Carbalkoxycarbenes

ALAN P. MARCHAND* and NOLAN MAC BROCKWAY**

Departments of Chemistry, University of Oklahoma, Norman, Oklahoma 73069, and Midwestern University, Wichita Falls, Texas 76308

Received March 19, 1973 (Revised Manuscript Received August 17, 1973)

Contents

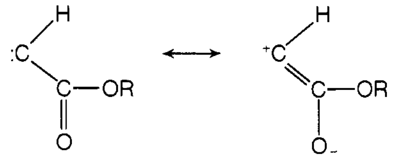
I. Introduction

Interest in carbenes as highly reactive intermediates in organic chemistry dates back to the last century. In the late 1940's and early 1950's, interest surged in the study of the chemical and physical properties of divalent carbon species as convenient laboratory techniques were developed for preparing and studying these highly reactive species. In the mid-1950's, it was recognized that methylene, :CH_2, produced *via* direct photolytic decomposition of diazomethane was extremely reactive, leading Doering to label this species as "the most indiscriminate reagent in organic chemistry."[1] It was also demonstrated experimentally about this time that methylene could be produced in different spin states, each of which had associated with it a particular pattern of chemical behavior and individual physical properties.[2,224]

Although of considerable mechanistic interest, reactions of "hot" methylene were of limited synthetic value owing to the high reactivity and consequent low selectivity of the photolytically produced carbene. However, it was found empirically by a large number of investigators that substitution of one or both of the methylene hydrogen atoms either by a heteroatom (or substituent group containing a heteroatom adjacent to the carbene carbon atom) which contained an unshared pair of electrons or, alternatively, by conjugatively electron-withdrawing substituents could have a stabilizing effect on the carbene. This, in turn, could increase the selectivity of the carbene relative to methylene in its reactions with various substrates, and it could thereby render the carbene as a viable synthetic intermediate.

Carbalkoxycarbenes, :$CHCO_2R$, particularly the species having R = CH_3 or CH_2CH_3, have been extensively studied from both mechanistic and synthetic standpoints. The reactions of carbalkoxycarbenes have been known for quite some time,[3,4] but it is only within the last 25 years that chemists have begun to focus attention upon them with an eye toward gaining an understanding of the detailed mechanisms of these reactions.

In carbalkoxycarbenes, stabilization results from the electron-withdrawing resonance effect of the carbalkoxy group (eq 1). This same factor should also cause carbalkoxycarbenes to be more electrophilic than methylene itself, a prediction which has been amply demonstrated experimentally.



(1)

Although a number of review articles have appeared (particularly within the last 10 years) which deal with various aspects of carbene chemistry,[5-23] they generally have been concerned in only a superficial way (with one notable exception[17]) with the chemistry of carbalkoxycarbenes. Indeed, a number of mechanistically very interesting and potentially synthetically useful reactions of carbalkoxycarbenes (such as carbene-promoted HX eliminations and C–X "insertion" reactions) have gone generally unnoticed in most of the broader reviews which have dealt with the chemistry of a wide variety of carbenes.

---

* Author to whom inquiries should be addressed at the University of Oklahoma.

** Midwestern University. Present address: Solvent Manufacturing Co., Inc., Midwest City, Okla. 73110.

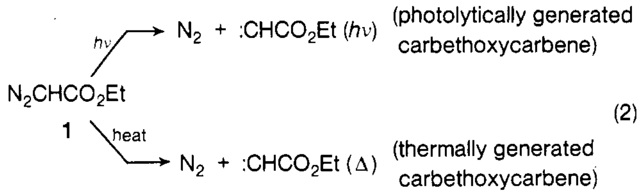
It is our purpose in this review to focus attention upon the chemistry of monocarbalkoxycarbenes, particularly carbethoxycarbene and carbomethoxycarbene, without undue duplication of material which has appeared elsewhere in more generalized carbene chemistry reviews. To accomplish this purpose, we have undertaken a survey of the literature through February 1973, covering principally carbethoxycarbene, carbomethoxycarbene, and reactions of their diazo precursors (ethyl diazoacetate and methyl diazoacetate, respectively). Reactions which might reasonably be expected to proceed *via* carbene (or carbenoid) intermediates have been emphasized, but occasionally noncarbene (or carbenoid) reactions of the diazo precursor have been mentioned where their mechanisms have proved to be especially interesting or in cases where these reactions appear to be of unusual synthetic utility.

Discussions of the chemistry of biscarbalkoxycarbenes, particularly involving biscarbethoxy- and biscarbomethoxycarbene, occur frequently throughout the review. When this has been done, it has been for purposes of comparison with the corresponding monocarbalkoxycarbene, and we have not attempted to be thorough in our presentation of the chemistry of biscarbalkoxycarbene species.

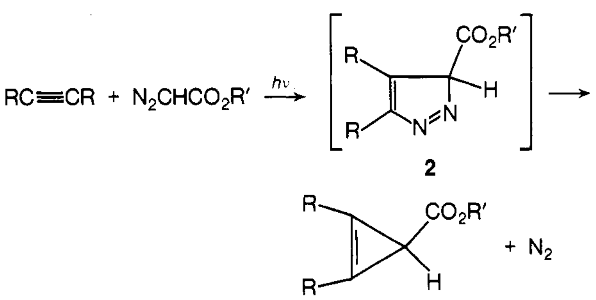
II. Spin States of Carbalkoxycarbenes

A. Methods of Generating Carbalkoxycarbenes: Carbenes *vs.* Carbenoids

Both carbomethoxycarbene and carbethoxycarbene are conventionally prepared from the corresponding diazo ester. This may be accomplished thermally (*ca.* 150°) or photolytically (eq 2). Photolytic decomposition of **1** can be carried out either *via* direct photolysis or *via* photolysis in the presence of known photosensitizers, such as benzophenone.[24,25] The thermal decomposition of **1** can be carried out at temperatures well below 150° when performed in the presence of a metal catalyst.[26,27] Copper bronze or Cu(II) have been widely used for this purpose; however, the reactive intermediate produced in this way is termed a "carbenoid," and its chemistry has been shown to involve both the elements of :$CHCO_2R$ and the metal in the catalyst (to which it is complexed; *vide infra*).[26-28]

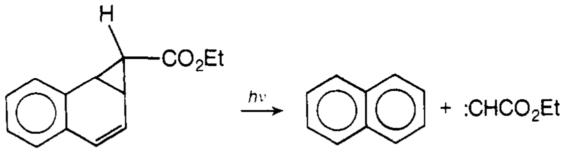


Let us first consider the "free" carbene produced either photolytically or thermally from **1**. In addition to the question of the spin state of the reacting species, :$CHCO_2R$ (*hν*) (*i.e.*, whether singlet or triplet), the whole question of the nature of photochemical reactions involving diazo esters is greatly complicated by the possibility that the excited diazo ester itself (and not a divalent carbon species derived from it) may in fact be the reacting species.[25,30,31] This phenomenon might manifest itself in, *e.g.*, addition reactions of carbalkoxycarbenes to carbon–carbon triple bonds, through intermediate pyrazolenine formation, followed by photodecomposition of the pyrazolenine intermediate (**2**) to afford cyclopropenes[32-36] (eq 3). Similarly, the addition of excited diazo compounds to carbon–carbon double bonds can occur to afford pyrazolines which photodecompose to cyclopropanes.[37-39]



(3)

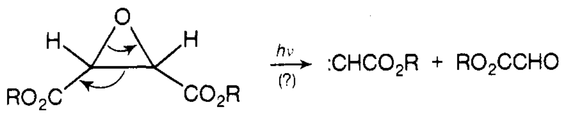
One obvious way to alleviate the difficulties attendant with the generation of "free" carbenes from diazo precursors is to find alternative pathways which do not involve diazo compounds. In the case of carbalkoxycarbenes this has only been successfully accomplished in one instance, involving photocycloelimination of carbethoxycarbene from 7-carbethoxybenzonorcaradiene (**3**)[40-42] (eq 4). Yields in this reaction are low (*ca.* 8%, as determined *via* trapping experiments), and the product is accompanied by considerable tar. Consequently, no quantitative comparison of the reactions of the carbene produced from **3** with those of the species produced *via* photodecomposition of ethyl diazoacetate has been performed.



3

(4)

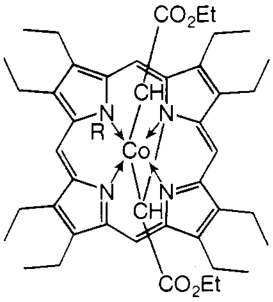
Other methods for generating carbalkoxycarbenes can be envisioned; for example, one might consider attempting a photocycloelimination from a suitably constructed oxirane[42] (eq 5). However, thus far only *vic*-diaryloxiranes have been used successfully as (phenyl)carbene precursors in this way.[42] Alternatively, *thermal* cycloelimination processes can be envisioned, but, again, there has been no report forthcoming in the carbene literature to suggest that processes of this type can be successfully employed for the preparation of carbalkoxycarbenes.[43] Similarly, photolysis or thermolysis of diazirines, although a useful method for preparing a number of substituted methylenes, has not been successfully utilized for the generation of carbalkoxycarbenes.[42-50]



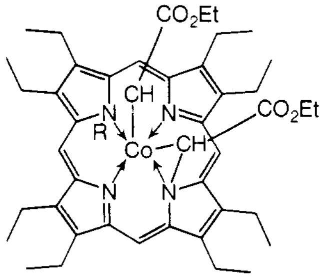
(5)

A final potential precursor for carbalkoxycarbenes merits consideration. There are a large number of examples of stable transition metal–carbene complexes.[51] The possibility exists that reactions which displace the carbene from these complexes might be capable of affording the "free" (noncomplexed) carbene whose chemical reactions could then be compared with those of the corresponding carbene generated photolytically from a diazo precursor. However, with very few exceptions, such transition metal–carbene complexes are stable only when the carbene moiety is *nucleophilic* (*i.e.*, :CXY, where X and Y are lone-pair substituents).[51] Two notable exceptions to this statement are the complexes **4** and **5** which are formed upon reaction of ethyl diazoacetate with cobalt(III) octaethylporphyrin.[52-54]

In lieu of satisfactory alternative precursors for carbalkoxycarbenes, only indirect evidence has been brought to bear on the question of carbene intermediates in diazo ester photolyses *vs.* direct reaction of the photoexcited



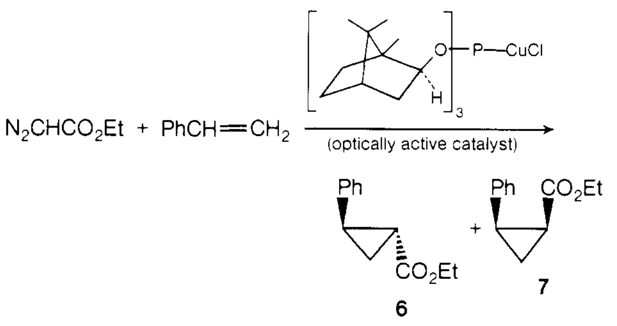
4, R = CH_2CO_2Et



5, R = CH_2CO_2Et

diazo ester. Particularly important in this regard has been the demonstration that the chemical reactivity of phenylcarbene[55] and of 4,4-dimethylcyclohexadienylidene[56] when generated in the same spin state from different precursors is precursor independent. Evidence mitigating against the intermediacy of pyrazolines in stereospecific reactions of diazoacetic esters with olefins under photolytic or thermal (80–100°) conditions has recently been cataloged in an excellent review by Dave and Warnhoff.[17] Nevertheless, the important question of the exact nature of the reacting species in diazoacetic ester decompositions remains yet to be convincingly answered.

Thermal decompositions of diazo esters in the presence of metal catalysts, especially Cu(0), Cu(I), or Cu(II), leads to the formation of carbalkoxycarbenoids. Important evidence suggesting that the reacting species in metal-catalyzed diazo ester–olefin reactions involves a carbene–metal complex is provided by a number of independent observations that ethyl diazoacetate in the presence of optically active homogeneous Cu(I) or Cu(II) catalysts reacts with olefins to afford optically active ethyl cyclopropanecarboxylates in low optical yield[26,57,58] (eq 6–8). Furthermore, in the Cu(I) catalyzed reaction of ethyl diazoacetate with cyclohexane, increasing the steric bulk of the ligand on copper in homogeneous catalysts of the type $(RO)_3PCuCl$ was found to produce systematic changes in the exo/endo ratio among the product 7-carbethoxynorcaranes.[26] It was concluded that this result offered further proof of the presence of a carbene–metal complex as the reacting species in these Cu(I) catalyzed additions of ethyl diazoacetate to olefins.[26] The observation that homogeneous catalysis of the reaction between ethyl diazoacetate and cyclohexene by $(ArO)_3PCuCl$ (where Ar = meta- and para-substituted benzenes) produced systematic changes in the syn/anti ratio in the product 7-carbethoxynorcaranes was interpreted as suggesting that the $:CHCO_2Et$ moiety, the metal atom in the catalyst, and the olefinic substrate are all involved in the transition state leading to product[27] (for an opposing view, see discussion in section III.A.1).

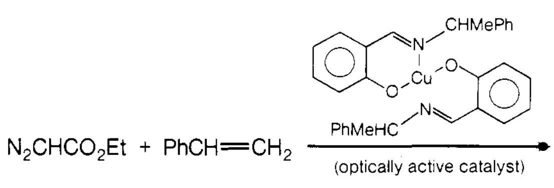


(6)

6

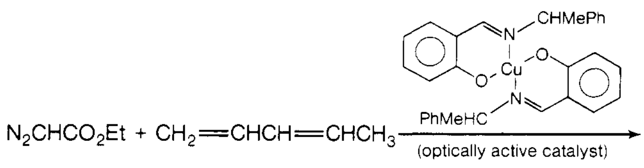
7

(optical yield = 3%, ref 26)



6 + **7** (7)

(optical yield = 6%, ref 57)



optically active 1-ethoxycarbonylcyclopropanes (ref 58) (8)

In addition to the commonly employed copper catalysts, a potential new route to carbalkoxycarbene–metal complexes is suggested by the recent study of Alper and Partis.[59] These investigators have suggested that an unstable alkylidenylcarbeneiron tetracarbonyl complex may be formed when carbomethoxymethylenetriphenylphosphorane

$$\mathrm{MeO_2C{-}\overset{-}{C}H{-}\overset{+}{P}Ph_3}$$

is treated with various iron carbonyls. The future systematic exploration of the chemistry of this unique iron carbonyl complex of carbomethoxycarbene should prove to be of great interest.

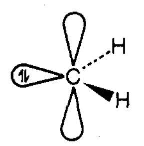
Comparison of the chemical properties among $:CHCO_2R$ ($h\nu$), $:CHCO_2R$ (Δ), and carbalkoxycarbenoids is deferred to sections III–VI. Before continuing with a discussion of the chemistry of these species, it is worthwhile to briefly examine the environmental conditions under which reactions of these highly energetic intermediates are carried out. With liquid substrates, the reaction of ethyl diazoacetate (prepared essentially free from contaminating ethyl chloroacetate by Searle's method[60]) is simply performed using an excess of the substrate as solvent. For the corresponding reaction with solid substrates, a suitable solvent must be found which is both inert toward ethyl diazoacetate and capable of dissolving reasonably high concentrations of the diazo ester and the solid substrate. Hexafluorobenzene has been extensively utilized as solvent in reactions involving carbenes (such as fluorenylidene[61,62]) which are less reactive than carbethoxycarbene. However, cyclopentadienylidene[63] and $:CHCO_2Et$ ($h\nu$)[64] have been found to add to a fluorinated carbon–carbon double bond in hexafluorobenzene. It is also important to note that hexafluorobenzene has been utilized as an "inert" solvent to promote singlet–triplet intersystem crossing in $:C(CO_2Me)_2$[23]; however, $:CHCO_2Et$ ($h\nu$) apparently does not suffer decay from a singlet to a triplet electronic configuration when generated in the presence of hexafluorobenzene.[65,65a]

Freon E-4, a perfluorinated polyether, has been successfully used as solvent in reactions involving $:CHCO_2Et$ (Δ).[66] The major drawback may be the low solubility of substrates in this solvent, rendering it useful in mechanistic studies but not for larger scale, preparative reactions. Perfluorinated aliphatics do not appear to be suitable solvents for such reactions owing to their immiscibility with ethyl diazoacetate.[67,67a]

B. Methods Used to Determine the Spin State of the Reacting Carbene Species

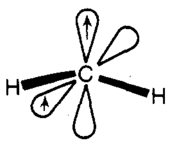
1. *Stereochemical Studies: Addition*

Methylene has long been known to exist in two different configurations[68c]: the bent, singlet ($^1A_1$) methylene (**8a**)[68a] and the more nearly linear, triplet ($^3B_1$) methy-



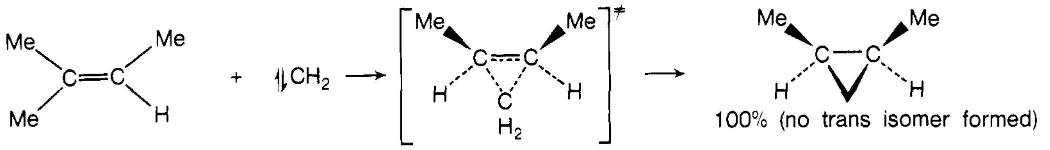
∠HCH≃102° (exptl value[68a])

8a



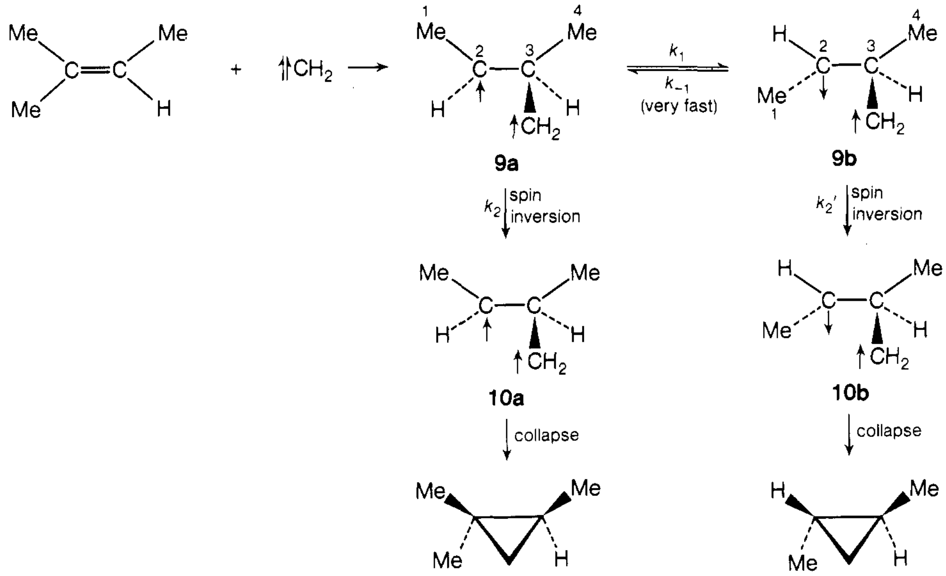
∠HCH≃136° (exptl value[68b])

8b



100% (no trans isomer formed)

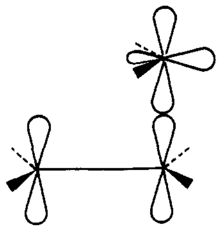
(9)



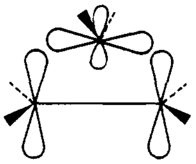
(10)

lene (**8b**).[68b] The classical chemical approach to demonstrating the spin state of the reacting methylene species in solution (or in the gas phase) is based upon the stereochemistry of its addition to olefins.[69-74] In essence, the argument presented by Skell and his coworkers is that singlet carbenes add stereospecifically (in concerted fashion), while triplet carbenes may add nonstereospecifically. The argument is illustrated in eq 9 and 10 for the addition of methylene to *cis*-2-butene. The extent of nonstereospecific addition of the triplet carbene will depend upon the relative rates of rotation about the C_2–C_3 bond in the diradicals **9a** and **9b** relative to spin inversion (to afford **10a** and **10b**, respectively, which subsequently undergo ring closure to *cis*- and *trans*-1,2-dimethylcyclopropane, respectively). A number of factors can influence this balance of rates, notably solvent cage effects[75] (which might tend to hinder free rotation about the C_2–C_3 bond in **9a** and **9b**, thus hindering k_1,k_{-1} relative to k_2,k_2') or unusually rapid (*i.e.*, heavy atom catalyzed) intersystem crossing (which again would increase k_2,k_2' relative to k_1,k_{-1}). The situation is further confounded in photolytic reactions of diazo compounds, where rapid singlet–triplet intersystem crossing may occur in the diazo precursor.[76-79] Any of these factors can alter the stereoselectivity of addition by triplet carbenes from 50% cis, 50% trans addition, the limiting values which might be attained in a completely nonstereospecific process.

In spite of these difficulties, Skell's criterion appears to work well in practice in distinguishing between singlet and triplet reacting carbene species, and over the years it has found extensive practical application as well as having withstood a barrage of criticism.[68,69,80,81] Theoretical justification has been forthcoming from Hoffmann,[82,83] whose extended Hückel theory (EHT) calculations account for the stereospecificity of singlet methylene additions and for the nonstereospecificity of triplet methylene additions to olefins through detailed examination of the energy profile for the addition of methylene to ethylene. Singlet methylene addition is found to be concerted, proceeding *via* an unsymmetrical reaction pathway (*e.g.*, **11a**), the most symmetrical approach (**11b**) being symmetry forbidden.[84] The resulting complex with ethylene correlates with the ground state of a cyclopropane. In contrast, triplet methylene addition proceeds through a complex of an excited configuration of methylene with ground-state ethylene; this complex correlates with a stereochemically mobile (excited triplet) trimethylene configuration. Interestingly, this argument is novel in that it is *not* based upon differences in spin state *per se.* Similar considerations have recently been applied to carbenoid addition processes.[85]



11a



11b

No corresponding calculations have been performed for carbalkoxycarbene additions from which predictions of their electronic structure might be made. However, formylmethylene (:CHCHO) has been subjected to EHT scrutiny.[86] The results may be of interest in the present context since both the CHO and CO_2R functional groups behave qualitatively as conjugative, electron-withdrawing substituents. Thus, formylmethylene is a "p^2" carbene, whose σ orbital is formally empty, rendering it a highly electrophilic species[83] for which EHT calculations predict a *linear singlet* ground state.[86] Selective stablization of the singlet ground state of :CHCHO is provided by interaction of one of the methylene p orbitals (and not the other) with low-lying unoccupied (π^*) levels of the CHO group.[87,88]

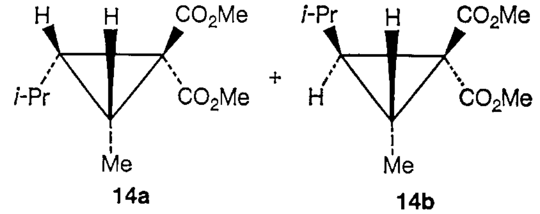
Let us now consider experimental evidence bearing on the question of the spin state of carbalkoxycarbenes produced by decomposition of diazoacetic esters. Here, it is emphasized that evidence is brought to bear on the spin state of the *reacting* species (which does not necessarily correspond to the ground state of the carbene). The first study of the stereochemistry of addition of carbomethoxycarbene to olefins was that of Doering and Mole;[89] the carbene produced photolytically from methyl diazoacetate was reported to add in a stereospecific cis fashion to *cis*- and *trans*-2-butene.[90] A recent study of the addition of :CHCO$_2$Me ($h\nu$) to *cis*- and *trans*-2-butenes has revealed that the carbene produced *via* direct photolysis of methyl diazoacetate adds in a highly stereoselective cis manner to the olefin substrates, whereas the corresponding benzophenone sensitized photolysis affords addition products in which substantial (but not complete) loss of stereospecificity has occurred.[23] Cis addition has also been demonstrated for the reactions of :CHCO$_2$Et (Δ) with *cis*- and *trans*-stilbenes.[37] D'yakonov and coworkers have likewise found essentially stereospecific cis addition in the reactions of carbethoxycarbenoid (generated *via* copper sulfate catalyzed decomposition of ethyl diazoacetate) with *cis*- and *trans*-stilbenes,[91] 4-octenes,[91,92] 5-decenes,[93] and 1,2-diphenylethylenes.[94] The mechanistic implications of the results obtained for carbethoxycarbenoid additions to olefins will be discussed later (section III.A).

It has been pointed out that *both* the singlet and triplet states of a given carbene must be observed in order to support a claim of determination of spin state of that carbene in a particular reaction.[68c] An attempt to provide the necessary comparison between singlet and triplet states of photolytically generated carbalkoxycarbenes has been made by Jones and his collaborators.[23,24,30] Direct photolysis of dimethyl diazomalonate has been shown by these investigators to afford a reactive intermediate whose chemical properties differ markedly from those of the corresponding species produced *via* benzophenone sensitized photodecomposition of the same diazo ester. It is thought that the reacting species produced in the direct and sensitized photodecompositions of dimethyl diazomalonate are singlet and triplet biscarbomethoxycarbene, respectively.[23,24,30] An alternative possibility remains, *i.e.*, that the excited diazo compound (singlet and triplet, respectively) is itself the reacting species in solution (see section II.A). Although arguments have been presented which favor the former interpretation,[24] the actual identity of the reacting species in diazo ester photodecompositions must still be regarded as an open question. The ambiguity inherent in this situation must necessarily restrict attempts at mechanistic rationalization.

The results of the photolytic reactions of dimethyl diazomalonate with *cis*- and *trans*-4-methyl-2-pentene[24] are shown in Table I. Control experiments have established that the products **14a** and **14b** formed in the reactions shown in Table I were stable to the reaction conditions. Although Jones suggests that the reacting carbene produced *via* direct photolysis of dimethyl diazomalonate has a singlet electronic configuration, he does not explain why the addition is only 90–92% stereoselective cis (rather than 100% stereospecific). It is altogether possible that the direct photolytic decomposition of dimethyl diazomalonate in solution is not a "multiplicity specific"[95-103] reaction (*i.e.*, the carbene is not formed exclusively in one spin state or the other, but instead it is formed predominantly in one state and to a lesser extent in the other). In this vein, it is interesting to note that in a recent study of the benzophenone sensitized photolysis of dimethyl diazomalonate in the presence of *cis*-4-methyl-2-pentene, the ratio of products (cis/trans dimethyl 2-isopropyl-3-methylcyclopropane-1-dicarboxylate) was influenced by the presence of dimethyl sulfide, the ratio being greater when the sulfide was present than was observed in the absence of added dimethyl sulfide.[104] (No such effect was found in this reaction when Freon 113 was used as an added diluent instead of dimethyl sulfide.[104]) Additional experiments led Jones to conclude that the singlet :C(CO$_2$Me)$_2$ ($h\nu$) is an electrophilic species which is highly sensitive to steric factors in the olefin substrate,[24,30] whereas the behavior of the triplet carbene conformed with expectations intuitively predicted on the basis of "radical-like" character.[24]

TABLE I. Product Distributions in the Reactions of Dimethyl Diazomalonate with *cis*- (13a) and *trans*-4-Methyl-2-pentene[24] (13b)

$$\underset{\mathbf{12}}{\mathrm{N_2C(CO_2Me)}} + \underset{\substack{\mathbf{13a},\ \text{cis isomer}\\ \mathbf{13b},\ \text{trans isomer}}}{\mathrm{Me_2CHCH{=}CHMe}} \xrightarrow[-\mathrm{N_2}]{h\nu}$$

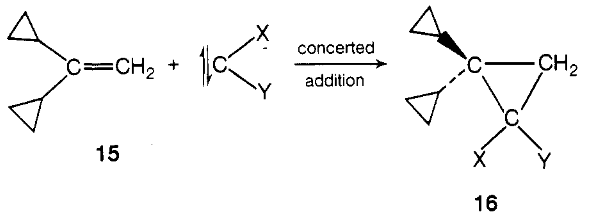


14a **14b**

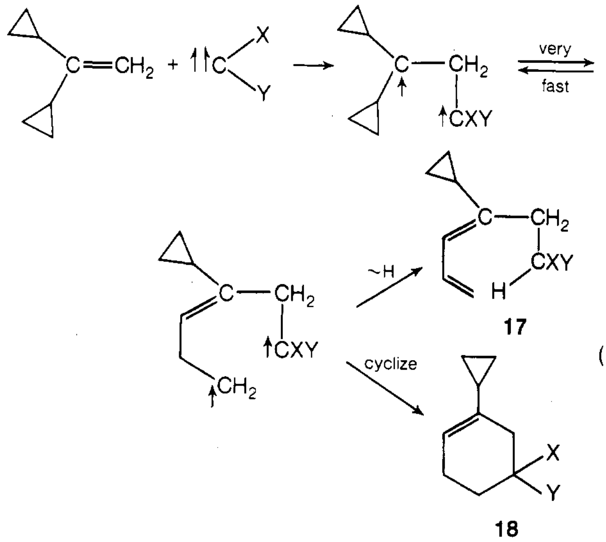
Conditions	Product ratios 14a	Product ratios 14b	Total yield of products, %
12 + **13a**	92	8	39.8
12 + **13b**	10	90	24.3
12 + **13a** + Ph$_2$C=O	10	90	43.0
12 + **13b** + Ph$_2$C=O	14	86	...

A corresponding study of direct *vs.* benzophenone sensitized photolysis of ethyl diazoacetate has been performed.[105] Direct photolysis afforded ethoxyketene *via* Wolff rearrangement (section VI.B), whereas benzophenone sensitized photolysis of ethyl diazoacetate afforded a (presumably triplet) carbene which added in a nonstereospecific manner to olefins and abstracted hydrogen to form ethyl acetate. Thermolysis of ethyl diazoacetate at 140° produced what is probably the lowest lying singlet :CHCO$_2$Et which added stereospecifically to olefins but did not afford ethoxyketene.[105]

Before leaving the subject of the use of stereochemical criteria in carbene addition reactions to determine the spin state of the reacting carbene, it is worthwhile to examine an alternative criterion proposed recently by Shimizu and Nishida.[106] These investigators have suggested utilizing 1,1-dicyclopropylethylene (**15**) as substrate for this purpose. Here, addition of a reacting singlet carbene (:CXY) can proceed in the usual concerted manner to afford **16**, whereas the existence of a reacting triplet carbene is revealed by the observation of rearranged products (*i.e.*, **17** or **18**) as shown in eq 11 and eq 12. The usefulness of this method has been demonstrated for the reactions of singlet and triplet fluorenylidene with **15**.[106] More recently, the reaction of **15** with ethyl diazoacetate in the presence of copper sulfate has been reported.[107] In this reaction, only the addition product (**16**, X = H, Y = CO$_2$Et) was observed; no trace of rearranged products corresponding to **17** or **18** was reported.[107] In this reaction, only the addition product (**16**, X = H, Y = CO$_2$Et)



(11)



(12)

was observed; no trace of rearranged products corresponding to **17** or **18** was reported.[107]

The corresponding reactions with :$CHCO_2R$ ($h\nu$) and :$CHCO_2R$ (Δ) have not yet been investigated at the time of writing of this review. However, it should be mentioned that Hendrick[25] has observed furan formation in the reactions of triplet biscarbomethoxycarbene (generated *via* benzophenone sensitized photolysis of methyl diazomalonate) with alkynes. Furan formation most likely arises *via* cyclization of an intermediate diradical, a situation analogous to Shimizu's observations[106] for reactions of triplet carbenes with 1,1-dicyclopropylethylene.

2. *Stereochemical Studies: Insertion*

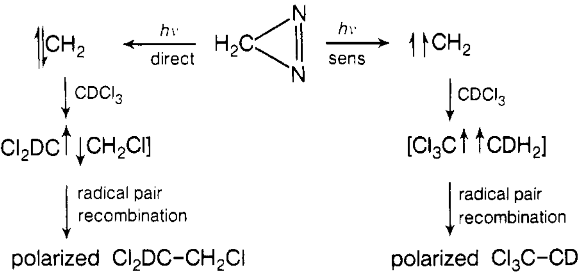
An additional criterion which has occasionally been utilized to assign spin state in a reacting carbene is carbon-hydrogen bond insertion, alleged to be observable for singlet carbenes but not for the corresponding triplet species.[108-110] This "insertion" (in reality, most likely a two-step process involving abstraction of hydrogen by the *triplet* carbene to form a radical pair which rapidly recombines) has, however, been observed for reactions of triplet :$CHCO_2R$ and :$C(CO_2R)_2$[23] and for reactions of other triplet carbenes with hydrocarbons.[111] Therefore, the observation of carbon-hydrogen "insertion" products in carbene reactions does *not* constitute good evidence that the carbene in question is reacting in a singlet electronic configuration.

On the positive side, there is growing evidence that singlet and triplet carbalkoxycarbenes afford qualitatively different results in carbon-hydrogen insertion reactions with the same alkane as substrate. Some discussion of this subject appears in section IV.B (see also the discussion of reactions of singlet *vs.* triplet carbalkoxycarbenes with carbon-*halogen* bonds in section IV.C).

3. *Chemically Induced Dynamic Nuclear Polarization (CIDNP) Studies*

The CIDNP phenomenon is relatively new,[112,113] having independently been discovered by Bargon, Fischer, and Johnson,[114-116] and by Ward and Lawler.[117-119] In the CIDNP method, the existence of a radical intermediate in a reaction is implicated through nuclear magnetic resonance (nmr) investigation of the product of that reaction as it is being formed. Polarization of the product by radical precursors may be observed experimentally as enhanced absorption or as emission (negative peaks) in the nmr spectrum of the product.[113] The observed signal directions are determined by the initial electron spin multiplicity of the radical pair; evidence bearing on the electron spin multiplicity of the radical pair and, consequently, of its precursor, is thereby obtained.[96] Theoretical explanation for this phenomenon has been forwarded by Closs and coworkers[95,97,120] and by Kaptein and Oosterhoff[99,100] (*i.e.*, the "radical-pair" model). A set of simple selection rules based on the radical-pair model has been developed to permit qualitative prediction of the effects of CIDNP on the nmr spectrum of products of radical reactions.[121]

In view of the diradical nature of triplet carbenes, the potential (radical) abstracting ability of singlet carbenes, and the experimental difficulties attendant with direct observation of these highly reactive intermediates, the application of CIDNP techniques to the determination of the spin states of reacting carbenes would seem to be both inevitable and desirable. Indeed, CIDNP phenomena have recently been observed for a number of carbene reactions, although the application of this technique to the study of carbene processes is still in its nascent state.[112] Methylene has been the subject of extensive CIDNP investigation in its reactions with alkyl halides and polyhalomethanes[122-126] and with alkylated aromatic compounds.[127] Singlet methylene reacts with carbon tetrachloride to afford products derived from carbon-chlorine bond "insertion" and chlorine atom abstraction.[122] Singlet methylene produced *via* direct photolysis of diazirine abstracts chlorine from $CDCl_3$ to form a (singlet) radical pair which combines in-cage to give polarized $Cl_2DC\text{-}CH_2Cl$.[123] Similar reaction of triplet methylene produced *via* sensitized photodecomposition of diazirine forms a (triplet) radical pair by *deuterium* atom abstraction from $CDCl_3$; recombination of the resulting radical pair then affords polarized $Cl_3C\text{-}CDH_2$[123,128] (eq 13).



