

## COPPER, SILVER AND GOLD

## ANNUAL SURVEY COVERING THE YEAR 1975

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## ABBREVIATIONS

acac	=	acetylacetonate
aq	=	aqueous
COD	=	1,5-cyclo-octadiene
COT	=	cyclo-octatetraene
Cp	=	cyclopentadienyl
DMF	=	dimethylformamide
DPM	=	1,2-bis(diphenylphosphino)methane
LDC	=	lithium dimethylcuprate
RT	=	room temperature
THF	=	tetrahydrofuran
TREN	=	2,2',2"-triaminotriethylamine
TRIPHOS	=	1,1,1-tris(diphenylphosphinomethyl)ethane

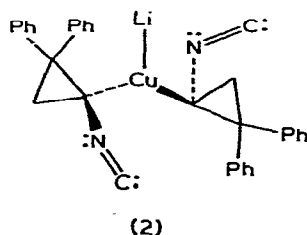
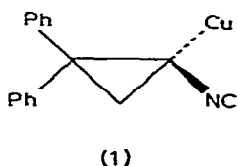
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## I Organocopper compounds

A survey on copper(I) complexes has appeared [1]. A review on the organic chemistry of metal vapours discusses Cu, Ag and Au interactions of alkyl halides to give alkyl radicals and metal halides [2]. Some copper-carbon bonded complexes were referred to in a survey on the inorganic chemistry of ylides [3]. A review has appeared which includes Group IB arylmetal cluster compounds [3a].

The compounds  $\text{Cu}\{\text{C}(\text{CF}_3)_2\text{CN}\}_2$  and  $\text{Ag}\{\text{C}(\text{CF}_3)_2\text{CN}\}$  have been prepared from  $(\text{CF}_3)_2\text{CHCN}$  and suitable copper or silver salts in 20% acetic acid [4]. The formation of the first optically active organocopper(I) compound (1) having an asymmetric C atom attached to copper(I) is reported. The chiral cuprate (2) was also prepared [5]. A series of papers on (dimethylamino)-phenylcopper compounds have appeared [6-10]. 2,6-Dimethoxy-, 2,4,6-trimethoxy-, 2-(dimethylamino)- and 4-(dimethylamino)phenylcopper compounds were synthesised by treating the corresponding lithio derivative with  $\text{CuBr}$  in ether solution at  $0^\circ$  [6]. A series of hydrocarbon-soluble 2-[(dimethylamino)methyl]phenyl- and substituted phenylcopper complexes have been isolated and shown to be tetrameric in benzene. The X-ray structural determination of 5-methyl-2-[(dimethylamino)methyl]phenylcopper, which was done elsewhere, was discussed together with possible bonding modes [7,8]. The 1:1  $[\text{RCu}-\text{CuBr}]_n$  [9] and the 2:1  $[2\text{RCu}-\text{MX}]_n$  [10] ( $\text{M} = \text{Cu}$ ,  $\text{X} = \text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ;  $\text{M} = \text{Ag}$ ,  $\text{X} = \text{Br}$ ) compounds have been characterised from interactions of 2-[(dimethylamino)methyl]phenylcopper ( $\text{RCu}$ ) with the appropriate metal halide. During the formation of the 1:1 complex with other cupric halides, the dimer R-R, 2-halo-substituted benzylamine, R-halide and small amounts of



N,N-dimethylbenzylamine RH were produced and these formations were discussed in terms of an intramolecular electron transfer redox reaction taking place in an inner sphere activated intermediate of the type  $R_4Cu_3X \text{ --- } X-CuX (CuX)_{n-1}$  [9]. Pure phenylcopper and substituted phenylcopper derivatives have been used in the one step synthesis of triorganotin halides from diorganotin halides [11]. The cuprous trimethylsilylacetylide  $CuC\equiv CSiMe_3$  was formed from  $Cu(OBu^t)$  and  $Me_3SiC\equiv CH$ . This acetylide, though a solid, was too unstable to undergo Castro coupling reactions but did form trimethylsilylethynyl ketones with acid chlorides [12].  $(CuCN)_4(DMF)_2$   $RR^1(OH)C\equiv CBr$  has been isolated as an intermediate in the conversion of the acetylene to butynenitriles using  $CuCN$  as a catalyst in aq. DMF solutions [15].

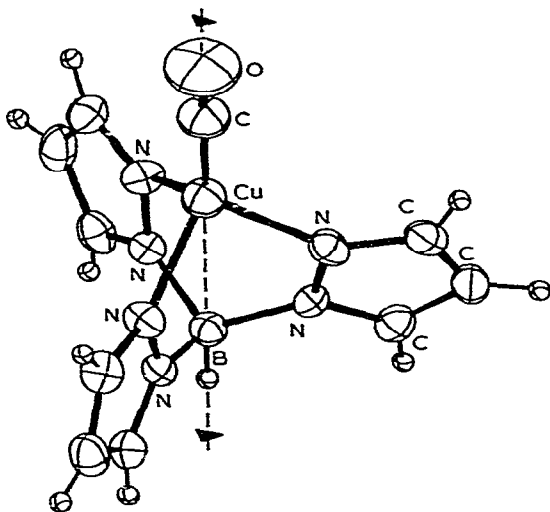
The  $^{13}C$  NMR spectra of a variety of isocyanide complexes have been studied. Some  $\pi$ -back bonding occurs in zero oxidation state complexes but it is not important in positive oxidation state compounds. A metal triad shielding trend was observed [14]. A new synthetic method of preparing organocopper(I) isocyanide complexes utilising active hydrogen compounds has been reported. Typical reactions involved

$$CHXYZ + \frac{1}{2}Cu_2O + \frac{1}{2}C_4H_9NC \xrightarrow{-H_2O} CHXYZCu(\frac{1}{2}C_4H_9NC)_2$$

for  $X=Y=COMe$ ,  $Z=H$ ;  $X=Y=CO_2Et$ ,  $Z=H$ ;  $X=COMe$ ,  $Y=CO_2Et$ ,  $Z=H$ ;  $X=CN$ ,  $Y=CO_2Me$ ,  $Z=H$  and  $X=Y=CO_2Et$  with  $Z=Et$ . When these reaction solutions were refluxed enamines  $XYC=CHNHR$  were formed via insertion reactions [15]. A unique structural investigation of a copper-carbonyl linkage has appeared with the X-ray crystallographic determination of [hydrotris(1-pyrazolyl)-borato]copper(I) carbonyl (3). Significant bond parameters observed were  $Cu-C = 1.76\text{\AA}$ ,  $Cu-N = 2.05\text{\AA}$  and  $C-C = 1.12\text{\AA}$  [16]. Poly(pyrazolyl)borate complexes of Cu and Ag, including  $Cu(CO)\{B(pz)_4\}$ , contained coordinated and free pyrazolyl groups which interchanged rapidly in the  $^1H$  NMR time scale at RT. Limiting spectra were observed at  $-100^\circ$  [17]. The products of the co-condensation reaction of copper atoms with CO at  $10-15^\circ K$  have been investigated. The carbonyls  $Cu(CO)_2$ ,  $Cu(CO)$  and  $Cu_2(CO)_6$  were

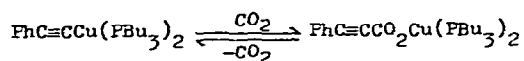
established and computation of isotopic frequencies for the CO stretching modes of triangular  $\text{Cu}(\text{CO})_3$  and linear  $\text{Cu}(\text{CO})_2$  were in close agreement with observed values. The IR data for  $\text{Cu}_2(\text{CO})_6$  were consistent with a structure containing a Cu-Cu bond [18]. Solutions of  $\text{H}_2\text{SO}_4$  containing copper carbonyl species have been used to carbonylate primary, secondary and tertiary alcohols to the corresponding acids [19]. The carbonylation of piperidine by CO in the presence of  $\text{CuCl}_2$  is a chain reaction initiated by radicals formed on oxidative dehydrogenation of piperidine and on decomposition of a piperidine- $\text{CuCl}_2$  complex [20].

Heating  $\text{CH}\equiv\text{CCH}=\text{CH}_2$  with  $\text{HgCl}_2$  in toluene gave a 95% yield of  $\text{ClHgCH}=\text{CHCH}=\text{CHCl}$  which on treatment with  $\text{CuCl}$  in MeCN at RT gave 84% of  $\text{CH}\equiv\text{CCH}=\text{CH}_2$  ( $\text{CuCl}_2$ )<sub>2</sub> [21]. Other olefin complexes of copper(I) were prepared from



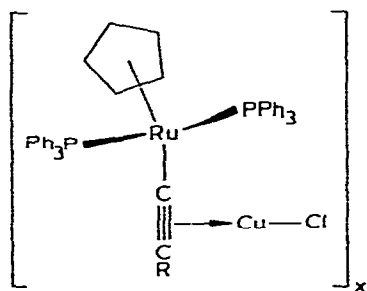
(3)

copper(I) acetate and 1,5-hexadienes, 1,4-hexadienes, COD and COT, forming  $\text{Cu}(\text{O}_2\text{CMe})_2(\text{olefin})$ . With 2,5-bicyclo[2.2.1]heptadiene  $\text{Cu}(\text{O}_2\text{CMe})(\text{olefin})$  was isolated [22]. Reaction between  $\text{CpRuCl}(\text{PPh}_3)_2$  or *cis*- $[\text{ReCl}(\text{CO})_3(\text{PPh}_3)_2]$  with  $\text{Cu}(\text{C}_2\text{R})$  has given a series of products formulated as (4), (5) and (6) [23]. A reversible insertion of  $\text{CO}_2$  into the metal-carbon bond in  $\text{PhC}\equiv\text{CCu}(\text{PBu}_3)_2$  under mild conditions has been noted [24] e.g.



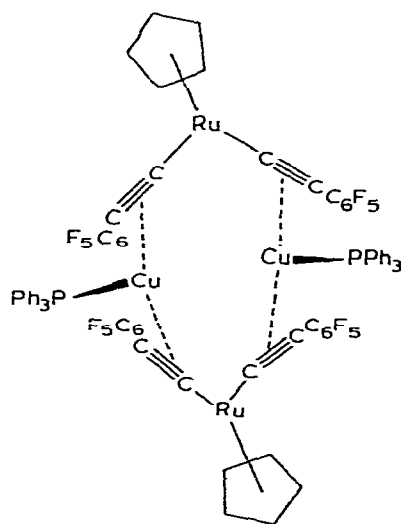
Bubbling  $\text{CO}_2$  through a THF solution of  $\text{CuMe}(\text{PPh}_3)_2$  gave  $\text{MeCO}_2\text{Cu}(\text{PPh}_3)_2$  which converted to  $\text{MeCO}_2\text{Cu}(\text{CO}_2)(\text{PPh}_3)_2$  with prolonged reaction times.

Both these complexes produced  $\text{MeCO}_2\text{H}$  with  $\text{HCl}$  gas [25]. The incorporation of  $\text{CO}_2$  into  $\text{Cu}(\text{II})$   $\psi$ -ephedrinates has been compared with the reactions of  $\text{CO}_2$  with amines and amino alcohols to form carbamates, and shown to be a reaction of  $\text{CO}_2$  with the ligand only [26]. The reaction of arylcopper with dinitrophenylmethane in the presence of  $\text{PPh}_3$  formed  $\text{Cu}(\text{dnmp})(\text{PPh}_3)_2$  and benzene. A structural elucidation of the copper product characterised the dnmp ion as (7) [27].

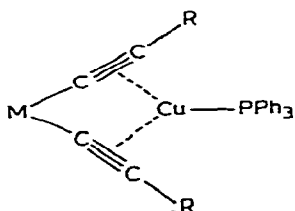


(4;  $x = 2$  for  $\text{R} = \text{Ph}$

$x = 1$  for  $\text{R} = \text{Ph}, p\text{-MeC}_6\text{H}_4$  or  $\text{Me}$ )



(5)



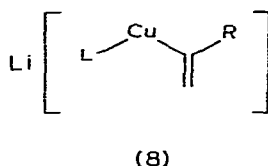
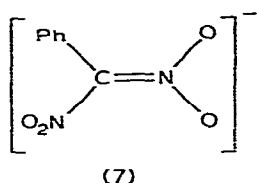
(6)  $\text{M} = \text{Re}(\text{CO})_3\text{PPh}_3$  for  $\text{R} = \text{C}_6\text{F}_5$

$\text{M} = \text{CpRu}$  for  $\text{R} = \text{MeC}_6\text{H}_4$  or  $\text{FC}_6\text{H}_4$

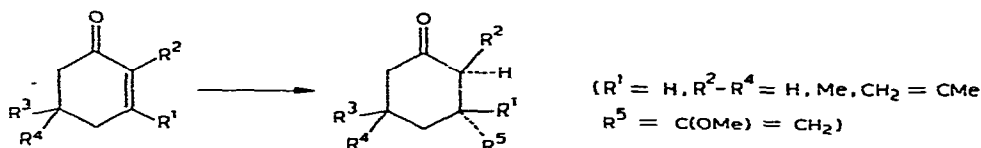
## II Reactions of lithium organocuprates

## 1. With enones and related compounds

Predominantly 1,2-additions were obtained with a variety of  $\alpha,\beta$ -unsaturated carbonyl compounds at low temperature using (8; R = CO<sub>2</sub>Me, CO<sub>2</sub>Et, L = 1-hexyne; or R = H, L = Me). Quantitative additions of (8; R = CO<sub>2</sub>Me, L = 1-hexyne) at -78° to simple cyclic ketones were also observed with

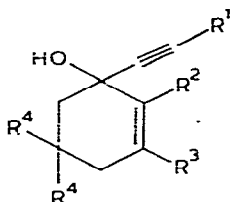


this reagent [28]. Preparation of the new cuprates (8; R = CH(OEt)<sub>2</sub>, L =  $\text{LiCE(OEt)}_2$  or  $\text{Bu}^t\text{C}\equiv\text{C}$ ) is reported together with their 1,4-conjugate alkylations of  $\alpha,\beta$ -unsaturated carbonyl compounds. Of these two new cuprates (8; L =  $\text{Bu}^t\text{C}\equiv\text{C}$ ) is the least reactive, failing to add to the more hindered dienones [29]. Reagents for coupling and 1,4-addition of a masked acyl ion have been synthesised from  $\alpha$ -ethoxyvinyl lithium and purified CuI [30].  $\text{R}_2\text{CuLi}$  (R =  $\alpha$ -methoxyvinyl), prepared from RLi and CuI-Me<sub>2</sub>S mixtures at -40°, reacted with cyclohexanones to give 1,4-adducts (Scheme 1) and with PhCH<sub>2</sub>Br to form PhCH<sub>2</sub>C(CMe)=CH<sub>2</sub> [31]. Some induction of asymmetry has been observed with additions of organocuprates containing chiral centres. For example the complex prepared from the alcoholate of (-)-N-methylephedrine, methyl lithium and CuI produced 16.5% of  $\alpha$ -methylbenzyl alcohol exhibiting a specific rotation  $[\alpha]_D + 6.6^\circ$  from benzaldehyde [32]. To avoid side reactions resulting from the presence of Cu(II) compounds and other metal salt impurities in the Cu(I) salt used to form

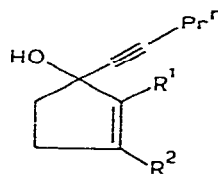


(Scheme 1)

lithium organocuprates, use of the readily prepared  $\text{CuBr}(\text{Me}_2\text{S})$  has been demonstrated, and the procedure used is illustrated with several addition reactions to enones [33]. When reaction conditions in cuprate formation and consequent reactions are such that competing decomposition of the cuprate occurs, then the  $\text{CuH}$  species formed can cause reduction of the organic product. It was found however in the reactions of several epoxides with  $\text{Bu}^n_2\text{CuLi}$  that byproducts resulting from reductions were practically eliminated in the presence of excess  $\text{Bu}^n\text{Li}$ . Other data from this study however suggested that the side reaction leading to reduction during a conjugate addition reaction could be attributed to partial decomposition of the cuprate reagent to form a  $\text{CuH}$  derivative, which is an effective reductant only if an organolithium reagent is present in the mixture [34]. Conjugate reduction of enones (substituted in both the  $\alpha$  and  $\beta$ -position) is readily effected by  $\text{LiAlH}_4$ - $\text{CuI}$  mixtures in THF [35].



