$\pi_1-\pi_4$	
	10.2[a]	n_2	
	11.2	n_3	
	11.8	n_4	
2c	9.6−9.5	$n_1, \pi_1-\pi_4$	190
	10.0	n_2	
	11.0[a]	n_3	
2e	8.8	n_1	190
	9.6−10.3	$\pi_1-\pi_4$	
	10.1	n_2	
	11.0	n_3	
2h	8.84	n_1	190
	10.24	n_2	
	11.20	n_3	
2j	8.9	n_1	94
	9.6	π_1, π_2	
	10.1	n_2	
	11.2	n_3	
	11.5	n_4	
2k	9.1	n_1	190
	9.4−10.4	$n_2, \pi_1-\pi_4$	
	11.3	n_3	
	12.1	n_4	
81	8.75	n_1	173
	10.0	n_2	
82a	8.75	n_1	173
	10.0	n_2	
82b	8.3	n_1	86
	9.6	n_2	
	9.7	$2\pi_1$	
	9.9	$2\pi_2$	
	10.7	n_3	
85	8.5	n_1	84
	9.66	n_2	
	10.2	2π	
	10.3	n_3	

[a] No distinct band in spectrum.

Figure 8. Correlation between the first PE bands of benzophenone, benzil, diphenyltriketone (**1a**), diphenyltetraketone (**2a**), and diphenylpentaketone (**3a**). Strongly overlapping bands of the phenyl groups are indicated by shaded areas.

Table 9. Vertical Ionization Energies, $I_{v,j}$, of *vicinal* Pentaketones: Diphenyl Pentaketone (3a), Di(*p*-tolyl) Pentaketone (3e), and Di-*tert*-butyl Pentaketone (3i) (All values in eV)

compound	$I_{v,j}$	assignment	ref
3a	8.9	n_1	4
	9.7	$\pi_1-\pi_4$	
	9.9	n_2	
	10.8	n_3	
	$(11.6)^a$	n_4	
	$(12.0)^a$	n_5	
3e	9.0	n_1	173a
	9.75	$\pi_1-\pi_4$	
	11.0	n_2	
	11.6	n_3	
3i	9.0	n_2	173a
	9.8	n_2	
	11.0	n_3	
	$(11.5)^a$	n_4	
	$(12.0)^a$	n_5	

^{a} No distinct band in spectrum.

that semiemperical and ab initio methods can be used for the assignment of the low-energy PE bands. All the calculations reveal that the through-bond interaction between the C—C σ frame and the 2p lone pair at the oxygen atoms dominates. The through-space interaction between the 2p lone pairs at the oxygen atoms plays a minor role.

B. Electronic Absorption Spectra (Tables 10 and 11; Figures 9–11)

1. Vicinal Triketones

Vicinal triketones are colored, and depending on the substituents or ring size, the color varies between green and yellow. Calvin and Wood[171] were among the first chemists to discuss the electronic absorption spectrum of dimethyltriketone (**1g**). They noticed a long-wavelength shift between the first band of the yellow-colored diacetyl to the orange-colored **1g**. A considerable number of *vic*-triketones have been prepared and their electron absorption spectra reported. In Table 10 we list the first absorption bands of a number of cyclic triketones with and without a π-system adjacent to the triketone moiety.
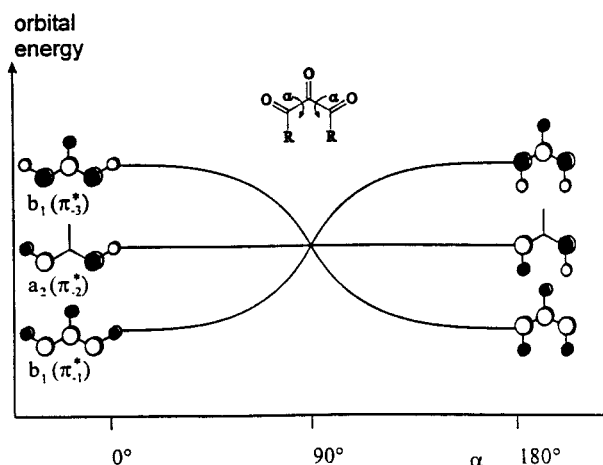

Figure 9. Schematic drawing of the orbital energies and the wave functions of the three π^* orbitals of a *vic*-triketone unit.

A comparison between the first three bands of tetramethylcyclopentane-1,2,3-trione (**202**, $\alpha_1 = \alpha_2 = 0°$), 1,5-dimethylbicyclo[3.1.0]hexane-2,3,4-trione (**12b**, $\alpha_1 \approx 17°$, $\alpha_2 \approx -18°$), bicyclo[3.2.1]octane-2,3,4-trione (**205**, $\alpha_1 = 7°$, $\alpha_2 = -9°$), bicyclo[3.2.2]nonane-2,3,4-trione (**206**, $\alpha_1 = \alpha_2 = 12°$), and 4,4,6,6-tetramethyl-cyclohexane-1,2,3-trione (**63b**, $\alpha_1 = 20°$, $\alpha_2 = -23°$) shows a hypsochromic shift with increasing nonplanarity of the triketone moiety. CNDO/S-CI calculations on these species predict that the first three bands can be assigned to the following configurations: first band, $\pi_{-1}^* \leftarrow n_+$; second band, $\pi_{-2}^* \leftarrow n_+$, $\pi_{-1}^* \leftarrow n_0$; third band, $\pi_{-3}^* \leftarrow n_+$, $\pi_{-2}^* \leftarrow n_0$, $\pi_{-1}^* \leftarrow n_-$.