(13)

Photolytic decomposition of methyl diazoacetate in the presence of carbon tetrachloride and deuteriochloroform affords methyl 2,3,3,3-tetrachloropropionate and methyl 3-deuterio-2,3,3-trichloropropionate, respectively.[129] The slow decay of the observed emission signals due to these (polarized) products (relaxation time = *ca.* 70 sec) suggested that the products of the reaction were still being formed after irradiation ceased. Primarily on the basis of this observation, a free radical *chain* mechanism was forwarded for the reactions of :$CHCO_2Me$ ($h\nu$) with carbon tetrachloride and deuteriochloroform.[129] However, this conclusion has recently been reconsidered in the light of the radical-pair theory of CIDNP which does *not* allow spin polarization in a radical induced decomposition step (*i.e.*, $\cdot CCl_3 + N_2CHCO_2Me \rightarrow Cl_3C\text{-}\dot{C}H\text{-}CO_2Me$) or in a chain transfer step (*i.e.*, $Cl_3C\text{-}\dot{C}H\text{-}CO_2Me + CCl_4 \rightarrow Cl_3C\text{-}CHCl\text{-}CO_2Me + \cdot CCl_3$).[130] Thus, the original conclusion[129] that free radical chain processes are operative in these reactions is probably not warranted. The observed CIDNP effects are instead consistent with expectations based on the alternative abstraction–recombination process.[130] This conclusion may have important bearing on other carbon–halogen "insertion" reactions of carbalkoxycarbenes which have previously been postulated to proceed *via* radical chain processes; discussion of some of these reactions appears in section IV.C.

CIDNP studies of reactions of $:CHCO_2Me$ ($h\nu$) with polyhalomethanes have provided evidence to support the following important conclusions: (1) the carbene generated *via* direct photolysis of methyl diazoacetate reacts in a *singlet* electronic configuration with polyhalomethanes,[125,131] (2) an abstraction–recombination mechanism for "insertion" of this carbene into carbon–halogen bonds in polyhalomethanes is important and (3) in addition to in-cage radical recombination, an alternative mechanism exists whereby the radicals "escape" from the solvent cage prior to recombination. Under "escape" circumstances, encounter between (free) $\cdot CHClCO_2Me$ and (free) $\cdot CCl_3$ (produced from the reaction of $:CHCO_2Me$ ($h\nu$) with carbon tetrachloride) induces the same type of polarization as would have been obtained had those radicals been generated by reaction of *triplet* $:CHCO_2Me$ with CCl_4.[130]

In this way, the usefulness of the CIDNP technique in exploring carbene reactions and in establishing the spin state of the reacting carbene species has been demonstrated. It is anticipated that this powerful technique will continue to be exploited in future years.

III. The Addition Reaction

An excellent review of addition reactions of carbalkoxycarbenes with alkenes, alkynes, heterocyclics, and benzenoid hydrocarbons covering the literature to mid-1970 has appeared.[17] Also, a review of the stereoselectivity of carbene additions to olefins has been recently published (1969).[16] In section III, some of the conclusions reached in these reviews will be critically summarized, and more recent work which has appeared since the time of publication of these reviews will be discussed.

A. Additions to Carbon–Carbon Double and Triple Bonds

1. Additions to Alkenes and Alkynes: Stereochemistry, Stereoselectivity, and Mechanism

This subject has been recently reviewed;[16,17] the following points serve to summarize what appear to be the general points of agreement among investigators who have studied addition reactions of carbalkoxycarbenes to unsaturated systems.

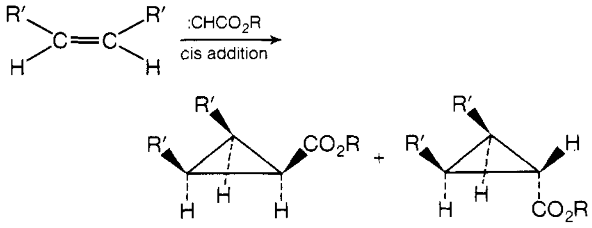
(1) Reactions of diazo esters with olefins (or alkynes) to form cyclopropane (or cyclopropene) carboxylates can occur in any of three ways: (a) with loss of nitrogen from the diazo ester to form the free carbene which reacts directly with the unsaturated substrate; (b) *via* 1,3-dipolar cycloaddition of the diazo ester to the alkene (or alkyne) to form pyrazolines (or pyrazolenines) which subsequently lose nitrogen and close to the product cyclopropane (or cyclopropene); (c) *via* nucleophilic (or radical) attack of the diazo ester on the substrate followed by loss of nitrogen and ring closure.[17] Diazo esters react with alkynes to produce cycloprop-1-ene-3-carboxylates which, in the presence of copper sulfate, can react with a second mole of diazo ester to afford bicyclobutane derivatives.[132]

(2) Carbalkoxycarbenes and carbenoids behave as electrophilic species. However, the carbenoid is a less reactive species than either $:CHCO_2R$ ($h\nu$) or $:CHCO_2R$ (Δ). There is evidence to suggest that the transition state for addition of carbalkoxycarbenoids to olefins involves the carbene, the metal catalyst, and the substrate,[26,27] although this interpretation has recently been questioned (*vide infra*).

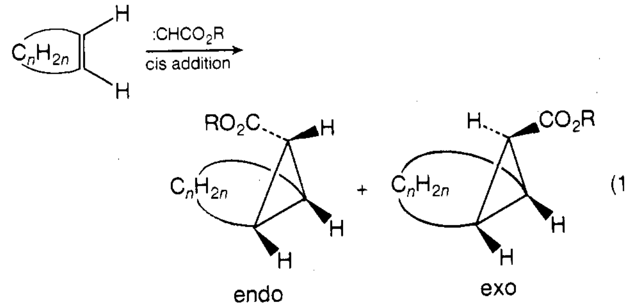
(3) The reaction of carbalkoxycarbenes produced via *direct* photolysis of the corresponding diazo ester[23,89,90] or of carbalkoxycarbenoids[26,27] with olefins to form cyclopropanes is a stereospecific (or, at the very least, a highly stereoselective) process. This has led a number of investigators to postulate that this results from concerted reaction of a singlet carbene with the olefinic substrate, a conclusion which, although generally accepted, has not survived without criticism.[66]

(4) Regardless of the conditions under which they are produced, carbalkoxycarbenes (or carbenoids) show little discrimination between various substituted olefins.[133,134] Conflicting results have been reported regarding the ability of carbalkoxycarbenes (or carbenoids) to discriminate in their reactions with carbon–carbon double *vs.* triple bonds in alkenynes or with mixtures of alkenes and alkynes.[136] Recent results suggest that carbethoxycarbenoid adds to the double and triple bonds of 2-hexen-4-yne to give the corresponding cyclopropanecarboxylates and cyclopropenecarboxylates in the ratio 1:1.6.[137] Previous reports indicated that catalytic reactions of ethyl diazoacetate with alkenynes occurred preferentially with the *double* bond.[138-140] Recent studies indicate that carbethoxycarbene shows discrimination in its reaction with chloroprene, the preferred position of attack being the more highly substituted double bond; with *cis*-1-chlorobuta-1,3-diene, attack at the terminal, unsubstituted double bond was preferred.[141] With *cis*- and *trans*-1,3-pentadiene (**19a** and **19b**, respectively), ethyl diazoacetate affords all possible isomers of ethoxycarbonylvinylcyclopropane in the thermal (100°), uncatalyzed reaction and in the copper sulfate catalyzed thermal (40°) reaction.[39] The relative reactivity of the double bonds in **19a** and **19b** was found to be cis-1,2 > trans-1,2 > trans-3,4 > cis-3,4.[39] In view of the foregoing, the best that can be said at present is that carbalkoxycarbene and carbenoid additions to olefins and alkynes are subject to both steric and electronic influences in the substrate, the outcome of the addition reactions being determined by a subtle blend of both effects (*vide infra*).

(5) With cis additions of carbalkoxycarbenes to substituted olefins, the question of stereoselectivity arises in the formation of cis- *vs.* trans-substituted cyclopropanecarboxylates (eq 14). With cyclic olefins, exo and endo products are possible (eq 15). In general, trans products predominate in the former and exo products in the latter case, the preference in each case being more pronounced for the catalytic reaction (involving carbalkoxycarbenoid) than for the photochemical reaction with diazoacetic esters.[16,26,27] This demonstrates the importance of (unfavorable) nonbonded interactions in the transition state between the substrate and the carbene (or carbenoid) in



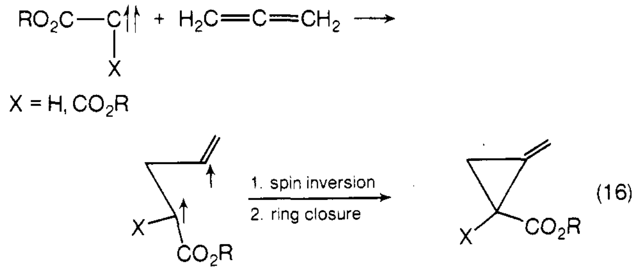
(14)



(15)

determining the cis/trans or exo/endo stereoselectivity of the addition reaction.

(6) The photolytic reactions of methyl diazoacetate and of dimethyl diazomalonate with allene has recently been investigated.[23] In both cases, sensitized and direct (unsensitized) photolyses afforded methylenecyclopropanes *via* simple addition of the carbene to one of the two allenic double bonds. The sensitized additions in both cases were found to proceed more rapidly than the corresponding unsensitized reactions. There was no evidence for the intermediacy of a trimethylenemethane intermediate in the benzophenone sensitized reactions. The favored mechanism for the reaction of carbalkoxycarbenes with allene is shown in eq 16.[23]



$X = H, CO_2R$

(16)

The question of the nature of the reacting species in the "copper-catalyzed" additions of carbalkoxycarbenoids to olefins has been the subject of much debate.[16,17] A precise knowledge of the structure of the catalyst-carbene "complex" is vital to understanding the detailed mechanism of these reactions. Perhaps a more basic question to ponder regards the identity of the active catalytic species itself! The answer to this latter question has been successfully pursued recently for copper catalyzed reactions of dimethyl and di-*tert*-butyl diazomalonates with olefins;[142,143] the results of these investigations have important bearing on the corresponding monocarbalkoxycarbenoid reactions. It has been found that soluble catalysts afford nearly doubled yields of cyclopropane-containing products as are obtained when heterogeneous catalysts are employed in reactions of diazomalonates with cyclic olefins.[144,145] Furthermore, the presence of peroxides has been found to convert soluble (trimethyl phosphite) copper(I) halides into a new catalyst which is superior in catalytic activity to the original material.[144,145] Rather than acting in such reactions as an initiator of a free radical chain reaction, the peroxide instead appears to be serving simply as an oxidizing agent, producing undefined Cu(II) salts in solution. It is these Cu(II) salts which are now believed to be the actual catalytic species, and not Cu(I) or Cu(0) as was previously supposed.[146-148] Indeed, copper(II) fluoroborate has proved to be the best catalyst thus far examined for promoting diazomalonate ester decompositions.[147]

In another study, the (trialkyl phosphite)copper(I) halide catalysts system employed by Moser[26,27] has been recently reexamined.[135] Two important effects were observed for the reaction of dimethyl diazomalonate with 1-methylcyclohexene in the presence of this catalyst system: (1) the addition of common (halide) anions depressed the yields of all identifiable products, and (2) dramatic changes in the distribution of products occurred with change in the nature of the counterion, Z^-, in catalyst systems $(MeO)_3P\text{-}CuZ$.[135] The first result was taken as evidence that displacement of the counterion in the catalyst by the diazo compound occurs in either the rate-determining step of the reaction or in a preequilibrium step. The second result was considered to have provided evidence that the nature of the leaving group, Z, influences the effective spin multiplicity of the carbenoid, *i.e.*, that there exists a competition between apparent singlet and triplet processes, the outcome of which is determined, at least in part, by the nature of the counterion in the catalyst. This interpretation, however, is suspect as the recognition of the intervention of "triplet" processes was based solely on the observation of allylic carbon-hydrogen insertion by the carbene (in contrast to Moser.[26,27] who reported no carbon-hydrogen insertion in (trialkyl phosphite)copper(I) halide catalyzed reactions of diazoacetic esters with olefins). The possibility that this apparent "insertion" process might in reality result from a radical chain process was apparently not considered.[135]

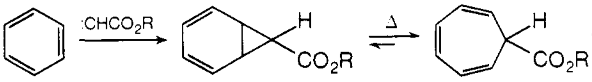
Perhaps the most interesting feature of this recent work was the authors' contention that "none of these results requires invoking a complex involving olefin, catalyst, and diazo compound or carbene as suggested by Moser."[135] These authors instead prefer a model in which the initial (and rate-controlling) interaction involves only the diazo ester and the soluble catalyst, with displacement of the counterion associated with the catalyst. The electrophilic attack on the olefin by the carbenoid is viewed as occurring *subsequent to* the rate-determining step. The role of the olefin in stabilizing the transition state (which occurs prior to its suffering attack by the carbene) is seen essentially as a solvation effect.[135]

In summary, it can be safely stated that the naive models for the transition states of addition reactions of carbalkoxycarbenes (or carbenoids) to olefins which organic chemists have found convenient to employ over the years are indeed grossly insufficient representations. The enormous complexity of these processes (and especially those involving transition metal catalysts) has only recently come to be fully appreciated.[149] The need for a higher level of theoretical aproach and for systematic experimental investigation is apparent.

2. *Additions to Benzenoid Aromatic Systems*

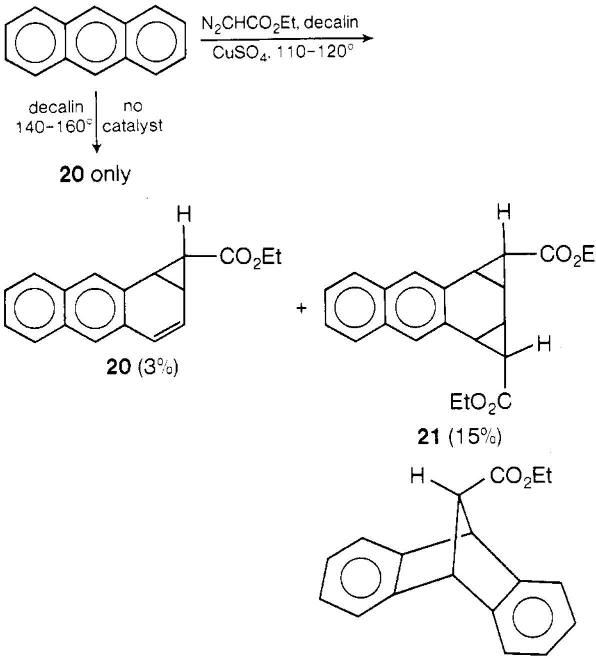
This subject has recently been reviewed as an adjunct to the more general subject of additions of carbenes to unsaturated systems.[150,151] Some general observations which emerge from these reviews are as follows.

(1) The addition of monocarbalkoxycarbenes to benzene and benzene derivatives produces noncaradienes which rapidly undergo valence tautomerism to the corresponding tropilidene[152] (eq 17). With substituted benzenes, this reaction affords mixtures of substituted cycloheptatrienecarboxylates which often give rearranged products under the conditions of their formation. In such cases, the isomer ratios observed will not correspond to the kinetically controlled ratios.[153]



(17)

(2) Additions of monocarbalkoxycarbenes or carbenoids to polynuclear aromatics such as naphthalene,[154] anthracene,[155-158] and phenanthrene[158] afford stable cyclopropanecarboxylates. The copper sulfate catalyzed reaction of ethyl diazoacetate with anthracene is especially interesting, as a monoadduct (**20**) and a diadduct (**21**) are formed along with a third product (**22**) which is formed *via* an unusual 1,4-addition of the carbenoid to the 9,10 positions of anthracene,[155-157,159] as shown in eq 18. However, it is unlikely that **22** is a primary product of this reaction.

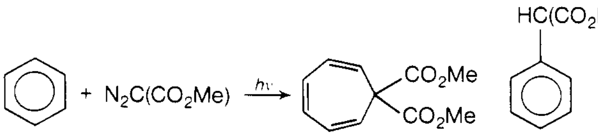


20 (3%) **21** (15%) **22** (2%)

(18)

(3) Very few mechanistic studies have been performed in connection with monocarbalkoxycarbene addition reactions with benzenoid hydrocarbons. The reaction of $:CHCO_2Et$ (Δ) with monosubstituted benzenes is a rare example of such a study. A linear free energy correlation of the relative rates of consumption of the aromatic substrates with Hammett σ_p values for the substituents in the monosubstituted benzene substrates revealed the existence of a linear relationship between these quantities with $\rho = -0.38$, indicative of the electrophilic character and highly indiscriminate nature of the thermally generated carbene.[66] Addition reactions of carbalkoxycarbenes with benzenoid aromatics have proved to be useful synthetic methods for the preparation of azulenes and tropolones.[150,151]

(4) Despite a report to the contrary,[160] biscarbomethoxycarbene has recently been found to be capable of reacting with benzene.[23] This occurs in the manner shown in eq 19.[23] The sensitized photolysis probably proceeds *via* a diradical which can either close to afford the norcaradiene (which then valence tautomerizes to the tropylidene), or it can suffer hydrogen shift to give the phenylmalonate.[23]

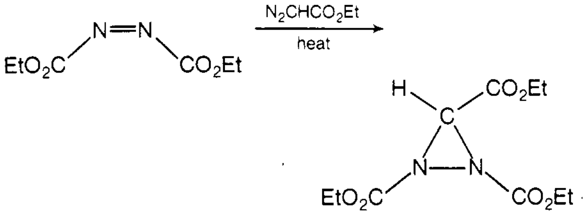


(19)

product ratio, direct photolysis: 2.7 : 1
product ratio,
Ph$_2$C=O sensitized photolysis: 1.6 : 1

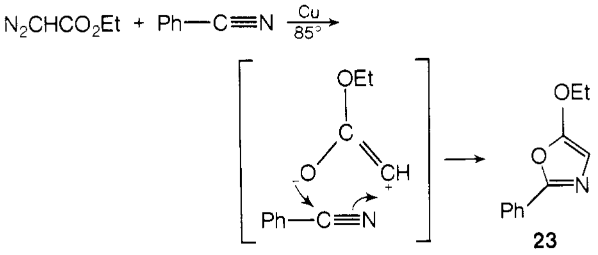
3. *Additions to Other π Systems*

Besides undergoing addition reactions with unsaturated hydrocarbon systems, carbalkoxycarbenes undergo a number of interesting and often synthetically useful addition reactions with systems containing unsaturated linkages of the type $-X{=}Y-$ or $-X{\equiv}Y$, where one or both of the atoms X, Y may be heteroatoms. One of the earliest examples of reactions of this type is the thermal reaction of ethyl diazoacetate with diethyl azodicarboxylate[161] (eq 20).



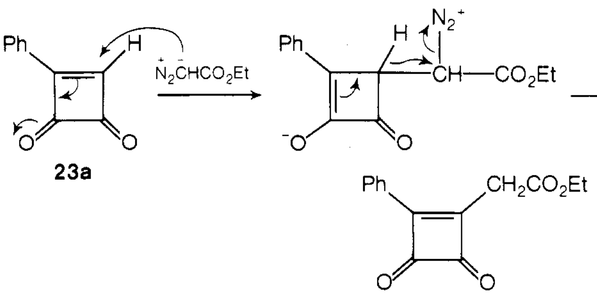
(20)

The addition of carbethoxycarbene to acrylonitrile proceeds in the usual fashion to afford *cis*- (49%) and *trans*- (40%) 1-cyano-2-ethoxycarbonylcyclopropane.[162] However, the corresponding reaction with benzonitrile has been reported to produce an oxazole (**23**) *via* 1,3-dipolar cycloaddition of carbethoxycarbene to the CN group[163] (eq 21). Addition of carbalkoxycarbenes to the $-C{=}N-$ linkage in imines affords the corresponding aziridine.[164,165]



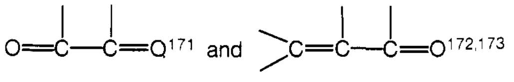
(21)

Diazoacetic esters undergo a number of interesting reactions with ketones and thioketones; these have been reviewed recently.[166,167] Most of these reactions involve copper (or copper sulfate) catalysis, and it is interesting to note that oxiranes or thiiranes (which might be obtained by simple addition of carbalkoxycarbenoid to the C-O or C-S double bond, respectively) are *not* observed. Ethyl diazoacetate reacts with simple ketones to afford enol ethers.[168,169] An addition–elimination mechanism has recently been proposed for the reaction of ethyl diazoacetate with 1-phenyl-1-cyclobutene-3,4-dione, (**23a**, an α,β-unsaturated ketone) as indicated in eq 22.[170] Note, however, that it is the undissociated diazoester and *not* the carbene which is considered to be the attacking (in this case, nucleophilic) reagent. Unusual examples of



(22)

1,4-addition of carbalkoxycarbenes to systems containing the linkages

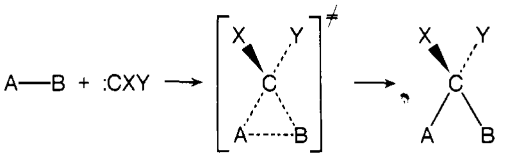


have been reported.

IV. The Insertion Reaction

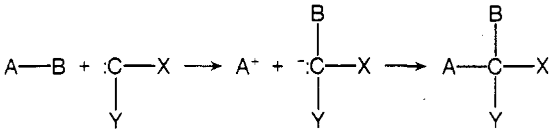
A. General Mechanistic Considerations

In the most general sense a carbene insertion reaction is one in which the carbene :CXY attacks a bond A-B, cleaving the A-B σ bond and forming new σ bonds between the carbene and each of the functionalities A and B (eq 23). The term "insertion" is reserved for those

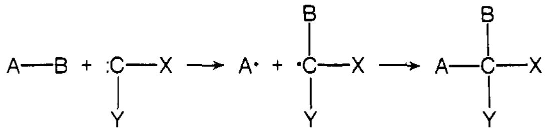


(23)

reactions where cleavage of the A-B bond and formation of the A-C and B-C bonds occur in concert. The alternative stepwise process, abstraction followed by recombination, may afford "insertion-type" products *via* a dipolar or diradical process (eq 24 and eq 25, respectively).

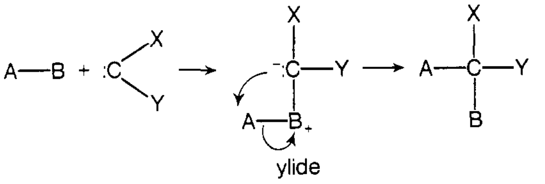


$$\text{A—B} + :\underset{\text{Y}}{\text{C}}\text{—X} \longrightarrow \text{A}^{+} + {}^{-}\!:\overset{\text{B}}{\underset{\text{Y}}{\text{C}}}\text{—X} \longrightarrow \text{A—}\overset{\text{B}}{\underset{\text{Y}}{\text{C}}}\text{—X} \quad (24)$$



$$\text{A—B} + :\underset{\text{Y}}{\text{C}}\text{—X} \longrightarrow \text{A}\cdot + \cdot\overset{\text{B}}{\underset{\text{Y}}{\text{C}}}\text{—X} \longrightarrow \text{A—}\overset{\text{B}}{\underset{\text{Y}}{\text{C}}}\text{—X} \quad (25)$$

When B is a heteroatom containing one or more unshared pairs of electrons, a third mechanistic possibility may be operative involving intermediate ylide formation as shown in eq 26. This process bears a formal resemblance to the familiar Stevens rearrangement, and it might analogously be expected to proceed with retention of configuration at atom A (see sections IV.C and IV.D).



(26)

As envisioned above, insertion of a *singlet* carbene into A*-B (where the asterisk denotes that atom A is asymmetric) *via* a three-center transition state should result in a product, A*CXYB, in which the configuration of the asymmetric atom is *retained.* A triplet carbene may "insert" *via* abstraction-recombination, the stepwise process affording the opportunity for the intermediate (ion or radical) A* to racemize. The situation is confounded, however, by a third possibility: singlet carbenes have been demonstrated in some instances to be capable of giving "insertion" products *via* a radical abstraction-recombination mechanism. However, this process is probably restricted to reactions which involve initial attack of the carbalkoxycarbene on heteroatomic substrates; it should not be important in carbon-hydrogen insertion reactions (see section IV.C.3).

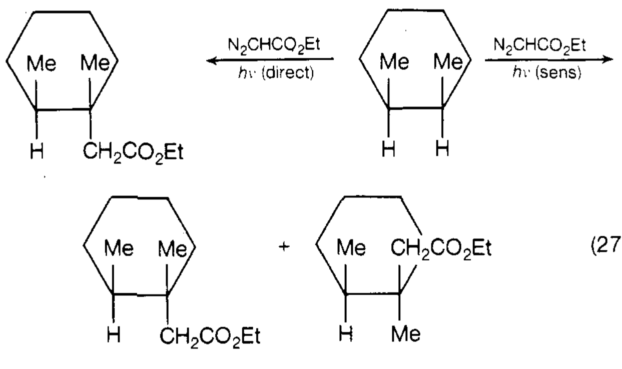
Relatively little is known concerning the detailed mechanism of carbalkoxycarbene insertion reactions. These are not pleasant reactions to work with; although more selective in their insertion reactions with, *e.g.*, alkanes than is methylene, carbalkoxycarbene insertion reactions nevertheless afford gross mixtures of isomeric esters whose separation is generally tedious. These insertion reactions of carbalkoxycarbenes are therefore seldom attractive from a synthetic viewpoint. These same features which detract from their synthetic utility also render mechanistic studies difficult. Nevertheless, efforts in this direction have met with some success. A general accounting of what is known about these reactions is presented in the following sections.

B. Insertion into Carbon-Hydrogen Bonds: Stereochemistry and Selectivity

The general subject of carbene insertions into carbon-hydrogen bonds has been recently reviewed.[111] The following points summarize some significant observations which have been reported regarding the stereochemistry and mechanism of carbon-hydrogen bond insertion by carbalkoxycarbenes.

(1) A critical experiment establishing the stereochemistry of carbon-hydrogen bond insertion by :CHCO$_2$Me ($h\nu$) has been performed utilizing methyl (−)-(*S*)-2-methoxypropionate as substrate.[174] The product of carbon-hydrogen insertion, dimethyl (+)-(*R*)-2-methoxy-2-methylsuccinate (isolated in low yield), was formed with 99 ± 4% *retention* of configuration at the asymmetric carbon atom in the substrate. No corresponding study has been performed with :CHCO$_2$R (Δ). Carbalkoxycarbenoids produced by copper-catalyzed decompositions of diazoacetic esters with rare exceptions[135,175-177] do not insert into carbon-hydrogen bonds. Reactions of these species in solution with alkanes afford carbene dimers (maleate and fumarate esters),[26,27,178,179] trimers,[180] and tetramers.[181,182]

(2) The photolytic reaction of ethyl diazoacetate with *cis*-1,2-dimethylcyclohexane has been studied; insertion into a tertiary carbon-hydrogen bond occurs with complete retention of the cis stereochemistry.[65] Interestingly, the corresponding photosensitized process was observed to be nonstereospecific[65] (eq 27). Similarly, direct photolysis of dimethyl diazomalonate in the presence of 2,3-dimethylbutane gave qualitatively different results than were obtained for the corresponding benzophenone sensitized reaction,[23,24] as indicated in eq 28 and 29. The utility of such observations as a diagnostic tool for assigning spin state of the reacting carbalkoxycarbene remains yet to be fully exploited, although the above results are strongly suggestive in this regard.



(27)

In these *photolytic decompositions of diazomalonic* ester, it has been generally observed that the sensitized decomposition affords a slightly more selective interme-

$$N_2C(CO_2Me)_2 + Me_2CHCHMe_2 \xrightarrow[\text{46\% yield of C–H insertion products}]{h\nu\text{ (direct)}} \qquad (28)$$

$$\underset{\substack{\textbf{24}\\ \text{insertion ratio}\\ 3°/1° = 13}}{C_6H_{13}CH(CO_2Me)_2} + \underset{\substack{\textbf{25}\\ \text{(trace)}}}{H_2C(CO_2Me)_2} + \underset{\substack{\textbf{26}\\ \text{(trace)}}}{(MeO_2C)_2CHCH(CO_2Me)_2}$$

$$N_2C(CO_2Me)_2 + Me_2CHCHMe_2 \xrightarrow[\text{13\% yield of C–H insertion products}]{h\nu\text{(sens)}}$$

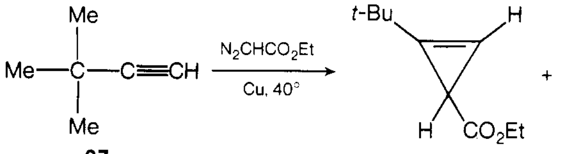
$$\underset{\substack{\text{insertion}\\ \text{ratio}\\ 3°/1° = 20}}{\textbf{24}} + \underset{(23\%)}{\textbf{25}} + \underset{(38\%)}{\textbf{26}} \qquad (29)$$

diate than is obtained *via* direct photolysis. Yields of "insertion" products are much lower in the sensitized decompositions. Jones[23] has suggested that this results from a change in mechanism in going from direct to sensitized photolytic decompositions of diazo esters. The former condition affords a singlet carbene capable of direct insertion into carbon-hydrogen bonds whereas the latter affords a triplet carbene which affords "insertion" products *via* radical abstraction-recombination.[23]

(3) Studies of relative rates of carbalkoxycarbene insertions into carbon-hydrogen bonds of alkanes have generally revealed an order of preference tertiary > secondary > primary. Furthermore, $:CHCO_2R$ ($h\nu$) shows greater selectivity toward insertion into carbon-hydrogen bonds than does methylene, $:CH_2$ ($h\nu$), while $:C(CO_2R)_2$ ($h\nu$) shows even greater selectivity in this regard than does the corresponding monocarbalkoxycarbene.[24,183-186] This has led a number of investigators to postulate a transition state for carbon-hydrogen insertion by carbalkoxycarbenes which involves the creation of partial positive charge on the carbon atom of the carbon-hydrogen bond which suffers attack. Further evidence to support this postulate is found in the demonstrated reluctance of the bridgehead carbon-hydrogen bonds in norbornane[187] and nortricyclene[188] to undergo insertion by carbalkoxycarbenes (despite the fact that these are formally tertiary positions). This should not, however, be regarded alone as firm evidence for a *dipolar* transition state; the reluctance of these same substrates toward undergoing *radical* attack (resulting in substitution of C-H by C-X) at their bridgehead positions is well known.[189] Nevertheless, taken together with the other stereochemical and selectivity evidence mentioned above, the observations of unusually low reactivity of bridgehead carbon-hydrogen bonds toward carbalkoxycarbenes are clearly consistent with a one-step (concerted) mechanism (and should not be regarded as indicative of the two-step mechanism) for singlet carbon-hydrogen bond insertion by carbalkoxycarbenes.

(5) Insertion of carbalkoxycarbenes into carbon-hydrogen bonds of alkenes, arenes, and (rarely) alkynes is known, but this reaction pathway competes poorly with addition of the carbene to unsaturated bonds in these systems.[111] The rate ratio for carbomethoxycarbene insertion into vinylic carbon-hydrogen bonds *vs.* addition to an alkene double bond is roughly 0.045;[89] the corresponding ratio for biscarbomethoxycarbene is roughly 0.03.[24] One exception to this generalization occurs for the reaction of carbethoxycarbene with ketene diethyl acetal, which affords *only* carbon-hydrogen insertion products (methylene reacts with this substrate to afford products of both carbon-hydrogen insertion and carbon-carbon double bond addition).[190]

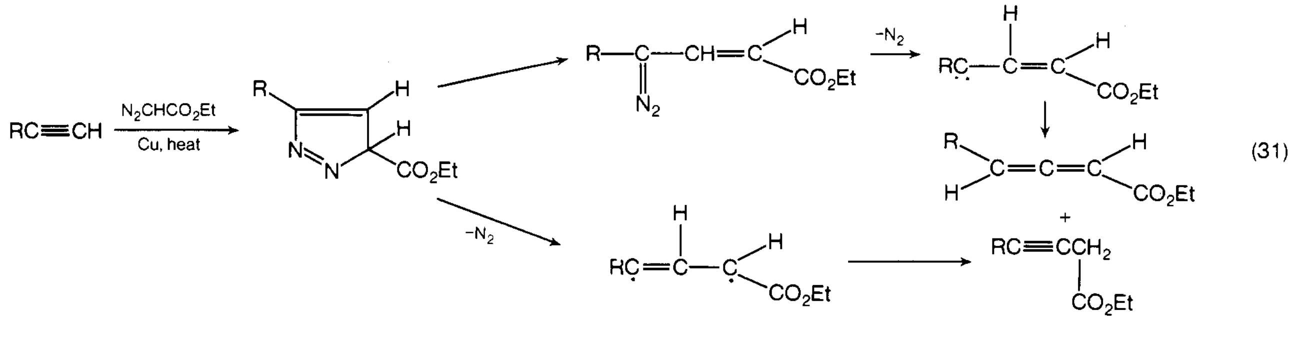
Carbethoxycarbene generated photolytically from ethyl diazoacetate has been found to add to the triple bond of 4-octyne about 21 times faster than it inserts into a single carbon-hydrogen bond.[185] Interestingly, there appeared to be no preference shown for insertion into the methylene group "allylic" to the triple bond (relative to insertion into the remaining carbon-hydrogen bonds in 4-octyne), in contrast with that which is usually found for, *e.g.*, methylene insertions into carbon-hydrogen bonds at true allylic positions.[191] In their study of the photolytic reaction of ethyl diazoacetate with 4-octyne, Lind and Deutschman obtained a *ca.* 10% yield of ethyl 6-decynoate, the product expected from insertion of carbethoxycarbene into the acetylenic carbon-hydrogen bond.[185] In contrast to this report, the results of a more recent study have led to the conclusion that $:CHCO_2R$ ($h\nu$) will insert into aliphatic but *not* acetylenic carbon-hydrogen bonds.[192] Carbethoxycarbenoid generated thermally (40°) from ethyl diazoacetate in the presence of copper reacts with 3,3-dimethyl-1-butyne (**27**) to afford the corresponding cyclopropenecarboxylate (**28**) in low yield along with traces of two other products, **29** and **30**[177] (eq 30). At higher temperatures (100°), reactions of this type afford only allenic and acetylenic esters; the product of addition of the carbenoid to the triple bond is not observed.[177] Allenic and acetylenic esters formed in reactions of this type have recently been shown to be primary reaction products (*i.e.*, they are not formed *via* subsequent rearrangement of initially formed cyclopropenecarboxylate adducts).[192] These unusual products are instead believed to arise during the breakdown of an initially formed pyrazolenine[192] (eq 31). As envisaged above, the formation of products of the type **29** and **30** in reactions



27 **28**

t-BuC≡CCH$_2$CO$_2$Et + t-BuCH=C=CHCO$_2$Et +
29 **30**

diethyl maleate and fumarate (30)



(31)

of carbalkoxycarbenoids with alkynes is *not* to be construed as evidence for the ability of these carbenoids to insert into carbon-hydrogen bonds.

C. "Insertion" into Carbon-Halogen Bonds

In this section and the one which follows, consideration will be given to "insertion" reactions involving attack by carbalkoxycarbenes at C-X bonds where X is a lone-pair substituent. We must therefore consider mechanisms involving intermediate ylide formation as a prelude to abstraction-recombination in addition to the concerted insertion and simple abstraction-recombination mechanisms which were considered in connection with carbon-hydrogen insertion reactions of carbalkoxycarbenes.