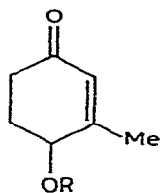
- (9) a;  $\text{R}^1 = \text{Pr}^n, \text{R}^2 = \text{R}^3 = \text{R}^4 = \text{H}$   
 b;  $\text{R}^1 = \text{Pr}^n, \text{R}^2 = \text{Me}, \text{R}^3 = \text{R}^4 = \text{H}$   
 c;  $\text{R}^1 = \text{Pr}^n, \text{R}^2 = \text{H}, \text{R}^3 = \text{R}^4 = \text{Me}$   
 d;  $\text{R}^1 = \text{Bu}^n, \text{R}^2 = \text{R}^3 = \text{R}^4 = \text{H}$   
 e;  $\text{R}^1 = \text{Bu}^n, \text{R}^2 = \text{H}, \text{R}^3 = \text{R}^4 = \text{Me}$



- (10) a;  $\text{R}^1 = \text{R}^2 = \text{H}$   
 b;  $\text{R}^1 = \text{allyl}, \text{R}^2 = \text{H}$

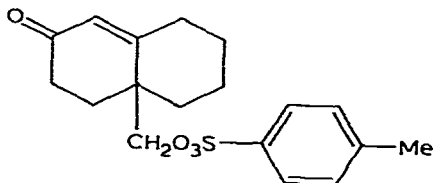
Results from mechanistic studies of conjugate addition of organocuprates to  $\alpha, \beta$ -unsaturated ketones indicate that the addition proceeds by a transfer of 2 electrons from the reagent to the  $\alpha, \beta$ -unsaturated ketone giving presumably a complex dianion and an organocopper(III) species. Electrophilic attack at the  $\beta$ -carbon by this  $\text{Cu(III)}$  species then gives the required product [36]. It has been found that the alkyne groups (e.g. pent-1-ynyl and hex-1-ynyl) of dilithium trialkylcuprates are transferred regioselectively to cyclic enones to afford (85-95%) the corresponding pure 1,2-adducts (9) and (10) only in the presence of

hexamethylphosphoric triamide [37]. LDC reactions with the conjugated enones (11), (12) and (13) followed by  $\text{NH}_4\text{Cl}$  hydrolysis gave 67% of a 1:4 mixture of the enones (14) and (15), 71% of the cyclohexanone (16) and 86% of the cyclopropane (17) respectively. One -electron transfer from the Cu to the enone produced a radical anion which underwent a 1,2-elimination (or alkylation) when the leaving group was good, and methyl transfer

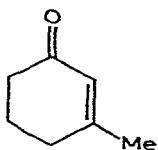


(11) R = Ac

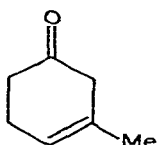
(12) R = tetrahydropyranyl



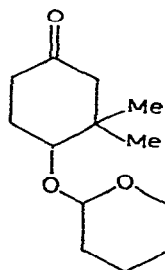
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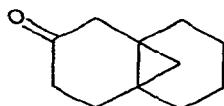
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(15)



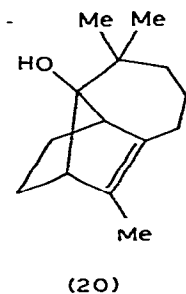
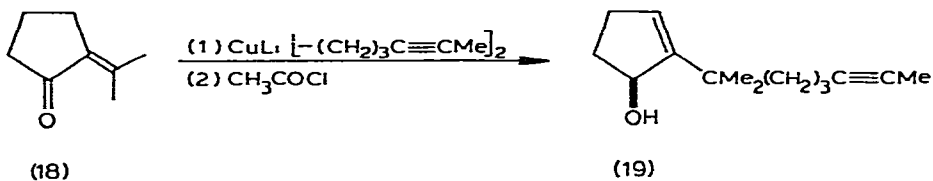
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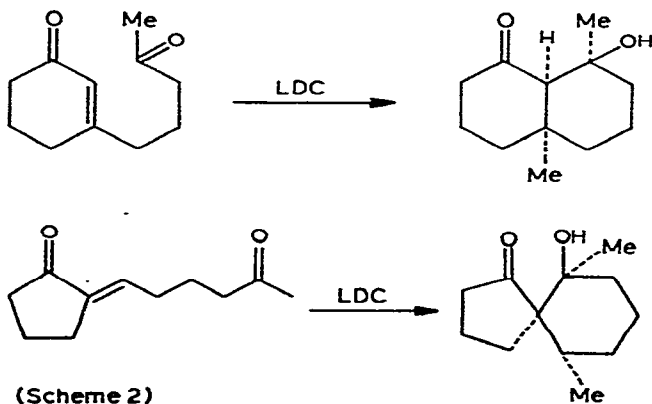
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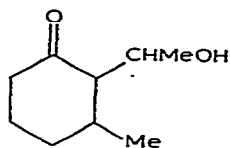
when the leaving group was poor [38]. A short stereospecific total synthesis of longifolene has been developed. The key step is the novel cyclization of the acetylenic cyclopentenol (19), synthesised via cuprate additions to (18), to give the tricyclic bridged-ring alcohol (20) in 75% yield [39]. Cyclohexenone gave 97% (21), a product of an aldol condensation, when treated with LDC in ether followed by  $\text{ZnCl}_2$  and excess  $\text{MeCHO}$  [40]. A regioselective intramolecular aldol condensation has been





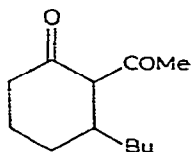
induced by LDC additions to  $\gamma$ -oxo- $\alpha,\beta$ -enones (scheme 2). Enolate anions or radical anions were suggested as intermediates [41]. A series of papers relating to the synthesis of prostaglandin or prostaglandin analogues involving cuprate additions have appeared [42-46]. Part of the synthesis of 7-oxoprostaglandins involved  $\text{Bu}_2\text{CuLi}$  reactions with 2-cyclohexenone which gave 97:3 mixtures of (22) and (23) on acetylation with  $\text{MeCOCl}$  and  $(\text{Me}_2\text{N})_3\text{PO}$  [42]. A bio-organic total synthesis of (-)-PGE<sub>2</sub> and (-)-PGE<sub>1</sub> has been accomplished via conjugate additions of organocuprates, derived from trans-3(S)-hydroxy-1-iodo-1-octene, to (24) ( $\text{R} = \text{Me}$ ,  $\text{R}^1 = \text{OH}$ ) or (25) [43]. A highly stereospecific method for the construction of the



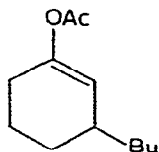


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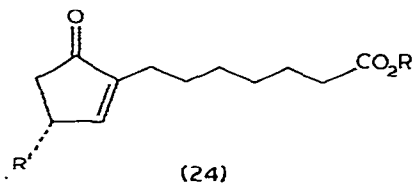
prostanic acid skeleton features conjugate additions of the C-8 vinyl-cuprates  $\text{Cu}\{\text{CH}=\text{CH}-\text{CHR}(\text{CH}_2)_4\text{Me}\}_n$  ( $\text{R} = \text{OCH}(\text{Me})\text{OCH}_2\text{Me}$ ,  $n = 2$ ;  $\text{R} = \text{H}$ ,  $n = 2$ ) to the  $\alpha$ -alkylated cyclopentenones (24) ( $\text{R} = \text{Et}$ ,  $\text{R}^1 = \text{OTHP}$ ). The synthesis depends on steric interaction to control the relative stereochemistry of the ring substituents at C11 to direct the attack of an octenyl cuprate from the opposite face of the 5-membered ring, giving, on protonation the thermodynamically more stable stereoisomeric prostenoate [44]. Alkylations of 4 different structural types of cycloalkanone enolate ions, which are generated regiospecifically via an organocopper reaction with an  $\alpha,\alpha$ -dibromoketone or a 2-cycloalkanone, have been investigated. Information on the relative rates of enolate alkylations versus enolate equilibrium was



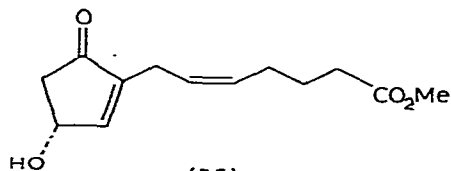
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(23)

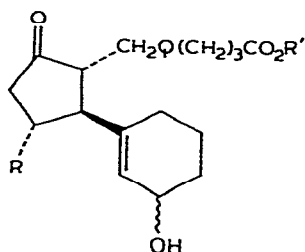


(24)

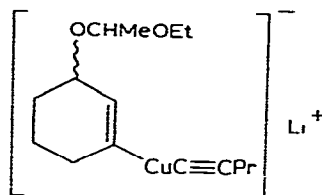


(25)

obtained and the work led to a new total synthesis of the decalin sesquiterpene valerane and to an efficient method for constructing model systems of the E-series of 11-deoxyprostaglandins [45]. Cyclopentenone heptanoate and -heptenoate esters formed (26) on treatment with (27) [46]. Reactions of LDC with several heterocyclic ketones resulted in a 1,4-addition and introduction of a methyl group on the heterocyclic ring (e.g. scheme 5) [47]. With (28) a new type of conjugate 1,4-addition



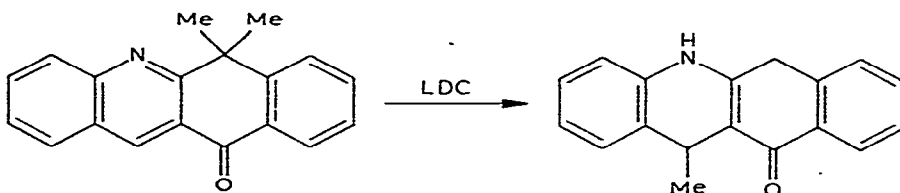
(26)



(27)

(R = H, OH; φ = CH<sub>2</sub>CH<sub>2</sub>, *cis*-CH=CH; R' = H, Me)

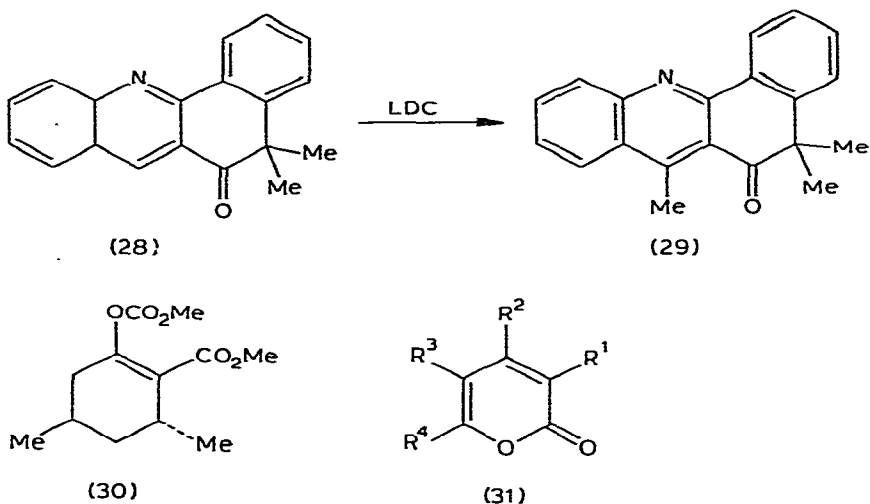
with LDC gave (29) [48]. Michael alkylation of 2-cycloalkenones with R<sub>2</sub>CuLi (R = Me, Bu, PhCH<sub>2</sub> or CH<sub>2</sub> = CH) and treatment with ClCO<sub>2</sub>Me gave the enol carbonates of cyclic β-keto esters (and in some cases the O-acylation products) which, with NaOH or NaOMe, underwent retro-Dieckmann cleavage to β-alkylalkanedioic acids or dimethyl esters. The reactions were highly stereoselective, e.g., 5-methyl-2-cyclohexenone with LDC gave (30), which with NaOMe-NaOH followed by saponification gave *d,l*-HO<sub>2</sub>CCH<sub>2</sub>CHMeCH<sub>2</sub>CHMeCH<sub>2</sub>CO<sub>2</sub>H. 2-Cyclopentenone, 2-cyclohexenone and several methyl-substituted derivatives and 2-cycloheptenone were similarly treated [49]. Treatment of the acetylene R<sup>4</sup>CH(OH)CHR<sup>3</sup>C≡CCOOH with R<sub>2</sub><sup>1</sup>CuLi and subsequent alkylation or acylation of the resultant vinyl anion produced the pyrones (51) [50].



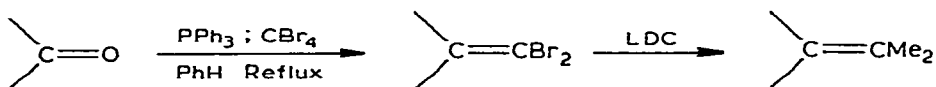
(Scheme 3)

## 2. Miscellaneous reactions

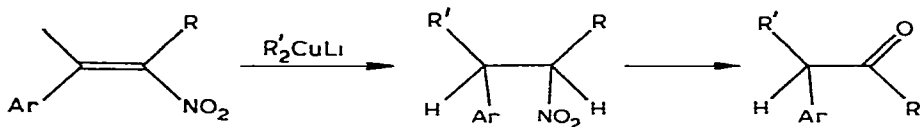
A series of alkylation reactions of bromoketones with cuprates has appeared [51-54]. Thus alkyllithium homocuprate additions to α,α'-dibromoketones gave monoalkylated ketones on hydrolysis, or dialkylated ketones if alkyl halides were added to the reaction intermediate [51].