These assignments permit rationalization of the strong dependence of the first band on the planarity of the triketone moiety. Since the HOMO (n_+) is nearly independent of the torsion angle, it is the LUMO (π_{-1}^*) which has to depend strongly on the torsion angle. Indeed, as shown in Figure 9 the two π^* MOs belonging to the irreducible representation b_1 depend very strongly on the torsion angle between the CO groups. In line with the assignment of the

Table 10. Electronic Absorption Spectra (λ_{max}[nm], ϵ[L·mol^{-1}·m^{-1}]) of *vicinal* Triketones in Acetonitrile: Indanetrione (4a), 1,2,3,5,6,7-Hexaoxo-*s*-hydrindacene (9), 1,2,3,6,7,8-Hexahydrohexaoxopyrene (10), Bicyclo[2.1.0]hexane-2,3,4-trione (12a), 1,5-Dimethylbicyclo[2.1.0]hexane-2,3,4-trione (12b), Cyclopentene-1,2,3-trione (13), 2*H*,3*H*-Dihydrophenalene-1,2,3-trione (17a), Cyclohepta-4,6-diene-1,2,3-trione (62), 4,4,6,6-Tetramethylcyclohexane-1,2,3-trione (63b), Tetramethylcyclopentane-1,2,3-trione (202), Bicyclo[3.1.1]heptane-2,3,4-trione (204), Bicyclo[3.2.1]octane-2,3,4-trione (205), Bicyclo[3.2.2]nonane-2,3,4-trione (206), Tetrahydro-2,2,6,6-tetramethyl-2*H*-pyran-3,4,5-trione (207), 4,4,6,6-Tetramethylcyclohexane-1,2,3,5-tetrone (208), 7,8-Dimethyltricyclo[5.2.1.1^{5,8}]undecane-2,3,4-trione (209), Bicyclo[3.2.0]heptane-2,3,4-trione (210), and 6,7-Dihydro-5*H*-benzocycloheptene-5,6,7-trione (242)

compound	λ_{max} (e)	ref
4a	583 (17), 390 (20), 328 (2550), 258 (20500), 231 (13400)	194
9	620 (52), 354 (2660), 265 (26500), 246 (20400)	194
10	533 (125), 355 (14100), 266 (11000), 234 (46800)	194
12a	597 (19), 345 (45), 270 (577), 233 (571)	187
12b	590 (20), 350 (173)	187
13	540 (9), 459 (14), 345 (17), 252 (1600), 220 (10300)	194
17a	526 (18), 395 (316), 345 (5130), 261 (3950), 230 (9600)	194
62	557 (19), 550 (2430)	194
63b	524 (27), 338 (36), 248 (219)	194
202	666 (9), 370 (28), 361 (164), 235 (197)	194
204	530 (17), 328 (27)	194
205	548 (16), 325 (36), 246 (238)	194
206	534 (24), 324 (40), 238 (451)	194
207	536 (24), 375 (48)	169
208	527 (27), 320 (143)	169
209	478 (17), 326 (33)	169
210	638 (20)	169
242	522 (28), 358 (6761)	69b

Table 11. Electronic Absorption Spectra (λ_{max}[nm], log ϵ[L·mol^{-1}·cm^{-1}]) of *N*,*N*,*N*,*N*-Tetramethyl- and *N*,*N*,*N*,*N*-Tetrabenzyloxopropanediamide (230a,b), *N*,*N*-Dimethyl-3-(dimethylamino)-2-oxo-3-thiooxopropane Amide (231a), *N*,*N*-Dibenzyl-3-dibenzylamino-2-oxo-3-thiooxopropane Amide (231b), *N*,*N*,*N*,*N*-Tetramethyl- and *N*,*N*,*N*,*N*-Tetrabenzyl-2-oxo-propanebis(thiodiamide) (232a,b), *N*,*N*-Dibenzyl-3-dibenzylamine2,3-dithiooxo-propaneamide (233b), *N*,*N*,*N*,*N*-Tetrabenzylthiooxopropanediamide (234b), Ethyl 3-Dimethylamino- and Ethyl 3-Dibenzylamino-2-oxo-3-thiooxopropanoate (235a,b), *N*,*N*-Dimethyl- and *N*,*N*-Dibenzyl-2,3-dioxo-3-phenyl-propanoate (236a,b), *N*,*N*-Dimethyl- and *N*,*N*-Dibenzyl-2,3-dioxo-3-phenylpropanethioamide (237a,b), Ethyl 4,4-Dimethyl-2,3-dioxopentanoate (238), *N*,*N*-Dibenzyl-4,4-dimethyl-2,3-dioxopentaneamide (239), *N*,*N*-Dibenzyl-4,4-dimethyl-2,3-dioxopentanethioamide (240b), and Ethyl 3-Phenyl-2,3-dioxopropanoate (241) (All data from ref 76 except last entry from ref 24)

compound	λ_{max} (log ϵ)	compound	λ_{max} (log ϵ)
230a[a]	347 (2.01), 255 (3.81), 212 (3.98)	**235b**[a]	384 (3.09), 300 (3.60), 259 (4.29)
230b[a]	350 (2.31), 257 (3.77), 218 (4.28)	**236a**[b]	405 (2.01), 268 (4.73)
231a[b]	366s (2.18), 296 (3.62), 252 (4.05)	**236b**[b]	418 (1.81), 263 (4.09)
231b[b]	370s (2.96), 269 (4.70)	**237a**[b]	405 (2.78), 318s (3.39), 266 (3.87)
232a[b]	376 (2.44), 302 (3.99), 267 (4.29)	**237b**[b]	407 (2.99), 323 (3.69), 267 (4.37)
232b[b]	370 (3.28), 307 (4.15), 272 (4.30)	**238**[b]	400 (1.72), 290s (1.93)
233b[b]	450s (2.90), 377 (2.85), 308 (4.03)	**239**[b]	414 (1.78), 256 (3.18), 250 (3.18)
234b[b]	566 (1.67), 287 (5.63), 247 (3.57)	**240b**[b]	412 (2.92), 317 (3.77), 297 (3.92)
235a[b]	366 (3.27), 299 (3.62), 255 (4.32)	**241**[c]	402 (1.43), 261 (3.30)