1. Reactions with Polyhalomethanes

There has been some suggestion that reactions of alkyl diazoacetates with polyhalomethanes may proceed *via* free radical chain mechanisms.[193] In an early study, Urry and Wilt[194,195] found that photolytic reactions of methyl diazoacetate with chloroform, carbon tetrachloride, and bromotrichloromethane produced the corresponding methyl polyhalopropionates which, under the conditions of the reaction, suffered dehydrohalogenation to give methyl polyhaloacrylates. A free radical chain mechanism was postulated on the basis of the identity of the products and by analogy to earlier studies[196,197] which involved the corresponding reactions of diazomethane with polyhalomethanes (Scheme I). However, it should be borne in mind that recent CIDNP studies do not provide support for a radical chain mechanism in such reactions[130] (*cf.* discussion in section II.3). This question certainly merits detailed reinvestigation, but it will become apparent from the ensuing discussion that other mechanistic alternatives (especially those involving the formation of an intermediate halonium ylide) have gained much support in recent years.

The photolytic reaction of methyl diazoacetate with bromotrichloromethane has also been reexamined recently.[130] Whereas Wilt reported having identified $Cl_2BrCCHClCO_2Me$, Cl_3CCCl_3, Br_2CHCO_2Me, $Cl_2C{=}CCl\text{-}CO_2Me$, and HBr as products of this reaction,[195] reinvestigation has led also to the isolation of two additional methyl tetrahalopropionates and methyl dichloroacetate.[130]

In addition to the studies of the photolytic reactions of methyl diazoacetate with carbon tetrachloride, chloroform, and bromotrichloromethane (discussed above), Urry and Wilt also studied the corresponding reactions with CH_2Br_2, CBr_2Cl_2, $CHBr_3$, CH_2Cl_2, $CHClBr_2$, $CHCl_2Br$, CH_2ClBr, and Cl_2CHCO_2Me.[195] In these reactions, C-X "insertion" products were generally observed in yields ranging from *ca.* 8 to 30%. Some significant general observations of possible mechanistic significance are as follows: (1) products of "insertion" into both carbon-chlorine and carbon-bromine bonds (affording methyl α-chloropropionates and methyl α-bromopropionates, respectively) were observed, but in substrates containing both chlorine and bromine, the major products were methyl α-chloro- (rather than α-bromo-) propionates; (2) the reactions displayed pseudo-zero-order kinetics; (3) products clearly resulting from free radical (or free radical chain) mechanisms (such as hexahaloethanes) were occasionally found; and (4) added diphenylamine, a commonly employed free radical scavenger, had only a slight inhibitory effect on the overall reaction rate.[195]

SCHEME I

Initiation

$$\mathrm{N_2CHCO_2Me \xrightarrow{h\nu} :CHCO_2Me + N_2}$$

$$\mathrm{:CHCO_2Me + Cl_3C{-}X \longrightarrow \cdot CCl_3 + \cdot CHXCO_2Me}$$

$$(\mathrm{X = Cl,\ Br,\ or\ H})$$

Propagation

$$\mathrm{\cdot CCl_3 + N_2CHCO_2Me \longrightarrow Cl_3C\dot{C}HCO_2Me + N_2}$$

$$\mathrm{Cl_3\dot{C}CHCO_2Me \xrightarrow{\sim Cl} Cl_2\dot{C}CHClCO_2Me}$$

$$\mathrm{Cl_2\dot{C}CHClCO_2Me + Cl_3CX \longrightarrow \cdot CCl_3 + Cl_2CXCHClCO_2Me}$$

$$\mathrm{\cdot CHXCO_2Me + Cl_3CX \longrightarrow \cdot CCl_3 + CHClXCO_2Me}$$

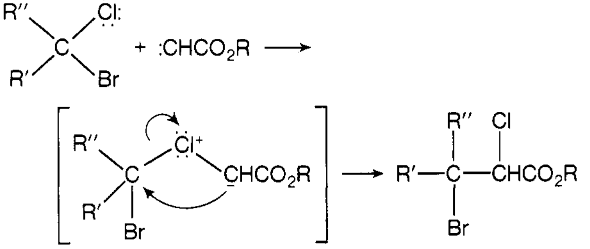
Termination

$$\mathrm{\cdot CHX{-}CO_2Me + \cdot CCl_3 \longrightarrow Cl_3C{-}CHX{-}CO_2Me}$$

$$\mathrm{2\cdot CCl_3 \longrightarrow Cl_3CCCl_3}$$

$$\mathrm{2\cdot CHXCO_2Me \longrightarrow MeO_2CCHXCHXCO_2Me}$$

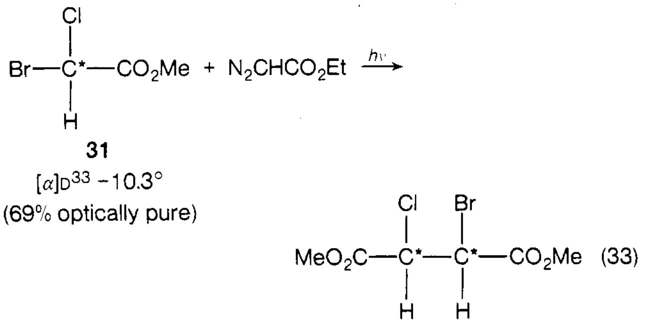
The preferred mechanism to account for the formation of the methyl propionates involved carbene attack at halogen with consequent ylide formation, followed by subsequent SNi-type displacement of the halogen involved in ylide formation (eq 32). Various competing free radical sequences were proposed to account for a number of minor reaction products. The observed preference for attack at chlorine over attack at bromine by the carbene in compounds of the type R_2CBrCl was accounted for in terms of the greater electronegativity of chlorine relative to bromine, with the consequent preference being shown by the electrophilic carbalkoxycarbene[195] (however, see further discussion regarding this point in sections IV.C.2 and IV.C.3).



(32)

Recently, arguments against the operation of a radical *chain* mechanism in the photolytic reaction of diazoacetic esters with carbon tetrachloride, chloroform, and methylene chloride have appeared.[198] When ethyl diazoacetate was decomposed in each of these substrates in turn in the presence of known radical chain initiators (such as benzoyl peroxide and perbenzoic acid), different products were obtained from those reported earlier by Urry and Wilt[194,195] (who had performed the corresponding photolytic reactions in the absence of added initiators). These results suggest that the photochemical decomposition of ethyl diazoacetate in the absence of added initiator affords a species which reacts quite differently with polyhalomethanes than does the corresponding species produced when this diazo ester is decomposed in radical fashion.

The question of the stereochemistry of these carbon-halogen "insertion" reactions by carbalkoxycarbenes is of considerable mechanistic interest. In a widely quoted but as yet unpublished study, Doering has found that the corresponding reaction of $:CH_2$ ($h\nu$) with the carbon-chlorine bond of optically active 2-chlorobutane proceeds with a high degree of racemization.[199] No corresponding information is available for carbalkoxycarbenes; however, there has been one report of the reaction of $:CHCO_2Me$ ($h\nu$) with optically active methyl chlorobromoacetate (**31**) which afforded optically active methyl α-chloro-α'-bromosuccinate (**32**)[200] as shown in eq 33. However, the configurational relationship between the optically active product and the reactant was never established for this reaction. This highly interesting result certainly merits reinvestigation as important information could thereby be gained regarding the stereochemistry of this carbon-halogen "insertion" reaction. Also, if labeled methyl diazoacetate (*e.g.*, $N_2{}^{14}CHCO_2Me$) were employed, one could determine the relative extent of C-Cl *vs.* C-Br "insertion" by the carbene in forming the chlorobromosuccinate ester (**32**) in this reaction.



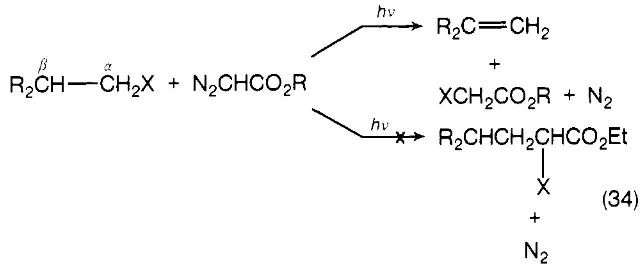
$$\mathrm{Br{-}\overset{Cl}{\underset{H}{C^*}}{-}CO_2Me + N_2CHCO_2Et \xrightarrow{h\nu} MeO_2C{-}\overset{Cl}{\underset{H}{C^*}}{-}\overset{Br}{\underset{H}{C^*}}{-}CO_2Me} \quad (33)$$

31
$[\alpha]_D{}^{33}$ -10.3°
(69% optically pure)

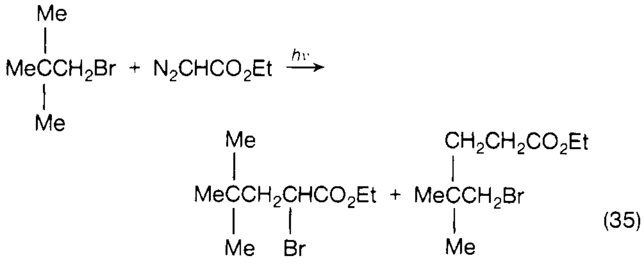
32
$[\alpha]_D{}^{33}$ -2.4°
(unknown optical purity)

2. *Reactions with Monohaloalkanes*

Reactions of carbalkoxycarbenes with monohaloalkanes have received little attention. One reason for this as we shall see later (section V) is that, generally, these compounds appear to be more prone to react whenever possible with $:CHCO_2R$ ($h\nu$) to give olefins (*via* HX elimination, when there is a β carbon-hydrogen bond present) as indicated in eq 34. In a system such as neopentyl bromide (which does not contain any β carbon-hydrogen bonds), carbon-bromine "insertion" is observed to predominate over carbon-hydrogen insertion by factor of 4 (despite the 9:1 statistical predominance of primary carbon-hydrogen bonds over carbon-bromine bonds in the substrate;[201] see eq 35). It is especially interesting to note that no rearranged products were observed in this reaction.[201] This argues against the operation of a mechanism whereby an intermediate ylide breaks down to form the carbon-bromine "insertion" product *via* dipolar abstraction of bromine with subsequent recombination of ionic fragments; the ease of carbonium ion rearrangements (1,2-methyl shifts) accompanying neopentyl halide or tosylate solvolyses is well known.[202] The high degree of selectivity displayed by $:CHCO_2Et$ ($h\nu$) in its reaction with carbon-bromine *vs.* primary carbon-hydrogen bonds in neopentyl bromide suggests that carbon-bromine "insertion" reactions of this type involving suitably constructed alkyl halides as substrates (*i.e.*, those which cannot readily eliminate HX *via* β-elimination) may be of synthetic value.



$$\mathrm{R_2\overset{\beta}{C}H{-}\overset{\alpha}{C}H_2X + N_2CHCO_2R \xrightarrow{h\nu} R_2C{=}CH_2 + XCH_2CO_2R + N_2}$$
$$\mathrm{R_2\overset{\beta}{C}H{-}\overset{\alpha}{C}H_2X + N_2CHCO_2R \overset{h\nu}{\not\longrightarrow} R_2CHCH_2\underset{X}{C}HCO_2Et + N_2} \quad (34)$$



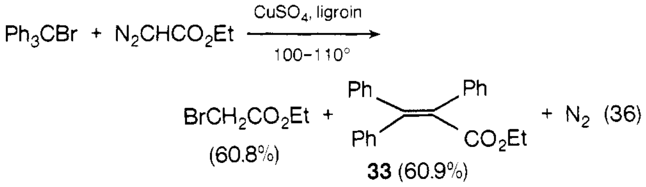
$$\mathrm{Me\overset{Me}{\underset{Me}{C}}CH_2Br + N_2CHCO_2Et \xrightarrow{h\nu} Me\overset{Me}{\underset{Me}{C}}CH_2\underset{Br}{C}HCO_2Et + Me\overset{CH_2CH_2CO_2Et}{\underset{Me}{C}}CH_2Br} \quad (35)$$

observed product ratio: 4 1

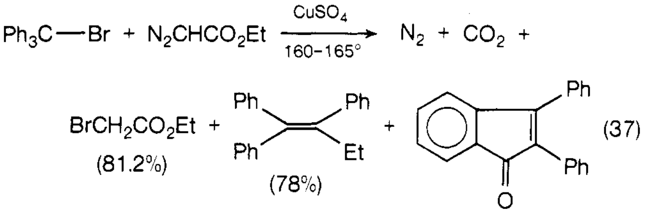
Wilt[195] reported that *tert*-butyl chloride failed to react with $:CHCO_2Et$ ($h\nu$). However, in a later reinvestigation of this reaction, Franzen[203] reported having observed the formation of trace amounts of "insertion" products in this reaction. A more recent study has shown the major products of the *tert*-butyl chloride-$:CHCO_2Et$ ($h\nu$) reaction to be isobutylene and ethyl bromoacetate[201] (see section V). Simple monohaloalkanes have been reported by D'yakonov and Vinogradova[204] to undergo no carbon-halogen bond "insertion" by carbethoxycarbenoid, although haloacetic esters were often isolated in such reactions (along with diethyl fumarate).

3. *Reactions with Benzylic and Allylic Systems*

The copper sulfate catalyzed reaction of ethyl diazoacetate with triphenylmethyl bromide in refluxing petroleum ether solvent (bp 100-110°) afforded ethyl bromoacetate and ethyl 2,3,3-triphenylacrylate (**33**)[205] (eq 36). When the solvent was omitted and the temperature was raised to 160-165°, the yield of ethyl bromoacetate increased somewhat; compound **33** was not formed, but two new products, 1,2,2-triphenyl-1-butene and 2,3-diphenylindenone (**34**), were observed[205] (eq 37). The corresponding copper catalyzed reactions of ethyl diazoacetate with diphenylmethyl bromide and with benzyl bromide have also been reported[205] (eq 38 and 39, respectively). The mechanisms of these reactions are not known (*vide infra*).



33 (60.9%)

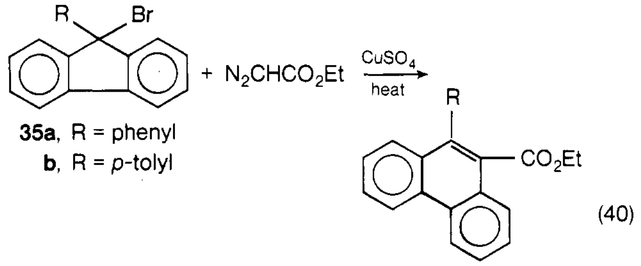


34 (trace)

$$\mathrm{Ph_2CHBr + N_2CHCO_2Et \xrightarrow[80^\circ]{CuSO_4} \underset{(31.2\%)}{PhCHBrCHPhCO_2Et} + \underset{(17.2\%)}{BrCH_2CO_2Et}} \quad (38)$$

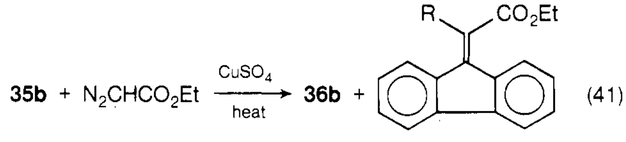
$$\mathrm{PhCH_2Br + N_2CHCO_2Et \xrightarrow[120^\circ]{Cu} diethyl\ fumarate + \text{“undistillable tar”}}$$
$$\Big\downarrow \text{60°, Zn dust, 50% HOAc-EtOH} \quad (39)$$
$$\mathrm{PhCH_2CH_2CO_2Et + other\ products}$$

Similar reactions of ethyl diazoacetate with triphenylmethyl chloride, diphenylmethyl dichloride, 9-bromofluorene, and 9,9-dibromofluorene, all in the presence of copper catalysts, have also been studied.[193] In all cases, free radical *chain* mechanisms were postulated to account for the observed reaction products. Whereas 9-bromofluorene reacted with ethyl diazoacetate in the presence of copper sulfate to afford only 9,9′-bifluorenylidene and ethyl bromoacetate,[193] the corresponding reaction with 9-phenyl-9-bromofluorene (**35a**) afforded a condensation product in which a novel ring expansion had occurred to give ethyl 10-phenyl-9-phenanthrenecarboxylate (**36a**)[206] (eq 40). With 9-*p*-tolyl-9-bromofluorene (**35b**), two condensation products were observed:[206] the ring-expanded product (**36b**) and a second product, **37**, analogous to the ethyl triphenylacrylate (**33**) which had earlier been found in the corresponding copper catalyzed reaction of triphenylmethyl bromide with ethyl diazoacetate[205] (see eq 40 and eq 41).



35a, R = phenyl
b, R = *p*-tolyl

36a, R = phenyl
b, R = *p*-tolyl



37, R = *p*-tolyl

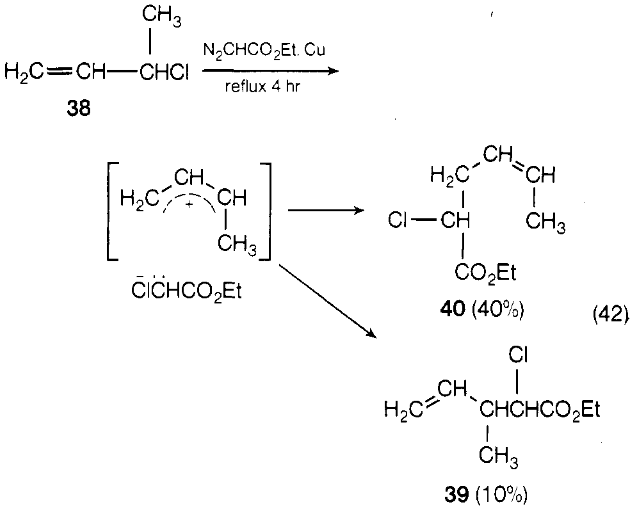
A free radical chain mechanism was suggested for the formation of **36** and **37** in these reactions as indicated in Scheme II. Interestingly, further investigation of the mother liquor obtained in the copper sulfate catalyzed reaction of ethyl diazoacetate with **35a** was reported to afford 9-phenyl-9-ethoxyfluorene as an additional reaction product.[206] It is difficult to account for the formation of this material in terms of the above free radical chain mechanism.

It is worth noting that there is no compelling evidence which demands that a radical chain mechanism be operative in the reactions discussed above. In fact, there is an increasing body of evidence which suggests that the major reaction path followed by diazo ester reactions with allylic and benzylic halides involves halonium ylide intermediates, and that these reactions do not proceed primarily *via* radical chain mechanisms.[206a] Some years ago, the reaction of benzal chloride with ethyl diazoacetate at 160–175° was reported to afford only ethyl α-chlorocinnamate (24%); a mechanism postulating the intermediacy of a chloronium ylide was suggested for this reaction.[69] More recently, it has been shown that under appropriate circumstances stable halonium ylides can be *isolated* from reactions of carbenes with substrates containing carbon–halogen bonds.[207,208]

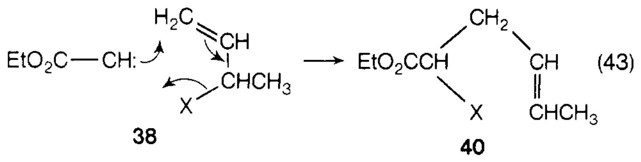
Reactions of allylic halides with diazoacetic ester have been more thoroughly and systematically studied than have the corresponding reactions with aralkyl halides. The results obtained for reactions involving the former system have probable bearing on mechanistic interpretations for those involving the latter.

Early studies of the reaction of carbethoxycarbenoid with allyl chloride indicated a slight preference for carbon–chlorine bond "insertion" relative to addition to the carbon–carbon double bond of the substrate.[209] The corresponding reactions with allyl bromide[210] and allyl iodide[204] resulted in the formation of ethyl 2-bromo-4-pentenoate (up to 70%) and ethyl 2-iodo-4-pentenoate (70%), respectively; in neither case were any cyclopropane-containing products observed. With 2,3-dichloropropene, carbethoxycarbenoid was observed to give mainly addition products along with some ethyl 2,4-dichloro-4-pentenoate (the product of "insertion" into the allylic carbon–chlorine bond).[211] The corresponding reaction with 2,3-dibromopropene afforded exclusively ethyl 2,4-dibromo-4-pentenoate, whereas only tars and diethyl fumarate could be obtained with 1,3-dibromopropene as substrate.[212]

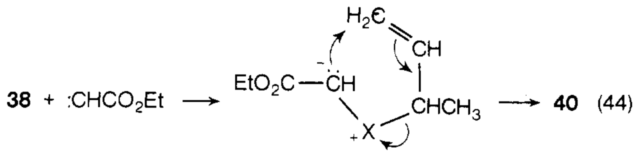
In agreement with the earlier findings of the Russian workers, Phillips[213] observed exclusive formation of ethyl 2-halo-4-pentenoate in the reactions of carbethoxycarbenoid with allyl bromide and allyl iodide. The reaction of carbethoxycarbenoid with α-methylallyl chloride (**38**) afforded 10% of the unrearranged carbon–chlorine "insertion" products (**39**) and 40% of a *rearranged* isomeric product (**40**) under reaction conditions where both the reactants and products were demonstrated to be stable. The intermediacy of an ion pair capable of affording an SN2′ rearrangement was suggested[213] (eq 42).



A concerted mechanism for the formation of **40** kinetically in indistinguishable from the above SN2′ mechanism was also considered (eq 43).



A third possibility for the formation of **40** in the above reaction might involve (reversible or irreversible) prior halonium ylide formation as indicated in eq 44. As envisioned above, the rearrangement of the halonium ylide to form **40** is essentially a symmetry allowed, thermal [2,3] sigmatropic rearrangement.[84] The rearranged carbon–



SCHEME II

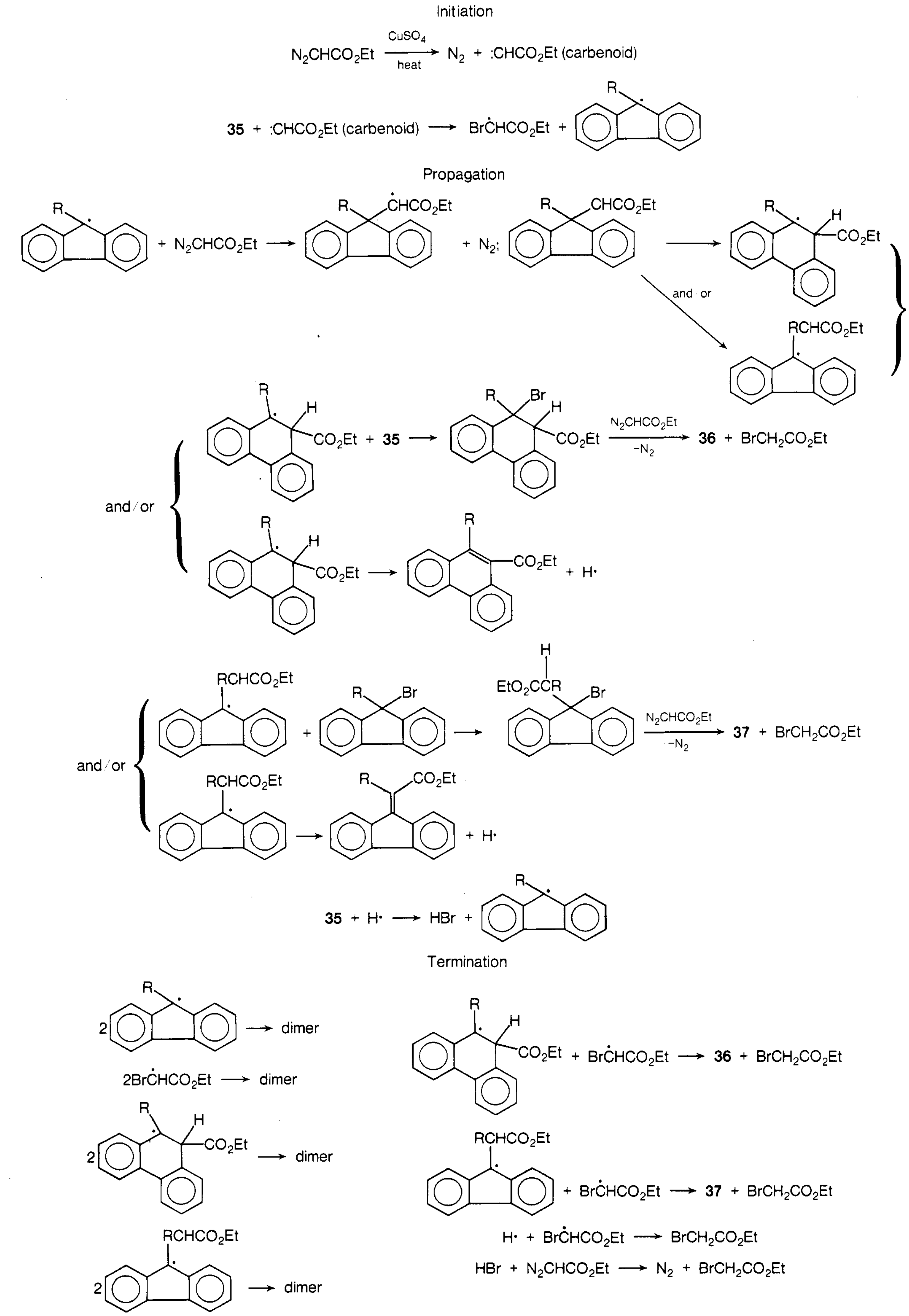

Initiation
$N_2CHCO_2Et \xrightarrow[heat]{CuSO_4} N_2$ + :CHCO$_2$Et (carbenoid)
35 + :CHCO$_2$Et (carbenoid) → BrĊHCO$_2$Et +
Propagation
+ N$_2$CHCO$_2$Et →
+ N$_2$;
and/or
and/or
+ 35 →
$\xrightarrow[-N_2]{N_2CHCO_2Et}$ 36 + BrCH$_2$CO$_2$Et
+ H·
and/or
$\xrightarrow[-N_2]{N_2CHCO_2Et}$ 37 + BrCH$_2$CO$_2$Et
+ H·
35 + H· → HBr +
Termination
2 → dimer
2BrĊHCO$_2$Et → dimer
2 → dimer
2 → dimer
+ BrĊHCO$_2$Et → 36 + BrCH$_2$CO$_2$Et
+ BrĊHCO$_2$Et → 37 + BrCH$_2$CO$_2$Et
H· + BrĊHCO$_2$Et → BrCH$_2$CO$_2$Et
HBr + N$_2$CHCO$_2$Et → N$_2$ + BrCH$_2$CO$_2$Et
R
Br
H
CO$_2$Et
ĊHCO$_2$Et
CHCO$_2$Et
RCHCO$_2$Et
EtO$_2$CCR

TABLE II. Product Distributions for the Reactions of Diazo Esters with Allyl Chloride (41), β-Methylallyl Chloride (42), γ-Methylallyl Chloride (43), and Allyl Bromide (44)

Diazo ester	Substrate	Method of decompn of diazo ester	% yield of C–X "insertion" product	% yield of C=C addition product	Ref
$N_2C(CO_2Me)_2$	**41**	*hν* (direct)	53	23	220
$N_2C(CO_2Me)_2$	**41**	*hν* ($Ph_2C{=}O$ sens)	5	88	220
$N_2C(CO_2Me)_2$	**41**	110°, CuCl	32	3	221
N_2CHCO_2Et	**41**	*hν* (direct)	21	18	220
N_2CHCO_2Et	**41**	*hν* ($Ph_2C{=}O$ sens)	7	69	220
$N_2C(CO_2Me)_2$	**42**	*hν* (direct)	25	22	220
$N_2C(CO_2Me)_2$	**42**	*hν* ($Ph_2C{=}O$ sens)	Trace	86	220
$N_2C(CO_2Me)_2$	**42**	110°, CuCl	35	4	221
N_2CHCO_2Et	**42**	*hν* (direct)	57	30	219
N_2CHCO_2Et	**42**	*hν* ($Ph_2C{=}O$ sens)	6	85	220
$N_2C(CO_2Me)_2$	**43**	*hν* (direct)	38	15	220
$N_2C(CO_2Me)_2$	**43**	*hν* ($Ph_2C{=}O$ sens)	Trace	49	220
$N_2C(CO_2Me)_2$	**43**	110°, CuCl	35	Trace	221
N_2CHCO_2Et	**43**	*hν* (direct)	16	8	219
N_2CHCO_2Et	**43**	80°, 60 min, CuCl	9	2	219
N_2CHCO_2Et	**43**	80°, 9 min, CuCl	12	3	219
N_2CHCO_2Et	**43**	80°, 60 min, Cu	6	3	219
$N_2C(CO_2Me)_2$	**44**	*hν* (direct)	38	6	220
$N_2C(CO_2Me)_2$	**44**	*hν* ($Ph_2C{=}O$ sens)	4	30	220

chlorine "insertion" product (**39**) can be visualized as a Stevens-type rearrangement of the halonium ylide intermediate. Recent CIDNP studies suggest that these reactions in, *e.g.*, sulfonium ylides, take place *via* homolytic fragmentations.[104,214–218]

The suggestion of a chloronium ylide intermediate has recently been forwarded to account for the observed course of the reactions of carbethoxycarbenoid,[219] $:CHCO_2Et$ (*hν*),[220] biscarbomethoxycarbenoid,[221] and $:C(CO_2Me)_2$ (*hν*)[222] with allylic halides. Interestingly, the relative yields of C–X "insertion" products and carbon–carbon double bond addition products were found to be strongly dependent on the mode of decomposition of the diazo ester; the results for allyl chloride (**41**), β-methylallyl chloride (**42**), γ-methylallyl chloride (**43**), and allyl bromide (**44**) are summarized in Table II. A dramatic change in the "insertion"/addition ratio was observed in each case upon changing from direct photolysis to sensitized photolytic conditions, reflecting the difference in reactivity (and, consequently, selectivity) between the singlet and triplet carbalkoxycarbenes. From these results, it was concluded that singlet carbalkoxycarbenes produced *via* direct photolysis of diazo esters preferentially attack the halogen atom in allylic halides to afford predominantly C–X "insertion" products, whereas the corresponding triplet carbenes generated by benzophenone sensitized photolyses preferentially add to the carbon–carbon double bonds in these substrates.[221]

Support for this interpretation of the differing behavior of carbalkoxycarbenes produced *via* direct photolyses *vs.* sensitized photolyses of diazo esters was obtained *via* the observation of a solvent effect on the "insertion"/addition ratio in the photolytic reaction of dimethyl diazomalonate with allyl chloride.[222] Dilution with methylene halides was found to decrease the value of this ratio, the observed value approaching that obtained in the benzophenone sensitized reaction. Not only does this implicate the triplet carbene in the photolytic reaction when carried out in the presence of heavy-atom-containing "inert" solvents[61,208,223] and in the benzophenone sensitized reaction, but it also suggests that the carbene produced by direct photolysis of dimethyl diazomalonate (*i.e.*, singlet $:C(CO_2Me)_2$ is in a higher energy electronic configuration than is that produced *via* photosensitized decomposition of the diazo ester.[224] (It should be noted that a factor which limits the reliability of the methylene halide dilution studies is that these solvents are *not* inert to $:C(CO_2Me)_2$ (*hν*), and the observed results could reflect preferential entrapment of the singlet carbene with consequent lowering of the "insertion"/addition ratio in the products.)[222]

Perhaps the strongest single piece of evidence to support the postulated intermediacy of ylides in "insertion" reactions of carbalkoxycarbenes into C–X bonds (X being a lone-pair atom) is the observation that $:C(CO_2Me)_2$ (*hν*) reacts with aliphatic sulfides to form *stable* sulfonium ylides.[104,225,226] Subsequent reactions of these stable ylides have also been studied, and they have been found to afford the same types of products as are obtained in reactions of $:C(CO_2Me)_2$ (*hν*) with the parent sulfides.[104,225,226] These subjects and related observations will be discussed in more detail in sections IV.D and V.

D. Miscellaneous "Insertion" Reactions

In the previous section, we considered "insertion" reactions into carbon–halogen bonds resulting from initial attack by carbalkoxycarbenes at halogen atoms (in the halonium ylide mechanism). Corresponding "insertion" reactions have been observed for C–X bonds, where X is a lone-pair atom other than halogen. Mechanisms involving the formation of ylide intermediates of the type

$$R{-}\overset{+}{X}{-}\overset{-}{C}YCO_2R \quad (Y = H \text{ or } CO_2R)$$

have been postulated for a number of these reactions. Taken together with the results of Ando and coworkers regarding carbalkoxycarbene reactions with allylic halides,[219–222] these studies offer a significant body of evidence to support the suggestion of intermediate ylide formation in the "insertion" reactions of carbalkoxycarbenes into C–X bonds, where atom X possesses an unshared electron pair.

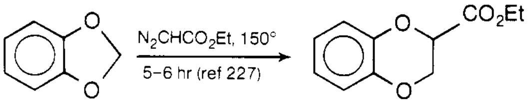
1. Reactions with C–O, C–S, and C–N Bonds

Cyclic acetals,[169,227] thioacetals,[228,229] orthoesters,[228] and trithioorthoesters[228] have been observed to undergo

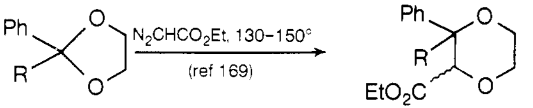
TABLE III. Product Distributions for the Reactions of Ethyl Diazoacetate with Alkyl Allyl Sulfides[219]

Substrate	N_2CHCO_2Et, mmol	Mode of decompn of diazo ester	% yield of C=C addition product (cis, trans)	% yield of C-S insertion product
$MeCH{=}CHCH_2SEt$	1.8	*hν* (direct)	6	23
$MeCH{=}CHCH_2SEt$	1.9	*hν* (direct)	7	19
$MeCH{=}CHCH_2SEt$	1.8	90°, 2 min, CuCl	. . .	95
$MeCH{=}CHCH_2SEt$	1.8	90°, 2 hr, Cu	. . .	85
$MeCH{=}CHCH_2SEt$	2.0	80°, 24 hr, no catalyst	5	25
$H_2C{=}CHCH_2S$-*n*-Bu	4.4	*hν* (direct)	10	15
$H_2C{=}CHCH_2S$-*t*-Bu	4.4	*hν* (direct)	13	16
$H_2C{=}C(Me)CH_2S$-*n*-Bu	4.4	*hν* (direct)	15	23

ring expansions when allowed to react with ethyl diazoacetate at elevated temperatures (eq 45 and 46). An oxonium ylide mechanism was suggested for the formation of **46** from **45**[169] (eq 47). The corresponding open-chain compounds also undergo carbon-oxygen or carbon-sulfur "insertion" as indicated in eq 48.