The bromoketones  $R^1CMe_2COCBr_2R^2$  ( $R^1 = Me, Et$ ;  $R^2 = H, Et, CHMe_2, CMe_3$ ) were alkylated by  $R_2CuLi$  ( $R = Me, CHMe_2, Et$ ) to give respectively  $R^1CMe_2COCHRR^2$  [52]. The monobromoketone  $Me_2CHCOCBrMe_2$  gave 90%  $Me_2CHCOCMe_3$  with LDC [53]. Regiospecific introduction of a primary, secondary or tertiary alkyl group on the ketone site initially brominated was achieved by this latter method. The mechanism was said to involve concomitant halogen-metal exchange and nucleophilic substitution. These two mechanisms coexisted in substitutions by primary or secondary alkyl groups but only nucleophilic substitution was possible with tertiary alkyl groups [53]. A new synthesis of  $\beta$ -alkyl  $\alpha,\beta$ -unsaturated ketones via alkylations of the corresponding  $\beta$ -bromo derivative has been demonstrated by reacting a series of cyclic  $\beta$ -bromo  $\alpha,\beta$ -unsaturated ketones with various lithium phenylthio(alkyl)cuprate reagents (alkyl = Me, Bu, sec-Bu, tert-Bu) [54]. An efficient method for converting ketones into 1,1-dibromoalkenes is reported (scheme 4) [55]. Conjugate addition of lithium organocuprates to nitroolefins has shown this to be a route to ketones (scheme 5) [56]. The reagent prepared by mixing LDC and MeLi reacted with cyclohexanones to produce axial alcohols with high stereoselectivity and in high yield. This 4-tert-butylcyclohexanone, 4-methyl-trans-2-decalone and 2-methylcyclohexanone with the above reagent gave 94,



(Scheme 4)



Ar = 4-ClC<sub>6</sub>H<sub>4</sub>; R = Me

= Ph; R = H

= 2-pyridyl, R = Me

(Scheme 5)

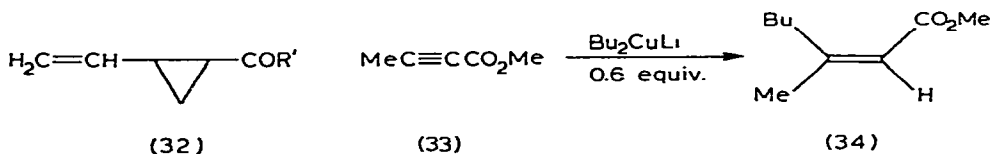
90 and 97% equatorial methylation respectively. The reagent was shown to be superior to other reagents for the high yield equatorial methylation of conformationally biased cyclohexanones [57]. The aldehydes 4-RC<sub>6</sub>H<sub>4</sub>CHO (R = MeO, H, F) and LDC gave >90% of 4-RC<sub>6</sub>H<sub>4</sub>CH(OH)Me in Et<sub>2</sub>O at -10°.

Similarly Me(CH<sub>2</sub>)<sub>5</sub>CHO formed > 90% of Me(CH<sub>2</sub>)<sub>5</sub>CH(OH)Me [58].

The cuprates R<sub>2</sub>CuLi (R = Me, Bu, Ph, H<sub>2</sub>C=CMe) formed 63-98% of

RCH<sub>2</sub>CH=CHCH<sub>2</sub>CH<sub>2</sub>COR<sup>1</sup> (R<sup>1</sup>=Me, Ph) with the vinylcyclopropane (32) [59].

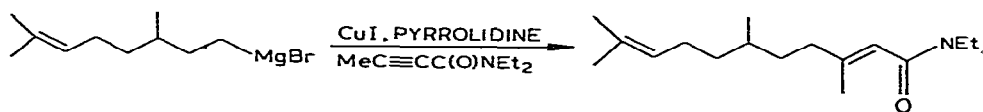
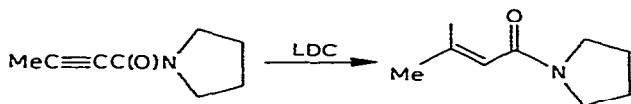
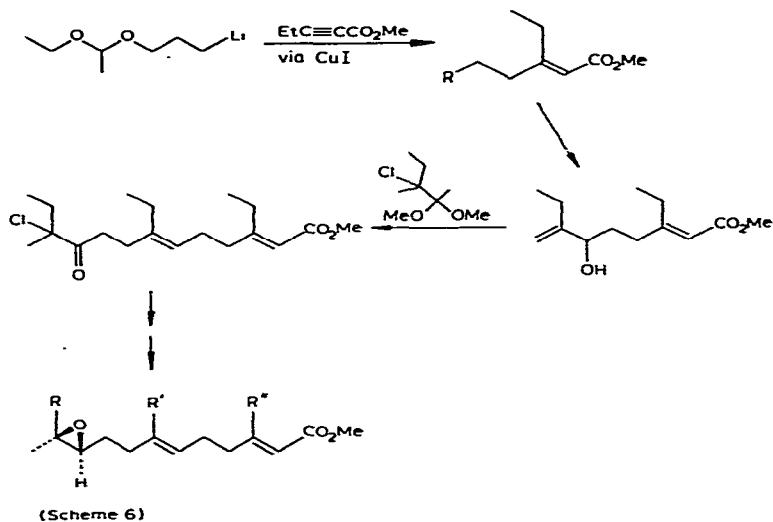
The conjugate addition of various n-butylcopper reagents to methyl 2-butynoate has been studied in some detail. Of special synthetic significance was the finding that both alkyl groups of an organocuprate complex may be transferred to an acetylenic ester. Thus 1 equivalent of (33) reacted



completely with 0.6 equivalent of Bu<sub>2</sub>CuLi to give a high yield of (34).

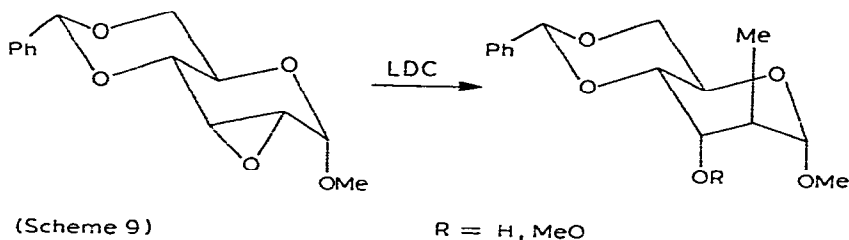
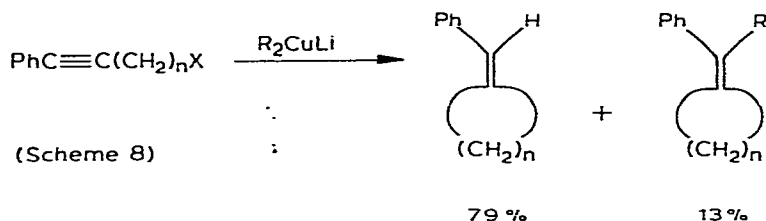
With mixed cuprates e.g. Bu(Me)CuLi, the butyl group was selectively transferred to (33). The stereoselective conjugate addition of organo-copper(I) species to α,β-acetylenic esters, as applied to the synthesis of trisubstituted double bonds, has been utilised in the preparation of

the juvenile hormone analogue Me(2E,6E)-3,7-diethyl-cis-10,11-epoxy-11-methyl-2,6-tridecadienoate (scheme 6). These conjugate additions were also applied to acetylenic amides (scheme 7) [60]. Lithium dialkylcuprates are reported to cyclise acetylenic alcohols in high yield (scheme 8) [61]. The oxirane rings of carbohydrate 2,3-anhydro sugars can be opened stereospecifically by LDC (scheme 9) [62]. The formation of allenes by reactions of lithium diorganocuprates on propargylic acetates



(Scheme 7)

is proposed to occur via an allenic copper derivative. The results appear to rule out radical or cationic mechanisms [63].  $\alpha,\beta$ -Epoxy silanes reacted with organocuprates in a regio- and stereospecific manner to give good yields of  $\beta$ -hydroxyalkylsilanes which can be stereospecifically converted

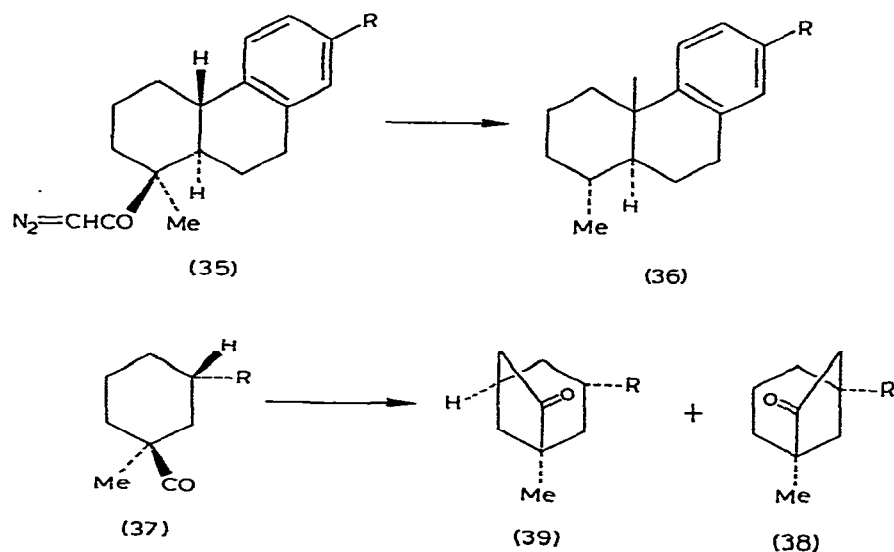
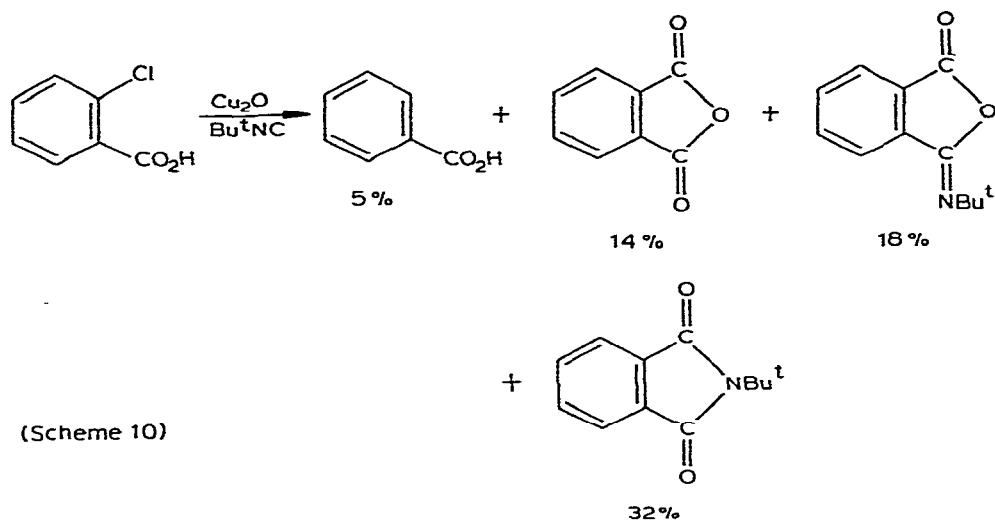


into olefins in high yields under mild conditions. Thus cis-1-pentenyl-trimethylsilane was converted to the cis-epoxide which on treatment with  $\text{Pr}_2\text{CuLi}$  in ether yielded erythro-5-trimethylsilyl-4-octanol [64].  $\text{PhOCH}(\text{Me})\text{CH}_2\text{CH}(\text{SePh})\text{CH}=\text{CH}_2$  reacted with LDC to give cis- and trans- $\text{PhOCHMeCH}_2\text{CH}=\text{CHEt}$  [65].

### III Reactions of organocopper and related reagents

A review on the synthesis of cyclic compounds via copper-isonitrile complexes has appeared [66], and reactions of 2-halo-1-olefin carboxylic acid with  $\text{Cu}_2\text{O}$  and isonitriles have been studied (scheme 10) [67].

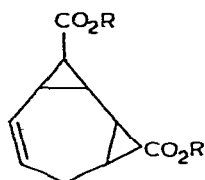
Partial rate data, asymmetric induction studies, interrupted experiments and additives studies have indicated that copper(I) phosphite complexes are destroyed during the course of reactions with dimethyl diazomalonate and ethyl diazoacetate. All evidence was consistent with the copper(I) being oxidised to copper(II), and copper(0) being oxidised by impurities in the olefin which most probably were peroxides.  $\text{Cu}(\text{acac})_2$  was found to be the most effective decomposing agent [68]. Carbenoid decomposition of the diazoketones (35) (R=H, OMe) in the presence of  $\text{Cu}_2\text{O}$  under tungsten filament lamp irradiation produced (36). Similar results were obtained



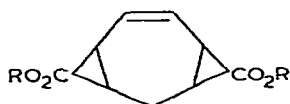
with (37) ( $R=Ph$ ,  $p\text{-MeOC}_6\text{H}_4$ ) which gave 55-60% of (38) and 10-15% of (39) [69]. The reaction of tropilidene with  $N_2CHCO_2R$  ( $R=Me$ ,  $Et$ ) and  $CuBr$  as catalyst gave mixtures of (40) and (41) which further formed (42) on additions of more diazoacid ester [70].  $N_2CHCO_2Et$  in  $(Me_2C=CH)_2$  decomposed in the presence of the copper catalyst (43) to give an isomeric mixture of chrysanthemic acid (44) [71]. The ratio of the 7-(45) to 6-membered (46) ring intramolecular cyclisation product increased with decreasing sol-



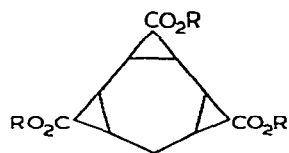
vent polarity in the  $[(C_6F_5)_3Cu]_4$  catalysed decomposition of (47). The ratio increased with increasing reaction temperature in the uncatalysed decomposition. The intermediacy of (48) and of ground and excited state  $S_0$  and  $S_1$  carbenes in this decomposition were discussed [72]. A comparison of the metal-promoted 1,3-dipolar addition of ketocarbenes to nitriles has shown copper trifluoromethanesulphonate to be a much more efficient catalyst than  $Pd(acetate)_2$ . The reduction of Cu(II) to Cu(I) is shown to be key step in the process [73].