[a] Ethanol. *[b]* Acetonitrile. *[c]* Methylene chloride. s refers to shoulder.

first few bands are the low extinction coefficients of the first bands. Low values are anticipated for "forbidden" $\pi^* \leftarrow$ n transitions. Note also that the first absorption bands of those triketones which are incorporated in a π-system: cyclopentene-1,2,3-trione (**13**), indanetrione (**4a**), *o*-tropoquinone (**62**), 2*H*,3*H*-dihydrophenalene-1,2,3-trione (**17a**), 1,2,3,6,7,8-hexa-hydrohexaoxo-pyrene (**10**), and 1,2,3,5,6,7-hexaoxo-*s*-hydrindacene (**9**) have low ϵ values which suggest an assignment of the corresponding bands to $\pi^* \leftarrow$ n transitions.

A detailed study of the absorption and emission spectra of indantrione (**4a**) has been reported.[192] The assignment of the first three excited states was based on the comparison with CNDO−CI calculations and solvent dependence.

The UV−vis spectra of a number of vinylogous tricarbonyls (**225**−**229**) have been reported and assigned on the basis of CNDO/S-CI calculations.[191] It is reported that the long-wavelength transition is

found between 446 and 550 nm. This band was assigned to $\pi^* \leftarrow$ n transition.

The electronic absorption spectra of mesoxalic acid diamides **230a,b**, mesoxalic acid thioamides **231a,b** and dithioamides **232a,b**, thio mesoxalic acid thioamide **233b**, thiomesoxalic acid diamide **234b**, ethyl mesoxalic acid thioamides **235a,b**, α,β-dioxoester-amides **236a,b** and **239**, α,β-dioxoesters **238**, **241**, and α,β-dioxothioamides **237a,b** and **240** have been listed in Table 11. As anticipated, the long-wave-length band of the esters, amides, and thioamides is shifted toward higher energy by more than 100 nm as compared to *vicinal* triketones. The only exception is found for **234b**, which is a genuine thioketone and shows a long-wavelength band at 566 nm.

The triketone unit in *vic*-triketones is one of the simplest chromophores known. Nevertheless, Figure 10 shows that the longest wavelength absorption maximum is very sensitive to structure varying from ca. 480 to ca. 670 nm, the maximum for di(*tert*-butyl)-
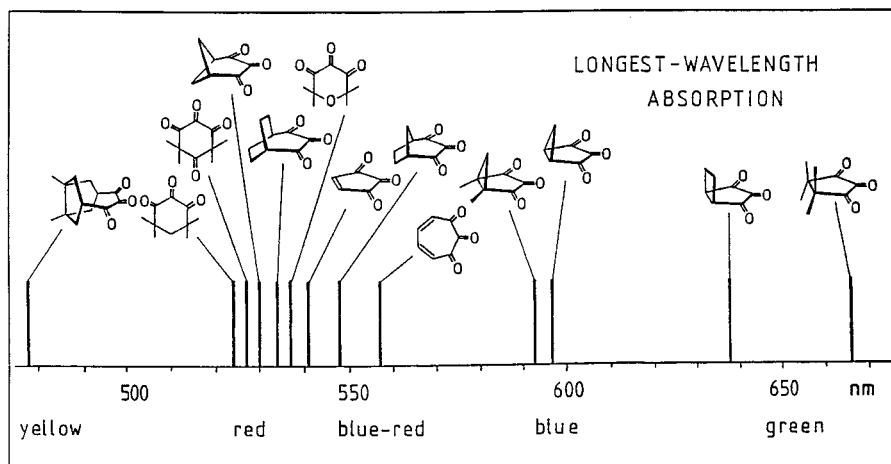
Figure 10. Comparison of the energies of the longest wavelength band of cyclic *vic*-triketones.

triketone is at even shorter wavelength (457 nm). "Translated" into color, this means a variation from yellow to blue and green. As with α-diketones, this change correlates with the planarity of the tricarbonyl unit (see Table 2). If the dihedral angles between the CO units are small or zero (e.g., tetramethylcyclopentane-1,2,3-trione (**202**), bicyclo[3.1.0]hexane-2,3,4-trione (**12a**)), the color is green or blue. If at least one CO group is bent out of the molecular plane (e.g., the hexanetriones **63**, **207**, **208** and the tricyclic trione **209**), the color is yellow to red.

2. Tetra- and Pentaketones (Tables 12 and 13)

The UV–vis spectra of open chain *vic*-tetraketones were reported many years ago by Horner and Maurer[193] and are summarized in the earlier review. What is new are data from cyclic tetraketones such as the cyclododecatetrone **81**,[81] the cyclotetradecatetrones **82a**[81] and **82b** and the [12]paracyclophanetetrone **84**,[83] the cyclic oxoundecanetetrone **85**,[84] the

Table 12. Electronic Absorption Spectra (λ_max[nm], ε[L·mol⁻¹·cm⁻¹]) of *vicinal* Tetraketones in Methylene Chloride Solution: 5,5,12,12-Tetramethylcyclododecane-1,2,3,4-tetrone (81), 5,5,14,14-Tetramethylcyclotetradecane-1,2,3,4-tetrone (82a), 1,4-Dioxa-7,7,12,12-tetramethylcyclotetradecane-8,9,10,11-tetrone (82b), 4,4,9,9-Tetramethyl[12]paracyclophane-5,6,7,8-tetrone (84), 1-Oxa-4,4,9,9-tetramethylcyclo-undeca-5,6,7,8-tetrone (85), and 1-Oxa-5,5,10,10-tetramethylcyclotrideca-6,7,8,9-tetrone (86)

compound	λ_{max} (ϵ)	ref
81	507 (43), 368 (97)	81
82a	553 (87), 385 (94)	81
82b	494 (120), 374 (1549), 300 (173)	86
84	507 (59), 402 (42)	83
85	460 (28), 362 (63), 294 (338), 226 (1202)	84
86	512 (25), 380 (134)	85