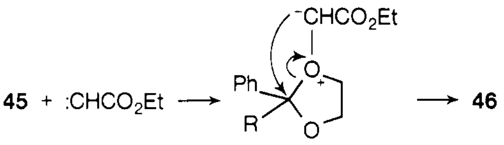
(45)



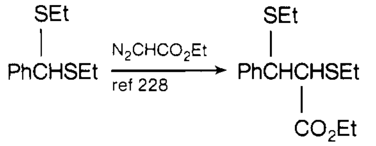
(46)

45a, R = H
b, R = Me

46a, R = H (48.5%, cis + trans)
b, R = Me (6.5%, cis + trans)



(47)



$$PhCH(SEt)SEt \xrightarrow[\text{ref 228}]{N_2CHCO_2Et} PhCH(SEt)CH(CO_2Et)SEt \qquad (48)$$

Similarly, carbon-oxygen "insertion" by carbalkoxycarbenes in their reactions with aliphatic ethers[57,230-232] (and the corresponding carbon-sulfur "insertions" with thioethers[104]) has been observed rarely. Generally, aliphatic ethers react with carbalkoxycarbenes to afford mixtures of carbon-hydrogen insertion products along with products arising *via* carbon-oxygen bond cleavage[233] (*cf.* section V). However, "insertions" by carbalkoxycarbenes and carbenoids into the *allylic* carbon-oxygen bond of allyl methyl ethers has recently been observed.[219,234,235]

Insertion into carbon-sulfur bonds has been observed for thermal (both copper catalyzed and uncatalyzed) and photochemical reactions of ethyl diazoacetate with alkyl allyl sulfides;[219] the results of these studies are summarized in Table III. In general, the C-X "insertion"/addition ratio was observed to be higher for corresponding reactions of alkyl allyl sulfides than for either alkyl allyl ethers or allyl chlorides, indicating the increased facility of attack of the carbene (or carbenoid) on carbon-sulfur bonds relative to carbon-oxygen or carbon-chlorine bonds. This may reflect the relative stabilities of the intermediate sulfonium, oxonium, and chloronium ylides, respectively, or it may instead be a kinetic effect. In contrast to :$C(CO_2Me)_2$ which was found to react with alkyl sulfides to afford stable sulfonium ylides,[225,226] :$CHCO_2Et$ instead gave products considered to arise *via* subsequent reaction of the (somewhat less stable) intermediate ylides.[219]

In general, :$C(CO_2Et)_2$ reacts with allylic sulfides and ethers to afford rearranged C-X "insertion" products. It is interesting to note that :$CHCO_2Et$ reacts with allylic ethers and chlorides to afford some nonrearranged C-X "insertion" products as well, although the corresponding reactions with allylic sulfides afford only rearranged "insertion" products.[219] Mechanistic details remain to be established which might qualitatively (or quantitatively) account for the observed differences between reactions of :$C(CO_2R)_2$ and :$CHCO_2R$ with carbon-sulfur, carbon-oxygen, and carbon-halogen bonds in allylic systems.

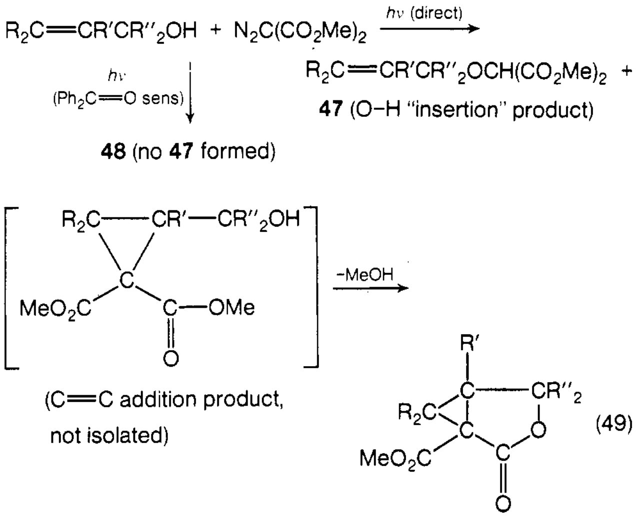
Diazomalonate ester decompositions in the presence of allyl sulfides and ethers under a variety of environmental conditions have recently been reported.[219,221,237] The results are in good general agreement with those of previous studies of this type. The relative ratio of C-X "insertion"/addition was dramatically decreased in the sensitized photolysis of the diazo ester as compared with that obtained from direct photolytic experiments. Generally, the corresponding carbenoid afforded exclusively C-X "insertion" products with $H_2C{=}CHCH_2XR$, (X = O or S; R = alkyl, except for the case of R = *t*-Bu, which effectively sterically hindered attack by the bulky carbenoid on the carbon-oxygen or carbon-sulfur bond, respectively, in the substrate). Interestingly, CuCl catalyzed thermal reactions of ethyl diazoacetate with allylic sulfides and ethers afforded *no* carbene dimers (diethyl maleate or fumarate), whereas these dimers were found to be the major products in the corresponding reaction with allyl chloride.[219]

Stable sulfonium ylides have been produced from the decomposition of dimethyl diazomalonate in the presence of alkyl and aryl sulfides and of dialkyl disulfides.[104,225,226,238] This behavior was expected for the case of reactions involving the carbene produced *via* direct photolysis of the diazo ester;[225,226] however, somewhat surprisingly,[237] the triplet carbene generated *via* benzophenone sensitized photolysis of the diazo ester and the corresponding carbenoid *both* likewise afforded stable sulfonium ylides.[104] These observations somewhat complicate attempts to explain why the courses of reactions of diazo esters with allyl chlorides, sulfides, and ethers are so greatly altered by changes in the mode of decomposition of the diazo esters (Tables II and III).

Reports of C-N bond "insertions" by carbalkoxycarbenes are relatively rare. One such example has been published for the photolytic and thermal reactions of ethyl diazoacetate with benzyldimethylamine.[239] For this reaction, the carbon-nitrogen "insertion" product, ethyl 2-dimethylamino-3-phenylpropionate, was observed along with ethyl 3-dimethylamino-3-phenylpropionate (the product of insertion of carbethoxycarbene into the benzylic carbon-hydrogen bond). Other examples have been reported recently for the reactions of allylamines with $:C(CO_2Me)_2$ ($h\nu$).[221] Along with addition products, these reactions afford rearranged carbon-nitrogen "insertion" products, although these reactions proceed to afford lower yields than were found previously for the corresponding C-X "insertion" reactions of $:C(CO_2Me)_2$ with allyl ethers and allyl sulfides.[221]

2. *Reactions with O-H, S-H, and N-H Bonds*

Carbalkoxycarbenes produced photolytically from diazo esters react with alcohols to give carbon-hydrogen and oxygen-hydrogen "insertion" products; these processes compete with Wolff rearrangement of the carbene (see section VI.B).[180,240,241] An early study of the reaction of allyl alcohol with carbethoxycarbenoid reported good yields of ethyl allyloxyacetate ($H_2C{=}CHCH_2OCH_2CO_2Et$, the oxygen-hydrogen "insertion" product, 52.5% yield) accompanied by a small amount of the corresponding addition product.[242] A more recent investigation of the reactions of dimethyl diazomalonate and ethyl diazoacetate with allylic alcohols has reported that the relative ratio of oxygen-hydrogen "insertion"/addition is sensitive to the mode of decomposition of the diazo ester.[234,243] Interestingly, the products of addition of $:C(CO_2Me)_2$ to the various allylic alcohols studied were not stable to the reaction conditions, but instead they spontaneously lactonized with elimination of methanol.[243] Another interesting feature of this reaction is that the corresponding benzophenone sensitized photolysis of dimethyl diazomalonate produced a (presumably triplet) carbene which added to the double bond of allylic alcohols but did not "insert" into their oxygen-hydrogen bonds.[243] These results are summarized in eq 49. A mechanism involving intermediate oxonium ylide formation was proposed for the oxygen-hydrogen "insertion" reaction.



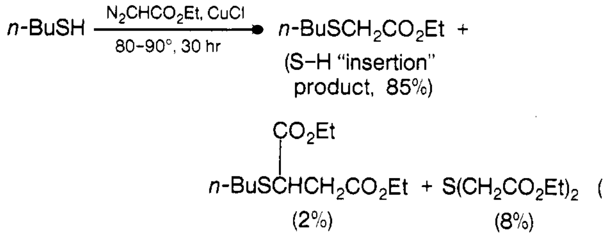
(49)

48 (γ-lactone)

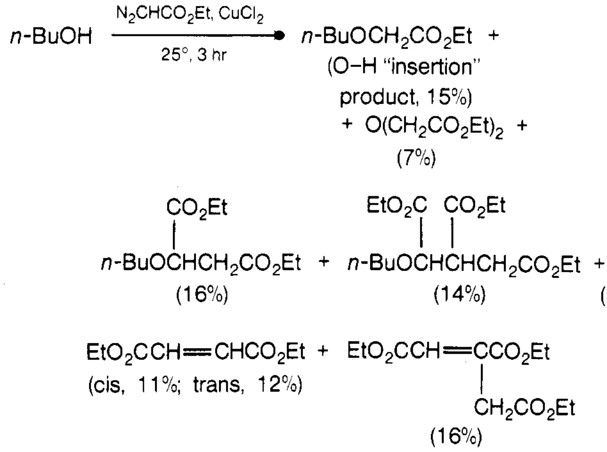
The results of a very recent study suggest that thermal decomposition (25°) of ethyl diazoacetate in the presence of catalytic amounts of rhodium salts (such as $Rh_2(OAc)_4$, $RhCl_3{\cdot}3H_2O$, and $(Ph_3P)_3RhCl$) in homogeneous solution produces a species capable of "inserting" into the oxygen-hydrogen bond of alcohols, water, and weak acids[243a] (eq 50). No products arising *via* carbon-hydrogen insertion by carbethoxycarbene (or carbenoid) were obtained in this reaction. A first-order dependence of the rate of the oxygen-hydrogen "insertion" reaction upon the catalyst concentration was noted, suggesting that complex formation (involving interaction between the metal catalyst and either the carbene or its diazo precursor) is kinetically important.

$$ROH + N_2CHCO_2Et \xrightarrow[\text{catalyst}]{25^\circ} \underset{(58\text{-}93\%)}{ROCH_2CO_2Et} + N_2 \qquad (50)$$

The copper catalyzed reactions of ethyl diazoacetate with alcohols and thiols have recently been studied.[180] In an earlier study, $:CHCO_2Et$ (Δ, 80°) was reported to have reacted with benzenethiol to afford ethyl phenylthioacetate, but aliphatic thiols gave no reaction under comparable conditions.[244] This same reaction with aliphatic thiols performed in the presence of cuprous chloride affords the sulfur-hydrogen "insertion" products in high yield and with a high degree of selectivity.[180] In contrast, alcohols afforded oxygen-hydrogen "insertion" products with ethyl diazoacetate in the presence of cupric chloride in a much less selective reaction. Some examples which illustrate this point are shown in eq 51 and eq 52.[180]

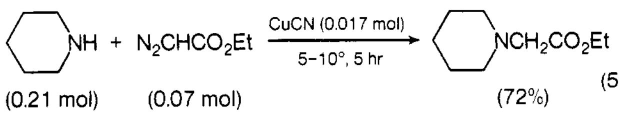


$$n\text{-BuSH} \xrightarrow[80\text{-}90^\circ,\ 30\text{ hr}]{N_2CHCO_2Et,\ CuCl} n\text{-BuSCH}_2CO_2Et \text{ (S-H "insertion" product, 85\%)} + n\text{-BuSCH(CO}_2\text{Et)CH}_2CO_2Et\ (2\%) + S(CH_2CO_2Et)_2\ (8\%) \qquad (51)$$

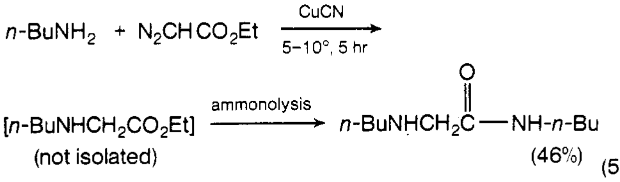


$$n\text{-BuOH} \xrightarrow[25^\circ,\ 3\text{ hr}]{N_2CHCO_2Et,\ CuCl_2} n\text{-BuOCH}_2CO_2Et \text{ (O-H "insertion" product, 15\%)} + O(CH_2CO_2Et)_2\ (7\%) + n\text{-BuOCH(CO}_2\text{Et)CH}_2CO_2Et\ (16\%) + n\text{-BuOCH(CO}_2\text{Et)CH(CO}_2\text{Et)CH}_2CO_2Et\ (14\%) + EtO_2CCH{=}CHCO_2Et \text{ (cis, 11\%; trans, 12\%)} + EtO_2CCH{=}C(CH_2CO_2Et)CO_2Et\ (16\%) \qquad (52)$$

The study of reactions of carbalkoxycarbenes with nitrogen-hydrogen bonds is practically virgin territory. In one such study, Saegusa and coworkers have reported nitrogen-hydrogen "insertion" by carbethoxycarbenoid in its reactions with primary and secondary amines[245] (eq 54 and 53, respectively). The conditions employed in these reactions are extremely mild (even for Cu(I) catalyzed thermal decompositions of ethyl diazoacetate), and one might question whether these reactions do indeed proceed *via* attack of carbethoxycarbenoid on the amines. Nevertheless, the observations of relatively good



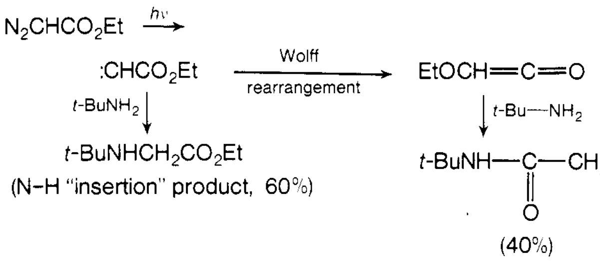
(53)



$$n\text{-BuNH}_2 + N_2CHCO_2Et \xrightarrow[5\text{-}10^\circ,\ 5\text{ hr}]{CuCN} [n\text{-BuNHCH}_2CO_2Et] \text{ (not isolated)} \xrightarrow{\text{ammonolysis}} n\text{-BuNHCH}_2C(=O)\text{—NH-}n\text{-Bu}\ (46\%) \qquad (54)$$

yields of products obtained under very mild conditions should serve to stimulate further inquiry into the generality of reactions of this type for synthetic purposes.

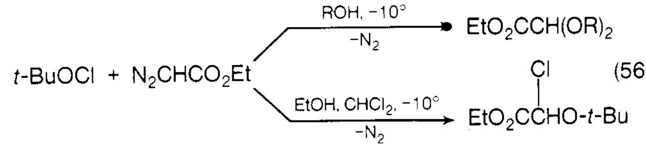
The reaction of :CHCO$_2$Et ($h\nu$) with *tert*-butylamine has been reported to afford the nitrogen-hydrogen "insertion" product along with a product resulting from Wolff rearrangement (section VI.B) of the carbene[164] (eq 55).



(55)

3. Reactions with O-Cl, S-Cl, and S-S Bonds

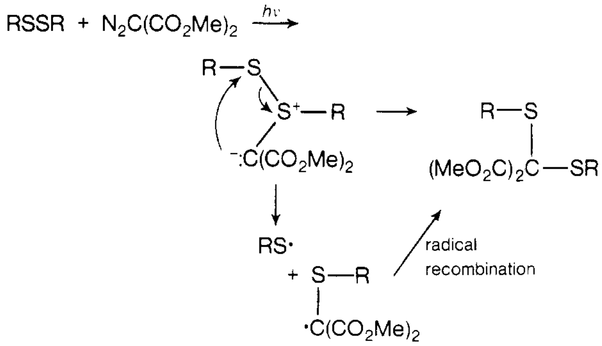
An example of oxygen-chlorine "insertion" has been reported for the reaction of ethyl diazoacetate with NO$_2$Cl.[246,247] Additionally, an interesting reaction of ethyl diazoacetate with *tert*-butyl hypochlorite has been reported recently[248-250] (eq 56). However, it is believed that these are ionic reactions initiated by attack of electrophilic chlorine in *t*-BuOCl on the diazo carbon atom. It is unlikely that carbenes are involved, considering the low temperatures at which these reactions are run (*e.g.*, −10°).



(56)

Ethyl diazoacetate has been found to react at −60° with EtSCl to afford EtSCHClCO$_2$Et, the sulfur-chlorine "insertion" product, in 71% yield.[251] Again, the very mild conditions employed in this reaction mitigate against the intermediacy of a carbene.

"Insertion" by :C(CO$_2$Me)$_2$ into the sulfur-sulfur bond of dialkyl disulfides has been reported.[104] This reaction has been suggested to proceed either *via* Stevens-type rearrangement of an intermediate sulfonium ylide or *via* homolytic cleavage of the sulfur-sulfur bond in this ylide followed by radical recombination.[104] These alternative processes are illustrated in eq 57.

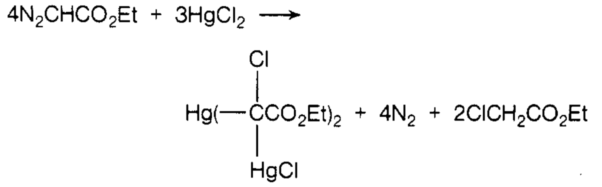


(57)

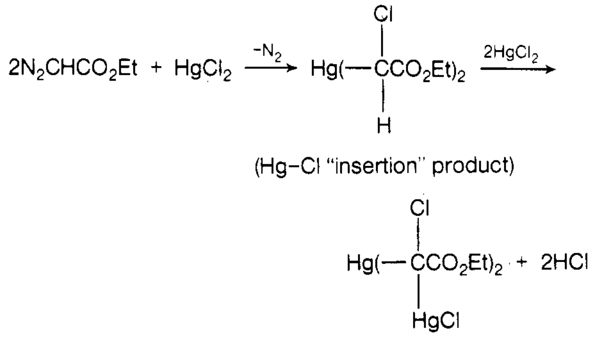
4. Reactions with Organometallic and Organometalloid Compounds

Review articles dealing in part with "insertions" of carbalkoxycarbenes into M-H and M-X bonds (where M = metal or metalloid) have appeared.[252-254] Insertion reactions of carbethoxycarbene into M-H bonds of group IV hydrides (*i.e.*, those of Si,[255] Sn,[256,257] and Ge[257,258]) have been studied. Often, reported yields in these reactions fell into a synthetically useful range (>50%).

Reactions of carbalkoxycarbenes with metal halides which very likely proceed with "insertion" of the carbene into the metal-halogen bond have been the subject of a number of investigations. An early report of the reaction of ethyl diazoacetate with HgCl$_2$ suggested that product formation *via* Hg-Cl bond "insertion" may have occurred[259] (eq 58). The ethyl chloroacetate formed in this reaction was thought to result from secondary reaction of ethyl diazoacetate with HCl liberated in the initial stages of the reaction[259] (eq 59):



$$4N_2CHCO_2Et + 3HgCl_2 \longrightarrow Hg(\text{—}\underset{HgCl}{\overset{Cl}{C}}CO_2Et)_2 + 4N_2 + 2ClCH_2CO_2Et \quad (58)$$

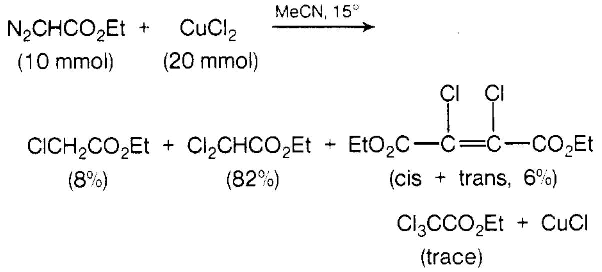


$$2N_2CHCO_2Et + HgCl_2 \xrightarrow{-N_2} Hg(\text{—}\underset{H}{\overset{Cl}{C}}CO_2Et)_2 \xrightarrow{2HgCl_2}$$

(Hg-Cl "insertion" product)

$$Hg(\text{—}\underset{HgCl}{\overset{Cl}{C}}CO_2Et)_2 + 2HCl \quad (59)$$

The corresponding reaction with cupric chloride has recently been studied.[260] In contrast to the reactions of ethyl diazoacetate with cuprous chloride and with other cupric salts (CuX$_2$, where X = CN, SO$_4$, and NO$_3$) which afforded only diethyl maleate and fumarate, the reaction with CuCl$_2$ was found to be considerably more complex (eq 60). No diethyl maleate or fumarate was formed in this reaction. However, when a 1:1 molar ratio mixture of N$_2$CHCO$_2$Et and CuCl$_2$ was allowed to react, some CuCl (formed by reduction of CuCl$_2$ which occurs during the reaction) catalyzed the decomposition of ethyl diazoacetate, affording diethyl maleate and fumarate in 30% yield (along with ClCH$_2$CO$_2$Et (16%), Cl$_2$CHCO$_2$Et (40%), and EtO$_2$C(Cl)C=C(Cl)CO$_2$Et (cis + trans, 3%)). The authors concluded that the reaction of ethyl diazoacetate with cupric chloride was much faster than the (competing) reaction with cuprous chloride, a result which complements the results of Wulfman's studies,[146,147] discussed earlier (section III.A.1). The detailed scheme which was suggested to account for the observed course of the reaction of ethyl diazoacetate with cupric chloride is shown in Scheme III.[260]

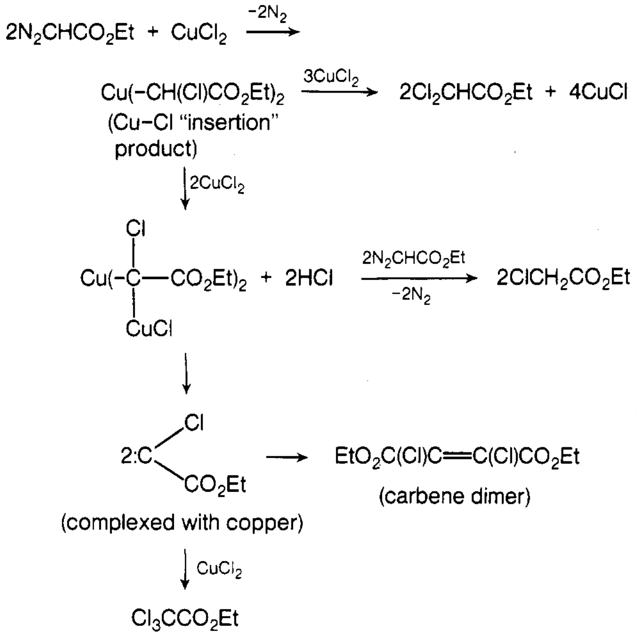


$$\underset{(10\ mmol)}{N_2CHCO_2Et} + \underset{(20\ mmol)}{CuCl_2} \xrightarrow{MeCN,\ 15°}$$

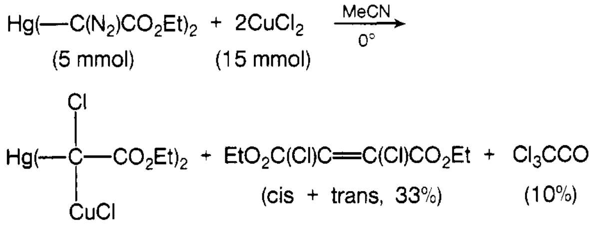
$$\underset{(8\%)}{ClCH_2CO_2Et} + \underset{(82\%)}{Cl_2CHCO_2Et} + \underset{(cis\ +\ trans,\ 6\%)}{EtO_2C\text{—}\overset{Cl}{C}=\overset{Cl}{C}\text{—}CO_2Et} + \underset{(trace)}{Cl_3CCO_2Et} + CuCl \quad (60)$$

Reactions of HgCl$_2$ and of CoCl$_2$ with ethyl diazoacetate at 80° were found to likewise afford mono-, di-, and trichloroacetate esters (the latter two only in trace quan-

SCHEME III

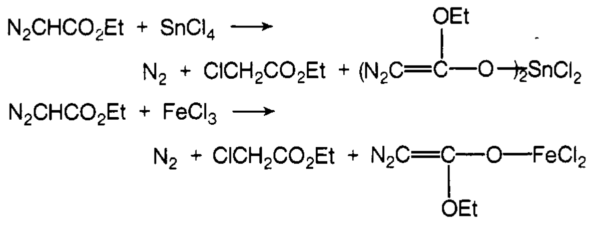


tities) along with solid organometallic complexes.[260] Interestingly, bis(diazoethoxycarbonylmethyl)mercury, $Hg(\text{-}C(N_2)CO_2Et)_2$, a popular precursor for "carbethoxycarbyne," [261-264] also reacts in a similar manner with cupric chloride[260] (eq 61).



$$\underset{(5\ \mathrm{mmol})}{\mathrm{Hg(\text{—}C(N_2)CO_2Et)_2}} + \underset{(15\ \mathrm{mmol})}{\mathrm{2CuCl_2}} \xrightarrow[0^\circ]{\mathrm{MeCN}} \mathrm{Hg(\text{—}\overset{Cl}{\underset{CuCl}{C}}\text{—}CO_2Et)_2} + \underset{(cis\ +\ trans,\ 33\%)}{\mathrm{EtO_2C(Cl)C{=}C(Cl)CO_2Et}} + \underset{(10\%)}{\mathrm{Cl_3CCO_2Et}} \quad (61)$$

In contrast to the foregoing, ferric chloride and tin(IV) chloride have been found to react with ethyl diazoacetate to afford ethyl chloroacetate plus metallic derivatives of the enol form of the diazo ester[265] (eq 63 and 62, respectively).



$$\mathrm{N_2CHCO_2Et + SnCl_4 \longrightarrow N_2 + ClCH_2CO_2Et + (N_2C{=}\overset{OEt}{C}\text{—}O\text{—})_{\frac{1}{2}}SnCl_2} \quad (62)$$

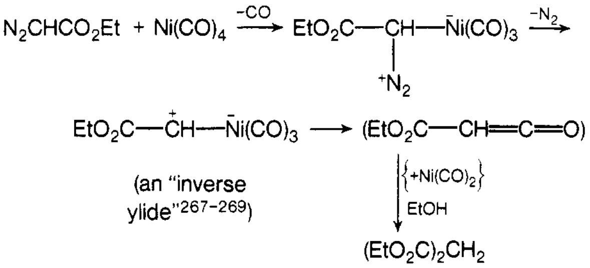
$$\mathrm{N_2CHCO_2Et + FeCl_3 \longrightarrow N_2 + ClCH_2CO_2Et + N_2C{=}\underset{OEt}{C}\text{—}O\text{—}FeCl_2} \quad (63)$$

An example of the reaction of ethyl diazoacetate with a transition metal carbonyl has been reported. Diethyl malonate is formed in low yield upon treatment of the diazo ester with $Ni(CO)_4$ at 55-60° in ethanol[266] (eq 64). A

$$\underset{(95\ \mathrm{mmol})}{\mathrm{N_2CHCO_2Et}} + \underset{(82\ \mathrm{mmol})}{\mathrm{Ni(CO)_4}} \xrightarrow[55\text{–}60^\circ]{\mathrm{EtOH\ (30\ ml)}} \underset{(8.5\%)}{\mathrm{H_2C(CO_2Et)_2}} \quad (64)$$

mechanism was proposed which does not involve the intermediacy of a carbene (eq 65).

There is a recent report of the reaction of ethyl diazoacetate with (π-allyl)nickel bromide, which is considered to proceed *via* formation of an intermediate carbethoxycarbene-nickel complex.[269a] Collapse of this complex with "insertion" of the carbene into a carbon-nickel bond

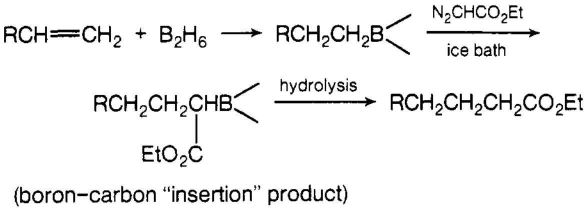


$$\mathrm{N_2CHCO_2Et + Ni(CO)_4 \xrightarrow{-CO} EtO_2C\text{—}\underset{^{+}N_2}{CH}\text{—}\bar{N}i(CO)_3 \xrightarrow{-N_2}}$$

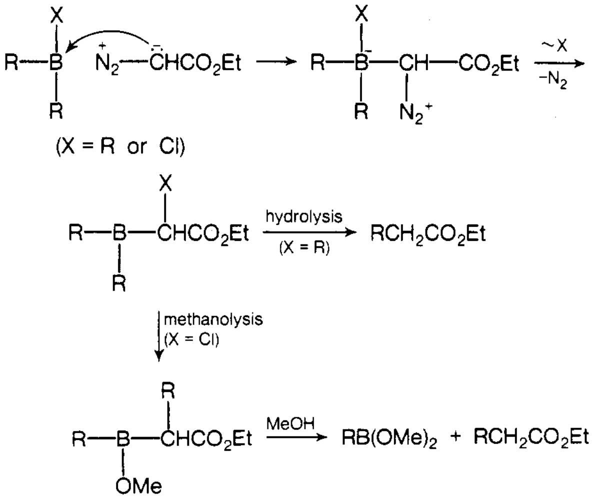
$$\underset{\text{(an "inverse ylide"}^{267-269})}{\mathrm{EtO_2C\text{—}\overset{+}{C}H\text{—}\bar{N}i(CO)_3}} \longrightarrow \mathrm{(EtO_2C\text{—}CH{=}C{=}O)} \xrightarrow[\mathrm{EtOH}]{\{+\mathrm{Ni(CO)_2}\}} \mathrm{(EtO_2C)_2CH_2} \quad (65)$$

was then proposed to account for the formation of the observed reaction products, ethyl *cis*- and *trans*-β-vinylacrylates).[269a]

Finally, we note in passing the reactions of ethyl diazoacetate with trialkylboranes which afford products which formally appear as products of $:CHCO_2Et$ "insertion" into boron-hydrogen and boron-carbon bonds. These comprise an important and synthetically useful class of reactions. Hydroboration of an olefin followed by reaction of the resulting trialkylborane affords (after hydrolysis) the homologated ester in *ca.* 40-80% yield[270-272] (eq 66). The corresponding reactions with dialkylchloroboranes have been found to occur at temperatures as low as −78°.[273] This approach offers the further advantage of accomodating olefins containing bulky alkyl substituents (which drastically reduce yields in the corresponding ethyl diazoacetate-trialkylborane reaction).[270-272] In both cases, it is unlikely that carbenes are involved. Instead, a mechanism has been proposed[273] which involves attack on the borane by undissociated ethyl diazoacetate (eq 67).



$$\mathrm{RCH{=}CH_2 + B_2H_6 \longrightarrow RCH_2CH_2B\!\!<\ \xrightarrow[\text{ice bath}]{N_2CHCO_2Et}\ RCH_2CH_2\underset{EtO_2C}{CH}B\!\!<\ \xrightarrow{\text{hydrolysis}} RCH_2CH_2CH_2CO_2Et} \quad (66)$$



$$\underset{(X\,=\,R\ \text{or}\ Cl)}{\mathrm{R\text{—}\overset{X}{\underset{R}{B}}\ \overset{+}{N_2}\text{—}\bar{C}HCO_2Et}} \longrightarrow \mathrm{R\text{—}\overset{X}{\underset{R}{\bar{B}}}\text{—}\underset{N_2^{+}}{CH}\text{—}CO_2Et \xrightarrow[-N_2]{\sim X}}$$

$$\mathrm{R\text{—}\overset{X}{\underset{R}{B}}\text{—}CHCO_2Et \xrightarrow[(X\,=\,R)]{\text{hydrolysis}} RCH_2CO_2Et}$$

$$\mathrm{R\text{—}\underset{OMe}{B}\text{—}\overset{R}{C}HCO_2Et \xrightarrow{MeOH} RB(OMe)_2 + RCH_2CO_2Et} \quad (67)$$

V. Carbalkoxycarbene-Promoted HX Eliminations

Of all the known reactions of carbalkoxycarbenes, only their ability to promote β-eliminations in systems such as aliphatic tertiary amines, ethers, sulfides, and halides (among others) to afford olefins in yields as high as 50-70% has gone all but unheralded in recent carbene chemistry reviews. Often, these elimination reactions have been discovered accidentally when investigators were attempting to observe C-X "insertion" reactions.