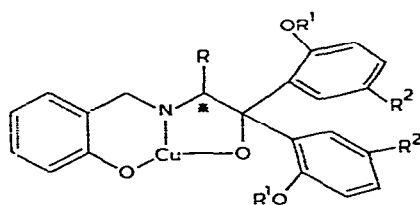
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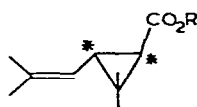
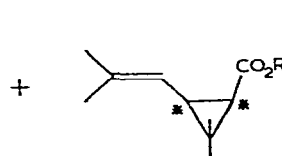
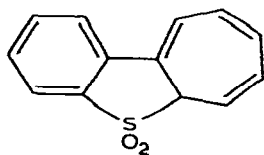
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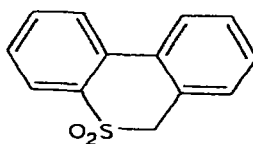
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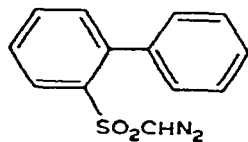
(43)

*trans*-(44)*cis*-(44)

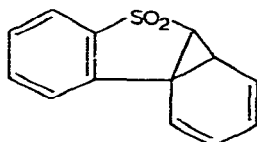
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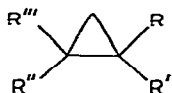


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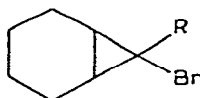


(48)

gem-Dibromocyclopropanes (49) and (50) ( $R=R'=\text{Br}$ ,  $R''=\text{H}$ ,  $R''=\text{Ph}$ ,  $\text{PhCH}_2\text{OCH}_2$ , hexyl) in THF were treated with BuLi and the resultant lithio derivatives (49, 50) ( $R = \text{Li}$ ,  $R' = \text{Br}$ ,  $R''=\text{H}$ ) on reaction with MeI, EtI and allyl bromide produced (49, 50) ( $R=\text{Me}$ , Et, allyl). Stereoselectivity in the monoalkylation was influenced by additions of  $(\text{Me}_2\text{N})_3\text{PO}$  and Cu(I) salts, and the products could be transformed into trisubstituted ethylenes



(49)

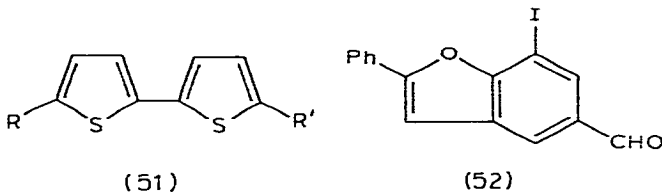


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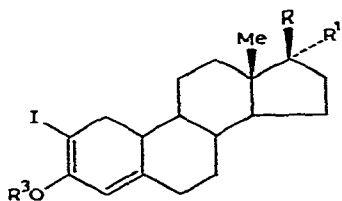
stereospecifically, or to alkylidenecyclopropanes [74]. The cyclopropanes (49) ( $R=\text{Me}$ ,  $R'=\text{CO}_2\text{Me}$ ;  $R = \text{CO}_2\text{Me}$ ,  $R' = \text{Me}$  for  $R'' = \text{CN}$  and  $R''' = \text{Me}$ ) were formed mainly as trans-isomers from  $\text{MeCHClCO}_2\text{Me}$  by successive treatment with  $\text{Me}_3\text{COCuPBu}_3$  and  $\text{CH}_2=\text{CMeCN}$  in DMF, THF or benzene [75].

Tertiary or secondary alkylcopper reagents readily add to conjugated dienes to give allylic organocopper derivatives [76]. Dialkenylchloroboranes react rapidly at  $0^\circ$  with three equivalents of MeCu to produce (E,E)-1,3-dienes of 99% stereochemical purity. The reaction provides a facile and stereoselective transformation of acetylenes into the corresponding (E,E)-1,3-dienes via hydroboration with  $\text{BH}_2\text{Cl}$  and can even be extended to the accommodation of a functional group [77]. The syn-addition of alkylcopper compounds to various alkynes,  $\text{HC}\equiv\text{C}-(\text{CH}_2)_n\text{Z}$  ( $n = 2,3$ ;  $Z = \text{NEt}_2$ , SEt, OR etc.), showed a regio-selectivity dependent upon various factors, the major factor being the nature of the function and the solvent. The vinylcopper derivatives thus obtained have been carboxylated, iodinated and alkylated [78]. Alkoxy and alkylthiovinyl organocuprous reagents have been used as intermediates in the stereospecific synthesis of heterosubstituted alkenes. Thus treatment of ethynyl ethyl ether with  $\text{RMgBr}$  ( $R = n\text{-heptyl}$ , Et), CuBr and  $\text{H}_2\text{O}$  (and  $\text{CO}_2$  and  $\text{I}_2$ ) gave  $\text{RC}(\text{OEt})=\text{CHR}'$  ( $R' = \text{H}$ ,  $\text{CO}_2\text{H}$ , iodo). Ethynyl ethyl

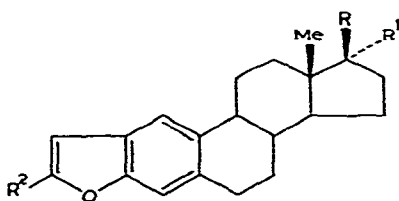
sulphide formed  $RCH=C(SET)R'$  [79]. Trans-addition of several Grignard reagents to primary  $\alpha$ -acetylenic alcohols catalysed by CuI is reported. The reactions represent a new example of stereospecific synthesis of allylic alcohols [80]. The structure of (51) ( $R=C\equiv CMe$ ,  $R'=C\equiv CH$ ) isolated from the flowers of Tagetes erecta was confirmed by synthesis from (51) ( $R=R'=I$ ) and  $CuC\equiv CCH(CMe)_2$  in six steps [81]. 4-Substituted 2,6-diiodo-phenols with cuprous arylacetylides gave 16-63% of 5-substituted 2-aryl-7-iodobenzofurans. For example 3,5,4-I<sub>2</sub>(HO)C<sub>6</sub>H<sub>2</sub>CHO with PhC $\equiv$ CCu formed (52) in 26% yield [82]. The diethynyl compounds (PhC $\equiv$ C)<sub>2</sub>Z<sup>-</sup> [Z = 4-C<sub>6</sub>H<sub>4</sub>COC<sub>6</sub>H<sub>4</sub>-4, 3-C<sub>6</sub>H<sub>4</sub>COC<sub>6</sub>H<sub>4</sub>-3, 4-C<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>-4, p-C<sub>6</sub>H<sub>4</sub>(C<sub>6</sub>H<sub>4</sub>-4)<sub>2</sub>, 9H-fluoren-2,7-ylene, 9-oxo-9H-fluoren-2,7-ylene, 2,8-dibenzofuranylene, 9,10-dihydro-9,10-dioxo-2,7-phenanthrylene, dibenzo[a,c]-phenazin-2,7-ylene] were prepared in 39-96% yields from IZI and CuC $\equiv$ CPh [83].



Treatment of (53) with  $CuC\equiv CR^2$  in refluxing pyridine gave (54) ( $RR^1 = O$ ,  $R^2 = Pr, Bu, Ph, n-C_6H_{13}, HOCH_2CH_2$ ;  $R = HO, R^1 = H, R^2 = Pr$ ) in 60 - 71% yields [84]. An  $S_N2'$  type substitution product (e.g. 55) was formed in excellent yield from the reaction of 1-alkylthioallylcopper reagents (e.g. isopropylthioallylcopper) with allylic halides (e.g. 2-cyclohexylidene-ethyl bromide) [85]. The alkylation of  $[RCR'=C(SMe)]_2Cu$  with excess MeI in THF gave 20-50% of cis- $RCR'=C=C=CRR'$  ( $R=Ph, R'=Me, Et, Me_2CH, Ph, H$ ;  $R=H, R'=Me(CH_2)_4, Me_3C$ ) [86]. The compounds  $p-MeC_6H_4S(O)_nCH_2CMe=CH_2$  ( $n=1,2$ ) were alkylated at the  $\alpha$ -CH<sub>2</sub> position by alkyl halides in the presence of BuLi. CuI lowered the yields and, in the case of  $CH_2=CHCH_2Br$ , the reaction with the para-compound ( $n=2$ ) led mainly to  $p-MeC_6H_4SO_2CH=CMeCH_2CH_2CH=CH_2$  [87]. Vinylcopper derivatives with 1-halo-1-alkynes in Et<sub>2</sub>O containing  $(Me_2NCH_2)_2$  followed by acid hydrolysis gave 77-84% of conjugated enynes.



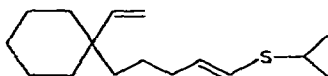
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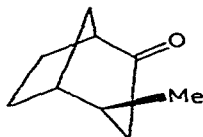
(54)

For example  $\text{BuCEt}=\text{CHCuMgI}_2$  and  $\text{BuC}\equiv\text{CI}$  formed  $\text{BuCEt}=\text{CHC}\equiv\text{CBu}$ . (*Z*)- $\text{PrCH}=\text{CHC}=\text{CCH}_2\text{OH}$  was prepared similarly and with  $\text{LiAlH}_4$  formed 96% of (*2E-4Z*)- $\text{Pr}(\text{CH}=\text{CH})_2\text{CH}_2\text{OH}$ , the acetate of which with  $\text{Cu(I)}$  and  $\text{BrMg}(\text{CH}_2)_8\text{OCHMeOEt}$  gave 75% of bombykol [88].

(56) was the only product formed when bicyclo[3.2.1]oct-3-en-2-one was treated with  $\text{MeMgI}$  and  $\text{CuCl}$  [89]. *N,N'*-Dimethyl-1,4-benzoquinone-diimine forms, with  $\text{MeLi}$  and  $\text{MeMgX}$ , 4- $\text{Me}_2\text{NC}_6\text{H}_4\text{NHMe}$  by 1,6-addition, 2,5-( $\text{MeNH}$ ) $_2\text{C}_6\text{H}_7\text{Me}$  by 1,4-addition and 4- $\text{MeNHC}_6\text{H}_4\text{NHMe}$  by reduction. The effect of the kind of reagent, solvation with  $\text{Et}_2\text{O}$  and THF, additions of  $\text{Cu(I)}$  or

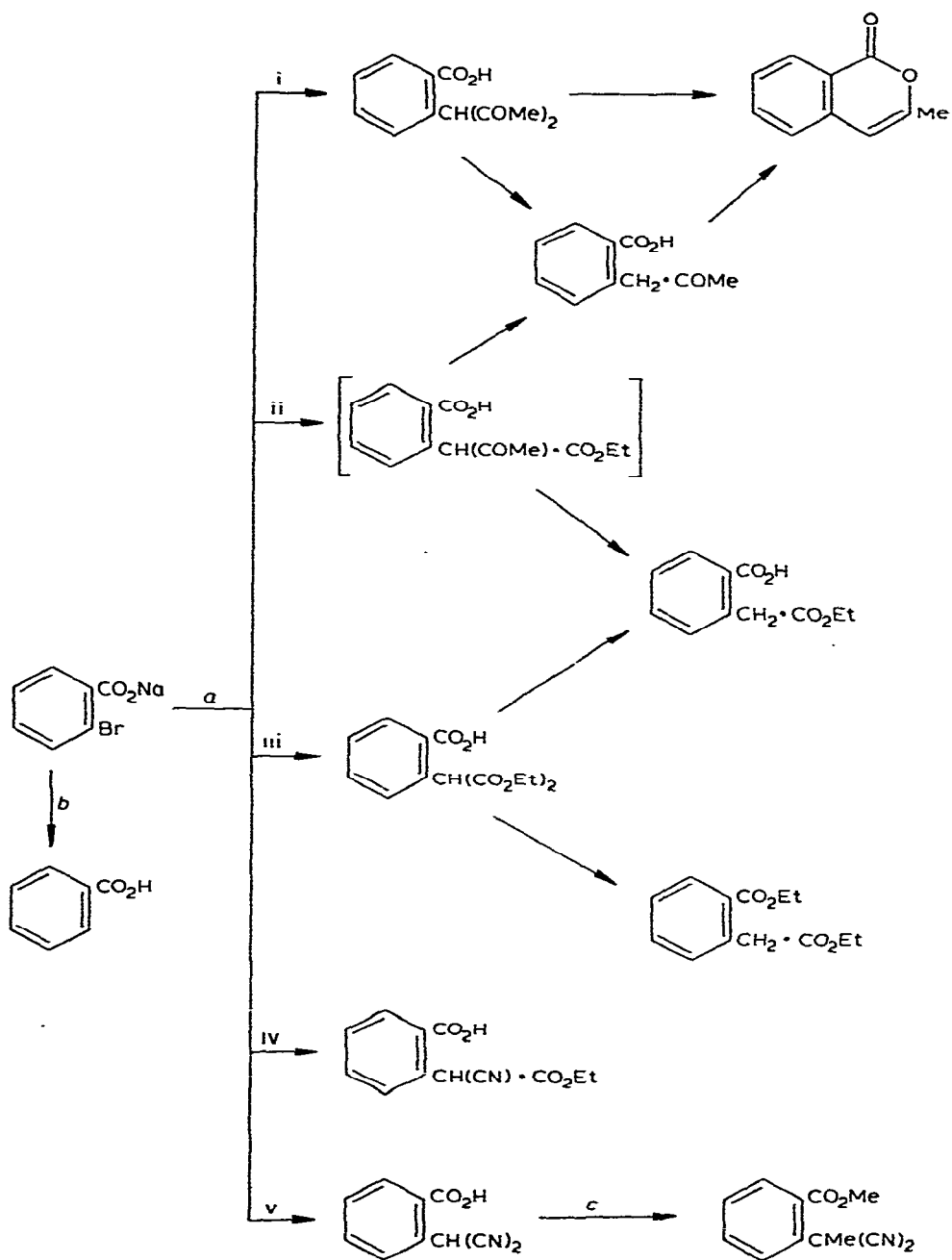


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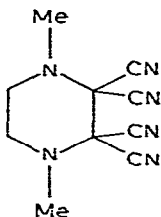


(56)

$(\text{Me}_2\text{NCH}_2)_2$  and temperature changes on these competing reactions have been studied [90]. 9-Alkyl and 9-arylanthracenes react with  $\text{CuBr}$  in methanol to give 10-alkyl (or aryl)-10-methoxyanthrones as the major product [91]. 2-Iodobenzene underwent substitution reactions with  $\text{CuCN}$  and  $\text{CuOR}$  ( $\text{R}=\text{Me}, \text{Et}, \text{Me}_2\text{CH}, \text{Me}_3\text{C}$ ) to yield 2-cyano- and 2-alkoxyazobenzenes [92]. Depending upon the choice of conditions, copper-catalysed reactions of aromatic bromocarboxylates with carbanions have given oxo-acids, isocoumarins and related products (scheme 11). The effective reaction intermediates are considered to be  $\text{Cu(II)}$  complexes incorporating the halogen carboxylate substrate and the carbamionic nucleophile [93]. Various saturated  $\alpha$ - or  $\beta$ -ethylenic or aryllic organocopper compounds have been



carboxylated under conditions very similar to those used with vinylcopper compounds. Catalytic amounts of  $P(OEt)_3$  enhanced the reaction and carboxylic acids were obtained in excellent yields [94]. Treatment of a range of vinyl iodides with various copper(I) and organocopper derivatives has effected substitution at the carbon with retention of configuration. Copper(II) carboxylates gave better yields of enol esters than the corresponding copper(I) salt [95]. Perfluoroalkylcopper compounds have been used in the preparation of some perfluoroalkyl-substituted acids and alcohols [96]. The use of  $(C_6F_5Cu)_4$  in the decarboxylation of a benzhydryl carboxylic acid has been described [97]. Fatty acid esters were synthesised in good yields by treating copper(I) "ate" complexes, formed from  $MeCu$  and primary or secondary Grignards reagents and esters of primary iodoalkylcarboxylic acids [98]. Four isomers of 1,3,5-undecatriene, (*E,E*)-, (*E,Z*)-, (*Z,E*)-, and (*Z,Z*)-, have been prepared (stereospecifically and nonstereospecifically), using either the Wittig reaction, thermal sigmatropic H shifts, or partial reduction of triple bonds by Zn or organocopper reagents [99]. Dry DMF formed (57) with acetyl chloride in the presence of  $CuCN$  and air [100].