Table 13. Electronic Absorption Spectra (λ_max[nm], ε[L·mol⁻¹·cm⁻¹]) of *vicinal* Pentaketones in Methylene Chloride Solution: Diphenyl Pentaketone (3a), Di-*p*-tolyl Pentaketone (3e), and Di-*tert*-butyl Pentaketone (3i)

compound	λ_{max} (ϵ)	ref
3a	547 (30), 457 (154)	4
3e	561 (136), 431 (207)	94
3i	559 (96), 436 (101), 352 (196)	4

cyclic oxotridecanetetrone **86**.[85] With the exception of **82b** and **85**, all show a long-wavelength band between 507 and 533 nm with low extinction typical for a $\pi^* \leftarrow n$ transition. In the case of the oxocyclodecanetetrone **85** and the dioxacyclotetradecatetrone **82b**, a hypsochromic shift of the first band to 460 and 494 nm, respectively, was observed.[84,86] This was explained by assuming an interaction between the 2p orbital(s) of the ether oxygen(s) and the lowest π^* orbital of the C_4O_4 of **85** and **82b**, respectively.[84,86] X-ray data (see section VII.A) and electrochemical studies (see section VIII.C) on **85** support this rationalization. In the case of di(*tert*-butyl)pentaketone (**3i**)[4] and diphenylpentaketone (**3a**),[4] the long-wavelength band was observed between 545 and 560 nm. To conclude the chapter on the UV–vis spectra, we have correlated in Figure 11 the wavenumbers of the first absorption bands of the diaryl ketones in the series from benzophenone to diphenyl pentaketone. For the first members of the series, we find a linear decrease with increasing number of CO groups. As anticipated from the other studies, a leveling off in the shift to longer wavelengths was observed as the number of CO groups increased.

C. Reduction Potentials. Correlation with Spectra (Figure 12, Tables 14 and 15)

Half-wave potentials recorded for a number of *vic*-triketones are collected in Table 14.[187,194] At first glance there seems to be no correlation with any of the properties of these species. More detailed consideration suggests a correlation between the first band in the UV–vis spectra of tetramethylcyclopentane-1,2,3-trione (**202**), bicyclo[3.1.0]hexane-2,3,4-trione (**12a**), bicyclo[3.2.1]octane-2,3,4-trione (**205**), bicyclo[3.2.2]nonane-2,3,4-trione (**206**), and 4,4,6,6-tetramethylhexane-1,2,3-trione (**63b**) with the half-wave potentials. This selection was made because the long-wavelength band of these species was assigned to a $\pi_{-1} \leftarrow n_+$ transition (86–90%) and because the first ionization energies ($I_{v,1}(n_+)$) of these molecules vary only slightly. One could argue from these facts that the energy of the π_{-1}^* orbital should correlate with the first UV–vis band. This is indeed the case as shown in Figure 12.
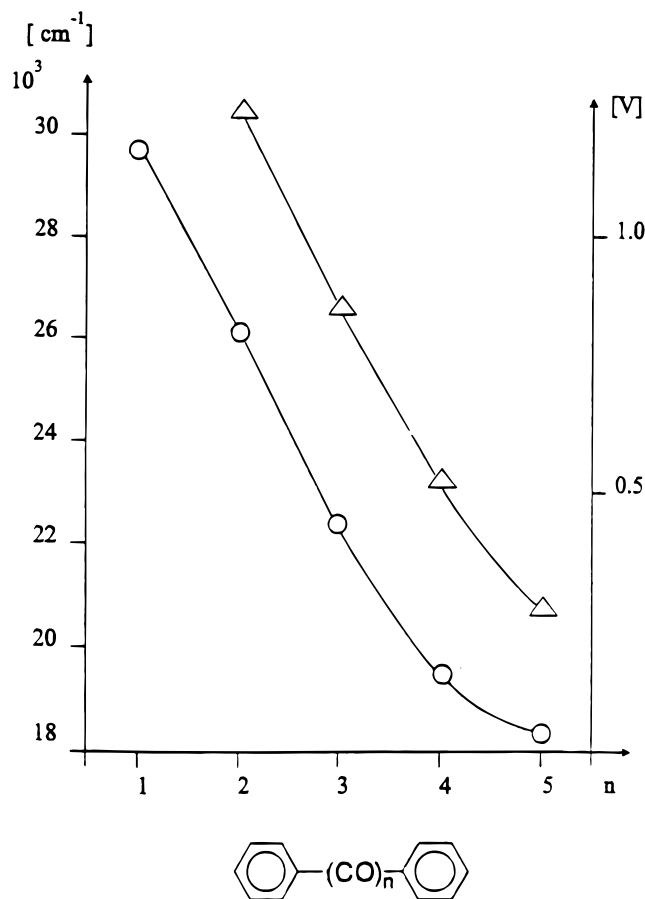
Figure 11. Correlation of the long-wavelength absorption band (arches, left scale) and the first reduction potential (triangles, right scale) of the diarylketones $C_6H_5-(CO)_n-C_6H_5$ from $n = 1$ (benzophenone) to $n = 5$ (diphenyl pentaketone, **3a**).
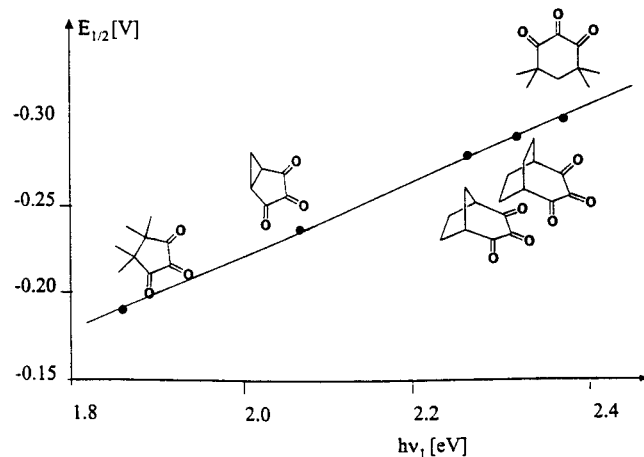

Figure 12. Correlation of the first reduction potential ($E_{1/2}$) and the long-wavelength absorption band of cyclic and bicyclic triketones.