TABLE IV. Carbalkoxycarbene-Promoted HX Eliminations

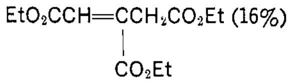
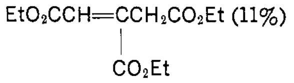
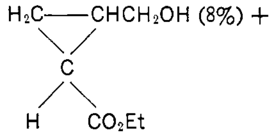
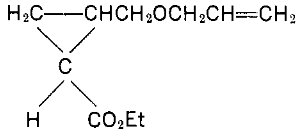
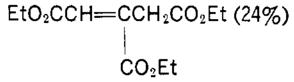
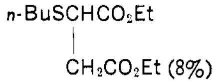
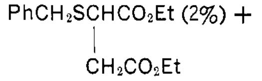
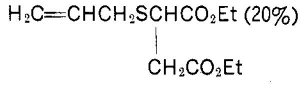
Diazo ester[a]	Method of decompn of diazo ester	Substrate	XCH$_2$CO$_2$R or XCH(CO$_2$R)$_2$ produced[b]	Other products[b]	Ref
			Reactions of Diazo Esters with (a) Alcohols		
A	Δ, CuCl$_2$	*n*-BuOH	n-BuOCH$_2$CO$_2$Et (15%) + O(CH$_2$CO$_2$Et)$_2$ (7%)	Products resulting from further reaction of n-BuOCH$_2$CO$_2$Et with :CHCO$_2$Et (30%) + diethyl maleate and fumarate (23%) + $\mathrm{EtO_2CCH{=}\underset{CO_2Et}{\underset{\vert}{C}}CH_2CO_2Et}$ (16%)	180
A	Δ, CuCl$_2$	PhCH$_2$OH	PhCH$_2$OCH$_2$CO$_2$Et (49%) + O(CH$_2$CO$_2$Et)$_2$ (5%)	Products resulting from further reaction of PhCH$_2$OCH$_2$CO$_2$Et with :CHCO$_2$Et (13%) + diethyl maleate and fumarate (15%) + $\mathrm{EtO_2CCH{=}\underset{CO_2Et}{\underset{\vert}{C}}CH_2CO_2Et}$ (11%)	180
A	Δ, CuCl$_2$	H$_2$C=CHCH$_2$OH	H$_2$C=CHCH$_2$OCH$_2$CO$_2$Et (17%) + O(CH$_2$CO$_2$Et)$_2$ (9%)	  (5%) + diethyl maleate and fumarate (31%) + $\mathrm{EtO_2CCH{=}\underset{CO_2Et}{\underset{\vert}{C}}CH_2CO_2Et}$ (24%)	180
			(b) Thiols		
A	Δ, CuCl	*n*-BuSH	n-BuSCH$_2$CO$_2$Et (85%) + S(CH$_2$CO$_2$Et)$_2$ (8%)	n-Bu$\mathrm{S\underset{CH_2CO_2Et}{\underset{\vert}{C}}HCO_2Et}$ (8%)	180
A	Δ, CuCl	PhCH$_2$SH	PhCH$_2$SCH$_2$CO$_2$Et (86%) + S(CH$_2$CO$_2$Et) (7%)	$\mathrm{PhCH_2S\underset{CH_2CO_2Et}{\underset{\vert}{C}}HCO_2Et}$ (2%) + PhCH=CHCO$_2$Et (1%)	180
A	Δ, CuCl	H$_2$C=CHCH$_2$SH	H$_2$C=CHCH$_2$SCH$_2$CO$_2$Et (63%) + S(CH$_2$CO$_2$Et)$_2$ (7%)	$\mathrm{H_2C{=}CHCH_2S\underset{CH_2CO_2Et}{\underset{\vert}{C}}HCO_2Et}$ (20%)	180
			(c) Aliphatic Ethers		
A	*hν*	Et$_2$O	EtOCH$_2$CO$_2$Et	H$_2$C=CH$_2$ (presumed)	[c]
B	*hν*	Et$_2$O	EtOCH$_2$CO$_2$Me	EtOCH(CH$_3$)CH$_2$CO$_2$Me + EtO(CH$_2$)$_3$CO$_2$Me	279
C	*hν*	Equimolar Et$_2$O + Me$_2$S	Not reported	$\mathrm{Me_2\overset{+}{S}{-}\overset{-}{C}(CO_2Me)_2}$ (73%) + {H$_2$C=CH$_2$ + C–H insertion products} (12%)	225
B	*hν*	*n*-Bu$_2$O	n-BuOCH$_2$CO$_2$Me (52%)	MeO$_2$CCH$_2$(C$_4$H$_8$)O-n-Bu (mixture of isomers)	279
A	Δ	*n*-Bu$_2$O	n-BuOCH$_2$CO$_2$Et (9%)	EtO$_2$CCH$_2$(C$_4$H$_8$)O-n-Bu (mixture of isomers, 24%) + MeCH$_2$C=CH$_2$ (6%)	276, 280
A	Δ	n-C$_7$H$_{15}$OMe	MeOCH$_2$CO$_2$Et (16%) + n-C$_7$H$_{15}$OCH$_2$CO$_2$Et (27%)	Not reported	276
A	*hν*	*i*-BuOMe	i-BuOCH$_2$CO$_2$Et (9–10%) + MeOCH$_2$CO$_2$Et (0.1–0.9%)	Mixture of C–H insertion products (9–18%)	274
A	*hν*	*sec*-BuOMe	*sec*-BuOCH$_2$CO$_2$Et (1.8–5.0%) + MeOCH$_2$CO$_2$Et (6.1–9.0%)	Mixture of C–H insertion products (8.5–20%) + mixture of butenes (8%; product ratio 1-:*trans*-2-:*cis*-2-butene = 52:33:15)	274

TABLE IV (continued)

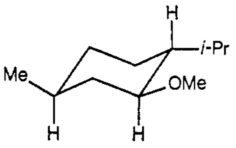
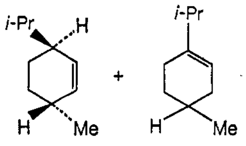
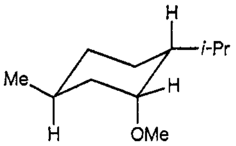
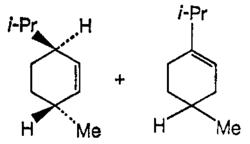
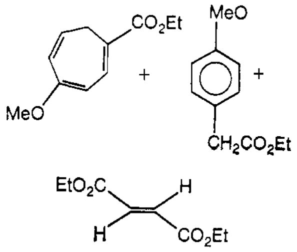
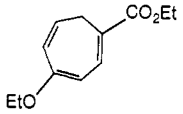
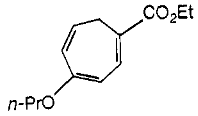
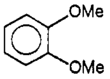
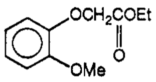
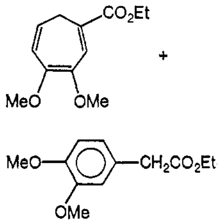
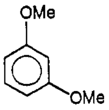
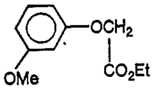
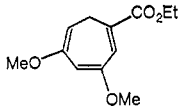
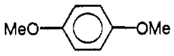
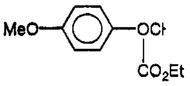
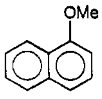
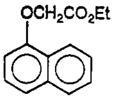
Diazo ester[a]	Method of decompn of diazo ester	Substrate	XCH_2CO_2R or $XCH(CO_2R)_2$ produced[b]	Other products[b]	Ref
A	hν		Not reported	 (36%) (64%)	274
A	hν		Not reported	 (17%) (64%)	274
			(d) Alkyl Aryl Ethers		
A	Δ	PhOMe	$PhOCH_2CO_2Et$ (2.5%)		276
A	Δ	PhOEt	$PhOCH_2CO_2Et$		227
A	Δ	PhO-*n*-Pr	$PhOCH_2CO_2Et$		276
A	Δ				276
A	Δ				276
A	Δ			Not reported	276
A	Δ			($C_{13}H_{12}O_3$) (unidentified, obtained after saponification of reaction product)	276
			(e) Dialkyl Sulfides		
A	hν	Et_2S	$EtSCH_2CO_2Et$ (7%)	Olefin not detected	219
A	hν	*sec*-BuSMe	*sec*-$BuSCH_2CO_2Et$ (5.7–8.7%) + $MeSCH_2CO_2Et$ (27.4–48%)	Mixture of C-H insertion products (0–1.8%) + mixture of butenes (49%; product ratio 1-:*trans*-2-:*cis*-2-butene = 52:31:17)	274
A	hν	*i*-BuSMe	*i*-$BuSCH_2CO_2Et$ (5.3–33%) + $MeSCH_2CO_2Et$ (3.2–11.0%)	Mixture of C-H insertion products (4.0%)	274

TABLE IV (continued)

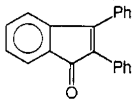
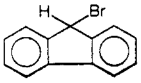
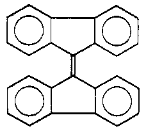
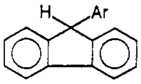
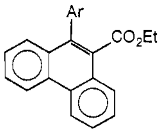
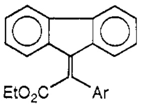
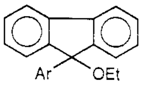
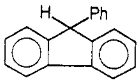
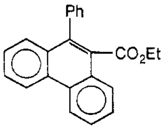
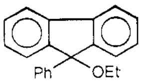
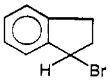
Diazo ester[a]	Method of decompn of diazo ester	Substrate	XCH_2CO_2R or $XCH(CO_2R)_2$ produced[b]	Other products[b]	Ref
A	$h\nu$	$t\text{-}Bu_2S$	$t\text{-}BuSCH_2CO_2Et$ (23%)	Olefin not detected	219
C	$h\nu$	$t\text{-}Bu_2S$	$t\text{-}BuSCH(CO_2Me)_2$	$H_2C(CO_2Me)_2$	*f*
			(f) Dialkyl Disulfides		
C	$h\nu$	MeSSMe	$MeSCH(CO_2Me)_2$ (44%)	$(MeS)_2C(CO_2Me)_2$ (2.2%)	104
C	$h\nu$ ($Ph_2C{=}O$ sens)	MeSSMe	$MeSCH(CO_2Me)_2$ (32%)	$(MeS)_2C(CO_2Me)_2$ (14%)	104
C	$h\nu$	EtSSEt	$EtSCH(CO_2Me)_2$ (41%)	$(EtS)_2C(CO_2Me)_2$ (trace)	104
C	$h\nu$ ($Ph_2C{=}O$ sens)	EtSSEt	$EtSCH(CO_2Me)_2$ (61%)	$(EtS)_2C(CO_2Me)_2$ (trace)	104
C	$h\nu$	$t\text{-}BuSS\text{-}t\text{-}Bu$	$t\text{-}BuSCH(CO_2Me)_2$ (6.2%)	$(t\text{-}BuS)_2C(CO_2Me)_2$ (13.2%) + $t\text{-}BuSSCH(CO_2Me)_2$ (3.3%)	104
C	$h\nu$ ($Ph_2C{=}O$ sens)	$t\text{-}BuSS\text{-}t\text{-}Bu$	$t\text{-}BuSCH(CO_2Me)_2$ (5%)	$(t\text{-}BuS)_2C(CO_2Me)_2$	104
			(g) Polyhalomethanes and Haloarylmethanes		
B	$h\nu$	$CHCl_3$	$ClCH_2CO_2Me$ (42.5%)	$Cl_2CHCHClCO_2Me$ (10%)	194
B	$h\nu$	$CBrCl_3$, $CHBr_3$, CBr_2Cl_2, CH_2Cl_2, CH_2ClBr, $CHCl_2Br$, $CHClBr_2$	X_2CHCO_2Me	Products of the types $X_3C\text{-}CX_3$, $X_2C{=}CYCO_2Me$, HBr, and various C-H insertion products	130, 194–196
A	Δ, $CuSO_4$	Ph_2CHBr	$BrCH_2CO_2Et$ (17.5%)	$PhCH(Br)CH(Ph)CO_2Et$ (32%)	205
A	Δ, $CuSO_4$ (100–110°)	Ph_3CBr	$BrCH_2CO_2Et$ (30.5%)	$Ph_2C{=}C(Ph)CO_2Et$ (31%)	205
A	Δ, $CuSO_4$ (160–165°)	Ph_3CBr	$BrCH_2CO_2Et$ (40.5%)	$Ph_2C{=}C(Et)Ph$ (39%) + CO_2 +  (trace)	205
A	Δ, $CuSO_4$		$BrCH_2CO_2Et$		206
A	Δ, $CuSO_4$	 (Ar = *p*-tolyl)	$BrCH_2CO_2Et$	 + (14%)  + (11%) 	206
A	Δ, $CuSO_4$		$BrCH_2CO_2Et$ (9.5%)	 + (6.5%) 	206
A	$h\nu$		$BrCH_2CO_2Et$	Unidentified	67

TABLE IV (continued)

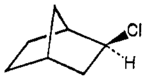
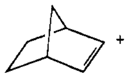
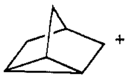
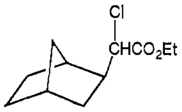
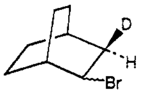
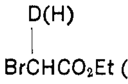
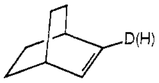
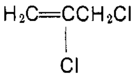
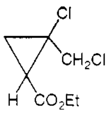
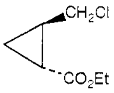
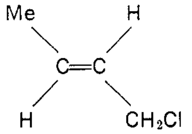
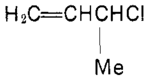
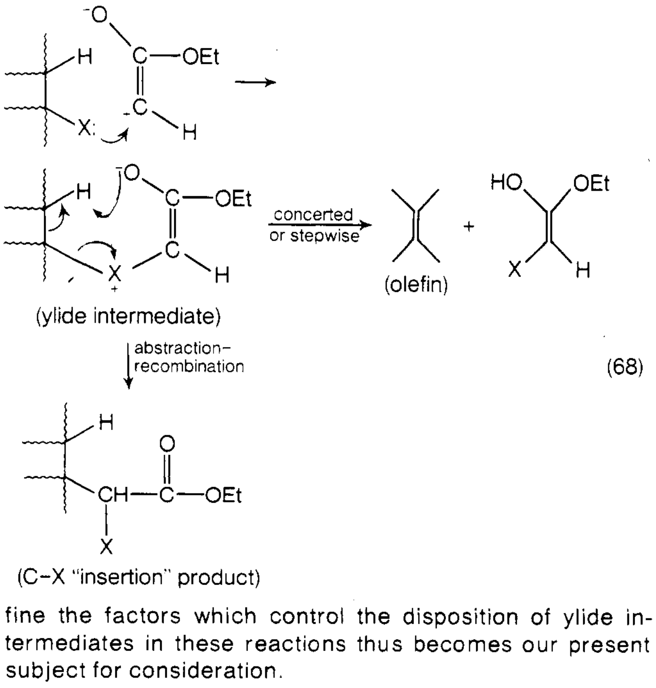
Diazo ester[a]	Method of decompn of diazo ester	Substrate	XCH_2CO_2R or $XCH(CO_2R)_2$ produced[b]	Other products[b]	Ref
			(h) Alkyl Halides		
A	*hν*	EtCl	$ClCH_2CO_2Et$ (30.8%)	C–H insertion products	67
A	*hν*	EtBr	$BrCH_2CO_2Et$ (93%)	$H_2C{=}CH_2$ + $EtCHBrCO_2Et$	203
A	*hν*	EtBr	$BrCHCO_2Et$ (41.2%)	$H_2C{=}CH_2$ + $EtCHBrCO_2Et$ + $MeCHBrCH_2CO_2Et$ (~5%) + $BrCH_2CH_2CH_2CO_2Et$	67
A	*hν*	D_3CCH_2Br	$BrCDHCO_2Et$ (41.2%) (no $BrCH_2CO_2Et$)	$D_2C{=}CH_2$ (no $HDC{=}CD_2$) + C–H insertion products	67, 201
A	*hν*	EtI	ICH_2CO_2Et (32.5%)	C–H insertion products	67
A	*hν*	*i*-PrCl	$ClCH_2CO_2Et$ (36.7%)	C–H insertion products	67
A	*hν*	*i*-PrBr	$BrCH_2CO_2Et$ (38.3%)	C–H insertion products	67
A	*hν*	*i*-PrI	ICH_2CO_2Et (40.6%)	C–H insertion products	67
A	*hν*	*sec*-BuCl	$ClCH_2CO_2Et$ (32.6%)	C–H insertion products	67
A	*hν*	*sec*-BuCl	Not reported	Mixture of butenes (31%; product ratio 1-:*trans*-2-:*cis*-2-butene = 57:26:17)	274
A	*hν*	*sec*-BuBr	$BrCH_2CO_2Et$ (37.1%)	C–H insertion products	67
A	*hν*	*sec*-BuBr	Not reported	Mixture of butenes (11%; product ratio 1-:*trans*-2-:*cis*-2-butene = 54:30:16)	274
A	*hν*	*sec*-BuI	ICH_2CO_2Et (37.3%)	C–H insertion products	67
A	*hν*	*sec*-BuI	Not reported	Mixture of butenes (45%; product ratio 1-:*trans*-2-:*cis*-2-butene = 57:28:15)	274
A	*hν*	*t*-BuCl	$ClCH_2CO_2Et$ (30.6%)	C–H insertion products	67
A	*hν*	*t*-BuCl	$ClCH_2CO_2Et$ (30%)	*t*-$BuCH(Cl)CO_2Et$ (7.5%)	203
A	*hν*	*t*-BuBr	$BrCH_2CO_2Et$ (38.6%)	C–H insertion products	67
A	*hν*	*t*-BuBr	$BrCH_2CO_2Et$ (35.5%)	$Me_2C{=}CH_2$	203
A	Δ, $CuSO_4$	*t*-BuBr	$BrCH_2CO_2Et$ (7.5%)	Diethyl fumarate (20%)	204
A	*hν*	*t*-BuI	ICH_2CO_2Et (33.9%)	C–H insertion products	67
A	*hν*		$ClCH_2CO_2Et$ (37.8%)	 (26.1%) +  (10.5%) +  (<1%) + diethyl maleate and fumarate (4%)	*d*
A	*hν*	 (Cis : trans = ~80 : 20)	 $\overset{\text{D(H)}}{\text{BrCHCO}_2\text{Et}}$ (d_0:d_1 = 33:67)	 d_0 : d_1 = 67 : 33, (indicative of ~80% stereoselective cis elimination)	67, 201
			(i) Allylic Halides		
A	Δ, $CuSO_4$	 $\underset{\text{Cl}}{\text{H}_2\text{C}{=}\text{C}}\text{CH}_2\text{Cl}$	$ClCH_2CO_2Et$ (2%)	 (cis 17.5%, trans 8.5%) + $H_2C{=}CClCH_2CHClCO_2Et$ + diethyl fumarate (8%)	211
A	Δ, $CuCl_2$	$H_2C{=}CHCH_2Cl$	$ClCH_2CO_2Et$ (8%)	 (4.4%) + $H_2C{=}CHCH_2CHClCO_2Et$ (6%) + diethyl fumarate (35%)	209

TABLE IV (continued)

Diazo ester[a]	Method of decompn of diazo ester	Substrate	XCH$_2$(COR) or XCH(CO$_2$R)$_2$ produced[b]	Other products[b]	Ref
A	Δ, Cu		ClCH$_2$CO$_2$Et (19%)	MeCH=CHCH$_2$CH(Cl)CO$_2$Et (36%) + H$_2$C=CHCH(Me)-CH(Cl)CO$_2$Et (25%)	213
A	Δ, Cu	 H$_2$C=CHCH(Me)Cl	ClCH$_2$CO$_2$Et (15%)	MeCH=CHCH$_2$CH(Cl)CO$_2$Et (40%) + H$_2$C=CHCH(Me)-CH(Cl)CO$_2$Et (10%)	213
A	Δ, Cu	H$_2$C=CHCH$_2$Br	BrCH$_2$CO$_2$Et	H$_2$C=CHCH$_2$CH(Br)CO$_2$Et (83% crude, 68% pure)	209, 210
A	Δ, Cu	H$_2$C=CHCH$_2$I	ICH$_2$CO$_2$Et (7.5%)	H$_2$C=CHCH$_2$CH(I)CO$_2$Et (70% crude, 47% pure)	204
			(j) Tertiary Aliphatic Amines		
C	hν	Equimolar Et$_3$N + Me$_2$S	Et$_2$NCH(CO$_2$Me)$_2$ (trace)	Me$_2\overset{+}{S}$—$\overset{-}{C}$(CO$_2$Me)$_2$ (25%) + H$_2$C(CO$_2$Me)$_2$	225
A	hν	Et$_3$N	Et$_2$NCH$_2$CO$_2$Et	Et$_2$NCH(Me)CH$_2$CO$_2$Et (45%) + Et$_2$N(CH$_2$)$_3$CO$_2$Et	239
			(k) Miscellaneous		
A	hν	*sec*-BuOAc	Not reported	Mixture of butenes (39%; product ratio 1-:*trans*-2-:*cis*-2-butene = 53:34:13)	274
A	hν	RCH$_2$CH(Br)CO$_2$Et (R = Me or Ph)	BrCH$_2$CO$_2$Et	RCH=CHCO$_2$Et	e

[a] A = N$_2$CHCO$_2$Et; B = N$_2$CHCO$_2$Me; C = N$_2$C(CO$_2$Me)$_2$. [b] In cases where yields could be quoted, they are based on the amount of diazo ester consumed in the reaction. [c] J. Warkentin E. Singleton, and J. F. Edgar, *Can. J. Chem.*, **43**, 3456 (1965). [d] A. P. Marchand and W. R. Weimar, Jr., unpublished results. [e] A. P. Marchand and T. Y.-C. Lin, unpublished results. [f] See footnote 4 in ref 226.

The unravelling of the details of the mechanisms of these elimination reactions is especially tantalizing as these reactions generally appear to share one feature in common with C-X "insertion" reactions; *i.e.*, in all cases, initial attack of a carbalkoxycarbene at a lone-pair atom (*e.g.*, nitrogen, oxygen, sulfur, or halogen) can occur, offering a choice between abstraction–recombination (to form the "insertion" product) or some other pathway (resulting in the formation of α-substituted acetic esters and, occasionally, olefinic products; see eq 68). To define the factors which control the disposition of ylide intermediates in these reactions thus becomes our present subject for consideration.

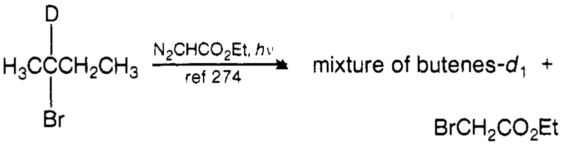


(68)

The scope of the carbalkoxycarbene-promoted HX elimination reaction is defined in Table IV, which represents the results of an exhaustive search of the literature for examples of this reaction type. In cases where the yields of the various reaction products were reported, recalculation of the literature values has been performed (whenever necessary) to ensure that the yields reported in Table IV are uniformly based on the number of moles of diazo ester *consumed* in the reaction. For the purpose of constructing this table, we have considered as an "HX elimination reaction" one in which the carbalkoxycarbene reacts with the substrate to cleave a C-X bond to produce observable amounts of XCH$_2$CO$_2$R (or XCH(CO$_2$R)$_2$). This definition permits us to consider substrates such as methyl aryl ethers and polyhalomethanes which do react with carbalkoxycarbenes to afford products of the type XCH$_2$CO$_2$R or XCH(CO$_2$R)$_2$ but are so constructed that they cannot afford olefins via β-elimination.

Let us consider first those reactions which can afford olefins *via* β-elimination. Photolytic decomposition of ethyl diazoacetate (200-W medium-pressure mercury lamp, Pyrex shield, 8.5 ± 0.5°) in the presence of alkyl halides has been found to afford olefins accompanied by α-halo esters in yields varying from *ca.* 30 to 40%[67] (see Table IV). In all of the reactions studied, olefin formation occurred to the extent of almost complete exclusion of products resulting from carbon–halogen "insertion" by the carbene. No clear trend emerges from inspection of the data in Table IV to correlate product yields with the type of alkyl halide employed (RX, where R = Cl, Br, or I) or its structure (primary, secondary, or tertiary alkyl halide). Indeed, the narrow range of yields of α-halo esters observed over the wide variation in structures of the alkyl halide substrates would seem to suggest that the critical factor in obtaining olefinic products is probably the availability of the carbene for reaction with the substrate (in competition with other processes, most notably self-condensation reactions involving the carbene and/or its diazo precursor). Nevertheless, when competition reactions are run among alkyl halides of the same structural type (*i.e.*, RX, where R is constant and X is varied among Cl, Br, and I), a clear order of reactivity emerges; the reactivity ratio X = Cl:Br:I = 1.0:1.5:2.2 has been observed for R = *t*-Bu.[67,201] Significantly, this order of reactivity (I > Br > Cl) is just the *opposite* of what Wilt has reported for reactions of :$CHCO_2Et$ ($h\nu$) with polyhalomethanes containing different halogen atoms in the same molecule.[195]

It has been demonstrated that open-chain alkyl halides possessing β-hydrogens preferentially afford olefins rather than carbon–halogen "insertion" products.[201,274] That these reactions are indeed β-eliminations has been demonstrated essentially simultaneously by two different groups through the use of appropriate specifically deuterated substrate systems (eq 69 and 70).



$$H_3C\overset{D}{\underset{Br}{C}}CH_2CH_3 \xrightarrow[\text{ref 274}]{N_2CHCO_2Et,\,h\nu} \text{mixture of butenes-}d_1 + BrCH_2CO_2Et \quad (69)$$

(no butenes-d_0 or $BrCHDCO_2Et$ formed)

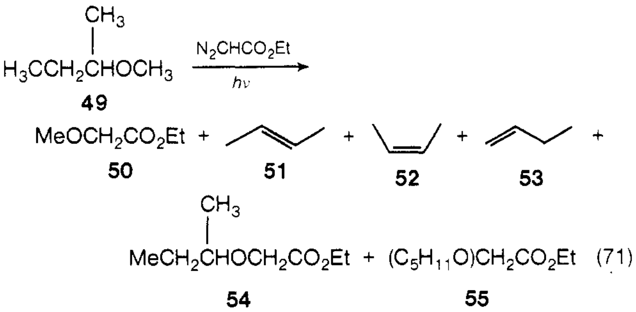
$$D_3CCH_2Br \xrightarrow[\text{ref 201}]{N_2CHCO_2Et,\,h\nu} D_2C{=}CH_2 + BrCHDCO_2Et \quad (70)$$

(no $D_2C{=}CDH$ or $BrCH_2CO_2Et$ formed)

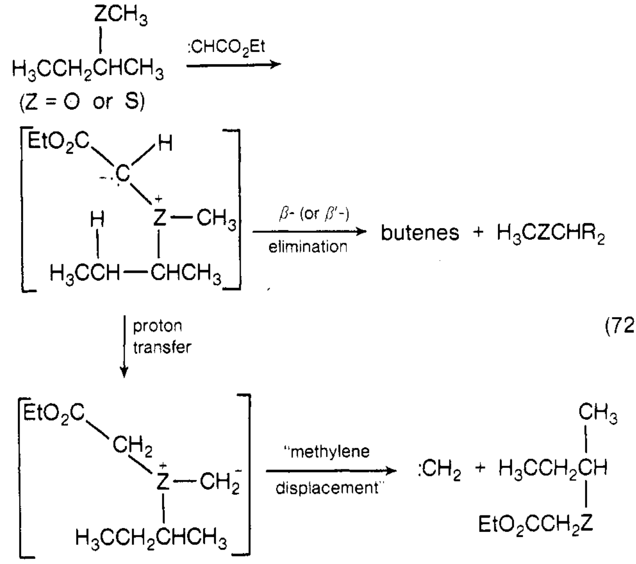
The results of mechanistic studies involving investigation of the carbethoxycarbene-promoted HX elimination reaction with alkyl halides and its stereochemistry appear to be consistent with expectations based on the postulated intermediacy of a halonium ylide.[201] This conclusion is also supported by the observation that reactions of :$CHCO_2Et$ ($h\nu$) with a variety of *sec*-butyl halides, with *sec*-butyl methyl ether and thioether, and with *sec*-butyl acetate afford mixtures of 1-butene, *trans*-2-butene, and *cis*-2-butene in a remarkably constant product ratio (Table IV). This observation argues strongly against an E2 elimination mechanism, the outcome of which is known to be sensitive to the steric requirements of the leaving group.[275]

It also appears that direct photolysis of ethyl diazoacetate affords a carbene which reacts in a singlet electronic configuration with alkyl halides. This is evidenced by the fact that the corresponding benzophenone photosensitized reaction of ethyl diazoacetate with ethyl bromide has been found to result in a severely depressed yield of ethyl bromoacetate (16.6%) compared with that obtained from direct photolytic reaction of ethyl diazoacetate with ethyl bromide (*ca.* 40%).[67]

The reactions of carbethoxycarbene with ethers and thioethers have also been extensively investigated by Freeman.[274] For example, the reaction of :$CHCO_2Et$ ($h\nu$) with *sec*-butyl methyl ether (**49**) affords elimination products (**50–53**), a "methylene displacement" product (**54**), and carbon–hydrogen insertion products (**55**) (eq 71). The course of reactions of this type has been accounted for in terms of subsequent fragmentation of an intermediate ylide (eq 72). Frequently (but not always), methylene displacement has been found to predominate over β-elimination in reactions of carbalkoxycarbenes with alkyl methyl ethers (in cases where the alkyl side chain possesses a β-hydrogen atom capable of undergoing elimination).[274,276] The fate of the methylene (:CH_2) displaced in this reaction has been accounted for *via* identification of small amounts of ethylene among the gases evolved in reactions of carbethoxycarbene with alkyl methyl ethers and thioethers.[274] This observation is particularly significant since *aryl* methyl ethers are known to react with carbethoxycarbene to afford ethyl aryloxyacetates,[276] although an accounting for the fate of the ether methyl group has never before appeared.



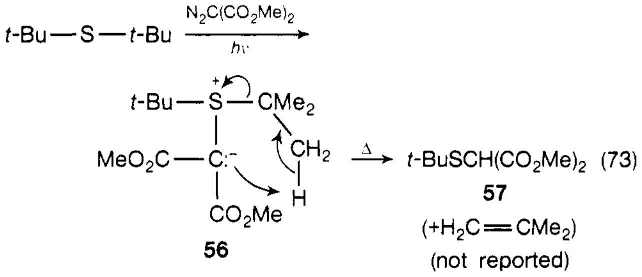
(71)



(72)

The stereochemistries of :$CHCO_2Et$ ($h\nu$)-promoted HX eliminations have been studied for reactions of the carbene with alkyl halides[201] and with alkyl methyl ethers[274] (Table IV). The results in both cases indicate that the elimination is not stereospecific (although highly stereoselective) cis, and each reaction probably proceeds *via* stepwise breakdown of its corresponding ylide intermediate. Particularly significant is the observation that the carbene-promoted elimination of HBr (and DBr) from 1-deuterio-2-bromobicyclo[2.2.2]octane proceeds stereoselectively (*ca.* 80%) cis, whereas the corresponding E2 elimination in that system (using KO-*t*-Bu in dry *t*-BuOH as the catalyst–solvent system) is a stereoselective (*ca.* 76%) trans elimination.[201]

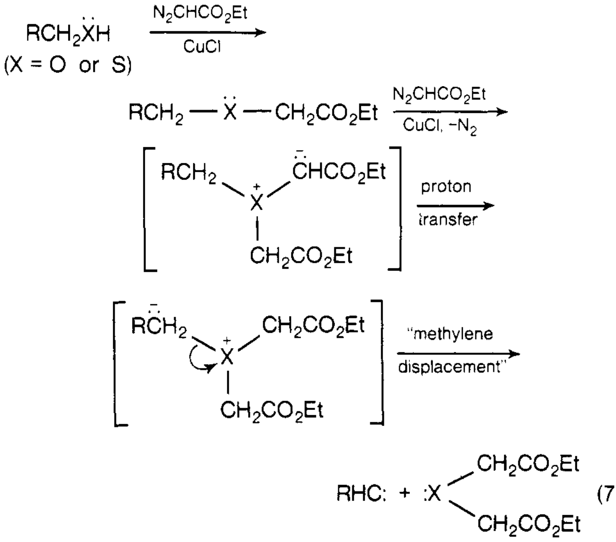
Evidence has recently been brought to bear on the intermediacy of sulfonium ylides in carbalkoxycarbene-promoted HX elimination reactions with dialkyl sulfides.[226,238] The isolation of stable dialkylsulfonium biscarbomethoxymethylides and their subsequent rearrangement to carbon–sulfur "insertion" products have already been discussed (section IV.D.1). In the present connection, it is worthwhile to note that under vapor phase chromatographic conditions, di-*tert*-butylsulfonium biscarbomethoxymethylide (**56**) has been reported to decompose to form several products, among which dimethyl malonate and *tert*-butylmercaptomalonate (**57**) have been found.[226,238] Compounds **57** can result from a thermally induced β-elimination reaction on the ylide intermediate (**56**) as shown in eq 73. The formation of dimethyl malonate in this reaction was not rationalized mechanistically.[226,238] Other examples of RSH eliminations upon



(73)

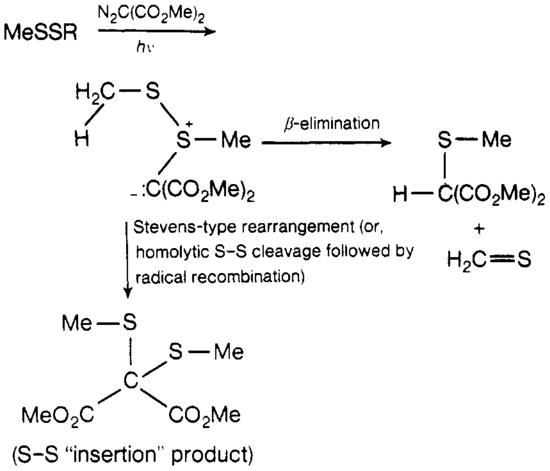
pyrolysis of stable sulfonium ylides of the type $R_2CHCR'_2SMeC(CO_2Me)_2$ (which afford olefins and dimethyl alkylthiomalonates) have been reported recently.[104]

The "methylene displacement" reaction discussed earlier in connection with reactions of carbethoxycarbene with ethers and thioethers[274] has also been observed for the corresponding reactions of carbethoxycarbenoid with alcohols and mercaptans.[180] For example, when 1:1 molar ratios of alcohol or thiol and ethyl diazoacetate were heated at 80–90° in the presence of a catalytic amount of cuprous chloride, a number of products were observed, among which were compounds of the type $X(CH_2CO_2Et)_2$ (where X = oxygen or sulfur, respectively; *cf.* discussion in section IV.D.2). The formation of these products can be envisioned as "methylene displacement" reactions which result from attack of a second mole of carbethoxycarbenoid on the initially formed X-H "insertion" product as indicated in eq 74. As envisioned in this equation, such "methylene displacement" reactions are actually α-elimination reactions, (*i.e.*, loss of H and X occur from the *same* carbon atom). The displaced methylene (RHC:) is then trapped by another mole of ethyl diazoacetate, affording products of the type $RCH{=}CHCO_2Et$.

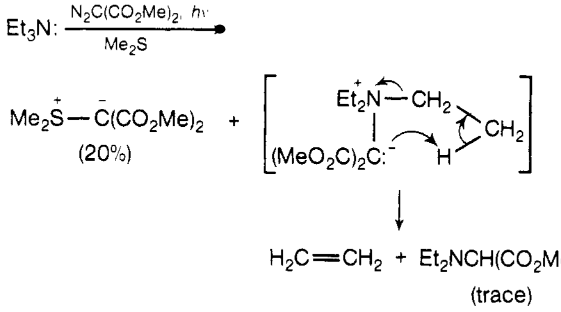


(74)

Elimination products have also been observed in photolytic reactions of dimethyl diazomalonate with dialkyl disulfides[104] and with trialkylamines.[225] Thus, the reaction of $:C(CO_2Me)$ ($h\nu$) with MeSSR afforded $MeSCH(CO_2Me)_2$ and $(MeS)_2C(CO_2Me)_2$ *via* an ylide intermediate[104] (eq 75). A similar elimination reaction occurs between $:C(CO_2Me)_2$ ($h\nu$) and triethylamine (eq 76).[225]

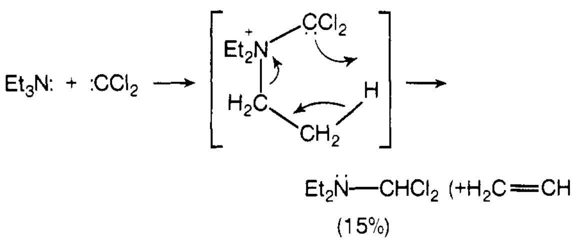


(75)

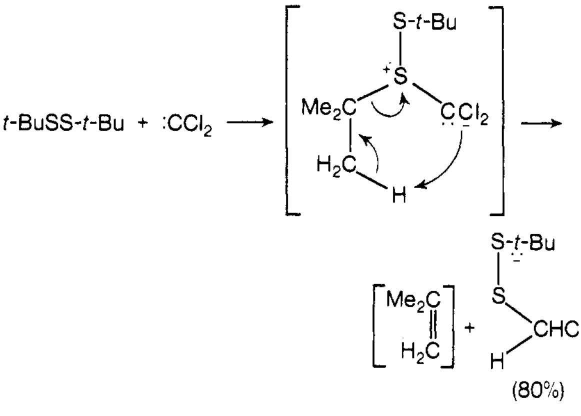


(76)

In concluding, it should be mentioned that a number of examples are known where carbenes other than carbalkoxycarbenes have been found to promote HX elimination reactions. For example, $:CCl_2$ (Δ) reacts with triethylamine to form diethyldichloromethylamine[277] and with di-*tert*-butyl disulfide to afford *tert*-butyl dichloromethyl disulfide[278] (eq 77 and eq 78, respectively). Also, photolytic decomposition of diazomethane in the presence of diethyl ether[279] or di-*n*-butyl ether[280] lead to olefin formation (ethylene and 1-butene, respectively). Again, a mechanism involving intermediate ylide formation seems likely for these reactions of methylene with dialkyl ethers.