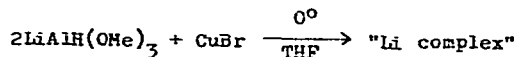


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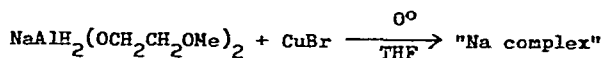
#### IV General catalytic reactions involving copper compounds

A simple preparation of copper hydride reagents which are efficient 1,4-reductants for both conjugated ketones and esters has been reported.

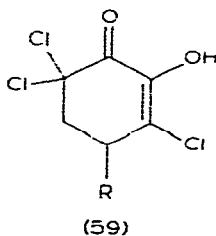
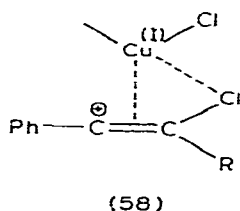
They were prepared by



and

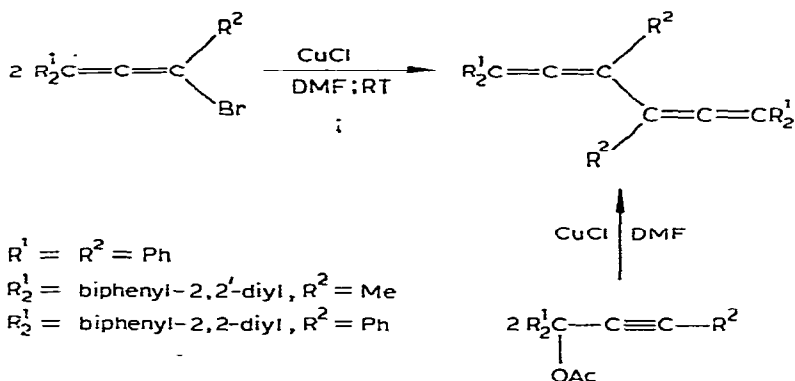


and addition of *sec*-butanol to these reactions allows reduction of acrylates. Labeling experiments established that  $\beta$ -hydrogen addition occurs from the copper and  $\alpha$ -additions from protons of the butanol [101]. Alkylphenyl acetylenes reacted with  $\text{CuCl}_2/\text{LiCl}$  or  $\text{CuCl}_2/\text{I}_2$  in  $\text{MeCN}$  to form dihalo-alkenes. *E*-addition was favoured except when a *tert*-butyl group is on the acetylene, when *Z*-addition predominates. The cationic intermediate (58) was proposed for these reactions [102]. At constant acetylene pressure, the copper-catalysed chlorination of  $\text{C}_2\text{H}_2$  to give  $\text{Cl}_2\text{C}=\text{CHCl}$  proceeded by two independent pathways, the first depending only on  $[\text{Cu}^{2+}]$  and the second depending upon  $[\text{Cu}^{2+}]$ ,  $[\text{Cu}^+]$  and  $[\text{H}_3\text{O}^+]$  [103]. Oxidative chlorination of  $\text{RC}=\text{CH}$  ( $\text{R}=\text{H}$ ,  $\text{Me}$ ,  $\text{CH}_2=\text{CH}$ ) in  $\text{NH}_4\text{Cl}$  with  $\text{CuCl}_2$  and  $\text{FeCl}_2$  gave  $\text{RC}=\text{CCl}$ .  $\text{C}_2\text{H}_2$  formed *trans*- $\text{ClCH}=\text{CHCl}$  [104]. Chlorination of  $\text{RCCH}_2\text{C}=\text{CC}=\text{CCH}_2\text{OR}$  ( $\text{R}=\text{H}$ ) in the presence of  $\text{CuCl}_2$  yielded  $\text{RCCH}_2(\text{CCl}=\text{CCl})_2\text{CH}_2\text{OR}$  ( $\text{R}=\text{H}$ ). Analogous chlorinations for  $\text{R}=\text{Me}$ ,  $\text{Et}$ ,  $\text{Pr}$  and  $\text{Bu}$  in  $\text{MeCN}$  proceeded stepwise giving initially  $\text{RCCH}_2(\text{CCl}=\text{CCl})_2\text{CH}_2\text{OR}$  ( $\text{R}=\text{Me}$ ,  $\text{Et}$ ,  $\text{Pr}$ ,  $\text{Bu}$ ) [105]. The olefins  $\text{R}_2\text{C}=\text{CR}^1\text{CR}^2=\text{CH}_2$  ( $\text{R}=\text{H}$ ,  $\text{R}^1=\text{Cl}$ ,  $\text{R}^2=\text{H}$ ,  $\text{Cl}$ ;  $\text{R}=\text{R}^2=\text{H}$ ,  $\text{R}^1=\text{Me}$ ) were halogenated by  $\text{CuX}_2$  ( $\text{X}=\text{Cl}$ ,  $\text{Br}$ ) in  $\text{MeCN}$  or  $\text{MeOH}$  to give 94.5% of  $\text{XCR}_2\text{CR}^1=\text{CR}^2\text{CH}_2\text{X}$  [106]. Reactions of cycloheptanone or 4-methylcycloheptanone with 50 molar equivalents of  $\text{CuCl}_2$  in 50% acetic acid resulted in ring contraction and chlorination to give (59) ( $\text{R}=\text{H}$ ,  $\text{Me}$ ) [107].



Cyclohexanones and  $\text{CuBr}_2$  produce polybrominated cyclohexanediones except when 3,5-dimethylcyclohexanone was used. A pyrocatechol and a phenol derivative were obtained from 4-methyl- and 3,5-dimethylcyclohexanone respectively [108]. A study on conditions affecting the  $\text{Cu(I)}$  induced reductive dehalogenation, hydrolysis or couplings of some aryl and vinyl halides at RT is reported [109]. Additions of hexamethylphosphoric

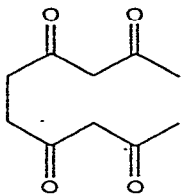
triamide was found to bring about an increase of cross-coupled products in the transition metal catalysed reaction of allylic chlorides (allyl, crotyl and methallyl) with Grignard reagents, the effect being most significant in copper(II) chloride catalysed reactions [110]. Conjugated diallenes were obtained in good yield from bromoallenes or prop-2-ynyl acetates with CuCl in DMF at RT (scheme 12). An allene radical is proposed as an intermediate [111]. The product (60) has been isolated from a cuprous chloride catalysed dimerisation of acetylacetonate [112]. 1,6-Diketones were obtained from  $\text{CH}_2=\text{CHMgCl}$  reactions with fatty acid methyl esters and CuCl [113]. The reaction of ketone enolates with  $\text{CuCl}_2$  in DMF at  $-78^\circ$  produces 1,4-diketones in satisfactory yields.



(Scheme 12)

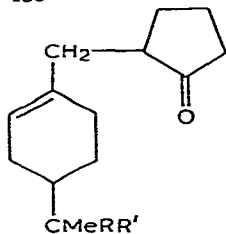
In the  $\text{CuCl}_2$ -promoted coupling of ketones having two different enolizable hydrogens (2-butanone etc.) a mixture of 1,4-diketones was formed with the less crowded 1,4-diketones predominating. The product yields and selectivities in the reaction depend upon alkyl substitution at the  $\alpha$ -carbon of the ketone. Increasing alkyl substitution at the coupling site results in a remarkable reduction in the yield of the coupled product. The reaction with methyl ketones ( $\text{MeCOCHR}^1$ ) furnished 1,4-diketones ( $\text{RR}^1\text{CHCOCH}_2\text{CH}_2\text{COCHR}^1$ ), arising from coupling at the methyl group, in high selectivities (80-90%), and in good yields (60-90%), together with other isomeric 1,4-diketones as minor products. This coupling reaction of ketones provides a general and convenient route to



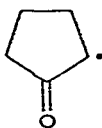


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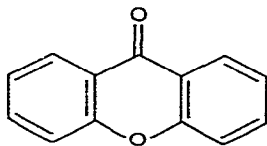
symmetrical 1,4-diketones  $\text{RCOCH}_2\text{CH}_2\text{COR}$ . The present method was successfully applied to some cross couplings of two different methyl ketones and of methyl ketone with acetate, leading to unsymmetrical 1,4-diketones ( $\text{RCOCH}_2\text{CH}_2\text{COR}^1$ ) and  $\gamma$ -keto esters ( $\text{RCOCH}_2\text{CH}_2\text{CO}_2\text{R}^1$ ) respectively. The cross coupling of acetone with 2-octanone gave undecane-2,5-dione, a precursor of dihydrojasnone, in satisfactory selectivity and yield [114]. The reaction of  $\beta$ -pinene with cyclopentanone in the presence of  $\text{Cu}(\text{OAc})_2$  gave 44% of (61) ( $\text{RR}^1=\text{CH}_2$ ) and 12% of its dihydroanalogue (61) ( $\text{R}=\text{H}$ ,  $\text{R}^1=\text{Me}$ ).  $\text{CuCl}$  similarly catalysed the addition which occurred via the radical (62).  $\beta$ -Pinene underwent similar additions with acetone and cyclohexanone [115]. Rapid RT Ullmann-type couplings and ammonolyses of activated aryl halides in homogeneous solutions containing copper(I) ions have been observed. Thus 2- $\text{IC}_6\text{H}_4\text{NO}_2$  with  $\text{F}_3\text{CSO}_3\text{Cu}$  and 5% aq.  $\text{NH}_3$  gave 92% of 2,2'-dinitrobiphenyl after 5 min. [116]. Xanthone side products formed (0.1-8%) in the reactions between a Cu(III)-salicylaldehyde complex and five aryl halides. For example the copper complex and  $\text{PhI}$  gave 8% of (63) which could be formed directly (50%) by heating  $\text{o-PhOC}_6\text{H}_4\text{CHO}$  with  $\text{CuBr}_2$  or  $\text{CuCl}_2$  in  $\text{PhNO}_2$  [117]. Ethyl 2-cyano-6-heptenoate reacted with  $\text{CuCl}_2$ ,  $\text{Cu}(\text{OAc})_2$  and  $\text{Cu}(\text{OPh})_2$  to give mixtures of ethyl 1-cyano-2-(chloromethyl)cyclopentanecarboxylate, its 2-methyl analogue and ethyl 1-cyano-2-methylenecyclopentanecarboxylate [118]. The cyclization of  $\text{CH}_2=\text{CRC}=\text{CMe}_2\text{OCH}_2\text{C}=\text{CH}$  ( $\text{R}=\text{H}$ ,  $\text{Me}$ ) to give the phthalans (64) was catalysed by  $\text{Et}_3\text{N-CuCl}$  or  $\text{Et}_3\text{N-Cu}(\text{OAc})$  in benzene or aq. solution [119]. The tetrahydropyranyloxy- and methoxy-alkynols and (Z)-alkenols  $\text{Me}_2\text{C}(\text{OR})\text{C}=\text{C}(\text{CH}_2)_2\text{OH}$  ( $\text{R}$  = tetrahydropyranyl) and (Z)- $\text{PrCH}(\text{OMe})\text{CH}=\text{CH}(\text{CH}_2)_2\text{OH}$  reacted with  $\text{MeMgI}$  and  $\text{CuI}$  to form  $\text{Me}_2\text{C}=\text{C}=\text{CMe}(\text{CH}_2)_2\text{OH}$  (56%) and (E)-



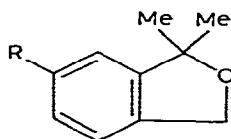
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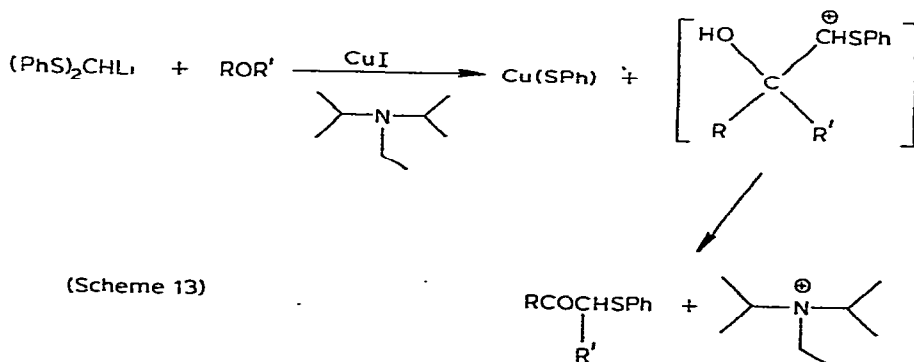


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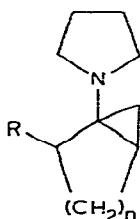


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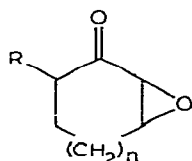
$\text{PrCH}=\text{CHCHMe}(\text{CH}_2)_2\text{OH}$  respectively [120]. Ring expansion or chain extensions of aldehydes and ketones via an  $\alpha$ -epoxythioether intermediate have been facilitated by  $\text{CuI}$  (scheme 13) [121]. Tertiary alkyl primary amines have been dealkylated by  $\text{CuCl}$  via their  $N,N$ -dichloroderivatives [122]. Cuprous ion, supplied as the soluble benzene complex of the trifluoromethanesulphonate salt, is capable of removing a thiophenoxide ion from  $S,S$ -diphenyl thioacetal or an  $S,S$ -diphenyl thioacetal to produce a carbocation which is stabilised by the remaining thiophenoxide group. The intermediate cation ordinarily loses a  $\beta$ -proton to give a high yield of vinyl phenyl sulphide. In addition to simple vinyl sulphides, 1-phenylthio-1,3-butadiene and ketene  $S,S$ -diphenyl thioacetal have been produced by this method. The internal capture of the cation by



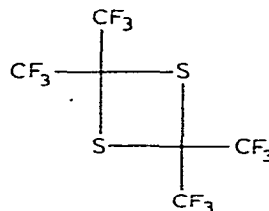
the O atom of a carbonyl group is demonstrated by the production of 2-phenyl-5-methylfuran from the reaction of cuprous ion with the Michael adduct of methyl vinyl ketone and the lithium cuprate salt derived from the S,S-diphenyl thioacetal of benzaldehyde [123]. A mild and simple means of converting vinyl bromides into vinyl acetates with CuI is reported [124]. Kinetics (2nd order) of the reaction of  $\text{BrC}_6\text{H}_4\text{R}$  ( $\text{R}=\text{H}$ ,  $m\text{-Br}$ ,  $m\text{-NO}_2$ ,  $p\text{-NO}_2$ ,  $p\text{-MeSO}_2$ ,  $p\text{-CO}_2\text{Na}$ ) with  $\text{KOCNa}$  in  $\text{MeOH}$ -pyridine at  $130^\circ$  were determined in the presence and absence of  $\text{CuBr}$  and correlated with Hammett  $\sigma$ -constants. The mechanism of the  $\text{CuBr}$ -catalysed reaction was discussed in terms of a single-electron transfer [125].  $\text{CuCl}_2$ -catalysed oxygenation of the bicycloalkanes (65) ( $n = 2-4$ ,  $\text{R}=\text{H}$ ;  $n=3$ ,  $\text{R}=\text{Me}$ ) in  $\text{MeCN}$  gave the epoxy ketones (66). The reaction occurred by oxidative cleavage of the cyclopropane ring and via a 1,2-dioxolane type intermediate [126]. The complexes  $\text{Cu}_2\text{L}_4$  ( $\text{L} = 1,3$ -diaryltriazene) accelerate the oxidation of cyclohexene and are converted in the process to  $\text{CuL}_2$  and  $\text{CuL}$ . Rate constants and activation energies were determined [127].  $\text{CuCl}_2$  and  $\text{IrCl}_3$  were less active catalysts than  $\text{RuCl}_3$  in converting  $\text{CH}_2=\text{CMeCH}_2\text{CH}$  to  $\text{Me}_2\text{CHCHO}$  in  $\text{CF}_3\text{CH}_2\text{OH}$  [128]. The activity of transition