The triones incorporating a π-system such as cyclopentene-1,2,3-trione (**13**), indanetrione (**4a**), 2H,3H-dihydrophenalene-1,2,3-trione (**17a**), 1,2,3,6,7,8-hexahydrohexaoxopyrene (**10**), and 1,2,3,5,6,7-hexaoxo-s-hydrindacene (**9**) do not show such a correlation. This is anticipated because the long-wavelength band in the UV–vis spectra of π-systems usually cannot be described by a single transition.

Table 14. Half-Wave Potentials (SCE) of Indanetrione (4a), 1,2,3,5,6,7-Hexaoxo-s-hydrindacene (9), 1,2,3,6,7,8-Hexahydrohexaoxopyrene (10), Bicyclo[3.1.0]hexane-2,3,4-trione (12a), 1,5-Dimethylbicyclo[3.1.0]hexane-2,3,4-trione (12b), Cyclopentene-1,2,3-trione (13), 2,3,4-Dihydrophenalene-1,2,3-trione (17a), 4,4,6,6-Tetramethylcyclohexane-1,2,3-trione (63b), Tetramethyl-cyclopentanetrione (202), Bicyclo[3.1.1]heptane-2,3,4-trione (204), Bicyclo[3.2.1]octane-2,3,4-trione (205), Bicyclo[3.2.2]nonane-2,3,4-trione (206), and 4,4,6,6-Tetramethylcyclohexane-1,2,3,5-tetrone (208) (All polarographic data were determined in acetonitrile solution)

compound	$E_{1/2}$ [V]	ref
4a	−0.28	194
9	−0.13	194
10	−0.09	194
12a	−0.24	194
12b	−0.32	194
13	−0.44	194
17a	−0.34	194
63b	−0.22	187
	−0.30	194
202	−0.19	194
204	−0.32	187
205	−0.24	187
	−0.29	194
206	−0.24	187
	−0.28	194
208	−0.08	187

Table 15. Comparison between Reduction Potentials and Long-Wavelength Absorption Bands of Di-*tert*-butylketone, -diketone, -triketone (1i), -tetraketone (2i), and -pentaketone (3i) and of Benzophenone, Diphenyldiketone, -triketone (1a), -tetraketone (2a), and -pentaketone (3a) (All data from ref 4)

compound	E_1[V]^a	λ_{max}[nm](ϵ)
t-buCO*t*-bu	>−2.0	295 (23)
t-buCOCO*t*-bu	−1.70	362 (16)
1i	−1.15	457 (33)
2i	−0.63	525 (85)
3i	−0.33	559 (96)
PhCOPh	>−2.0	337 (150)
PhCOCOPh	−1.25	380 (75)
1a	−0.88	450 (45)
2a	−0.52	515 (200)
3a	−0.27	547 (130)

^{a} The cyclovoltammetric data were obtained in CH_2Cl_2 with 0.1 mol/L n-$Bu_4N^+PF_6$ under argon with a glassy carbon electrode, using Ag/AgCl in LiCl/ethanol as reference and Pt as counterelectrode. Scan rate, 15 mV/s. $E_{1/2}$ $FeCp_2/FeCp_2^+ = 0.4$ eV.

Very little electrochemical data are available for *vic*-tetra- and pentaketones. In Table 15 the reduction potentials of the di-*tert*-butyl compounds (di-*tert*-butylmono-, di-, tri- (**1i**), tetra- (**2i**), and pentaketone (**3i**) as well as the diphenyl ketones benzophenone, benzil, diphenyl triketone (**1a**), tetra- (**2a**), and pentaketone (**3a**)) are listed. As anticipated, the reduction potentials decrease linearly at least to $n = 4$ (see Figure 11) as a function of increasing number of carbonyl groups. The figure suggests a leveling off of the reduction potentials. It seems to parallel the result of absorption data.

D. ESR Spectra (Tables 16 and 17)

ESR data of cyclic and acyclic triketones have been summarized recently.[195] To the best of our knowledge, there are only three reports of ESR investigations of

Table 16. Hyperfine Coupling Constants a(H) and g-Factors Derived from ESR Spectroscopic Investigations of the Radical Anions of Di-*tert*-butyldiketone, -triketone (1i), -tetraketone (2i), and -pentaketone (3i) as well as Diphenyldiketone, -triketone (1a), and -tetraketone (2a) (Data from ref 198)

compound	T [K]	a(H)[G]	a(H$_m$)[G]	a(H$_p$)[G]	g
t-buCOCO*t*-bu$^{•-}$	300	0.27 (18H)			2.0050
1i$^{•-}$	300	0.14 (18H)			2.0053
2i$^{•-}$	265	0.08 (18H)			2.0055
3i$^{•-}$	240	0.063 (18H)			2.0058
PhCOCOPh$^{•-}$	300	0.101 (4H)	0.034(4H)	0.115 (2H)	2.0050
1a$^{•-}$	300	−0.060 (4H)	0.019(4H)	−0.065 (2H)	2.0052
2a$^{•-}$	260	0.017 (4H)	0.006(4H)	0.017 (2H)	2.0056