(77)

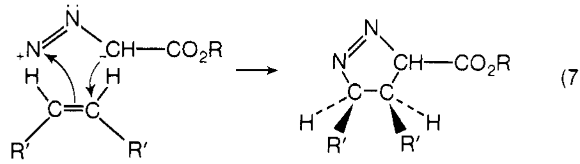


(78)

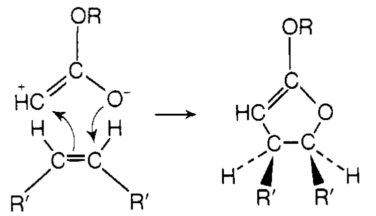
VI. Miscellaneous Reactions of Carbalkoxycarbenes

A. 1,3-Dipolar Cycloadditions

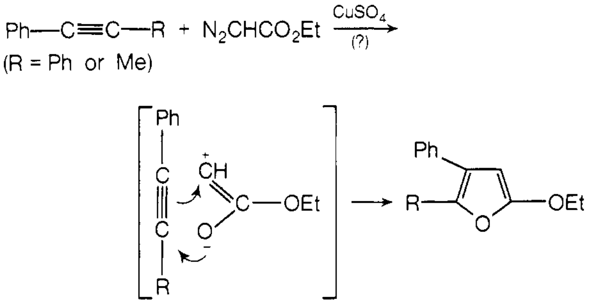
Diazo esters commonly afford products arising *via* 1,3-dipolar cycloaddition in their reactions with alkenes and alkynes (eq 79). This same kind of behavior is possible for the carbalkoxycarbenes derived from the diazo


(79)

esters, although such behavior is much less frequently encountered than for the corresponding reactions of the diazo esters themselves (eq 80). In this section, we shall be concerned exclusively with cycloaddition reactions of the carbene itself (and not those involving its diazo precursor).

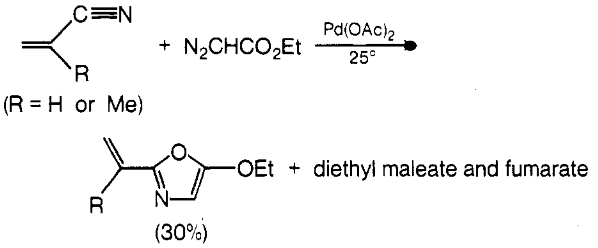

(80)

Early reports by a Russian group claimed to have observed 1,3-dipolar cycloaddition of carbethoxycarbenoid to tolane,[281] to 1-phenylpropyne,[282] and to other alkynes[283] (eq 81). However, careful reinvestigation of these reactions has revealed that the furan derivatives in each case were formed by subsequent copper sulfate catalyzed isomerization of the expected (and, indeed, initially formed) cyclopropene.[284-292] Thus, it appears that furan formation does *not* occur *via* 1,3-dipolar cycloaddition of carbalkoxycarbenoid to these alkynes.[293,294]


(81)

There are very few bona fide examples of 1,3-dipolar cycloadditions of carbalkoxycarbenes (or carbenoids) to unsaturated systems. One of these, the reaction of carbethoxycarbenoid with benzonitrile,[163] has been discussed previously (section III.A.3). In addition, oxazole formation has been reported for the reaction of :CHCO$_2$Et (Δ, 145–150°) with benzonitrile and with phenylacetonitrile, and for the reaction of carbethoxycarbenoid with acetonitrile.[163,295] A related carbalkoxycarbene, F$_3$CCOC(CO$_2$Et)=, has been found to display an unusual capacity for entering into 1,3-dipolar cycloaddition reactions with a variety of substrates.[296,297] Some illustrative examples are shown in Scheme IV. Interestingly, the carbene derived from photolytic decomposition of ethyl trifluoroacetyldiazoacetate shows no tendency to undergo the Wolff rearrangement in contrast with simple carbalkoxycarbenes (:CHCO$_2$R and :C(CO$_2$R)$_2$; see section VI.B), which may account for its unusual ability to promote 1,3-dipolar cycloaddition reactions.

An unusual reaction, formally a 1,3-dipolar cycloaddition of carbethoxycarbene to a C≡N group, has recently been realized for the Pd(OAc)$_2$ catalyzed reaction of ethyl diazoacetate with acrylonitrile[298] (eq 82). Simple cyclopropanation of the carbon–carbon double bond of acrylonitrile does not occur under the conditions shown in eq 82. Also, no pyrazoline is formed in this reaction, in contrast with what has been found previously for the thermal (*un*catalyzed) reaction of ethyl diazoacetate with acrylonitrile (which proceeds only *via* 1,3-dipolar cycloaddition of the *diazo ester* to the carbon–carbon double bond and does not involve attack at the nitrile functionality[5,162,299-301]).


(82)

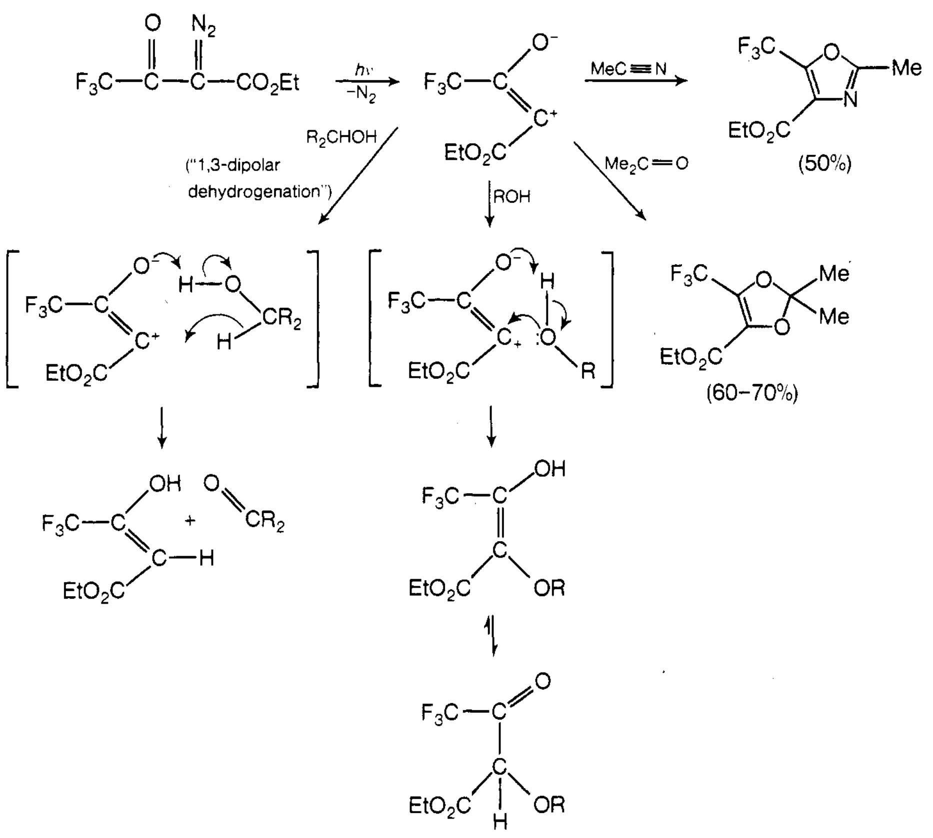
Furan formation has been noted for the benzophenone photosensitized reaction of dimethyl diazomalonate with alkynes.[25] However, singlet :C(CO$_2$Me)$_2$ ($h\nu$) fails to give this product in its reaction with alkynes, and it appears likely that furan formation in the case of the triplet carbene involves an intermediate (triplet) diradical. The furan formation probably does not represent a true example of 1,3-dipolar cycloaddition of a carbalkoxycarbene to an acetylene in this case.

One might inquire as to why 1,3-dipolar cycloaddition reactions are so seldom encountered in reactions of carbalkoxycarbenes with unsaturated substrates whereas the parent diazo compounds often react with alkenes and alkynes in this manner. One explanation might lie in the high reactivity of these carbenes relative to their corresponding diazo precursors, and in the inability of the cycloaddition process to compete effectively with other reactions which these carbenes can undergo. In the case of photolytically generated carbalkoxycarbenes, simple addition of the carbene to an unsaturated substrate and Wolff rearrangement of the carbene dominate to the exclusion of the competing 1,3-dipolar cycloaddition process. With carbenoids (generated *via* metal-catalyzed, thermal decompositions of diazo esters), the major side reaction is simple carbene dimerization to afford relatively large quantities of dialkyl maleate and fumarate which accompany addition products in reactions with alkenes and alkynes. However, carbalkoxycarbenes generated thermally (and noncatalytically) from diazo esters generally afford neither products resulting from Wolff rearrangement of the carbene nor large quantities of carbene dimers. It is not clear why 1,3-dipolar cycloaddition of simple carbalkoxycarbenes to unsaturated systems cannot compete more effectively with addition to these systems in the case of thermally generated carbalkoxycarbenes, and this question certainly merits further investigation.

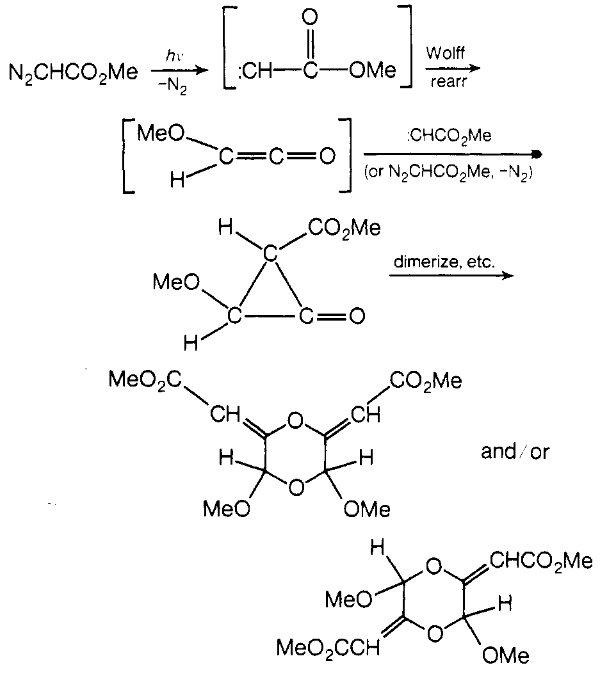
B. Wolff Rearrangement

Until relatively recently, carbalkoxycarbenes were thought to be incapable of undergoing the Wolff rearrangement.[302-305] However, in 1966, a report appeared which suggested that carbalkoxycarbenes were capable of undergoing intramolecular rearrangements.[306] In 1968, four isomeric carbomethoxycarbene tetramers were isolated among the products resulting from photolytic decomposition of methyl diazoacetate in benzene. A mechanism for their formation was suggested, one step of which involved Wolff rearrangement of carbomethoxycarbene[307] (eq 83). In that same year, independent observations of the photolytic decompositions of diazoacetic esters in alcohols revealed the existence of ethoxyacetic esters among the products. It was suggested that these esters were formed *via* Wolff rearrangement of the inter-

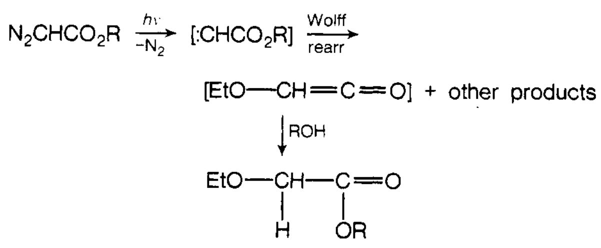
SCHEME IV



mediate carbalkoxycarbene to ethoxyketene which was then trapped by reaction with the alcohol present in the reaction mixture[240,241] (eq 84).

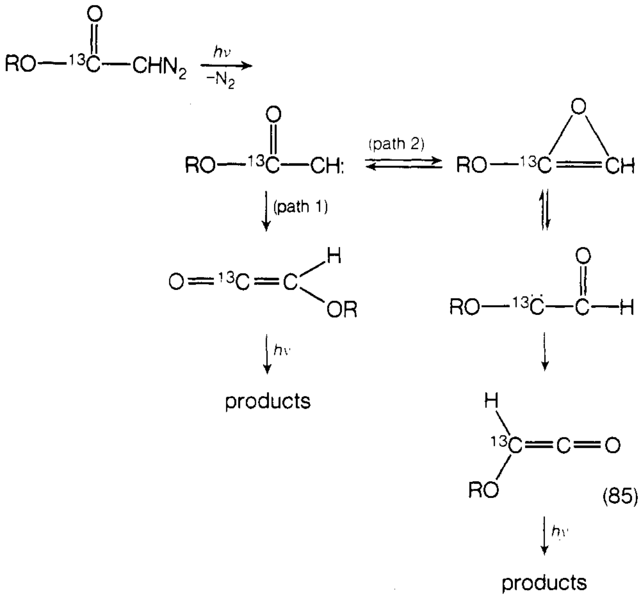


(83)



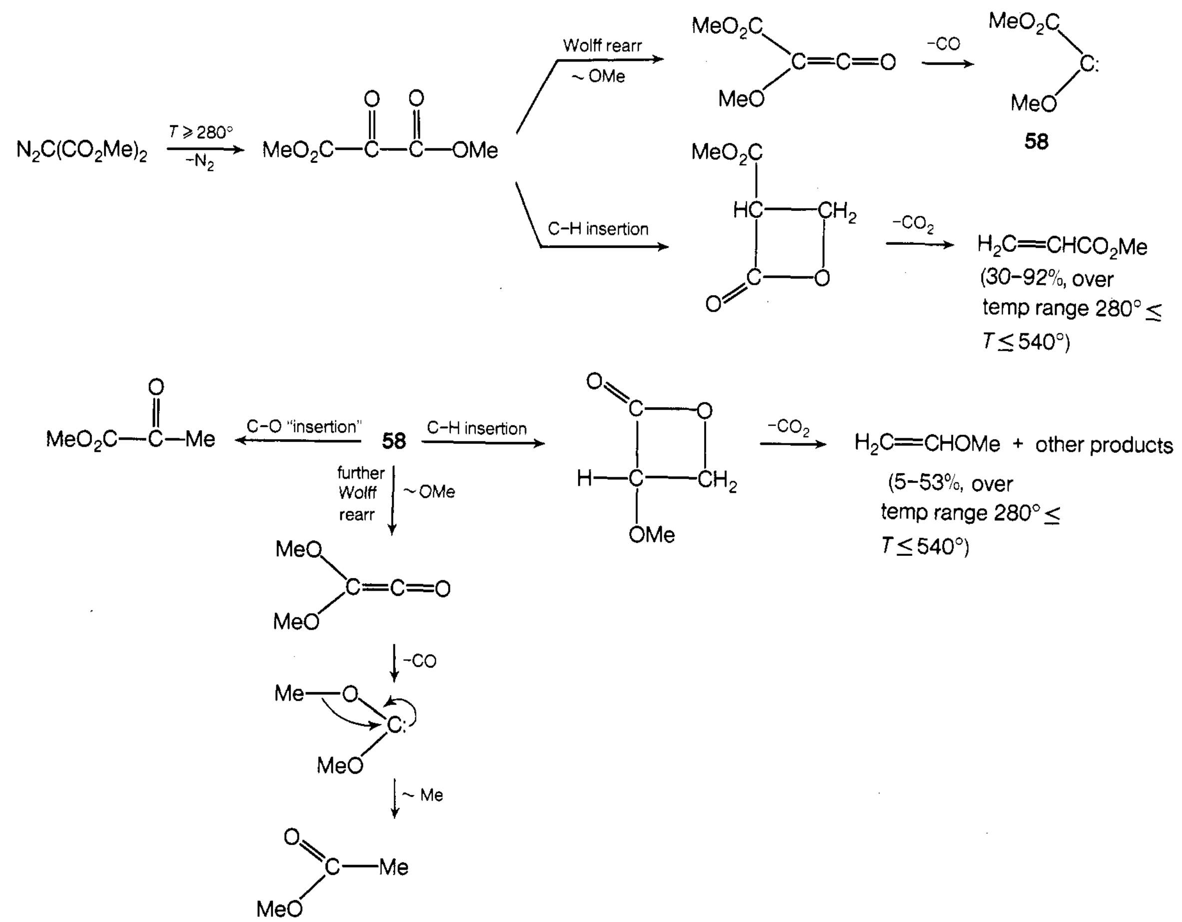
$$N_2CHCO_2R \xrightarrow[-N_2]{h\nu} [:CHCO_2R] \xrightarrow[\text{rearr}]{\text{Wolff}} [EtO{-}CH{=}C{=}O] + \text{other products} \xrightarrow{ROH} EtO{-}CH(H){-}C(OR){=}O \quad (84)$$

Since the time of these observations, Strausz and coworkers have systematically studied the detailed mechanism of the Wolff rearrangement of carbalkoxycarbenes and ketocarbenes. Their initial studies concentrated on vapor phase photolytic decompositions of ^{13}C-labeled methyl and ethyl diazoacetate. Isotopic analysis of the decomposition products by high resolution mass spectroscopy revealed the existence of two intramolecular rearrangement paths, one involving direct alkoxyketene formation (path 1) and the other involving intermediate oxirene formation, (path 2)[308] (eq 85). The isotopic analysis of the products indicated ≥28% oxirene participation (path 2) in the gas phase photolytic decomposition of methyl diazoacetate and ≥32% oxirene participation for



(85)

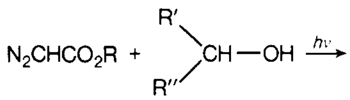
SCHEME V



the corresponding decomposition of ethyl diazoacetate.[308] Intermediate oxirene formation was similarly implicated in gas phase and condensed (solution) phase photodecompositions of α-diazo ketones.[309-312] These results superseded an earlier report which claimed to have shown that oxirene participation does not occur in the solution phase Wolff rearrangement of diazo ketones.[313]

Molecular orbital calculations (EHT) have suggested that oxirene formation (path 2) for the case of photolytically generated carbethoxycarbene is endothermic by *ca.* 100 kcal/mol whereas isomerization of even *ground-state* carbethoxycarbene to ethoxyketene is an exothermic process.[308,314] An important conclusion to arise from these calculations is that oxirene formation should be accessible only to photolytically generated carbalkoxycarbenes (or α-ketocarbenes) and not to the corresponding thermally generated carbene (which lacks sufficient excess vibrational energy to reach the transition state for oxirene formation).[308,314] In this connection, it is interesting to note that whereas the absence of a thermally induced Wolff rearrangement of monocarbalkoxycarbenes has been generally noted,[105,308,315] an example has nevertheless been reported for the case of biscarbomethoxycarbene[316,317] (Scheme V). Over the temperature range 280° $\leq T \leq$ 330°, the major product was observed to be methyl acrylate, whereas methyl vinyl ether was the predominant product over the range 360° $\leq T \leq$ 540°.[316] It was concluded that the thermal Wolff rearrangement of biscarbomethoxycarbene is an important reaction accompanying the gas-phase pyrolytic decomposition of methyl diazomalonate. Furthermore, the results suggested the following rough ordering of the relative ease of intramolecular reactions of the interesting carbalkoxycarbene intermediate, **58**: intramolecular insertion into the methoxyl carbon-hydrogen bond (ultimately leading to the formation of methyl vinyl ether) ≫ Wolff rearrangement (leading to methyl acetate) > intramolecular "insertion" into the methoxyl carbon-oxygen bond (leading to methyl pyruvate).[316]

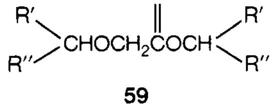
Incidental to the study of the Wolff rearrangement of carbalkoxycarbenes was the observation that rearrangement of carbomethoxycarbene and carbethoxycarbene in the presence of alcohols was accompanied by alkoxyl exchange[240,241,306,318] (eq 86). Control studies indicated



$$N_2CHCO_2R + R'R''CH—OH \xrightarrow{h\nu}$$

(products of reaction of $:CHCO_2R$ + $R'R''CHOH$) +

(products arising *via* Wolff rearr of $:CHCO_2R$) +

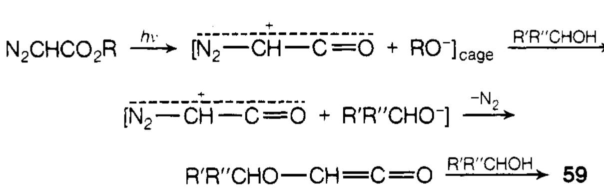


$$R'R''CHOCH_2COCHR'R'' \quad (86)$$

59

that the exchange is a photoinduced process; it does not involve carbenes nor does it occur in the starting materials (since no trace of exchanged insertion products could be detected).[318] Instead, a mechanism involving light-induced heterolysis of the diazoester was suggested,[318] (eq 87).

The question of the spin state of the reacting carbalkoxycarbene which is capable of undergoing the Wolff rearrangement has been given serious consideration by a number of research groups. The tendency of some keto-



$$N_2CHCO_2R \xrightarrow{h\nu} [\overset{+}{N_2-CH-C=O} + RO^-]_{cage} \xrightarrow{R'R''CHOH} [\overset{+}{N_2-CH-C=O} + R'R''CHO^-] \xrightarrow{-N_2} R'R''CHO-CH=C=O \xrightarrow{R'R''CHOH} \mathbf{59} \quad (87)$$

carbenes (produced *via* photolytic decomposition of α-diazo ketones) to undergo the Wolff rearrangement has been found to be drastically reduced when benzophenone is employed as a photosensitizer during the photolytic reaction.[319-321] Similar observations have been recorded for carbalkoxycarbenes produced *via* direct *vs.* benzophenone photolyses of diazo esters.[105,234,243] These results suggest that the reacting carbalkoxycarbenes which undergo the Wolff rearrangement in direct photolytic decompositions of diazoesters are in a singlet electronic configuration. A similar conclusion has been reached with regard to the oxirene pathway for the Wolff rearrangement of ketocarbenes and carbalkoxycarbenes.[308,322]

VII. Addendum

This section, added during revision of the manuscript, provides a brief account of material published since the submission of the original manuscript. Accordingly, coverage of the literature has been extended to August 1973.

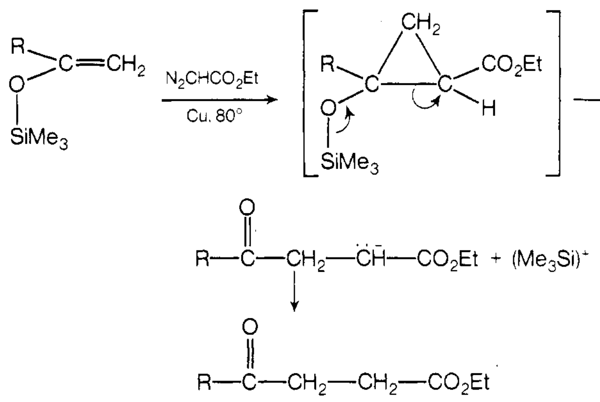
Two research groups have recently directed attention to the question of the *ground-state* electronic configuration of carbalkoxycarbenes. In both cases, this problem has been approached through examination of "internal heavy atom" effects; *i.e.*, diazo compounds possessing heavy metal atoms adjacent to the developing carbene center were studied. It was anticipated that the effect of the metal atom would be to promote fast single–triplet equilibration, thereby promoting rapid relaxation of the nascent carbene to its ground state, where its reactions could then be observed.

In the first of these studies, diazo esters of the general structure $(H_3C)_3MC(N_2)CO_2Et$ were prepared, where M = Si, Ge, Sn, and Pb.[323] The carbenes derived *via* photodecomposition of these diazo esters in all cases added stereospecifically cis (or nearly so) to the olefinic substrates studied. Additions to *cis*-2-butene afforded nearly equal amounts of the diastereoisomeric cyclopropane adducts. The authors concluded from this evidence that the ground state of each of these carbenes has the *singlet* electronic configuration.[323]

In a more recent study, Skell and coworkers[324,325] have studied the photodecompositions of diazoacetonitrile and α-methylmercuridiazoacetonitrile (**60**) in the presence of *cis*-2-butene. Whereas cyanocarbene gave 94% *cis*- and 6% *trans*-1-cyano-2,3-dimethylcyclopropanes, the carbene derived from **60** (*i.e.*, $MeHgC(CN)=$) afforded equal amounts of the diastereoisomeric adducts.[324] It was concluded that the α-methylmercuri group greatly accelerates intersystem crossing to the triplet ground state of $MeHgC(CN)=$. When this same reaction was studied using methyl methylmercuridiazoacetate as reactant, stereospecific addition to *cis*-2-butene was observed, suggesting a singlet electronic configuration for the ground state of $MeHgC(CO_2Me)=$.[324] Interestingly, it was found that $MeHgC(CO_2Me)=$ $(h\nu)$ did not undergo Wolff rearrangement to any significant extent. Furthermore, it was found to be incapable of affording carbon–hydrogen insertion products in its reactions with 2-methylpropene.[325] Thus, the introduction of the α-mercury atom was found to greatly alter the chemistry of $MeHgC(CO_2Me)=$ $(h\nu)$ relative to that of the mercury-free carbene.[325] It was also suggested that internal heavy atom effects offer a useful kinetic probe for examining ground-state spin multiplicities of carbenes.[324]

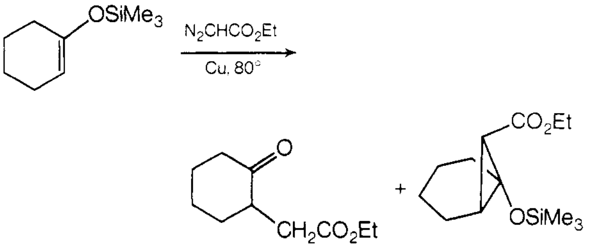
The studies described above suffer from the uncertainty that the reactions may involve the diazo precursors themselves and not the free carbenes. Also, even if free carbenes are involved in these reactions, there is no *necessary* correlation between the electronic configurations of the ground states of carbenes of the types $=CHCO_2R$ and $(H_3C)_3MC(CO_2R)=$ (M = heavy metal atom). Nevertheless, these studies are a welcome contribution to the carbalkoxycarbene literature, and they point the way for future studies of this kind.

Other addition reactions of carbalkoxycarbenes with unsaturated substrates, X = Y, have been reported. Copper-catalyzed, thermal decomposition of ethyl diazoacetate in the presence of trimethylsiloxyalkenes affords the cyclopropane, which further rearranges to afford γ-keto esters (eq 88).[326] This same reaction when carried out with 1-trimethylsiloxycyclohexene affords the corresponding γ-keto ester (**61**) in 80% yield along with a small quantity of the carbene adduct, **62** (eq 89).[326] This represents a useful (and perhaps general) synthetic method for the preparation of γ-keto esters from ketones containing at least one enolizable α-hydrogen atom.



(88)

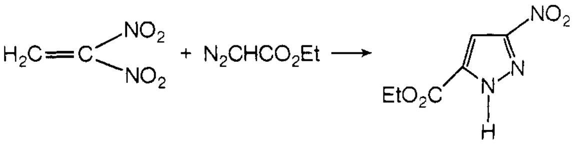
(80% isolated yield for R = Ph or *t*-Bu)



(89)

(80%) **61** (trace) **62**

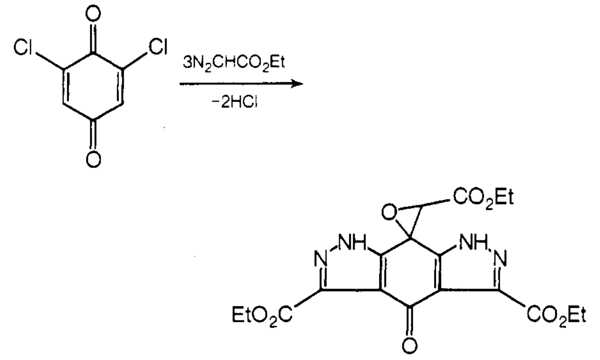
In its reaction with 2,3-bis(trimethylsiloxy)but-2-ene (an electron-rich olefin), carbethoxycarbenoid affords the corresponding cyclopropanated adduct in *ca.* 60% yield.[326] However, reaction of ethyl diazoacetate with 1,1-dinitroethylene (an electron-poor olefin) affords a pyrazole (**63**, eq 90).[327] An interesting addition reaction of ethyl diazoacetate with 2,6-dichloro-*p*-benzoquinone has been reported.[327a] Two moles of the diazo ester



(90)

63

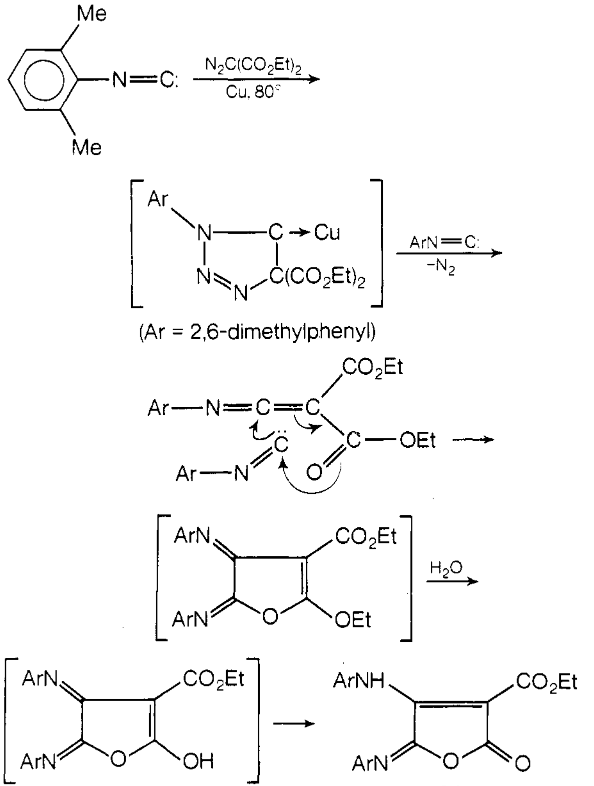
adds to the two benzoquinone carbon–carbon double bonds *via* 1,3-dipolar cycloaddition; a third mole of diazo ester affords the carbene which then adds across one of the benzoquinone *carbonyl* double bonds to afford an epoxide (eq 91).



(91)

Diazomalonic esters, unlike diazoacetic esters, do not normally react with aromatic compounds. However, in the presence of (trimethyl phosphite)copper(I) iodide, dimethyl diazomalonate has been found to react with 1,2,3,4-tetramethylbenzene.[67a] Although a total of eleven products were observed to result from this reaction, the major product (30%) was found to be dimethyl 2,3,4,5-tetramethylphenylmalonate. It was thought (on the basis of bond energy considerations) that this product arose *via* rearrangement of an intermediate norcaradiene, which was not isolated. In contrast, the corresponding reaction carried out in the presence of copper(II) fluoborate afforded at least 35 products. The major products included nearly all of the possible 1:1 and 2:1 (carbene: substrate) carbon–hydrogen bond insertion products.[67a]

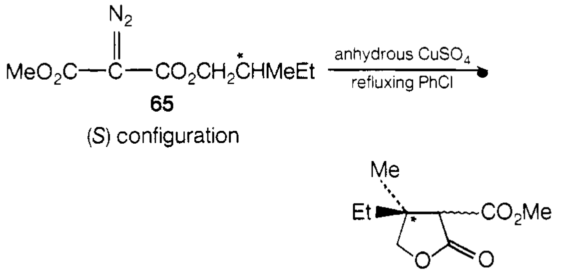
An interesting study of reactions of diazo esters with isonitriles has been reported recently. Copper-catalyzed, thermal (80°) reaction of ethyl diazoacetate with isonitriles has been found to afford triazoles; copper–isonitrile complexes were implicated as intermediates in these reactions.[328] Interestingly, the copper catalyzed, thermal decomposition of diethyl diazomalonate in the presence of 2,6-dimethylphenylisonitrile afforded 2-(2,6-dimethylphenylimino)-4-ethoxycarbonyl-5-oxyfuran (**64**, 15% yield); the suggested mechanism for this reaction is shown in eq 92.