(65)



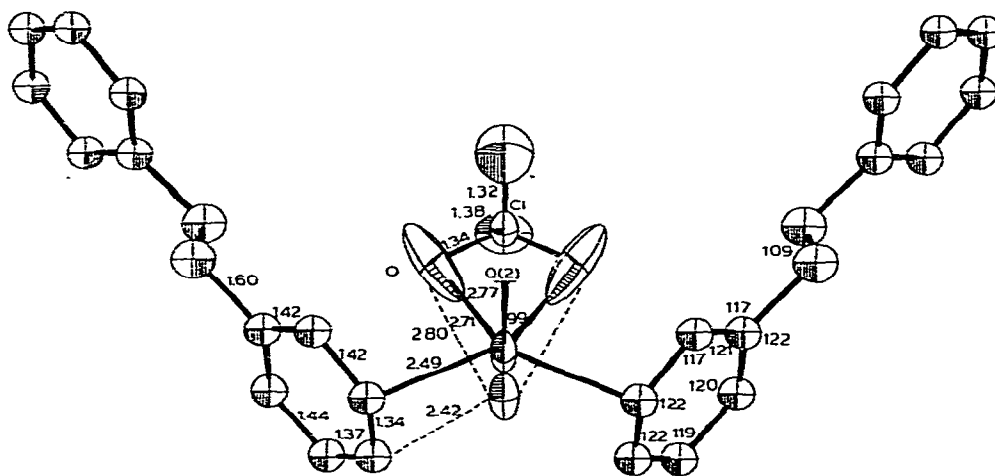
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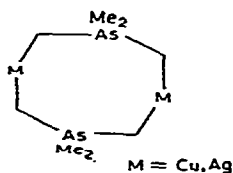
(67)

metal chlorides for cleaving the Si-Fh bond in  $\text{Me}_3\text{SiFh}$  in ethanol was found to decrease in the order  $\text{ReCl}_3 > \text{TiCl}_3 > \text{CuCl}_2 > \text{VCl}_3 > \text{CrCl}_3 > \text{NiCl}_2 > \text{CoCl}_2 > \text{MnCl}_2 > \text{FeCl}_2$  [129].  $\text{SiHCl}_3$  underwent a smooth reaction at RT with allyl chloride,  $\beta$ -methallyl chloride, crotyl chloride and  $\alpha$ -methallyl chloride to give the corresponding allyltrichlorosilanes in excellent yields in the presence of an equimolar amount of tertiary amine and a catalytic

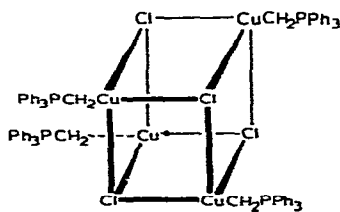
amount of  $\text{CuCl}$  [130]. The product and ease of oxidation of organomercury compounds  $\text{R}_2\text{Hg}$  or  $\text{RHgX}$  by copper salts in DMF under mild conditions was shown to depend on the nature of R and the copper salt used. Possible oxidation reaction mechanisms were considered [131]. Treatment of the 1,5-dithietane (67) in  $\text{KF-DMF}$  with hexafluoropropene in the presence of  $\text{CuBr}$  gave  $\text{RC}(\text{CF}_3)_2\text{SR}^1\text{DMF}$  ( $\text{R}=(\text{CF}_3)_2\text{CF}$ ,  $\text{R}^1=\text{Cu}$ ). Similar reactions of (67) with  $\text{MeOH}$  and  $\text{CuBr}$  or  $\text{AgNO}_3$  formed  $\text{RC}(\text{CF}_3)_2\text{SR}^1\text{DMF}$  ( $\text{R}=\text{MeO}$ ,  $\text{R}^1=\text{Cu}$  or  $\text{Ag}$ ) which further reacted with aryl iodides to produce the sulphide  $\text{RC}(\text{CF}_3)_2\text{SR}^1\text{DMF}$  ( $\text{R}=(\text{CF}_3)_2\text{CF}$ ,  $\text{OMe}$ ;  $\text{R}^1=\text{Ph}$  or substituted phenyl) [132].  $\text{PhN}(\text{O})=\text{NR}$  ( $\text{R}=\text{Bu}$ , cyclohexyl,  $\text{CO}_2\text{Et}$ ,  $\text{Ph}$ ,  $\text{Me}_2\text{NCO}$ ) were prepared (51-85%) from  $\text{PhNO}$  in  $\text{MeCN}$  by reacting with  $\text{RNCl}_2$  overnight at RT in the presence of  $\text{CuCl}$  [135]. Oxidations of  $\text{Me}_2\text{NNH}_2$  with  $\text{CuCl}_2$  gave  $[\text{Me}_2\text{N}=\text{N}]_2\text{Cu}_3\text{Cl}_3$ , which formed tetramethyl-2-tetrazene with  $\text{HCl}$  and  $\text{NH}_3$ .  $\text{CuBr}_2$  and



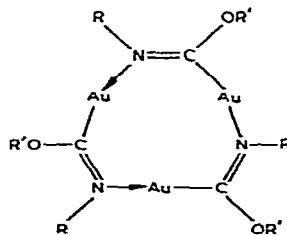
(68)



(69)



(70)



(71)

$\text{Me}_2\text{NNH}_2$  produced  $[\text{Me}_2\text{N}_2\text{CHN}_2\text{Me}_2]\text{Cu}_2\text{Br}_3$ , which gave a new formazan  $\text{Me}_2\text{N}=\text{NCH}=\text{NMe}_2$  on reactions with  $\text{NH}_3$  and  $\text{HBr}$  [154].

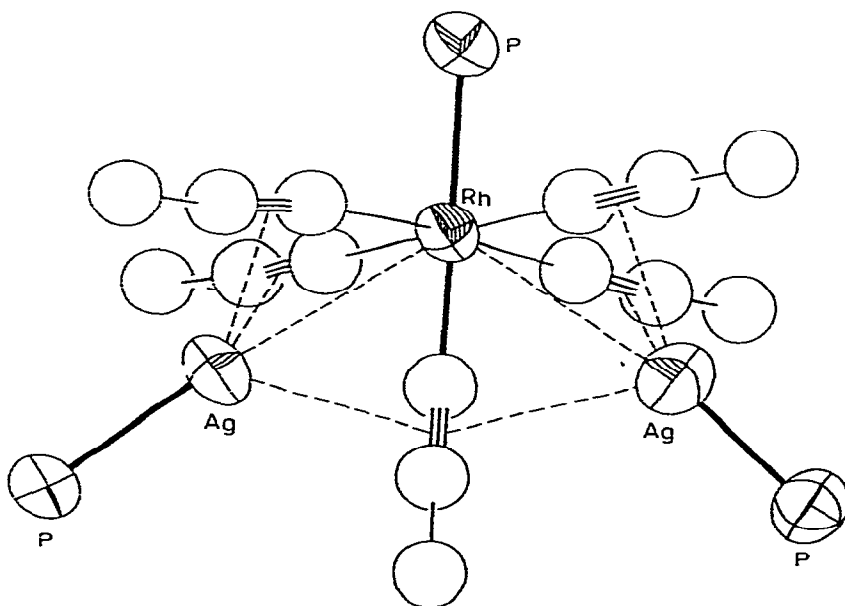
## V Silver-carbon bonds

Gmelin's Handbook of Inorganic Chemistry System No. 61, Silver, B section 5 has appeared and reviews organosilver compounds and organic silver salts [135].

The crystal structure of 1,2-diphenylethanesilver(I) perchlorate (68) has been resolved. The Ag-C bond length was  $2.49\text{\AA}$  [156]. The dimerisation of  $\text{Me}_3\text{As}=\text{CHR}$  with  $\text{CuCl}$  ( $\text{R}=\text{SiMe}_3$ ) and  $\text{Me}_3\text{AsAgCl}$  ( $\text{R}=\text{H}$ ) gave (69) [137]. The ylide complexes  $\text{Ph}_3\text{FCH}(\text{R})\text{MCH}(\text{R})\text{PPh}_3$  and  $[\text{Ph}_3\text{PCH}(\text{R})\text{MCl}]_n$  ( $\text{M}=\text{Cu}, \text{Ag}; \text{R}=\text{H}, \text{Me}, \text{CHMe}_2$ ) have been prepared from triphenylphosphorane ylides and  $\text{MCl}$  [138, 139]. The cubane structure (70) has been proposed for the latter complexes [139]. The isocyanide complexes  $[(\text{RNC})\text{AgCl}]_n$  have been prepared from  $\text{RNC}$  and  $\text{AgCl}$  and further react with alcoholic  $\text{KOH}$  to give the N-alkyliminomethyl derivatives  $[(\text{R}^1\text{O})(\text{RN})\text{CAG}]_3$  (71). The organic group from (71) has been transferred to other metals yielding  $\text{HgZ}_2$ ,  $\text{ClHgZ}$ ,  $[\text{AuZ}]_3$  and  $(\text{Ph}_3\text{P})_2\text{PtClZ}$  [ $\text{Z}=(\text{EtO})(\text{E}-\text{MeC}_6\text{H}_4\text{N})\text{C}-$ ] [140]. The IR and Raman spectra of copper and silver organoacetylides have been recorded and partially assigned by comparison with the published spectra of the parent alkynes. The Raman intensity distribution of the Cu compounds differed from that of the parent molecules far more than those of the silver complexes. The single strong Raman line in the  $\nu(\text{C}\equiv\text{C})$  region suggested only one C-Cu bond length [141].  $\text{AgC}\equiv\text{CPh}$  and the diazonium salts  $2,4\text{-RR}^1\text{C}_6\text{H}_3\text{N}_2^+ \text{X}^-$  ( $\text{R}=\text{H}, \text{R}^1=\text{H}, \text{MeO}, \text{Cl}, \text{Br}, \text{I}, \text{NO}_2, \text{CO}_2\text{Et}, \text{CN}; \text{R}=\text{CO}_2\text{Me}, \text{R}^1=\text{Cl}; \text{R}=\text{Ph}, \text{R}^1=\text{H}; \text{X}=\text{Cl}, \text{Br}$ ) produced the corresponding phenylazoethynylbenzenes  $2,4\text{-RR}^1\text{C}_6\text{H}_3\text{N}=\text{NC}\equiv\text{CPh}_3$  in ethanol- $\text{CHCl}_3$  mixtures [142].

Energies and bond populations have been calculated for several configurations of a 2:1 ethylene-silver(I)  $\pi$ -complex. The configuration in which  $\text{Ag}^+$  is at the centre and in the plane of a square formed by the two ethylene molecules was found to be unfavourable. Rotating one ethylene

molecule so that its  $\sigma_2$  orbitals become perpendicular to those of the other ethylene molecule lowers the energy of the system. As  $\sigma$  overlap (cyclobutane formation) increases,  $Ag^+$  is forced further out of the plane of the 2 ethylene molecules and the energy passes through an optimum [143].  $Ag$  atom-ethylene molecular complexes have been generated in Ne matrices and have been examined by ESR. The observed spectra were consistent with the bonding scheme in which the complex is formed by the dative bonds resulting from the interactions between the  $\pi$ -orbitals of the olefin and the valence orbitals of the  $Ag$  atom, the unpaired electron residing in the non-bonding  $d-p$  hybridized orbital of the latter [144]. A series of acids of formula  $RCH(CO_2H)_2$ ,  $RCH_2CO_2H$  and  $RH(CH_2CO_2H)_2$  with the R group containing an olefinic bond have been synthesised and reacted with a series of metal salts. Chelation via the olefin bond was only found to occur with  $Ag(I)$  salts [145]. Equimolar amounts of  $Ln(fod)_3$  ( $fod = C_3H_7COCHCOCMe_3$ ) and  $C_3F_7CO_2Ag$  act as shift reagents for alkenes in  $CCl_4$  or  $CDCl_3$  solutions [146]. The full paper on the crystal structure of  $RhAg_2(C=CC_6F_5)_5(PPh_3)_3$  (72) has appeared. The molecule contains



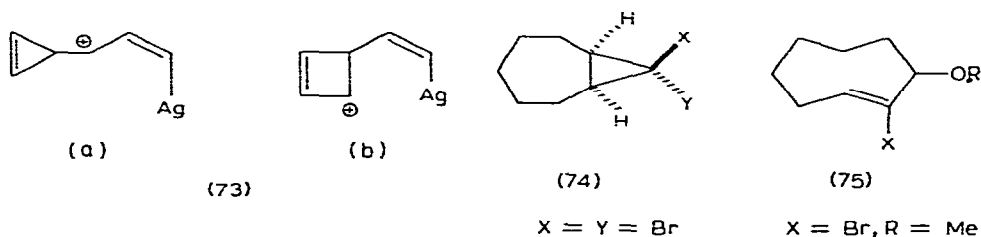
(72)

3 metal atoms in a bent arrangement  $\angle [Ag - Rh - Ag] = 110.5^\circ$ , with the rhodium octahedrally coordinated to one  $PPh_3$  ( $Rh-P = 2.34\text{\AA}$ ) and 5  $\sigma$ -acetylide ligands ( $Rh-C = 2.0\text{\AA}$ ). Each Ag is tetrahedrally bonded to one  $PPh_3$  and bonded asymmetrically to 3 acetylenic  $\pi$ -bonds. The structure is proposed as a zwitterionic association of  $[PPh_3Rh(C\equiv C_6F_5)_5]^{2-}$  and 2  $[PPh_3Ag]^+$  units held together by Ag- $\pi$ -acetylene bonds [147].

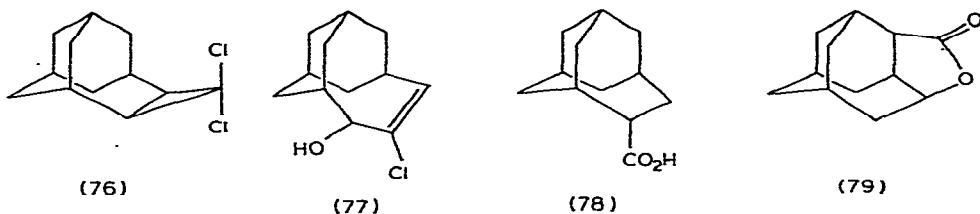
## VI Catalysis by silver salts

Preparative aspects of silver ion-catalysed rearrangements of polycyclic systems have been reviewed (90 refs.) [148].