Table 17. Hyperfine Coupling Constants a(H) from ESR Spectroscopic Investigations of the Radical Anions of Indanetrione (4a), o-Tropoquinone (62), and Cyclopentane-1,2,3-trione (243) (All values recorded at 298 K)

compound	a(H) [G]	ref
4a	0.097	200
62	H(4,7) 0.109	199
	H(5,6) 0.205	
243	H(4,5) 0.600(2)	198

acyclic *vic*-polyketones.[196−198] The radical anions of 1,3-diphenyl-1,2,3-propanetrione (**1a**)[195] and dimesityltetraketone (**2c**)[197] exist as free ions in dimethyl sulfoxide. In the case of **2c**, the contact ion pairs with Na$^+$, Cs$^+$, and Ba^{2+} were characterized by their ESR/ENDOR spectra showing temperature-dependent metal couplings of a_{Na^+} = 0.061 mT (190 K), a_{Cs^+} = 0.021 mT (190 K) and $a_{Ba^{2+}}$ = 0.145 mT (295 K).

Di(*tert*-butyl)diketone, -triketone (**1i**), -tetraketone (**2i**), and -pentaketone (**3i**) as well as the benzil, diphenyl triketone (**1a**), and diphenyl tetraketone (**2a**) were reduced with potassium metal in dimethoxyethane in the presence of Kryptofix 222 (see Table 16).[198] The coupling constants obtained decrease steadily, from the α-diketones to the *vic*-tetra- and pentaketones while the g-values increase. All radical anions are delocalized species. With increasing CO chain length, the magnitudes of the respective hyperfine constant splitting decrease considerably (Table 16). Each elongation of the CO chain shifts spin population from the terminal substituents into the extended π-system. The increase of the g-values is related to the growing spin−orbit coupling due to the interaction of the unpaired electron with the lone pairs at the oxygen atoms. The inverse correlation between g-values and the amount of spin population on the terminal substituents prove that the unpaired electron in the radical anions up to five CO units is fully delocalized.[198]

For the sake of completeness, we mention the reports on the radical anions of α,β-diketoesters such as dimethyl mesoxalate[195] and the methyl and ethyl esters of α,β-diketobutyric acid.[195]

In contrast to the few investigations on acyclic polyketones there are several reports on the radical anions of cyclic triketones.[196,199−202] The species investigated were the radical anions of cyclopentane-1,2,3-trione (**243**),[199,200] o-tropoquinone (**62**),[201] and indanetrione (**4a**).[196,202] These investigations revealed large coupling constants with the hydrogen atoms at 4 and 5 positions of **243** and smaller values for the coupling constants in **62** and **4a** (see Table 17). Besides these species, a number of radical anions of heterocyclic trionic systems were scrutinized. In detail, these were the radical anions of alloxan,[196,203] 1-benzyl- and 1-methyl-2,3,4-trioxo-pyrolidine,[204] N,N-dimethylalloxan,[205] ascorbic acid,[196,206] and 1,2-diphenylpyrazoline-3,4,5-trione.[207]

E. Other Spectra

1. NMR Spectra (Tables 18–21)

The NMR technique has developed rapidly since the earlier review and other resonances than hydrogen, e.g., ^{13}C and ^{17}O are available now. In particular, the readily available ^{13}C signals of *vic*-polyketones are very characteristic for the (CO)$_n$ moiety.

In Tables 18 and 19 we have summarized ^{13}C data of tri-, tetra-, and pentaketones. Unfortunately most *vic*-triketones described in the literature were prepared before ^{13}C NMR was readily available; therefore, our data are very limited. It is seen that for *vic*-triketones the ^{13}C signal varies between δ = 180−189 for the outer CO groups and 190−203 for the central CO groups (Table 18). Similar values are reported for the tetra- and pentaketones: lower δ values for the peripheral keto groups and higher ones for the central CO groups. The generalizations made in the earlier review on ^{13}C shifts appeared to be valid for all the compounds known so far.

Table 18. ^{13}C NMR Data of Diphenyltriketone (1a), Indanetrione (4a), Spiro[5.5]undecane-2,3,4-trione (37), 1,8,8-Trimethylbicyclo[3.2.1]octa-2,3,4-trione (40), o-Tropoquinone (62), 4,4,6,6-Tetramethylcyclohexane-1,2,3-trione (63b), 6,7-Dihydro-5H-benzocycloheptene-5,6,7-trione (242), 5-Methylcyclohexane-1,2,3-trione (244), 5,5-Dimethylcyclohexane-1,2,3-trione (245), 5-Phenylcyclohexane-1,2,3-trione (246), 4,4-Diphenylcyclohexane-1,2,3-trione (247), Tetrahydro-2H-furan-2,3,4-trione (248), and (2-Methyl-1,3-dioxolan-1-yl)butan-1,2,3-trione (249) [The spectra were recorded in CDCl$_3$ at 100 MHz except 62 (CD$_3$CN) and 242 ((CD$_3$)$_2$CO)]

	^{13}C resonances (δ) of CO groups			
compound	C(1)	C(3)	C(2)	ref
1a	188.5	188.9	192.8	3
4a	183.0	183.8	189.1	3
37	181.4	181.4	193.1	49
40	188.6	188.6	197.0	49
62	188.7	188.7	185.5	69
63b	189.0	189.0	197.0	209
242	193.4	187.5	194.9	69
244	182.0	182.0	192.2	49
245	181.7	181.7	192.8	49
246	192.0	192.0	203.5	49
247	185.1	185.1	193.6	49
248	154	180.3	190.0	208
249	190.4	195.0	203.4	210