(92)

64

Intramolecular carbon–hydrogen insertion by a carbalkoxycarbenoid in an optically active diazo ester (**65**) has recently been studied[329] (eq 93). The product lactone (**66**) was formed with net *retention* of configuration at the asymmetric (tertiary, asterisked) center. As similar intramolecular insertions into nontertiary positions were found to proceed only in low yield, it was concluded that intramolecular biscarbalkoxycarbenoid insertion reactions could be used to selectively functionalize nonactivated tertiary carbon–hydrogen bonds.[329]



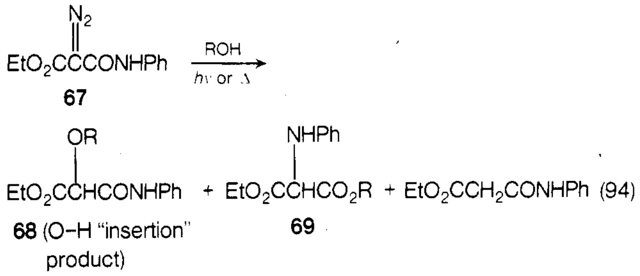
65

(*S*) configuration

66 (mixture of epimers)

(93)

Thermal and photochemical decompositions of ethyl diazomalonanilate (**67**) in the presence of alcohols have recently been studied.[330] The products of these reactions include the corresponding ethyl α-alkoxymalonanilates (**68**), ethyl α-*N*-phenylaminomalonates (**69**), and ethyl malonanilate (eq 94). Compound **68** was considered to result from "insertion" by singlet $EtO_2CC(CONHPh)=$ into the oxygen–hydrogen bond of the alcohol, whereas the mechanism of the formation of ethyl malonanilate was believed to involve the triplet carbene. Two alternative mechanisms were considered for the formation of **69**, (paths 1 and 2, eq 95).[330]

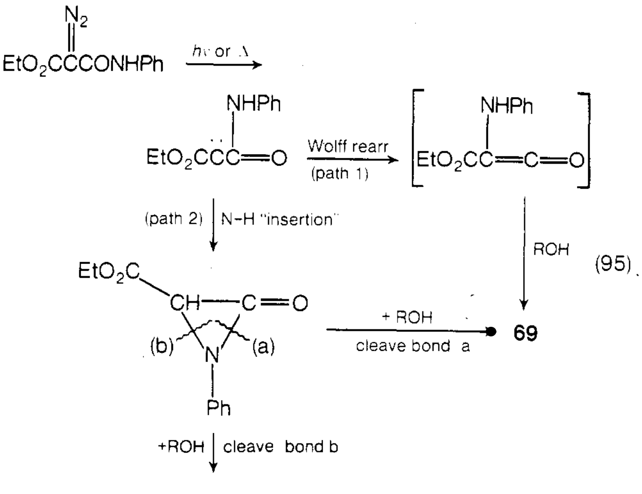


$$EtO_2C\overset{N_2}{\overset{\|}{C}}CONHPh \xrightarrow[h\nu \text{ or } \Delta]{ROH} EtO_2C\overset{OR}{\overset{|}{C}}HCONHPh + EtO_2C\overset{NHPh}{\overset{|}{C}}HCO_2R + EtO_2CCH_2CONHPh \quad (94)$$

67

68 (O–H "insertion" product)

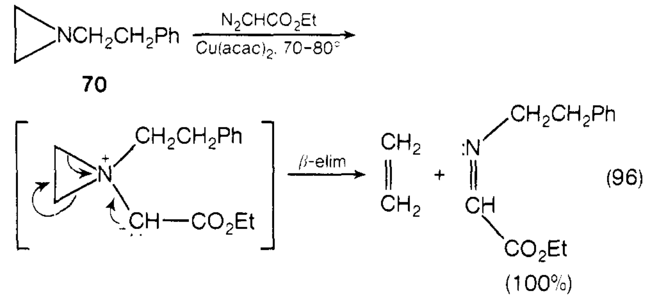
69



(95)

68

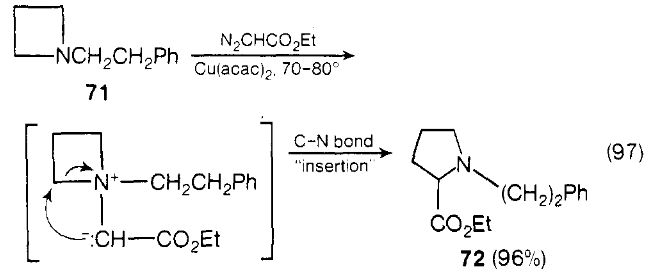
The effect of ring strain on the course of reactions of cyclic imines with carbethoxycarbenoid has recently been reported.[331] The reactions studied are illustrated in eq 96–98. The reaction with the aziridine (**70**) results in carbethoxy*carbenoid*-promoted β-elimination. Inspection of Table IV reveals that bona fide examples of *carbenoid*-promoted β-elimination reactions in which olefins have been identified among the products are relatively rare. The corresponding reaction with the azetidine (**71**) affords a pyrrolidine (**72**); this product results formally *via* carbethoxycarbenoid "insertion" into a carbon–nitrogen bond of **71**. No reaction was observed when 1-phenethylpyrrolidine (**73**) was treated with ethyl diazoacetate in the presence of Cu(acac)$_2$; only unreacted starting material was recovered. However, intermediate ylide formation was indicated when the reaction was repeated in the presence of added benzophenone. The authors concluded that the amount of ring-strain energy released in the fragmentation of the cyclic imines studied is an important factor in determining the course of their reactions with carbethoxycarbenoid.[331]



70

(100%)

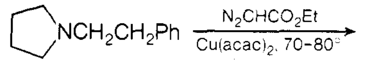
(96)



71

72 (96%)

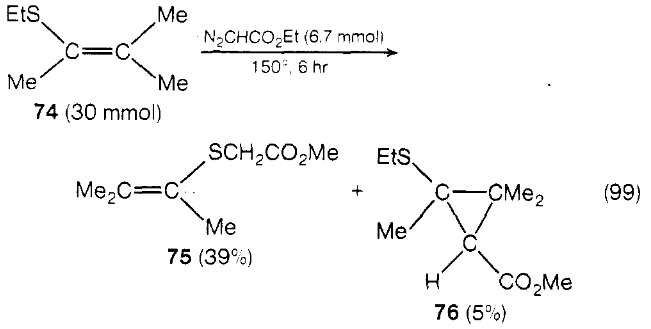
(97)



73

no reaction (cyclic imine recovered) (98)

Carbomethoxycarbene-promoted β-elimination has been reported for the reaction of :CHCO$_2$Me (Δ) with vinyl sulfides[332] (eq 99). Reaction with **74** afforded **75** as the major product, accompanied by a small amount of **76**, the product of addition of the carbene to the carbon–carbon double bond of **74**. A mechanism for the formation of **75** was formulated by analogy to the reaction of carbalkoxycarbenes with alkyl sulfides[219,238] (eq 100). Brief reviews by Japanese workers have appeared which document some of the evidence for the intermediacy of sulfonium ylides in the reactions of diazo esters with organosulfides and disulfides.[333,334]

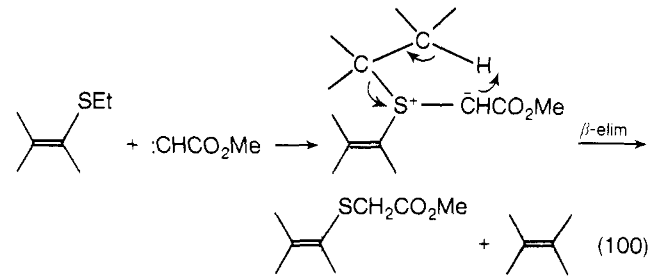


74 (30 mmol)

75 (39%)

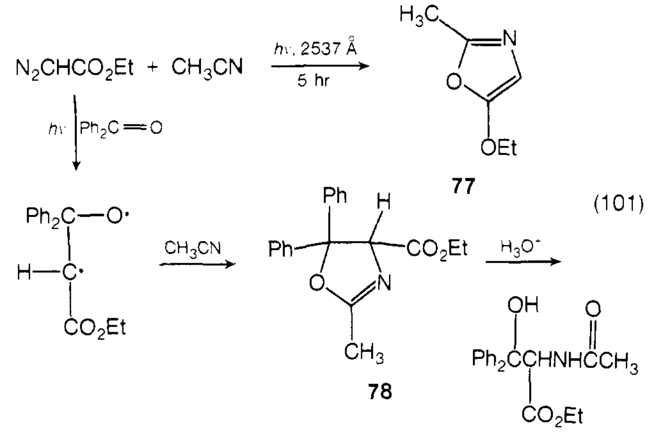
76 (5%)

(99)



(100)

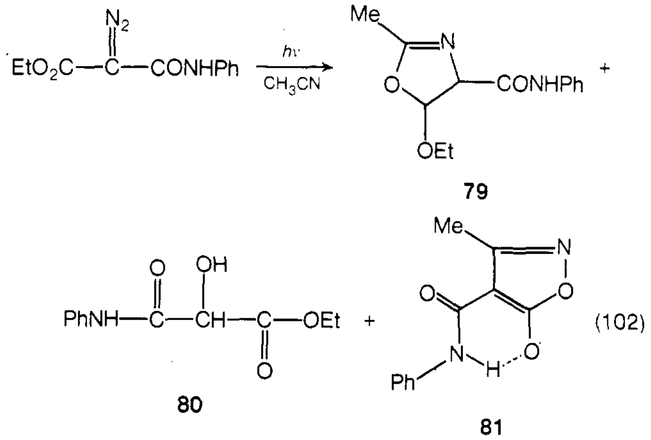
Buu and Edward[335] have reinvestigated 1,3-dipolar cycloaddition reactions of carbethoxycarbene with acetonitrile, (*cf.* discussion in sections III.A.3[163] and VI.A[295]). Direct photolysis of ethyl diazoacetate in the presence of acetonitrile affords an oxazole (**77**). However, the corresponding photolysis carried out in the presence of benzophenone results in reaction of the (presumably triplet) carbene with benzophenone, and the resulting diradical further reacts with acetonitrile to form an oxazoline (**78**, eq 101). Direct photolysis of ethyl diazomalonanilate in acetonitrile likewise affords an oxazole (**79**) *via* 1,3-dipolar cycloaddition, along with two other products (**80** and **81**, eq 102). The direct photolytic reaction affords **79** as the major product; however, the corresponding benzophenone sensitized reaction affords **81** as the major product, with *no* **79** formed.[335]



77

78

(101)



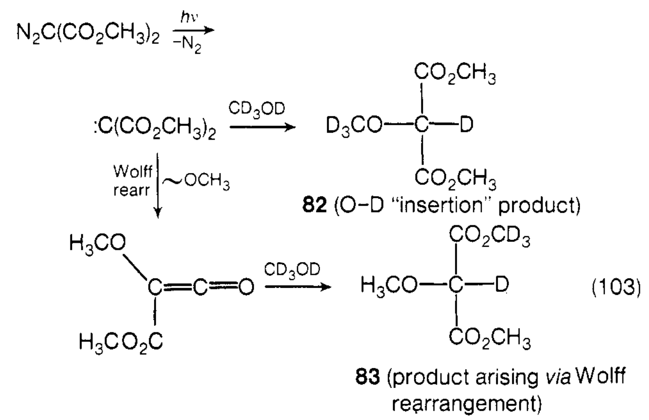
79

80

81

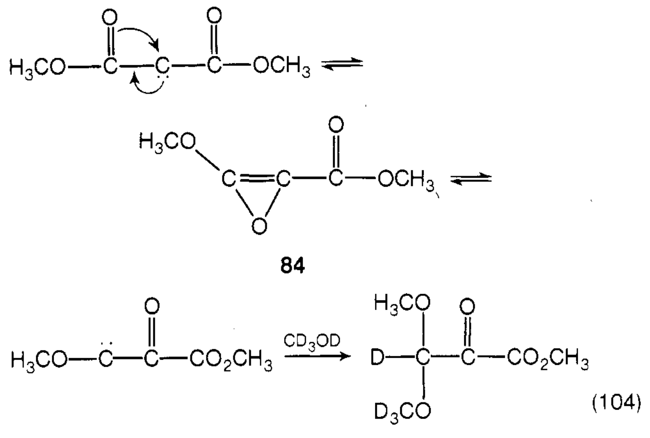
(102)

The Wolff rearrangement of carbalkoxycarbenes continues to receive attention. Photolysis of dimethyl diazomalonate in the presence of methanol-d_4 affords two products, **82** and **83**, in the ratio 9:4 (eq 103).[336] The absence of any product **85** suggests that an oxirene intermediate (**84**) is probably not involved (eq 104), and that


82 (O–D "insertion" product)

83 (product arising *via* Wolff rearrangement)

(103)

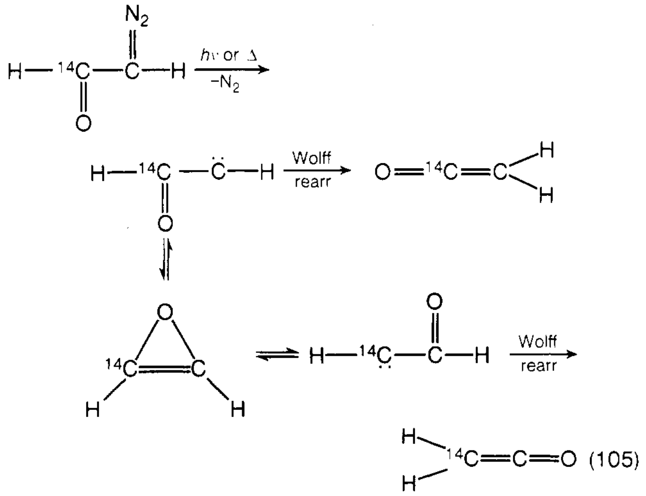

84

85 (not observed)

(104)

the Wolff rearrangement to **83** proceeds with methoxyl group migration, as indicated in eq 103.

A nonempirical molecular orbital calculation has recently been performed for oxirene and the isomeric formylcarbene which have been postulated as intermediates in the Wolff rearrangement of $O{=}CHCH{=}N_2$[337] (eq 105). The calculations suggest that ketene is more stable than either oxirene or formylcarbene by *ca.* 70 kcal/mol. Interestingly, oxirene and formylcarbene are predicted to have almost identical energies.[337]

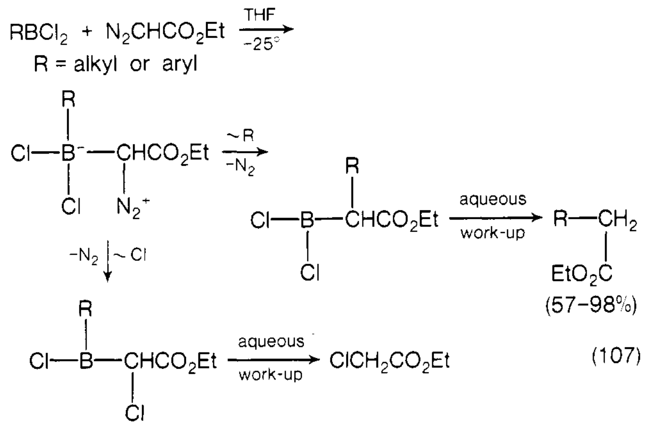

(105)

A convenient, high-yield procedure for the preparation of propargylic esters has recently appeared[338] (eq 106).

$$(RC{\equiv}C)_3B + N_2CHCO_2Et \xrightarrow[-N_2]{THF,\ -20^\circ} \xrightarrow{H_2O} RC{\equiv}CCH_2CO_2Et \quad (106)$$

(87–92%)

Also, alkyl- and aryldichloroboranes have been found to react with ethyl diazoacetate at low temperatures to afford substituted esters of the general structure RCH_2CO_2Et[339] (eq 107). This reaction appears to offer a useful method for converting alkenes or arenes to their corresponding two-carbon chain-lengthened ethyl esters.[339] The mild conditions utilized in these reactions are not compatible with mechanisms involving carbene intermediates (see discussion in section IV.D.4).



(107)

The material which follows has been added in proof. Some highlights of pertinent literature published between August, 1973, and May, 1974, are presented. Although coverage is necessarily not exhaustive, the references which are cited in connection with the paragraphs which follow should serve to indicate the directions being taken by carbalkoxycarbene research current at the time of publication of this review.

Studies directed toward elucidating the nature of the reactive intermediates in metal-catalyzed diazo ester decompositions continue.[340] Wulfman has recently shown that the Δ^1-pyrazoline derived from the reaction of dicyclopentadiene with dimethyl diazomalonate decomposes smoothly in the presence of copper(II) fluoroborate to afford the corresponding cyclopropane in essentially quantitative yield.[341] This result is especially intriguing since the nitrogen–nitrogen double bond in 7,8-diazatetracyclo$[3.3.0.0^{2,4}.0^{3,6}]$oct-7-ene appears to form a *stable* complex with copper(II).[342] The results of Wulfman's study demonstrate that Δ^1-pyrazolines, at least in some instances, can be catalytically decomposed by copper salts to afford cyclopropanes, suggesting that "carbalkoxycarbenoid additions" to double bonds may in such cases not involve divalent carbon species at all! In view of the complexity of these and related carbenoid reactions and the confused state of our present knowledge of their mechanisms,[343] the need for additional work is all too apparent.

The ability of biscarbalkoxycarbenoids to insert into allylic carbon–hydrogen bonds has been known for some time.[67a,344] Recently, insertion of carbethoxycarbenoid into *aliphatic* (nonallylic) carbon–hydrogen bonds has been effected utilizing high dilution techniques to minimize competing dimer formation (which results *via* attack of the carbenoid on excess diazo ester).[345] Thermal decomposition of methyl isobutyl diazomalonate in the presence of copper (131°, chlorobenzene solvent) has been reported to afford 3,3-dimethyl-2-carbomethoxybutyrolactone (62% yield).[346] This reaction is an example of an intramolecular carbon–hydrogen insertion by a biscarbalkoxycarbenoid.

A number of other interesting reactions of carbalkoxycarbenoids have been recently reported. The rhodium(II)-catalyzed reaction of ethyl diazoacetate with acetylacetone affords ethyl 3,5-dimethyl-2-furoate in 68% yield.[347] Lactones of 1-hydroxymethylcycloheptatriene-1-carboxylic acids have been prepared by intramolecular addition reactions involving the biscarbalkoxycarbenoids derived from substituted methyl benzyl diazomalonates.[348] In addition, a study of the stereoselectivity of carbethoxycarbenoid additions to 2,4-hexadienes has recently been reported.[349]

The reaction of 1-methyl-3-phenyl-4-oxo-3,4-dihydroquinazolinium bromide with ethyl diazoacetate in the presence of copper(II) sulfate (ethanol solvent) has been reported to afford 1-methyl-2-(1-ethoxy-1-ethoxycarbonylmethyl)-3-phenyl-4-oxo-1,2,3,4-tetrahydroquinazoline.[350] This is the first example of a reaction which proceeds *via* addition of carbethoxycarbenoid to a *positively charged* (carbon-nitrogen) double bond.

The photolytic reaction of methyl diazoacetate with polyhalomethanes has recently been reinvestigated utilizing CIDNP techniques.[351,352] Both ^1H and ^{13}C CIDNP patterns obtained for the reaction of methyl diazoacetate with chloroform and with carbon tetrachloride are in accord with a mechanism involving cage recombination of radical pairs[130] but are inconsistent with the radical chain mechanism which had been suggested previously.[129]

The benzaldehyde- and benzophenone-sensitized decompositions of methyl diazoacetate have recently been studied *via* CIDNP.[353] Triplet carbomethoxycarbene is thereby produced; in contrast to the behavior of the corresponding singlet carbene, this species is capable of abstracting hydrogen atoms from substrates such as cyclohexane.

A study of asymmetric induction in the addition of optically active diazoacetic esters to olefins in the presence of catalytic amounts of cuprous chloride has recently been reported.[354,355] The order of magnitude of induced asymmetry in the cyclopropanated products resulting from reaction of chiral diazoacetic esters, $N_2CHCO_2R^*$, with styrene was found to be R^* = menthyl > bornyl > amyl in the syn products and R^* = bornyl ≥ menthyl > amyl in the anti products.[355] Photolytic decomposition of (−)-menthyl diazoacetate in the presence of styrene afforded the syn-cyclopropanated product in significantly reduced optical yield as compared with that obtained from the same reaction when carried out in the presence of cuprous chloride.[355] Various transition state models were discussed to account for these results.

A number of reactions of diazo esters with heteroatom-containing substrates have been reported. Photodecomposition of ethyl diazoacetate in the presence of alkylthiotrimethylsilanes and alkoxytrimethylsilanes afforded silicon-sulfur and silicon-oxygen "insertion" products, respectively.[356] A likely mechanism for these reactions involves onium ylide formation followed by a 1,2-shift of the trialkylsilyl group from the onium site to the adjacent carbanionic center.

Reactions of carbalkoxycarbenes with alkylsilanes have been reported to afford both α and β carbon-hydrogen insertion products.[357] In addition, products arising *via* "insertion" of carbethoxycarbene into a silicon-carbon bond of 1,1,3,3-tetramethyl-1,3-disilacyclobutane have been observed (accompanied by the products of insertion of carbethoxycarbene into the primary and secondary carbon-hydrogen bonds of this substrate).[357]

Reactions of organosilicon hydride with methyl diazoacetate in the presence of copper powder have recently been studied.[358] Correlation of the relative rates of $:CHCO_2Me$ "insertion" into the silicon-hydrogen bonds of meta- and para-substituted phenyldimethylsilanes with Hammett σ constants (for the various phenyl ring substituents studied) afforded $\rho = -0.26$. Interestingly, the magnitude of this ρ value could be accounted for in terms of a mechanism involving electrophilic attack of *free* (noncomplexed) carbomethoxycarbene on the silicon-hydrogen bond of the substrate. The "insertion" process was considered to occur in concerted fashion, proceeding *via* a "very slightly polar transition state."[358] The authors suggested that the only function which the copper catalyst might serve in this reaction is to simply accelerate decomposition of the diazo ester (although no detailed mechanism for this catalytic decomposition process was specified).[358]

Arsonium ylides have been prepared *via* thermal decompositions of diazo esters in the presence of triphenylarsine.[359] The formation of arsonium ylides in this reaction is greatly facilitated by the presence of copper, copper-bronze, or copper salts. The stable triphenylarsonium ylides thus formed are of general synthetic value as reagents in Wittig reactions.

A number of new substituted carbalkoxycarbenes have recently been prepared and studied. Diazoacetic esters, $XC(N_2)CO_2R$, have been decomposed thermally or photolytically to afford the corresponding carbalkoxycarbenes ($=C(X)CO_2R$), where X = NO_2,[360] Cl,[361,362] Br,[361,362] I,[361,362] HgMe,[363] and Me_3Si.[364,365] In addition, halocarbalkoxycarbenes have been prepared from phenyl(dihalocarbalkoxymethyl)mercury compounds. Fluorocarbethoxycarbene has been generated *via* $PhHgCFBrCO_2Et$[366] and *via* $PhHgCFClCO_2Et$.[367] The related mercurials $PhHgCCl_2CO_2Me$ and $PhHgCBr_2CO_2Me$ have been found to transfer $=C(Cl)CO_2Me$ and $=C(Br)CO_2Me$, respectively, to olefins and to triethylsilane.[368] Phenylcarbomethoxycarbene has been prepared *via* photocycloelimination from the corresponding *vic*-diphenyloxirane.[369]

Reactions of singlet and triplet carbomethoxycarbene with benzonitrile have been studied recently.[370] Reaction of the singlet carbene with benzonitrile affords methyl 3-phenyl-2*H*-azirine-2-carboxylate. However, the corresponding triplet carbene species reacts with benzonitrile to form 5-methoxy-2-phenyloxazole.[370]

Recent MINDO/3 and NDDO calculations suggest that oxirenes may possess sufficient stability that they may occur as stable intermediates in reactions (such as the Wolff rearrangement).[371] This suggestion stands in disagreement with earlier conclusions which were based upon a theoretical study of the Wolff rearrangement of carbalkoxycarbenes utilizing the extented Hückel method.[314]

Recent results obtained from studies of the photolysis of diazoacetaldehyde in argon and in ethylene matrices suggest that ketene formation is much faster than is the reaction of ethylene with any intermediate species or excited state which may be thereby generated from this diazo compound.[372] Accordingly, it is unlikely that diazoacetaldehyde will prove to be a synthetically useful precursor of :CHCHO.

Acknowledgments. We thank Professors P. K. Freeman, D. S. Wulfman, and J. A. Landgrebe and Dr. H. D. Roth and Dr. R. Paulissen for providing us with information and results in advance of publication. We thank Dr. Roth for critically reading section II.B.3 of the manuscript and for forwarding numerous helpful suggestions. One of us (A. P. M.) gratefully acknowledges sabbatical leave support from the U. S. Educational Foundation in Belgium in the form of a Senior Fulbright/Hays Research Fellowship (1972-1973 academic year) and from the Institut de Chimie, Université de Liège (Belgium). Finally, we thank Dr. Nancy Wu Marchand for assistance with the preparation of the manuscript.

VIII. References and Notes

(1) W. von E. Doering, R. G. Buttery, R. G. Laughlin, and N. Chaudhuri, *J. Amer. Chem. Soc.*, **78**, 3224 (1956).
(2) G. Herzberg and J. Shoosmith, *Nature* (*London*), **183**, 1801 (1959).
(3) E. Buchner and T. Curtius, *Ber.*, **18**, 2371 (1885).
(4) E. Buchner and T. Curtius, *Ber.*, **18**, 2377 (1885).
(5) R. Huisgen, *Angew. Chem.*, **67**, 439 (1955).
(6) W. Kirmse, *Angew. Chem.*, **71**, 537 (1959).
(7) W. Kirmse, *Angew. Chem.*, **73**, 161 (1961).
(8) P. Miginiac, *Bull. Soc. Chim. Fr.*, 2000 (1962).
(9) E. Chinoporos, *Chem. Rev.*, **63**, 235 (1963).
(10) J. Hine, "Divalent Carbon," Ronald Press, New York, N. Y., 1964.
(11) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y.: (a) 1st ed, 1964; (b) 2nd ed, 1971.
(12) G. G. Rozantsev, A. A. Fainzil'berg, and S. S. Novikov, *Russ. Chem. Rev.*, **34**, 69 (1965).
(13) E. Muller, H. Kessler, and B. Zeeh, *Fortsch. Chem. Forsch.*, **7**, 128 (1966).
(14) (a) R. A. Moss, *Chem. Eng. News*, **47**, 60 (June 16, 1969); (b) *ibid.*, **47**, 50 (June 30, 1969).
(15) T. L. Gilchrist and C. W. Rees, "Carbenes, Nitrenes, and Arynes," Appleton-Century-Crofts, New York, N. Y., 1969.
(16) R. A. Moss, "Selective Organic Transformations," Vol. 1, B. S. Thyagarajan, Ed., Wiley, New York, N. Y., 1970, pp 35–88.
(17) V. Dave and E. W. Warnhoff, *Org. React.*, **18**, 217 (1970).
(18) L. P. Danilkina, M. I. Komendantov, R. R. Kostikov, T. V. Mandel'shtam, V. V. Razin, and E. M. Kharicheva, *Vestn. Leningrad Univ., Fiz. Khim.*, 123 (1970); *Chem. Abstr.*, **73**, 34367x (1970).
(19) G. W. Cowell and A. Ledwith, *Quart. Rev., Chem. Soc.*, **24**, 119 (1970).
(20) W. Kirmse, "Carbene, Carbenoide, und Carbenanaloge," Verlag-Chemie, Weinheim, 1969.
(21) C. A. Buehler, *J. Chem. Educ.*, **49**, 239 (1972).
(22) M. Jones, Jr., and R. A. Moss, Ed., "Carbenes," Vol. 1, Wiley, New York, N. Y., 1973.
(22a) D. Bethell, "Organic Reactive Intermediates," S. P. McManus, Ed., Academic Press, New York, N. Y., 1973, pp 61–126.
(23) For additional references, see footnote 3 in M. Jones, Jr., W. Ando, M. E. Hendrick, A. Kulczycki, Jr., P. M. Howley, K. F. Hummel, and D. S. Malament, *J. Amer. Chem. Soc.*, **94**, 7469 (1972).
(24) M. Jones, Jr., W. Ando, and A. Kulczycki, Jr., *Tetrahedron Lett.*, 1391 (1967).
(25) M. E. Hendrick, *J. Amer. Chem. Soc.*, **93**, 6337 (1971).
(26) W. E. Moser, *J. Amer. Chem. Soc.*, **91**, 1135 (1969).
(27) W. E. Moser, *J. Amer. Chem. Soc.*, **91**, 1141 (1969).
(28) The term "carbenoid" was originally applied to the divalent carbon species generated from organolithium reagents.[29] The term is now used generally to denote a metal-complexed carbene as differentiated from a noncomplexed or "free" carbene. Although carbenoids under some reactions characteristic of "free" carbenes (such as addition to carbon–carbon double bonds), they are not, in fact, simple divalent carbon species, as transition states of carbenoid reactions have been demonstrated to involve the metal atom of the catalyst (see text).
(29) G. L. Closs and R. A. Moss, *J. Amer. Chem. Soc.*, **86**, 4042 (1964).
(30) M. Jones, Jr., A. Kulczycki, Jr., and K. F. Hummel, *Tetrahedron Lett.*, 183 (1967).
(31) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, Chapter 8.
(32) R. Anet and F. A. L. Anet, *J. Amer. Chem. Soc.*, **86**, 525 (1964).
(33) G. L. Closs and W. A. Böll, *J. Amer. Chem. Soc.*, **85**, 3904 (1963).
(34) G. L. Closs and W. A. Böll, *Angew. Chem., Int. Ed. Engl.*, **2**, 399 (1963).
(35) G. L. Closs, W. A. Böll, H. Heyn, and V. Dev, *J. Amer. Chem. Soc.*, **90**, 173 (1968).
(36) G. Ege, *Tetrahedron Lett.*, 1665 (1963).
(37) W. M. Jones, *J. Amer. Chem. Soc.*, **81**, 3776 (1959).
(38) A. Pudovik, R. D. Gareev, L. A. Stabrovskaya, G. I. Evstaf'ev, and A. B. Remizov, *J. Gen. Chem. USSR*, **42**, 77 (1972), and references cited therein.
(39) I. S. Lishanskii, V. I. Pomerantsev, and L. D. Turkova, *J. Org. Chem. USSR*, **8**, 263 (1972).
(40) E. Ciganek, *J. Amer. Chem. Soc.*, **89**, 1458 (1967).
(41) J. S. Swenton and A. Krubsack, *J. Amer. Chem. Soc.*, **91**, 786 (1969).
(42) For reviews covering the generation of carbenes by photocycloelimination reactions, see G. W. Griffin, *Angew. Chem., Int. Ed. Engl.*, **10**, 537 (1971); G. W. Griffin and N. R. Bertoniere, ref 22, p 305; N. R. Bertoniere and G. W. Griffin, "Organic Photochemistry," Vol. 3, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1973, pp 115–195.
(43) For a review on generation of carbenes *via* thermally induced cycloelimination reactions, see R. W. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **10**, 529 (1971).
(44) H. M. Frey, *Advan. Photochem.*, **4**, 225 (1966).
(45) E. Schmitz, *Angew. Chem., Int. Ed. Engl.*, **3**, 333 (1964).
(46) J. P. Snyder, R. J. Boyd, and M. A. Whitehead, *Tetrahedron Lett.*, 4347 (1972).
(47) H. M. Frey and I. D. R. Stevens, *J. Chem. Soc.*, 3865 (1962).
(48) H. M. Frey and M. T. H. Liu, *J. Chem. Soc. A*, 1916 (1970).
(49) M. T. H. Liu and K. Toriyama, *J. Phys. Chem.*, **76**, 797 (1972).
(50) A. S. Shteinman, *J. Phys. Chem. USSR*, **44**, 779 (1970).
(51) (a) D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, **72**, 545 (1972); (b) D. J. Cardin, B. Cetinkaya, M. J. Doyle, and M. F. Lappert, *Chem. Soc. Rev.*, **2**, 99 (1973).
(52) See footnote 77 in ref 51a.
(53) A. W. Johnson, *Pure Appl. Chem., Suppl.*, **6**, 101 (1971).
(54) A. W. Johnson, *Pure Appl. Chem.*, **28**, 195 (1971).
(55) R. L. Smith, A. Manmade, and G. W. Griffin, *Tetrahedron Lett.*, 553 (1970).
(56) R. H. Levin and M. Jones, Jr., *Tetrahedron*, **27**, 2031 (1971).
(57) H. Nozaki, S. Moriuti, H. Takaya, and R. Noyori, *Tetrahedron Lett.*, 5239 (1966).
(58) I. S. Lishanskii, V. I. Pomerantsev, N. G. Illarionova, A. S. Khatchaturov, and T. I. Vakorina, *J. Org. Chem. USSR*, **7**, 1870 (1971). *cis*-1,3-Pentadiene was reported not to react with ethyl diazoacetate in the presence of the *S* enantiomer of the chelate catalyst (presumably under conditions where it did react in the presence of the corresponding *R* enantiomer).
(59) H. Alper and R. A. Partis, *J. Organometal. Chem.*, **44**, 371 (1972).
(60) N. E. Searle, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 424.
(61) M. Jones, Jr., and K. R. Rettig, *J. Amer. Chem. Soc.*, **87**, 4013 (1965).
(62) M. Jones, Jr., and K. R. Rettig, *J. Amer. Chem. Soc.*, **87**, 4015 (1965).
(63) M. Jones, Jr., *J. Org. Chem.*, **33**, 2538 (1968).
(64) D. M. Gale, *J. Org. Chem.*, **33**, 2536 (1968).
(65) J. D. Collins, Ph.D. Dissertation, University of Arkansas, 1970.
(65a) A referee has pointed out that the apparent singlet reactivity of $:CHCO_2Et$ ($h\nu$) when generated in the presence of hexafluorobenzene might instead arise *via* a situation in which a rapid singlet-triplet equilibration is established, with the singlet carbene reacting much more rapidly than does the triplet species. Such appears to be the case for phenylcarbene (see W. J. Baron, M. R. De Camp, M. E. Hendrick, M. Jones, Jr., R. H. Levin, and M. B. Sohn, ref 22, pp 64–73). However, the alternative suggestions remain to be tested experimentally.
(66) J. E. Baldwin and R. A. Smith, *J. Amer. Chem. Soc.*, **89**, 1886 (1967).
(67) N. M. Brockway, Ph.D. Dissertation, University of Oklahoma, 1970.
(67a) It has recently been reported that hexafluorobenzene appears to be completely inert toward biscarbomethoxycarbenoid; see B. W. Peace and D. S. Wulfman, *Synthesis*, 137 (1973).
(68) (a) G. Herzberg and J. W. C. Johns, *Proc. Roy. Soc., Ser. A*, **295**, 107 (1967); (b) E. Wasserman, W. A. Yager, and V. J. Kuck, *Chem. Phys. Lett.*, **7**, 409 (1970); (c) P. P. Gaspar and G. S. Hammond in ref 11a, pp 235–274.
(69) For a review, see W. Kirmse, ref 11b, Chapter 8.
(70) P. S. Skell and A. Y. Garner, *J. Amer. Chem. Soc.*, **78**, 3409 (1956).
(71) P. S. Skell and A. Y. Garner, *J. Amer. Chem. Soc.*, **78**, 5430 (1956).
(72) P. S. Skell and J. Klebe, *J. Amer. Chem. Soc.*, **82**, 247 (1960).
(73) W. von E. Doering and P. LaFlamme, *J. Amer. Chem. Soc.*, **78**, 5447 (1956).
(74) P. S. Skell and R. C. Woodworth, *J. Amer. Chem. Soc.*, **78**, 4496 (1956).
(75) H. M. Frey, *J. Amer. Chem. Soc.*, **82**, 5005 (1960).
(76) G. L. Closs and S. H. Goh, *J. Chem. Soc., Perkin Trans. 1*, 2103 (1972).
(77) W. Simons and B. S. Rabinovitch, *J. Phys. Chem.*, **68**, 1322 (1964).
(78) S. Ho, I. Unger, and W. A. Noyes, *J. Amer. Chem. Soc.*, **87**, 2297 (1965).
(79) B. S. Rabinovitch, K. W. Watkins, and D. F. Ring, *J. Amer. Chem. Soc.*, **87**, 4960 (1965).
(80) H. M. Frey, *Progr. React. Kinet.*, **2**, 131 (1964).
(81) B. J. Herold and P. P. Gaspar, *Fortschr. Chem. Forsch.*, **5**, 89 (1965).
(82) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).
(83) See J. F. Harrison in ref 11b, Chapter 5.
(84) R. B. Woodward and R. Hoffmann, *Angew Chem., Int. Ed. Engl.*, **8**, 781 (1969).
(85) I. Fleming and E. J. Thomas, *Tetrahedron*, **28**, 5003 (1972).
(86) R. W. Hoffmann, G. D. Zeiss, and G. W. Van Dine, *J. Amer. Chem. Soc.*, **90**, 1485 (1968).
(87) R. Gleiter and R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 5457 (1968).
(88) The electronic configuration of the ground state of carbalkoxycarbenes has not been firmly established; see discussions in sections III.A, IV.A, and, especially, in the Addendum (section VII).
(89) W. von E. Doering and T. Mole, *Tetrahedron*, **10**, 65 (1960).
(90) For a later reinvestigation of this reaction, see T. C. Neil, Ph.D. Dissertation, Pennsylvania State University, 1964.
(91) I. A. D'yakonov, M. I. Komendantov, K.-H. Fu, and G. L. Korichev, *J. Gen. Chem. USSR*, **32**, 917 (1962).
(92) I. A. D'yakonov and R. R. Kostikov, *J. Gen. Chem. USSR*, **34**, 3894 (1964).
(93) I. A. D'yakonov and R. R. Kostikov, *J. Gen. Chem. USSR*, **34**, 1385 (1964).
(94) I. A. D'yakonov, K.-H. Fu, G. L. Korichev, and M. I. Komendantov, *J. Gen. Chem. USSR*, **31**, 624 (1961).
(95) G. L. Closs and A. D. Trifunac, *J. Amer. Chem. Soc.*, **92**, 2183 (1970).
(96) G.L. Closs and A. D. Trifunac, *J. Amer. Chem. Soc.*, **92**, 2186

(1970).

(97) G. L. Closs and A. D. Trifunac, *J. Amer. Chem. Soc.*, **92**, 7227 (1970).

(98) G. L. Closs, C. E. Doubleday, and D. R. Paulson, *J. Amer. Chem. Soc.*, **92**, 2185 (1970).

(99) R. Kaptein and L. J. Oosterhoff, *Chem. Phys. Lett.*, **4**, 195 (1969).

(100) R. Kaptein and L. J. Oosterhoff, *Chem. Phys. Lett.*, **4**, 214 (1969).

(101) S. H. Glarum, Abstracts, 159th National Meeting of the American Chemical Society, Houston, Texas, Feb, 1970, No. ORGN-040.

(102) H. Fischer, *Z. Naturforsch. A*, **25**, 1957 (1970).

(103) M. Tomkiewicz and M. Cocivera, *Chem. Phys. Lett.*, **8**, 595 (1971).

(104) W. Ando, T. Yagihara, S. Tozune, I. Imai, J. Suzuki, T. Toyama, S. Nakaido, and T. Migita, *J. Org. Chem.*, **37**, 1721 (1972).

(105) See footnote 3 in T. DoMinh and O. P. Strausz, *J. Amer. Chem. Soc.*, **92**, 1766 (1970).

(106) N. Shimizu and S. Nishida, *Chem. Commun.*, 389 (1972).