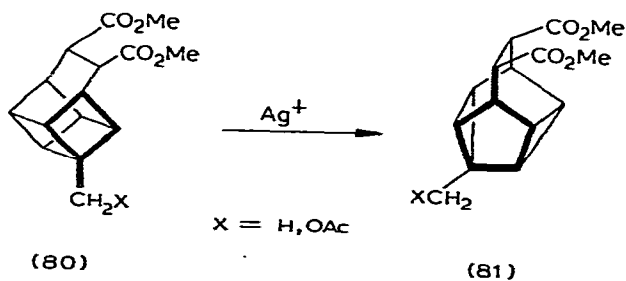
Evidence for the intermediates (73 a and b) has been obtained from the  $Ag(I)$  catalysed rearrangement of 1,1-bridged bicyclopropenyls [149]. The conversion of (74) into (75) with  $AgClO_4$  is virtually quantitative in NaOH. The preparation of medium sized rings of other halogenocyclopropanes was also studied [150]. Ring opening reactions of (76) with  $Ag(I)$



produced the 3 major products (77-79) [151]. Five papers related to the  $Ag(I)$  catalysed rearrangement of 1,8-bishomocubanes have appeared [152-156]. The unsymmetrical bishomocubanes (80) rearranged preferentially to (81) with  $Ag(I)$  and the mechanism of this rearrangement was discussed [152]. Kinetic data obtained from this reaction indicated that concerted and oxidative addition mechanisms are implausible. The bond switching process is triggered by electrophilic attack at the  $C_2 - C_5$  bond with direct formation of a delocalised cyclopropylcarbinyl cation. Such edge argentation accounts for all available kinetic data and conforms to theoretical conclusions that attack by  $Ag(I)$  at an edge bond



is energetically preferable to bidentate coordination with one of the cubyl faces [153]. To probe the effect of such groups as Ph, vinyl, cyclopropyl and ethoxy on the rate of Ag(I) catalysed homocubyl rearrangements, the isomerizations of 4-substituted homocubanes were compared with those of model compounds where direct resonance interaction in the transition state was not anticipated. In contrast to the kinetic behavior of homocubane and its 4-Me, 4-CH<sub>2</sub>OAc, 4-CO<sub>2</sub>Me and 4-CH<sub>2</sub>OMe derivatives, which conform to a linear  $\sigma$  free energy relationship ( $\rho = -2.33$ ), the first four compounds isomerized more rapidly than expected on this basis. The 4-Me<sub>3</sub>C substituent affects bond switching by a steric parameter and the  $k_{Ag}$  was smaller than projected. A D atom or CD<sub>3</sub> group at C<sub>4</sub> gave a small inverse isotope effect ( $k_H/k_D = 0.97$ ) in each instance. Introduction of a second substituent at C<sub>5</sub> does not lead to acceleration of the bond switching process. The contribution of C<sub>9</sub> substitution to the overall isomerisation rate also received limited scrutiny. All of these catalysed reactions followed a second order rate dependence with incursion of pre-equilibrium complex formation. The bond switchings appear to proceed by Ag(I)-induced electrophilic ring opening of the less substituted edge bond [154]. Kinetic studies on the influence of structural features on the 1,8-bishomocubane rearrange-





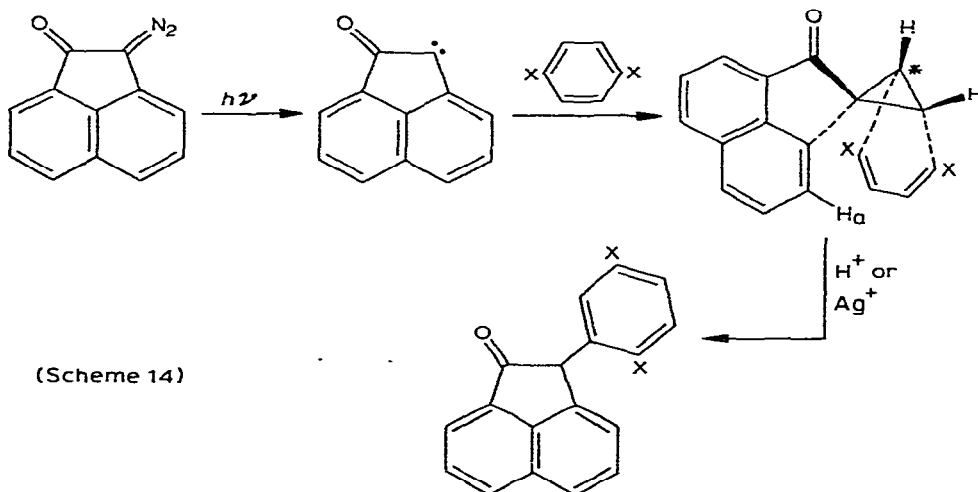
ment have shown that steric retardation with  $\text{PdI}_2(\text{PPh}_3)_2$  is a far more serious issue than it is with  $\text{Ag(I)}$  catalysis [155].



(82)

Tricyclanonone (82) has been prepared from 3-diazocamphor by adding a catalytic amount of silver ions to the THF solution [157].

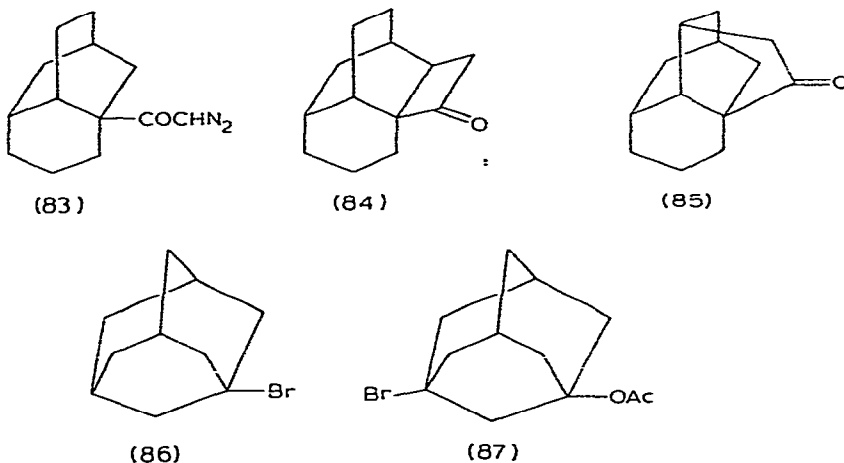
Norcaradienes, prepared from  $\alpha$ -oxocarbene additions to aromatic systems (scheme 14) [158]. Decomposition of (83) in toluene gave predominantly (84) with  $\text{Ag}_2\text{O}$  whilst (85) was the major reaction product with  $\text{CuSO}_4$  [159]. A versatile synthetic method for the preparation of symmetrical and asymmetrical carbodiimides  $\text{RN}=\text{C}=\text{NR}^1$  in which carbene-Pd(II) complexes of general formula  $\text{PdCl}_2(\text{RNC})[\text{C}(\text{NHR})\text{NHR}^1]$  were oxidised with  $\text{Ag}_2\text{O}$ , has been reported [160].



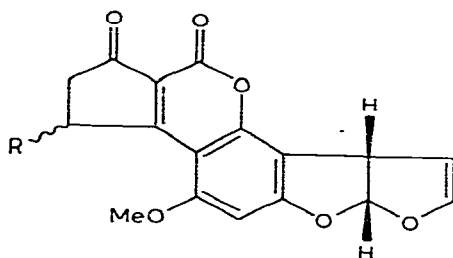
(Scheme 14)

1-Nitroadamantane has been synthesised from 1-adamantyl hexafluoroantimonate with  $\text{AgNO}_2$  [161]. The reactions of 2-bromooctane with an excess of  $\text{AgClO}_4$  in MeOH were found to be second order in  $\text{Ag(I)}$ . The

mechanism was discussed [162]. The reaction of (86) with silver acetate in  $\text{CCl}_4$  gave (87) as the major product [165]. The conversion of representative alkyl bromides and iodides to allyl fluorides with  $\text{Hg(II)}$  and  $\text{Ag(I)}$  fluorides has been shown to involve generation of intermediate alkyl carbonium ions by comparison of the product distribution obtained on conversion with those obtained on solvolysis of related alkyl derivatives. The C-F forming step is suggested as proceeding by the intermolecular transfer of fluoride from a halometallo-ate complex to a carbonium ion centre [164].



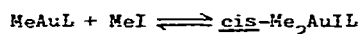
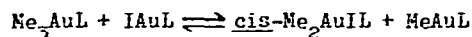
Oxidative demethylation of 2,5-dimethoxybenzaldehyde diacetate with 3 equivalents of  $\text{AgO}$  and  $6\text{N HNO}_3$  gave 96% benzoquinone-1,4-aldehyde diacetate [165]. The oxidation of aflatoxin  $\text{B}_1$  with  $\text{Ag}_2\text{O}$  gave a mixture of epimeric aflatoxins (88) ( $\text{R}=\text{CH}$ ) [166]. The reaction of  $[\text{PhC(CN)NO}_2]_2\text{Ag}$  with  $\text{CS}_2$  produced, in addition to  $\text{COS}$  and  $\text{AgS}$ , an oxime ether of benzoylcyanide of formula  $\text{PhC(CN)NO}_2\text{-ON=C(CN)Ph}$ . This latter product was characterised by an X-ray structural determination [167]. 1,4-Diketones have been synthesised from reactions of silyl enol ethers with  $\text{Ag}_2\text{O}$  in  $\text{DMSO}$  [168].



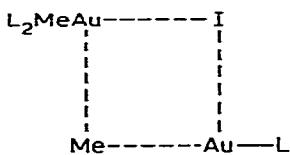
(88)

## VII Gold-carbon bonds

Fair substitution CIDMP effects have been used to study  $S_{\text{H}}2$  reactions of  $\text{PhCO}_2\cdot$  at the metal centres of  $\text{PbEt}_4$ ,  $\text{PbMe}_3\text{Cl}$ ,  $\text{SnEt}_4$ ,  $\text{SnMe}_3\text{Cl}$ ,  $\text{SnBu}_3\text{Br}$ ,  $\text{MeAuPPh}_3$  and cis- $\text{PtMe}_2(\text{PPh}_3)_2$ . The latter was much less prone to  $S_{\text{H}}2$  reactions than  $\text{MeAuPPh}_3$  [169]. The synthesis and reactivity of  $\text{Me}_2\text{Au(III)}$  complexes with TRIPHOS and TREN have been examined, and the products  $[\text{Me}_2\text{AuTRIPHOS}][\text{Me}_2\text{AuCl}_2]$  and  $\text{Me}_2\text{AuCl(TREN)}$  characterised. The latter underwent a reductive elimination [170, 171]. A quantitative conversion of  $\text{Me}_3\text{AuPPh}_3$  to  $\text{Li}[\text{Me}_4\text{Au}]$  using  $\text{LiMe}$  in ether solution has recently been effected. The physical data observed were consistent with square planar  $[\text{Me}_4\text{Au}]^-$  ions and solvated  $\text{Li}^+$  ions in solution. This system provides a good example of the declining significance of  $d_{\pi}$  back bonding as an explanation of the stabilisation of electron-rich systems. The analogous Au(I) product  $\text{Li}[\text{Me}_2\text{Au}]$ , formed from  $\text{LiMe}$  and  $\text{MeAuPPh}_3$ , also occurs as a solvent-separated ion pair [172].  $\text{MeI}$  additions to  $\text{MeAuL}$  ( $\text{L} = \text{PMe}_3$ ,  $\text{PMe}_2\text{Ph}$  and  $\text{PMePh}_2$ ) gave an equimolar mixture of  $\text{Me}_3\text{AuL}$  and  $\text{IAuL}$ . For  $\text{L} = \text{PMe}_3$  and  $\text{PMe}_2\text{Ph}$  a slower reaction then takes place to give cis- $\text{Me}_2\text{AuIL}$  and a mixture of cis- $\text{Me}_2\text{AuIL}$  and  $\text{IAuL}$  with  $\text{C}_2\text{H}_6$  when  $\text{L} = \text{PMePh}_2$ . Kinetic studies for  $\text{L} = \text{PMe}_3$  were done and found to be consistent with the mechanism



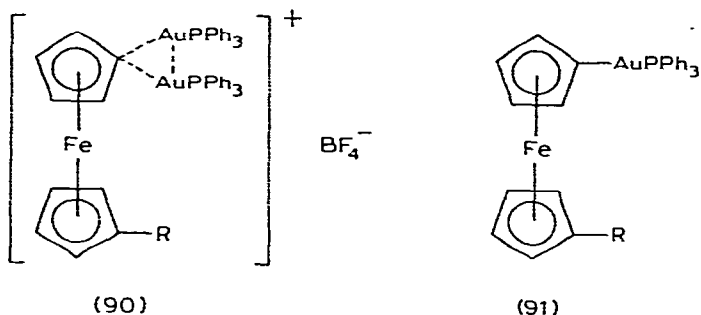
and a four centre transition state (89) was proposed [173]. Labelled alkylgold(I) and  $\text{CD}_3\text{Au(I)}$  complexes were utilised to investigate the



(89)