Table 19. ^{13}C NMR Data (δ) of *vic*-Tetra- and -Pentaketones: Diphenyl Tetraketone (2a), Di-*tert*-butyltetraketone (2i), 5,5-Dimethyl-1-phenylhexane-1,2,3,4-tetrone (2j), Diphenylpentaketone (3a), Di(*p*-tolyl)pentaketone (3e), Di(*tert*-butyl)pentaketone (3i), 2,2-Dimethyl-7-phenylhexane-3,4,5,6,7-pentone (3j), Di(*p*-fluorophenyl)pentaketone (3k), 5,5,12,12-Tetramethylcyclododecane-1,2,3,4-tetrone (81), 5,5,14,14-Tetramethylcyclotetradecane-1,2,3,4-tetrone (82a), 1,4-Dioxa-7,7,12,12-tetramethylcyclotetradecane-8,9,10,11-tetrone (82b), 4,4,9,9-Tetramethyl[12]paracyclophane-5,6,7,8-tetrone (84), 1-Oxa-4,4,9,9-Tetramethylcycloundecane-5,6,7,8-tetrone (85), and 1-Oxa-5,5,10,10-tetramethylcyclotridecane-6,7,8,9-tetrone (86) (The spectra were recorded in CDCl$_3$)

compound	chemical shift (δ) of carbonyl C atoms	ref
2a	192.8, 188.5	3
2i	204.8, 188.5	3
2j	205.3, 189.4, 189.0, 187.0	94
3a	190.1, 188.4, 182.4	4
3e	190.7, 187.9, 182.2	94
3i	204.9, 190.7, 182.2	4
3j	205.6, 191.0, 189.1, 183.3, 182.7	88
3k	190.2, 186.6, 181.6	94
81	206.5, 188.1	81
82a	207.3, 185.2	81
82b	200.9, 188.8	86
84	205.4, 185.3	83
85	203.5, 191.5	84
86	206.7, 184.8	85

Table 20. ^{13}C NMR Spectra of *N,N,N,N*-Tetramethyl- and *N,N,N,N*-Tetrabenzyloxopropanediamide (230a,b), *N,N*-Dimethyl-3-(dimethylamino)-2-oxo-3-thiooxopropane Amide (231a), *N,N*-Dibenzyl-3-dibenzylamino-2-oxo-3-thio-oxopropaneamide (231b), *N,N,N,N*-Tetramethyl- and *N,N,N,N*-Tetrabenzyl-2-oxo-propanebis(thioamide) (232a,b), *N,N*-Dibenzyl-3-dibenzylamino-2,3-dithio-oxopropaneamide (233b), *N,N,N,N*-Tetrabenzylthiooxopropanediamide (234b), Ethyl 3-Dimethylamino- and Ethyl 3-Dibenzylamino-2-oxo-3-thiooxopropanoate (235a,b), *N,N*-Dimethyl- and *N,N*-Dibenzyl-2,3-dioxo-3-phenylpropanoate (236a,b), *N,N*-Dimethyl- and *N,N*-Dibenzyl-2,3-dioxo-3-phenylpropanethioamide (237a,b), *N,N*-Dibenzyl-4,4-dimethyl-2,3-dioxopentaneamide (239), *N,N*-Dibenzyl-4,4-dimethyl-2,3-dioxopentanethioamide (240), and Ethyl 3-Phenyl-2,3-dioxopropanoate (241) (All data from ref 76 except last entry from ref 24)

compound	chemical shift (δ) of carbonyl C atoms		
	C1	C2	C3
230a	165.6	183.0	165.6
230b	166.3	182.2	166.3
231a	166.3	174.6	195.2
231b	167.1	173.4	196.8
232a	195.0	168.0	195.0
233b	196.9	167.2	196.0
234b	169.3	231.8	169.3
235a	162.1	172.3	193.3
235b	161.6	173.4	195.2
236a	191.9	185.5	165.3
236b	191.4	185.0	166.3
237a	193.0	175.7	194.8
237b	192.8	175.0	196.6
239	207.5	184.7	166.3
240	209.3	174.5	197.2
241	183.8	189.1	183.3

Table 20 summarizes ^{13}C data of mesoxalic acid diamides **230a,b**, mesoxalic acid thioamides **231a,b** and dithioamides **232a,b**, thio mesoxalic acid thioamide **233b**, thiomesoxalic acid diamide **234b**, ethyl mesoxalic acid thioamides **235a,b**, α,β-dioxoester-

Table 21. ^{17}O NMR Data of Diphenyltriketone (1a), Di(*p*-methoxyphenyl)triketone (1d), Di-*tert*-butyltriketone (1i), and Indanetrione (4a) (The spectra were recorded in CH$_3$CN at 65 °C. The width at half height is given in Hz. All data from ref 211)

compound	O(1), O(3)	$\nu_{1/2}$ [Hz]	O(2)	$\nu_{1/2}$ [Hz]
1a	545.5	350	573.4	270
1d	524	700	578	860
1i	608	775	531	485
4a	533.4	345	610.0	230

amides **236a,b** and **239b**, α,β-dioxoester **241**, and α,β-dioxothioamides **237a,b** and **240**. The ^{13}C data observed for the central (C2) carbon of **230**−**232** and **235** as well as of C-1 and C-2 of **236**−**241** correspond to those of other *vic*-polyketones.

In Table 21 some ^{17}O data of four triketones are summarized.[211] This comparison shows that the central oxygen atom in indanetrione (**4a**) is more strongly deshielded than in the other four samples.[211] This has been ascribed to the coplanarity of the three carbonyl groups in **4a**. The strong deshielding of the signals of the peripheral oxygens in di-*tert*-butyl triketone (**1i**) was explained by the steric hindrance of the *tert*-butyl groups.

2. Mass and IR Spectra

To the best of our knowledge, no detailed study of mass spectra or IR spectra of *vicinal* polyketones has been published since the last review.