(107) O. M. Nefedov, I. E. Dolgii, I. B. Shevedova, and R. N. Shafran, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1885 (1972); *Chem. Abstr.*, **77**, 164071g (1972).

(108) W. Lwowski and F. P. Woerner, *J. Amer. Chem. Soc.*, **87**, 5491 (1965).

(109) F. J. Duncan and R. J. Cvetanovic, *J. Amer. Chem. Soc.*, **84**, 3593 (1962).

(110) J. A. Bell, *Progr. Phys. Org. Chem.*, **2**, 1 (1964).

(111) W. Kirmse, ref 11b, Chapter 7.

(112) Review: see H. D. Roth, *Mol. Photochem.*, **5**, 91 (1973).

(113) Review: see S. H. Pine, *J. Chem. Educ.*, **49**, 664 (1972).

(114) J. Bargon, H. Fischer, and U. Johnson, *Z. Naturforsch. A*, **22**, 1551 (1967).

(115) J. Bargon and H. Fischer, *Z. Naturforsch. A*, **22**, 1556 (1967).

(116) H. Fischer, *Accounts Chem. Res.*, **2**, 110 (1969).

(117) H. R. Ward and R. G. Lawler, *J. Amer. Chem. Soc.*, **89**, 5518 (1967).

(118) H. R. Ward, *Accounts Chem. Res.*, **5**, 18 (1972).

(119) R. G. Lawler, *Accounts Chem. Res.*, **5**, 25 (1972).

(120) G. L. Closs, *J. Amer. Chem. Soc.*, **91**, 4552 (1969).

(121) R. Kaptein, *Chem. Commun.*, 732 (1971).

(122) H. D. Roth, *J. Amer. Chem. Soc.*, **93**, 1527 (1971).

(123) H. D. Roth, *J. Amer. Chem. Soc.*, **93**, 4935 (1971).

(124) H. D. Roth, *J. Amer. Chem. Soc.*, **94**, 1400 (1972).

(125) H. D. Roth, *Ind. Chim. Belg.*, **36**, 1068 (1971).

(126) Reactions of methyl diazoacetate with $CBrCl_3$, CH_3CH_2Cl, and chlorocyclohexane have been examined for CIDNP effects: H. D. Roth, personal communication.

(127) H. D. Roth, *J. Amer. Chem. Soc.*, **94**, 1761 (1972).

(128) Evidence for chlorine abstraction by *singlet* methylene in its gas-phase reaction with methyl chloride has recently been obtained by isotopic tracer studies $:CHT$ (singlet carbene) $+ CH_3Cl \rightarrow CHTCl + CH_3$ (T = tritium); see F. S. Rowland, P. S.-T. Lee, D. C. Montague, and R. L. Russel, *Discuss. Faraday Soc.*, **No. 53**, 111 (1972); see also K. Dees and D. W. Setser, *J. Chem. Phys.*, **49**, 1193 (1968); W. G. Clark, D. W. Setser, and E. E. Siefert, *J. Phys. Chem.*, **74**, 1670 (1970).

(129) M. Cocivera and H. D. Roth, *J. Amer. Chem. Soc.*, **92**, 2573 (1970).

(130) H. D. Roth, personal communication, Feb 5, 1973.

(131) This conclusion is confirmed by the observation that enhanced absorption is observed for $Cl_3CCHBrCO_2Me$ when formed during the reaction of $:CHCO_2Me$ ($h\nu$) with $CBrCl_3$.[130]

(132) W. Kirmse, ref 11b, p 369.

(133) P. S. Skell and R. M. Etter, *Chem. Ind.* (*London*), 624 (1958).

(134) In contrast, $:C(CO_2Me)_2$ ($h\nu$) appears to show increasing reactivity toward increasingly alkyl-substituted double bonds[30] whereas the corresponding carbenoid shows the opposite behavior.[135]

(135) D. S. Wulfman, B. W. Peace, and E. K. Steffen, *Chem. Commun.*, 1360 (1971).

(136) V. Dave and E. W. Warnhoff, ref 17, p 237.

(137) R. N. Gmyzina, I. A. D'yakonov, and L. P. Danilkina, *J. Org. Chem. USSR*, **6**, 2178 (1970).

(138) L. P. Danilkina and I. A. D'yakonov, *J. Org. Chem. USSR*, **2**, 1 (1966).

(139) I. A. D'yakonov and L. P. Danilkina, *J. Gen. Chem. USSR*, **34**, 738 (1964).

(140) I. A. D'yakonov and L. P. Danilkina, *J. Gen. Chem. USSR*, **32**, 994 (1962).

(141) I. A. D'yakonov, T. A. Kornilova, L. P. Danilkina, and L. F. Pakhomova, *J. Org. Chem. USSR*, **8**, 485 (1972).

(142) D. S. Wulfman, F. C. Carman, B. G. McGiboney, E. K. Steffen, and B. W. Peace, *Amer. Chem. Soc., Prepr., Div. Petrol. Chem.*, **16** (1), B81 (1971).

(143) D. S. Wulfman, E. K. Steffen, and B. W. Peace, Abstracts, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 28–April 2, 1971, No. ORGN-171.

(144) B. W. Peace, and D. S. Wulfman, *Chem. Commun.*, 1179 (1971).

(145) B. W. Peace, F. Carman, and D. S. Wulfman, *Synthesis*, 658 (1971).

(146) B. W. Peace and D. S. Wulfman, *Tetrahedron Lett.*, 3799 (1971).

(147) D. S. Wulfman and B. W. Peace, *Tetrahedron Lett.*, 3903 (1972).

(148) It should be noted that other transition metals have recently been found to effectively catalyze diazo ester decompositions and to thereby promote selective and nearly quantitative carbalkoxycarbene (or carbenoid) additions to olefins; see R. Paulissen, A. J. Hubert, and Ph. Teyssie, *Tetrahedron Lett.*, 1465 (1972).

(149) N. Bodor, M. J. S. Dewar, and J. S. Wasson, *J. Amer. Chem. Soc.*, **94**, 9095 (1972).

(150) V. Dave and E. W. Warnhoff, ref 17, pp 243–244.

(151) W. Kirmse, ref 11b, pp 387–393, 396.

(152) W. von E. Doering, G. Laber, R. Vonderwahl, N. F. Chamberlain, and R. B. Williams, *J. Amer. Chem. Soc.*, **78**, 5448 (1956).

(153) J. E. Baldwin and R. A. Smith, *J. Org. Chem.*, **32**, 3511 (1967).

(154) R. Huisgen and G. Juppe, *Chem. Ber.*, **94**, 2332 (1961).

(155) T. V. Domareva-Mandel'shtam, I. A. D'yakanov, and L. D. Kristol, *J. Org. Chem. USSR*, **2**, 2223 (1966).

(156) I. A. D'yakonov, T. V. Domareva-Mandel'shtam, and K. K. Preobrazhenskii, *J. Org. Chem. USSR*, **5**, 1095 (1969).

(157) T. V. Domareva-Mandel'shtam and I. A. D'yakonov, *J. Gen. Chem. USSR*, **34**, 3896 (1964).

(158) S. H. Graham, D. M. Pugh, and A. J. S. Williams, *J. Chem. Soc. C*, 68 (1969).

(159) It is worth noting that there are *no* bona fide examples of 1,4-addition of carbalkoxycarbenes which do not involve either gas phase reaction (with a high probability of hot molecule isomerizations) or copper-catalyzed reactions, or require forcing conditions which probably afford (secondary) 1,4-addition products *via* rearrangement of a primary product of the reaction.[23]

(160) E. Ciganek, *J. Org. Chem.*, **30**, 4366 (1965).

(161) E. Müller, *Chem. Ber.*, **47**, 3001 (1914).

(162) V. I. Ivanskii, I. A. D'yakonov, and A. P. Kuleshov, *J. Org. Chem. USSR*, **7**, 2190 (1971).

(163) R. Huisgen, H. J. Sturm, and G. Binsch, *Chem. Ber.*, **97**, 2864 (1964).

(164) P. Baret, H. Buffet, and J.-L. Pierre, *Bull. Soc. Chim. Fr.*, 2493 (1972).

(165) A. J. Speziale, C. C. Tung, K. W. Ratts, and A. Yao, *J. Amer. Chem. Soc.*, **87**, 3460 (1965).

(166) W. Kirmse, ref 11b, pp 434, 440.

(167) M. Regitz, *Synthesis*, 351 (1972).

(168) M. S. Kharasch, T. Rudy, W. Nudenberg, and G. Büchi, *J. Org. Chem.*, **18**, 1030 (1953).

(169) C. D. Gutsche and M. Hillman, *J. Amer. Chem. Soc.*, **76**, 2236 (1954).

(170) W. Reid, A. H. Schmidt, W. Kuhn, and A. Bierendempfel, *Tetrahedron Lett.*, 3885 (1972).

(171) A. Schönberg and N. Latif, *J. Chem. Soc.*, 446 (1952).

(172) D. L. Storm and T. A. Spencer, *Tetrahedron Lett.*, 1865 (1967).

(173) S. T. Murayama and T. A. Spencer, *Tetrahedron Lett.*, 4479 (1969).

(174) L. E. Helgen, Ph.D. Dissertation, Yale University, 1965.

(175) The formation of products of the type $RC{\equiv}CCH_2CO_2R$ has been reported for reactions of carbalkoxycarbenoids with terminal acetylenes.[176,177] However, their formation probably does not occur *via* direct carbon-hydrogen bond insertion (see discussion later in this section).

(176) V. K. Jones and A. J. Deutschman, Jr., *J. Org. Chem.*, **30**, 3978 (1965).

(177) M. Vidal, F. Massot, and P. Arnaud, *C. R. Acad. Sci., Ser. C*, **268**, 423 (1969).

(178) E. Ciganek, *J. Org. Chem.*, **30**, 4366 (1965).

(179) I. A. D'yakonov and A. G. Vitenberg, *J. Org. Chem. USSR*, **5**, 1019 (1969).

(180) T. Saegusa, Y. Ito, S. Kobayashi, K. Hirota, and T. Shimizu, *J. Org. Chem.*, **33**, 544 (1968).

(181) J. Owen and J. L. Simonsen, *J. Chem. Soc.*, 1424 (1932).

(182) J. Owen and J. L. Simonsen, *J. Chem. Soc.*, 1225 (1933).

(183) W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, **78**, 4947 (1956).

(184) W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, **83**, 1989 (1961).

(185) H. Lind and A. J. Deutschman, Jr., *J. Org. Chem.*, **32**, 326 (1967).

(186) A. D. Forbes and J. Wood, *J. Chem. Soc. B*, 646 (1971).

(187) M. R. Willcott, III, Ph.D. Dissertation, Yale University, 1963.

(188) R. R. Sauers and R. J. Kiesel, *J. Amer. Chem. Soc.*, **89**, 4695 (1967).

(189) E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **4**, 382 (1958).

(190) M. F. Dull and P. G. Abend, *J. Amer. Chem. Soc.*, **81**, 2588 (1959).

(191) F. H. Dorer and B. S. Rabinovitch, *J. Phys. Chem.*, **69**, 1964 (1965).

(192) M. Vidal, M. Vincens, and P. Arnaud, *Bull. Soc. Chim. Fr.*, 657 (1972).

(193) L. P. Danilkina, T. V. Domareva, and I. A. D'yakonov, *Vestn. Leningrad. Univ.*, **12**, No. 16, *Ser. Fiz. Khim.*, No. 3, 131 (1957); *Chem. Abstr.*, **52**, 6907g W**76**, 2594 (1954907g 1958).

(194) W. H. Urry and J. W. Wilt, *J. Amer. Chem. Soc.*, **76**, 2594 (1954).

(195) J. W. Wilt, Ph.D. Dissertation, University of Chicago, 1954.

(196) W. H. Urry and J. R. Eiszner, *J. Amer. Chem. Soc.*, **73**, 2977 (1951).

(197) W. H. Urry and J. R. Eiszner, *J. Amer. Chem. Soc.*, **74**, 5822 (1952).

(198) T. Migita, W. Ando, S. Kondo, H. Matsuyama, and M. Kosugi, *Nippon Kagaku Zasshi*, **91**, 374 (1970); *Chem. Abstr.*, **73**, 44856v (1970).

(199) See footnote 2 in ref 124.

(200) N. Bilow, Ph.D. Dissertation, University of Chicago, 1956.

(201) A. P. Marchand and N. M. Brockway, *J. Amer. Chem. Soc.*, **92**, 5801 (1970).

(202) A. Streitwieser, Jr., *Chem. Rev.*, **56**, 571 (1956).

(203) V. Franzen, *Justus Liebigs Ann. Chem.*, **627**, 22 (1959).

(204) I. A. D'yakonov and N. B. Vinogradova, *J. Gen. Chem. USSR*, **23**, 63 (1953).

(205) I. A. D'yakonov and N. B. Vinogradova, *J. Gen. Chem. USSR*, **23**, 255 (1953).

(206) I. A. D'yakonov and T. V. Domareva, *J. Gen. Chem. USSR*, **29**, 3064 (1959).

(206a) A referee has pointed out that the halonium ylide mechanism is not necessarily inconsistent with a radical chain mechanism. For the examples discussed above,[193,205,206] homolysis of the ylide would afford very stable radicals which might then escape from the cage and initiate a radical chain process. Similarly, radical intermediates might be involved in the reaction of neopentyl bromide with carbethoxycarbene.[201] The neopentyl *radicals* formed upon ylide *homolysis* might not rearrange prior to recombination. We are indebted to the referee for forwarding this suggestion.

(207) W. H. Pirkle and G. F. Koser, *J. Amer. Chem. Soc.*, **90**, 3598 (1968).

(208) W. H. Pirkle and G. F. Koser, *Tetrahedron Lett.*, 3959 (1968).

(209) I. A. D'yakonov and N. B. Vinogradova, *J. Gen. Chem. USSR*, **22**, 1393 (1952).

(210) I. A. D'yakonov and N. B. Vinogradova, *J. Gen. Chem. USSR*, **21**, 933 (1951).

(211) I. A. D'yakonov and T. V. Domareva, *J. Gen. Chem. USSR*, **25**, 1435 (1955).

(212) I. A. D'yakonov and T. V. Domareva, *J. Gen. Chem. USSR*, **25**, 899 (1955).

(213) D. D. Phillips, *J. Amer. Chem. Soc.*, **76**, 5385 (1954).

(214) U. Schöllkopf, G. Osterman, and J. Schossing, *Tetrahedron Lett.*, 2619 (1969).

(215) A. R. Lepley, *J. Amer. Chem. Soc.*, **91**, 1237 (1969).

(216) R. W. Jemison and D. G. Morris, *Chem. Commun.*, 1226 (1969).

(217) D. G. Morris, *Chem. Commun.*, 1345 (1969).

(218) J. E. Baldwin, W. F. Erickson, R. E. Hackler, and R. M. Scott, *Chem. Commun.*, 576 (1970).

(219) W. Ando, T. Yagihara, S. Kondo, K. Nakayama, H. Yamoto, S. Nakaido, and T. Migita, *J. Org. Chem.*, **36**, 1732 (1971).

(220) W. Ando, S. Kondo, and T. Migita, *J. Amer. Chem. Soc.*, **91**, 6516 (1969).

(221) W. Ando, S. Kondo, K. Nakayama, K. Ichibori, H. Kohoda, H. Yamato, I. Imai, S. Nakaido, and T. Migita, *J. Amer. Chem. Soc.*, **94**, 3870 (1972).

(222) W. Ando, S. Kondo, and T. Migita, *Bull. Chem. Soc. Jap.*, **44**, 571 (1971).

(223) E. Ciganek, *J. Amer. Chem. Soc.*, **88**, 1979 (1966).

(224) H. M. Frey, *J. Amer. Chem. Soc.*, **82**, 5947 (1960).

(225) W. Ando, T. Yagihara, S. Tozune, and T. Migita, *J. Amer. Chem. Soc.*, **91**, 2786 (1969).

(226) W. Ando, T. Yagihara, S. Tozune, S. Nakaido, and T. Migita, *Tetrahedron Lett.*, 1979 (1969).

(227) A. W. Johnson, A. Langemann, and J. Murray, *J. Chem. Soc.*, 2136 (1953).

(228) A. Schönberg and K. Praefcke, *Tetrahedron Lett.*, 2043 (1964).

(229) A. Schönberg and K. Praefcke, *Chem. Ber.*, **100**, 778 (1967).

(230) H. Nozaki, H. Takaya, and R. Noyori, *Tetrahedron Lett.*, 2563 (1965).

(231) H. Nozaki, H. Takaya, and R. Noyori, *Tetrahedron*, **22**, 3393 (1966).

(232) H. Nozaki, S. Moriuti, H. Takaya, and R. Noyori, *Tetrahedron*, **24**, 3655 (1968).

(233) W. Kirmse, ref 11b, pp 430–434.

(234) W. Ando, I. Imai, and T. Migita, *J. Org. Chem.*, **37**, 3596 (1972).

(235) An early report of the copper-catalyzed reaction of ethyl diazoacetate with vinyl ethyl ether mentioned only the formation of the addition product, ethyl 2-ethoxycyclopropane-1-carboxylate (63–70% yield).[236]

(236) I. A. D'yakonov and N. A. Lugovtsova, *J. Gen. Chem. USSR*, **21**, 921 (1951).

(237) W. Ando, K. Nakayama, K. Ichibori, and T. Migita, *J. Amer. Chem. Soc.*, **91**, 5164 (1969).

(238) W. Ando, T. Yagihara, and T. Migita, *Tetrahedron Lett.*, 1983 (1969).

(239) V. Franzen and H. Kuntze, *Justus Liebigs Ann. Chem.*, **627**, 15 (1959).

(240) H. Chaimovich, R. J. Vaughan, and F. H. Westheimer, *J. Amer. Chem. Soc.*, **90**, 4088 (1968).

(241) O. P. Strausz, T. DoMinh, and H. E. Gunning, *J. Amer. Chem. Soc.*, **90**, 1660 (1968).

(242) I. A. D'yakonov and N. D. Pirogova, *J. Gen. Chem. USSR*, **21**, 2201 (1951).

(243) W. Ando, I. Imai, and T. Migita, *Chem. Commun.*, 822 (1972).

(243a) R. Paulissen, H. Reimlinger, E. Hayez, A. J. Hubert, and Ph. Teyssie, *Tetrahedron Lett.*, 2233 (1973).

(244) E. Müller and A. Freytag, *J. Prakt. Chem.*, **146**, 56 (1931).

(245) T. Saegusa, Y. Ito, S. Kobayashi, K. Hirota, and T. Shimizu, *Tetrahedron Lett.*, 6131 (1966).

(246) W. Steinkopf and M. Kühnel, *Chem. Ber.*, **75B**, 1323 (1942).

(247) G. S. Skinner, *J. Amer. Chem. Soc.*, **46**, 731 (1924).

(248) B. Zwanenburg, W. Middlebos, G. J. K. Hemke, and J. Strating, *Recl. Trav. Chim. Pays-Bas*, **90**, 429 (1971).

(249) W. Middlebos, B. Zwanenburg, and J. Strating, *Recl. Trav. Chim. Pays-Bas*, **90**, 435 (1971).

(250) Similar reactions of other diazoalkanes with *t*-BuOCl have been reported; see H. Baganz and H.-J. May, *Angew. Chem., Int. Ed. Engl.*, **5**, 420 (1966).

(251) F. Weygand and H. J. Bestmann, *Chem. Ber.*, **89**, 1912 (1956).

(252) M. F. Lappert and J. S. Poland, *Advan. Organometal. Chem.*, **9**, 397 (1970).

(253) D. Seyferth, *Chem. Rev.*, **55**, 1155 (1955).

(254) D. Seyferth, *Pure Appl. Chem.*, **23**, 391 (1970).

(255) K. A. W. Kramer and A. N. Wright, *J. Chem. Soc.*, 3604 (1963).

(256) M. Lesbre and R. Buisson, *Bull. Soc. Chim. Fr.*, 1204 (1957).

(257) F. Rijkens, M. J. Janssen, W. Drenth, and G. J. M. van der Kerk, *J. Organometal. Chem.*, **2**, 347 (1964).

(258) M. Lesbre and J. Satze, *C. R. Acad. Sci. Paris*, **247**, 471 (1958).

(259) A. N. Nesmeyanov and G. S. Povch, *Chem. Ber.*, **67B**, 971 (1934).

(260) T. Saegusa, Y. Ito, T. Shimizu, and S. Kobayashi, *Bull. Chem. Soc. Jap.*, **42**, 3535 (1969).

(261) T. DoMinh, H. E. Gunning, and O. P. Strausz, *J. Amer. Chem. Soc.*, **89**, 6785 (1967).

(262) O. P. Strausz, T. DoMinh, and J. Font, *J. Amer. Chem. Soc.*, **90**, 1930 (1968).

(263) U. Schöllkopf and N. Rieber, *Angew. Chem., Int. Ed. Engl.*, **6**, 884 (1967).

(264) F. Gerhart, U. Schöllkopf, and H. Schumacher, *Angew. Chem., Int. Ed. Engl.*, **6**, 74 (1967).

(265) A. N. Nesmeyanov and A. E. Segalevich, *Bull. Acad. Sci. URSS, Classe Sci. Chim.*, 8 (1942); *Chem. Abstr.*, **37**, 3055^3 (1943).

(266) C. Rüchardt and G. N. Schrauzer, *Chem. Ber.*, **93**, 1840 (1960).

(267) Such "inverse ylides" have been proposed earlier to account for the course of copper-catalyzed reactions of diazomethane with aromatic hydrocarbons.[268,269]

(268) E. Müller, H. Kessler, H. Fricke, and W. Kiedaisch, *Justus Liebigs Ann. Chem.*, **675**, 63 (1964).

(269) E. Müller and H. Fricke, *Justus Liebigs Ann. Chem.*, **661**, 38 (1963).

(269a) I. Moritani, Y. Yamamoto, and H. Konishi, *Chem. Commun.*, 1457 (1969).

(270) J. Hooz and S. Lincke, *J. Amer. Chem. Soc.*, **90**, 6891 (1968).

(271) J. Hooz and D. M. Gunn, *J. Amer. Chem. Soc.*, **91**, 6195 (1969).

(272) J. Hooz and D. M. Gunn, *Tetrahedron Lett.*, 3455 (1969).

(273) H. C. Brown, M. M. Midland, and A. B. Levy, *J. Amer. Chem. Soc.*, **94**, 3662 (1972).

(274) P. K. Freeman, personal communication, Oct 14, 1970.

(275) H. C. Brown and O. H. Wheeler, *J. Amer. Chem. Soc.*, **78**, 2199 (1956).

(276) G. B. R. De Graaf, J. H. van Dijk-Rothuis, and G. van de Kolk, *Recl. Trav. Chim. Pays-Bas*, **74**, 143 (1955).

(277) M. Saunders and R. W. Murray, *Tetrahedron*, **11**, 1 (1960).

(278) S. Searles, Jr., and R. E. Wann, *Tetrahedron Lett.*, 2899 (1965).

(279) V. Franzen and L. Fikentscher, *Justus Liebigs Ann. Chem.*, **617**, 1 (1958).

(280) G. B. R. De Graaf and G. van de Kolk, *Rec. Trav. Chim. Pays-Bas*, **77**, 224 (1958).

(281) I. A. D'yakonov and M. I. Komendantov, *J. Gen. Chem. USSR*, **29**, 1726 (1959).

(282) I. A. D'yakonov and M. I. Komendantov, *Vestn. Leningrad. Univ.*, **11**, No. 22, *Ser. Fiz. Khim.*, No. 4, 166 (1956); *Chem. Abstr.*, **52**, 2762i (1958).

(283) I. A. D'yakonov, M. I. Komendantov, I. Gokhmanova, and R. Kostikov, *J. Gen. Chem. USSR*, **29**, 3809 (1959).

(284) R. Breslow and D. Chipman, *Chem. Ind. (London)*, 1105 (1960).

(285) I. A. D'yakonov and M. I. Komendantov, *J. Gen. Chem. USSR*, **31**, 3246 (1961).

(286) I. A. D'yakonov and M. I. Komendantov, *J. Gen. Chem. USSR*, **31**, 3618 (1961).

(287) I. A. D'yakonov, M. I. Komendantov, and S. P. Korshunov, *J. Gen. Chem. USSR*, **32**, 912 (1962).

(288) I. A. D'yakonov and M. I. Komendantov, *J. Gen. Chem. USSR*, **33**, 2387 (1963).

(289) M. I. Komendantov, I. A. D'yakonov, I. Gokhmanova, and R. Kostikov, *J. Org. Chem. USSR*, **1**, 201 (1965).

(290) M. I. Komendantov, I. A. D'yakonov, and T. S. Smirnova, *J. Org. Chem. USSR*, **2**, 561 (1966).

(291) M. I. Komendantov, T. S. Smirnova, and I. A. D'yakonov, *J. Org. Chem. USSR*, **3**, 1858 (1967).

(292) I. A. D'yakonov, M. I. Komendantov, and T. S. Smirnova, *J. Org. Chem. USSR*, **5**, 1689 (1969).

(293) W. Kirmse, ref 11b, p 375.

(294) V. Dave and E. W. Warnhoff, ref 17, p 237.

(295) R. Huisgen, H. König, G. Binsch, and H. J. Sturm, *Angew. Chem.*, **73**, 368 (1961).

(296) F. Weygand, *Angew. Chem.*, **73**, 70 (1961).

(297) F. Weygand, H. Dworschak, K. Koch, and S. Konstas, *Angew. Chem.*, **73**, 409 (1961).

(298) R. Paulissen and Ph. Teyssie, unpublished results; R. Paulissen, personal communication, March 9, 1973.

(299) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 565, 633 (1963).

(300) R. Huisgen, H. Staugl, H. J. Sturm, and H. Wagenhofer, *Angew. Chem.*, **73**, 170 (1961).

(301) S. M. Gurvich and A. P. Terent'ev, *Sb. Statei Obshch. Khim., Akad. Nauk SSSR*, **1**, 409 (1953); *Chem. Abstr.*, **49**, 1047i (1955).

(302) W. E. Bachmann and W. S. Struve, *Org. React.*, **1**, 38 (1942).

(303) F. Weygand and H. J. Bestmann, *Angew. Chem.*, **72**, 535 (1960).

(304) F. Weygand and H. J. Bestmann, *Newer Methods Prep. Org. Chem.*, **3**, 451 (1964).

(305) W. Kirmse, ref 11b, pp 490–491.

(306) J. Shafer, P. Baronowsky, R. Lausen, F. Finn, and F. H. Westheimer, *J. Biol. Chem.*, **241**, 421 (1965).

(307) G. O. Schenck and A. Ritter, *Tetrahedron Lett.*, 3189 (1968).

(308) D. E. Thornton, R. K. Gosavi, and O. P. Strausz, *J. Amer. Chem. Soc.*, **92**, 1768 (1970).

(309) I. G. Csizmadia, J. Font, and O. P. Strausz, *J. Amer. Chem. Soc.*,

90, 7360 (1968).

(310) G. Frater and O. P. Strausz, *J. Amer. Chem. Soc.*, **92**, 6654 (1970).

(311) J. Fenwick, G. Frater, K. Ogi, and O. P. Strausz, *J. Amer. Chem. Soc.*, **95**, 124 (1973).

(312) For an exception, see Z. Majerski and C. S. Redvanly, *Chem. Commun.*, 694 (1972).

(313) V. Franzen, *Justus Liebigs Ann. Chem.*, **614**, 31 (1958).

(314) I. G. Csizmadia, H. E. Gunning, R. K. Gosavi, and O. P. Strausz, *J. Amer. Chem. Soc.*, **95**, 133 (1973).

(315) J. Gelhaus and R. W. Hoffmann, *Tetrahedron*, **26**, 5901 (1970).

(316) D. C. Richardson, M. E. Hendrick, and M. Jones, Jr., *J. Amer. Chem. Soc.*, **93**, 3790 (1971).

(317) It should be noted that **58** has been reported *not* to suffer Wolff rearrangement at 140°.[315]

(318) T. DoMinh, O. P. Strausz, and H. E. Gunning, *J. Amer. Chem. Soc.*, **91**, 1261 (1969).

(319) M. Jones, Jr. and W. Ando, *J. Amer. Chem. Soc.*, **90**, 2200 (1968).

(320) A. Padwa and R. Layton, *Tetrahedron Lett.*, 2167 (1965).

(321) The suppression of intramolecular rearrangements of alkylcarbomethoxycarbenes has also been noted when these carbenes are produced *via* benzophenone sensitized photodecomposition of the parent diazo ester; see M. B. Sohn and M. Jones, Jr., *J. Amer. Chem. Soc.*, **94**, 8280 (1972).

(322) S. A. Matlin and P. G. Sammes, *Chem. Commun.*, **11** (1972).

(323) U. Schöllkopf, B. Bánhidai, and H.-U. Scholz, *Justus Liebigs Ann. Chem.*, **761**, 137 (1972).

(324) P. S. Skell, S. J. Valenty, and P. W. Humer, *J. Amer. Chem. Soc.*, **95**, 5041 (1973).

(325) P. S. Skell and S. J. Valenty, *J. Amer. Chem. Soc.*, **95**, 5042 (1973).

(326) R. LeGoaller and J.-L. Pierre, *C. R. Acad. Sci., Ser. C*, **276**, 193 (1973).

(327) A. L. Fridman, F. A. Gabimov, and V. D. Surkov, *J. Org. Chem. USSR*, **8**, 2505 (1972).

(327a) B. Eistert, J. Riedinger, G. Küffner, and W. Lazik, *Chem. Ber.*, **106**, 727 (1973).

(328) M. Muramatsu, N. Obata, and T. Takizawa, *Tetrahedron Lett.*, 2133 (1973).

(329) H. Ledon, G. Linstrumelle, and S. Julia, *Tetrahedron Lett.*, 25 (1973).

(330) N. T. Buu and J. T. Edward, *Can. J. Chem.*, **50**, 3719 (1972).

(331) Y. Hata and M. Watanabe, *Tetrahedron Lett.*, 4659 (1972).

(332) W. Ando, H. Fujii, T. Takeuchi, H. Higuchi, Y. Saiki, and T. Migita, *Tetrahedron Lett.*, 2117 (1973).

(333) W. Ando, *Int. J. Sulfur Chem., Part B*, **7**, 189 (1972).

(334) T. Migita and W. Ando, *Asahi Garasu Kogyo Gijutsu Shoreikai Kenkyu Hokoku*, 317 (1972); *Chem. Abstr.*, **78**, 123954g (1973).

(335) N. T. Buu and J. T. Edward, *Can. J. Chem.*, **50**, 3730 (1972).

(336) K.-P. Zeller, *Chem.-Ztg.*, **97**, 37 (1973).

(337) A. C. Hopkinson, *J. Chem. Soc., Perkin Trans. 2*, 794 (1973).

(338) J. Hooz and R. B. Layton, *Can. J. Chem.*, **50**, 1105 (1972).

(339) J. Hooz, J. N. Bridson, J. G. Calzada, H. C. Brown, M. M. Midland, and A. B. Levy, *J. Org. Chem.*, **38**, 2574 (1973).

(340) T. Sato, T. Mori, and J. Shinoda, *Bull. Chem. Soc. Jap.*, **46**, 1833 (1973).

(341) D. S. Wulfman and R. S. McDaniel, Jr., submitted for publication.

(342) B. M. Trost, R. M. Cory, P. H. Scudder, and H. B. Neubold, *J. Amer. Chem. Soc.*, **95**, 7813 (1973).

(343) R. G. Salomon and J. K. Kochi, *J. Amer. Chem. Soc.*, **95**, 3300 (1973).

(344) D. S. Wulfman, B. W. Peace, and R. S. McDaniel, Abstracts, 9th Midwest Regional Meeting of the American Chemical Society, Lawrence, Kans., Oct 25–26, 1973, No. 323.

(345) L. T. Scott and G. J. DeCicco, *J. Amer. Chem. Soc.*, **96**, 322 (1974).

(346) H. Ledon, G. Linstrumelle, and S. Julia, *Bull. Soc. Chim. Fr.*, 2071 (1973).

(347) R. Paulissen, E. Hayez, A. J. Hubert, and P. Teyssie, *Tetrahedron Lett.*, 607 (1974).

(348) H. Ledon, G. Linstrumelle, and S. Julia, *Tetrahedron*, **29**, 3609 (1973).

(349) P. H. Mazzocchi and H. J. Tamburin, *J. Org. Chem.*, **38**, 2221 (1973).

(350) Y. Yamada, T. Oine, and I. Inoue, *Bull. Chem. Soc. Jap.*, **47**, 339 (1974).

(351) H. Iwamura, Y. Imahashi, and K. Kushida, *Chem. Lett.*, 259 (1974).

(352) H. Iwamura, Y. Imahasi, and K. Kushida, *J. Amer. Chem. Soc.*, **96**, 921 (1974).

(353) H. D. Roth, personal communication, April 19, 1974; H. D. Roth and M. L. Manion, manuscript submitted for publication.

(354). P. E. Krieger and J. A. Landgrebe, Abstracts, 9th Midwest Regional Meeting of the American Chemical Society, Lawrence, Kans., Oct. 25–26, 1973, No. 324.

(355) P. E. Krieger, Ph.D. Dissertation, University of Kansas, 1974.

(356) W. Ando, K. Konishi, T. Hagiwara, and T. Migita, *J. Amer. Chem. Soc.*, **96**, 1601 (1974).

(357) W. Ando, K. Konishi, and T. Migita, *J. Organometal. Chem.*, **67**, C7 (1974).

(358) H. Watanabe, T. Nakano, K.-I. Araki, H. Matsumoto, and Y. Nagai, *J. Organometal. Chem.*, **69**, 389 (1974).

(359) I. Gosney and D. Lloyd, *Tetrahedron*, **29**, 1697 (1973).

(360) U. Schöllkopf and P. Tonne, *Justus Liebigs Ann. Chem.*, **753**, 135 (1971).

(361) U. Schöllkopf, F. Gerhart, M. Reetz, H. Frasnelli, and H. Schumacher, *Justus Liebigs Ann. Chem.*, **716**, 204 (1968).

(362) M. Reetz, U. Schöllkopf, and B. Banhidai, *Justus Liebigs Ann. Chem.*, 599 (1973).

(363) S. J. Valenty and P. S. Skell, *J. Org. Chem.*, **38**, 3937 (1973).

(364) W. Ando, T. Hagiwara, and T. Migita, *J. Amer. Chem. Soc.*, **95**, 7518 (1973).

(365) W. Ando, T. Hagiwara, and T. Migita, *Tetrahedron Lett.*, 1425 (1974).

(366) D. Seyferth and R. A. Woodruff, *J. Org. Chem.*, **38**, 4031 (1973).

(367) D. Seyferth and R. A. Woodruff, *J. Fluorine Chem.*, **2**, 214 (1972/73).

(368) D. Seyferth, R. A. Woodruff, D. C. Mueller, and R. L. Lambert, Jr., *J. Organometal. Chem.*, **43**, 55 (1972).

(369) G. W. Griffin and N. Bertoniere, ref 22, pp 318–328, and references cited therein.

(370) M. I. Komendantov, V. N. Novinskii, and R. R. Bekmukhametov, *J. Org. Chem. USSR*, **9**, 431 (1973).

(371) M. J. S. Dewar and C. A. Ramsden, *Chem. Commun.*, 688 (1973).

(372) A. Krantz, *Chem. Commun.*, 670 (1973).