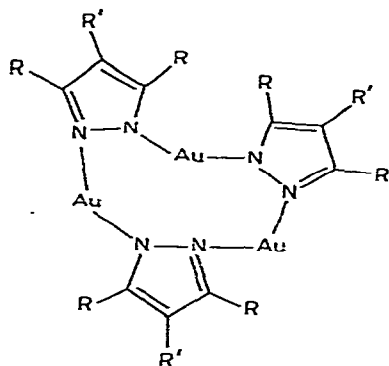
reaction mechanism and solvent effects for the formation of  $\text{Me}_3\text{AuPPh}_3$  from cis- $\text{Me}_2\text{AuIPh}_3$  and  $\text{MeAuPPh}_3$ . The data ruled out a redox reaction and suggested a simple alkyl transfer via a gold(III)-gold(I) alkyl-bridged species [174]. PhSH reacted with  $\text{MeAuL}$ ,  $\text{Me}_3\text{AuL}$  and cis- $\text{PtMe}_2\text{L}_2$  ( $\text{L} = \text{FMe}_n\text{Ph}_{3-n}$ ;  $n = 0-5$ ) to give  $\text{CH}_4$  and  $\text{PhSAuL}$ , cis- $\text{Me}_2\text{Au(SPh)L}$  and trans- $\text{PtMe(SPh)L}_2$  respectively. The Au(I) and Pt(II) reactions occurred via free-radical chain mechanisms but the Au(III) complexes formed by a non-radical route. Competitive reactions gave an order of reactivity for these complexes [175]. A series of reactions in which methyl and halogen groups were exchanged between Au(I), Au(III), Pd(II) centres has been studied. The exchange reactions probably followed an  $\text{S}_{\text{E}}2$  (cyclic) mechanism and reactivity and methylating power orders were given for the series of complexes used [176]. The interaction of phosphorus ylides with Au(I) and Au(III) compounds has produced the series, e.g.  $\text{MeAuCH}_2\text{FMe}_3$ ,  $[\text{Me}_3\text{PCH}_2\text{AuFMe}_3]\text{X}$ ,  $[\text{Me}_3\text{PCH}_2\text{AuCH}_2\text{FMe}_3]\text{X}$  [177]  $[\text{Me}_2\text{P}(\text{CH}_2)_2\text{Au}]_2$  [178] and  $\text{Me}_3\text{AuCH}_2\text{FMe}_3$  [179]. Thermal decomposition of  $[\text{Me}_2\text{Au}(\text{CH}_2\text{FMe}_3)_2]\text{Br}$  gave  $[(\text{Me}_3\text{PCH}_2)_2\text{Au}]\text{Br}$  which further reacted with halogens to form cis- and trans-isomers of the corresponding Au(III) halide ylide [179]. Oxidative additions to other Au-ylide systems were studied [178]. Treatment of  $\text{EtC}_6\text{H}_5=\text{CH}_2$  with  $\text{AuXPPh}_3$  ( $\text{X}=\text{halide}$ ) gave  $\text{EtC}_6\text{H}_5\text{CH}_2\text{AuPPh}_3$  [180].  $\text{Ph}_3\text{PAuCH}_2\text{CHO}$  was prepared from the reaction of  $\text{CH}_2=\text{CHOBu}$  and  $(\text{Ph}_3\text{PAu})_3\text{O}^+\text{BF}_4^-$  [181]. The complexes  $\text{C}_6\text{X}_5\text{AuL}$  ( $\text{X}=\text{Cl}$  [182],  $\text{Br}$  [183],  $\text{L}=\text{PPh}_3$ ;  $\text{X}=\text{Cl}$  [184],  $\text{F}$  [185],  $\text{L}=\text{AsPh}_3$ ) have been characterised. Oxidative addition reactions with halogens have given Au(III) products for  $\text{X}=\text{Cl}$  and  $\text{Br}$  and  $\text{L}=\text{PPh}_3$  and  $\text{AsPh}_3$  [182, 183]. For  $\text{X}=\text{F}$ , with  $\text{Br}_2$  and  $\text{I}_2$ , cleavage of the Au-C bond occurred [184]. Substitution reactions of  $\text{XAu}(\text{C}_6\text{F}_5)_2\text{AsPh}_3$  ( $\text{X}=\text{Cl}, \text{ClO}_4$ ) with the anions

$Y = \text{NO}_3^-, \text{MeCO}_2^-, \text{NO}_2^-, \text{CF}_3\text{CO}_2^-, \text{CN}^-, \text{SCN}^-, \text{N}_3^-$  and  $\text{PhCl}_2^-$  produced  $\text{YAu}(\text{C}_6\text{F}_5)_2 \text{AsPh}_3$  [185]. Diferrocenylmercury compounds and  $\text{MeAuPPh}_3$  in the presence of  $\text{HBF}_4$  have given (90) which formed (91) with  $\text{NaCl}$  [186]. A preliminary account of the crystal structure determination of 1-hydroxy-2,3,4,5-tetraphenylaura-cyclopentadiene dimer has appeared. The complex was



prepared from dilithiotetraphenylbutadiene with metal halides at low temperature [187]. Reactions of  $[(\text{RNC})_2\text{Au}]^+$  ( $\text{R} = \text{p-MeC}_6\text{H}_4, \text{C}_6\text{H}_{11}$ ) with alcohols  $\text{ROH}$  ( $\text{R} = \text{Me}, \text{Et}$ ) and amines  $\text{R}'\text{RNH}$  ( $\text{R} = \text{H}, \text{R}' = \text{p-FC}_6\text{H}_4, \text{p-MeC}_5\text{H}_4, \text{C}_6\text{H}_5\text{CH}_2, \text{Me}, \text{C}_6\text{H}_{11}, \text{o,o}'\text{-[Me}_2\text{CH]}_2\text{C}_6\text{H}_3; \text{R} = \text{Me}, \text{R}' = \text{Ph}$ ) have given mono- and bis-carbene complexes depending upon R. In the case of  $[\{\text{p-MeC}_6\text{H}_4\text{NH}(\text{EtO})\text{C}\}_2\text{Au}]\text{ClO}_4$ , geometrical isomers were separated by fractional crystallisation. In some cases substitution of a carbene ligand in bis-carbene complexes has given formamidines by rearrangement of the carbene group e.g.  $[\{\text{p-MeC}_6\text{H}_4\text{NH}\}_2\text{C}\}_2\text{Au}]\text{ClO}_4$  and  $\text{PPh}_3$  gave  $[\{\text{p-MeC}_6\text{H}_4\text{NH}\}_2\text{C}\}\text{AuPPh}_3]\text{ClO}_4$  and  $\text{HC}(\text{=NC}_6\text{H}_4\text{Me-p})\text{NHC}_6\text{H}_4\text{Me-p}$  [188]. The mass spectral fragmentations of  $[\text{Au}(\text{CR}=\text{NR}^1)]_3$  ( $\text{R} = \text{OMe}, \text{R}^1 = \text{Me}, \text{Et}$ ) and (92) ( $\text{R} = \text{R}^1 = \text{H}; \text{R} = \text{Me}, \text{R}^1 = \text{H}, \text{Et}$ ) have been determined [189].

Formation constants of  $\text{AuClL}$  and  $\text{AuBrL}$  complexes have been obtained by potentiometric titrations of  $[\text{Au}(\text{MeCN})_2]^+$  in  $\text{MeCN}$  at  $-20^\circ$  for  $\text{L} = \text{PPh}_3, \text{AsPh}_3, \text{SbPh}_3, \text{FMePh}_2, \text{FMe}_2\text{Ph}, \text{Me}_2\text{S}, \text{Me}_2\text{Te}, \text{MeNC}$  and  $\text{ArNC}$ .  $\text{Au}^+$  behaves as a typical class B metal. A general linear relation between  $\log K$ 's of corresponding  $\text{AuXL}$  complexes suggesting that  $\text{AuBr}$  discriminates better than  $\text{AuCl}$  between soft ligands breaks down when considering each family of ligands.  $[\text{Au}(\text{diolefin})_2]^+$  complexes are



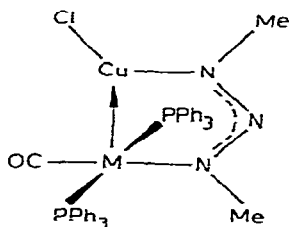
(92)

not sufficiently more stable than  $[\text{Au}(\text{MeCN})_2]^+$  to be isolated however, but they may be obtained in the solid state from  $\text{Et}_4\text{N}[\text{AuCl}_2]$  and  $\text{AgClO}_4$  in acetone solutions containing an excess of the diolefin [190].

IR stretching frequencies of the linear metal-metal bonded systems  $[\text{M}'-\text{Au}-\text{M}']^-$  ( $\text{M}'=\text{Mn}(\text{CO})_5$ ,  $\text{Co}(\text{CO})_4$ ,  $\text{CpMo}(\text{CO})_3$ ,  $\text{CpFe}(\text{CO})_2$ ) have been measured and correlations established between oxidation states and coordination number of  $\text{M}^1$  in linear  $\text{M}''-\text{M}'-\text{M}''$  systems ( $\text{M}'=\text{Pd}(\text{II})$ ,  $\text{Pt}(\text{II})$ ,  $\text{Hg}(\text{II})$  and  $\text{Au}(\text{I})$  and the corresponding  $\nu(\text{M}'-\text{M}'')$  [191].

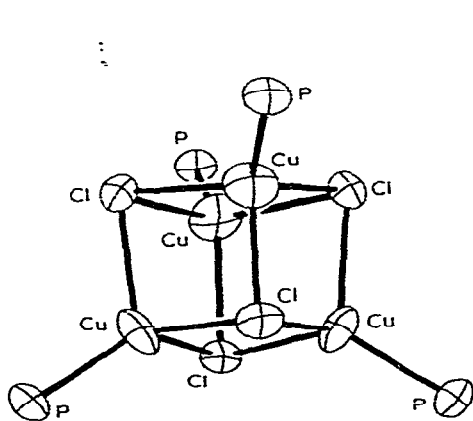
#### VIII Complexes of general interest

A review on the coordination chemistry of NO contains some references to intermediate Cu-NO complexes in the Cu(I) catalysed reduction of NO by  $\text{SnCl}_2$  [192]. The series of metal-metal bonded complexes  $[\text{L}_2(\text{CO})\text{M}(\text{C}(\text{RNNNR}')\text{X})]$  ( $\text{M}=\text{Rh}$ ,  $\text{Ir}$ ,  $\text{L}=\text{PPh}_3$ ,  $\text{PMe}_2\text{Ph}$ ,  $\text{AsPh}_3$ ,  $\text{X}=\text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ) of structure (95) has been prepared from  $[\text{Cu}(\text{RNNNR}')]\text{X}$  ( $n=4$ ,  $\text{R}=\text{R}'=\text{Me}$ ;  $n=2$ ,  $\text{R}=\text{R}'=\underline{p}$ -tolyl,  $\text{R}=\text{Me}$ ,  $\text{R}'=\underline{p}$ -tolyl) and  $\text{MX}(\text{CO})\text{L}_2$  [193]. Forty carbonyl complexes derived from the general formula  $[\text{Me}_4\text{N}][\text{M}'\{\text{M}(\text{CO})_3\text{Cp}\}_2]$  ( $\text{M}'=\text{Cu}$ ,  $\text{Ag}$ ;  $\text{M}=\text{Cr}$ ,  $\text{Mo}$ ,  $\text{W}$ ) have been synthesised [194]. The compounds  $\text{Me}_3\text{PAuSR}$  ( $\text{R}=\text{CMe}_3$ ,  $\text{Et}$ ),  $(\text{Me}_3\text{PAu})_2\text{S}$ ,  $\text{Me}_3\text{PAuSCH}_2\text{CH}_2\text{SAuPMe}_3$  and  $[\text{Ph}_3\text{PAu}]_3\text{Se}^+\text{Cl}^-$  are reported [195].  $\lambda^3$ -Phosphorins form  $\text{RPh}_2\text{C}_5\text{H}_2\text{PM}$  ( $\text{R}=\text{Ph}$ ,  $\text{PhCH}_2$ ,  $\text{Me}$ ;  $\text{M}=\text{AgO}_2\text{CCF}_3$ ,  $\text{CuCl}$ ,  $\text{AuCl}$ ) and  $[\text{Ph}_3\text{C}_5\text{H}_2\text{P}(\text{OMe})\text{Au}]_3$  from some suitable corresponding metal salt

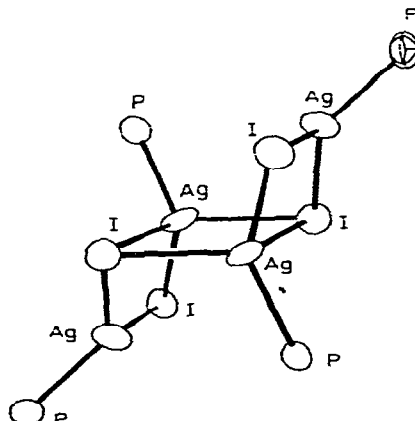


(93)

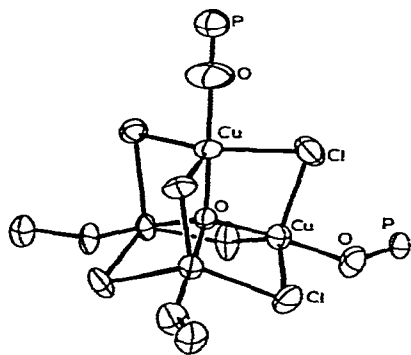
[196, 197]. Addition of  $\text{Cl}_2$  to  $\text{AuBr}(\text{PEt}_3)_2$  in  $\text{CHCl}_3$  at  $25^\circ$  resulted in the rapid formation of all six isomers of the type  $\text{AuBr}_{3-x}\text{Cl}_x(\text{PEt}_3)_2$  ( $x=0-3$ ) as shown by NMR. After 24 h. significant amounts of Au(I) were found in the solution [198]. 2,3- $\mu$ -[Bis(triphenylphosphine)cuprio] pentaborane(9), -1-methylpentaborane(9) and -1-methylpentaborane(9) were synthesised [199] and reaction of 2,3- $\text{C}_2\text{B}_4\text{H}_7^-$  with organometallic reagents of Al, Ga, Rh, Au and Hg effected insertion of the metal atom into a bridging position on the base of the pyramidal carborane cage, with the metal apparently linked to the cage by a B-M-B 3-centre 2-electron bond [200]. The crystal structure of  $\{(\text{Ph}_3\text{P})_2\text{Cu}\}_2\text{B}_{10}\text{H}_{10}\cdot\text{CHCl}_3$  has been solved [201], as have  $[\text{Cu}(\text{MeCN})_4]\text{ClO}_4$  [202],  $[\text{Ag}\{\text{P}(\text{OMe})_3\}_2\text{NO}_3]_2$  [203] and  $\text{AuBr}(\text{AsPh}_2)$  [204]. A series of X-ray structural determinations on molecules having an  $\text{M}_4\text{X}_4$  core have recently been reported. Those solved with a "cubane" type geometry (e.g. 94) were  $[\text{PEt}_3\text{MX}]_4$  ( $\text{M}=\text{Cu}$ ,



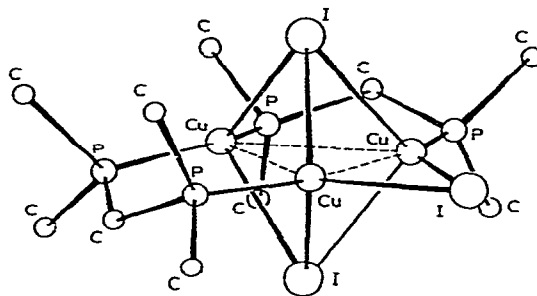
(94)



(95)



(96)



(97)

$X=\text{Cl, Br}$ ; [205];  $M=\text{Ag}$ ,  $X=\text{I}$  [206]) and those having a "step" structure (*c-g*. 95) were  $[\text{PPh}_3\text{MI}]_4$  ( $M=\text{Cu}$  [207];  $\text{Ag}$  [208]) and  $(\text{CuX})_2\text{DPM}$  ( $X=\text{Br, I}$  [209]). The stereochemical variations in the series  $[\text{R}_3\text{YMX}]_4$  ( $Y=\text{P, As}$ ;  $M=\text{Cu, Ag}$ ;  $X=\text{Cl, Br, I}$ ) have been rationalised in terms of van der Waals interactions among the ligands. Aerobic oxidation of  $[\text{PEt}_3\text{CuCl}]_4$  produced  $\text{Cu}_4\text{OCl}_6(\text{OPEt}_3)_4$  which was solved crystallographically (96). The central  $\mu_4$ -oxide ion is linked uniformly to all four copper atoms with  $\text{Cu}-\text{O} = 1.90\text{\AA}$  (mean) [210]. The structure of  $(\text{CuI})_3(\text{DPM})_2$  has been resolved (97) [211].

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