IX. Addendum

The following papers appeared or have been brought to our knowledge after this manuscript had been essentially completed.

A Review Article. A review[212] article appeared in Russian entitled "Oxidative methods in the synthesis of *vicinal* di- and poly-carbonyl compounds". Some of the methods presented in section II and III of the present review are discussed briefly in this article.

Attempted Complex Formation with Ninhydrin. Attempts by Leinweber et al.[213] to prepare a tricarbonylchromium complex of ninhydrin (**4b**) by direct complexation were not successful. The oxidation of tricarbonyl(η^6-1,3-indandione)chromium(0) with dimethyldioxirane gave the ninhydrin complex in 75% yield in equilibrium with the indantrione (**4a**) complex. The latter reacted in hetero-Diels−Alder reactions with dienes with diastereoselective formation of spiro-anellated pyran derivatives.

Photochemistry of Indanetrione (4a; Scheme 56). Netto-Ferreira and co-workers[214] have investigated the photochemical reactions of **4a** with a variety of unsaturated compounds. Excitation of **4a** into a higher excited state ($\lambda \approx 300$ nm) in the presence of 2,3-diphenyl-1,4-dioxene proceeded with a quantum yield of approximately unity in a variety of solvents (acetonitrile, dichloromethane, and benzene) to give the oxetane **250**. None of the cyclic six-membered product **251**, a type of product often observed with α-diketones, was detected. Isomerizaton of pure *cis*- or *trans*-stilbene was observed, a process which would be significantly endothermic if the lowest triplet state of **4a** was involved as a

Scheme 56
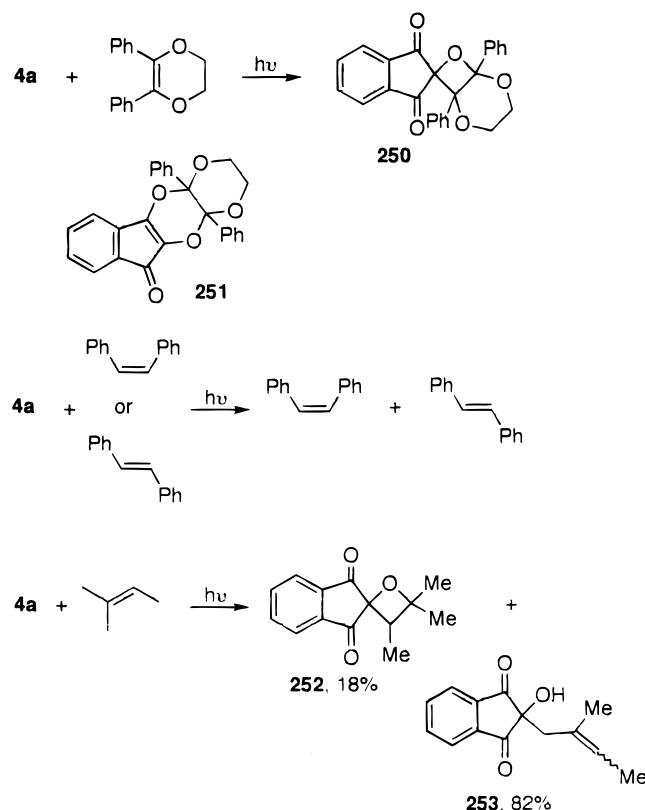
sensitizer. The major process involved with olefins having allylic hydrogen atoms was addition of the olefin to **4a** as illustrated for 2-methyl-2-butene in Scheme 56. Here again, quantum yields were approximately unity in a number of solvents. Abstraction of allylic hydrogen followed by coupling of the resulting two radicals was suggested.

Rearrangement Reactions of Hydrated *vic*-Triketones. G. Kollenz et al. contributed to the mechanism of the ring contraction of several cyclic *vic*-triketones or derivatives thereof, e.g., 1,5-dihydro-2*H*-1,5-benzodiazepine-2,3,4-trione hydrate,[215] 2,2-dichloro-6-methyl-4*H*-1-thiochroman-3,4-dione,[216] as well as the redoxdisproportionation of 2,2-dihydroxaphenalene-1,3(2*H*)-dione.[217] The investigations were carried out by means of ^{14}C labeling. These reactions had also been investigated earlier by F. Arndt, B. Eistert, and co-workers.[218]

Cycloadditions. [4+2]-Cycloadditions of diethyl mesoxalate with 2-alkyl-1-ethoxy-1,3-butadiene afforded in high yields diethyl 3-alkyl-2-ethoxy-5,6-dihydro-2*H*-pyran-6,6-dicarboxylates.[219] The Diels–Alder reaction of 2-methyl-1(1-phenylalkoxy)butadienes with cyclic triketones such as alloxan and ninhydrin proceeds smoothly at room temperature in excellent yields and high diastereoselectivity.[220]

Oxidative Cleavage of Iodonium Ylides. The reactions via phenyliodonium ylides (see Scheme 11) and subsequent oxidation by ozone were used by Schank and La Vecchia[210] to prepare tetracarbonyls such as dimethyl 2,3-dioxobutanedioate, methyl 2,3,4-trioxopentanoate, methyl 5-methyl-2,3,4-trioxohexanoate, methyl 4-cyclopropyl-2,3,4-trioxobutanoate, methyl 4-phenyl-2,3,4,trioxobutanoate, hexane-2,3,4,5-tetrone, and 6-methylheptane-2,3,4,5-tetrone. The

closest they came to *vic*-pentacarbonyls was the syntheses of methyl 5,5-dimethoxy-2,3,4-trioxohexanoate. In this work[210] the reaction of triketones as well as *vicinal* tetracarbonyls with water, diazoalkanes, as well as *o*-phenylenediamine was studied also.

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