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HOMOGENEOUS CATALYSIS IN THE DECOMPOSITION OF DIAZO COMPOUNDS BY COPPER CHELATES

ASYMMETRIC CARBENOID REACTIONS

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Abstract—Bis(acetylacetonato)copper(II) catalyzes thermal decomposition of diphenyldiazomethane in benzene to afford tetraphenylethylene and benzophenone azine. The absence of 1,1,2,2-tetraphenylethane among the products is explained by assuming a copper carbenoid in which the carbene moiety is attached to the central copper atom as the fifth ligand. The apparently electrophilic nature of this carbenoid is illustrated by isolating cyclopropylamines upon reaction with enamines. Chemical evidence for the postulated coordination has been obtained by observing several instances of asymmetric synthesis, which proceed under influence of a chiral copper chelate, bis[N-(*R*)-α-phenethylsalicylaldiminato]copper(II), and its enantiomer. Following products have been obtained in partially resolved form from reactions of methyl or ethyl diazoacetate and diazomethane with appropriate optically inactive substrates: ethyl *cis*- and *trans*-2-phenylcyclopropanecarboxylate, methyl *cis*- and *trans*-3-phenyltetrahydrofuran-2-carboxylate, *trans*-1-methyl-2-phenylcyclopropane, *trans*-bicyclo[10.1.0]-*cis*-4,*trans*-8-tridecadiene and *trans*-bicyclo[10.1.0]-tridecane. Intramolecular cyclization of allyl diazoacetate and of 1-diazo-6-phenyl-*trans*-5-hexene-2-one occurs smoothly in the presence of the same copper chelate to afford 3-oxabicyclo[3.1.0]-hexan-2-one and 6-phenylbicyclo[3.1.0]hexan-2-one both in partially resolved state. The mechanism of these carbenoid reactions is discussed on the basis of further additional observations.

MODIFIED carbenes are produced in the decomposition of diazo compounds catalyzed by copper or its salts.[1] The resulting species show highly selective reactivities and are of value in synthetic applications.[2] We have been interested in examining the behaviour of such copper carbenoids in a homogeneous system and this paper comprises several aspects of reactions of diazo compounds in the presence of soluble copper chelates.*

Modified diphenylcarbene†

Thermal decomposition of diphenyldiazomethane (I) proceeds slowly in benzene to give benzophenone azine (II)[5] and in hydrogen-donating solvents 1,1,2,2-tetraphenylethane (III). Diphenylcarbene as produced under such a condition is a typical triplet carbene which abstracts hydrogen from the solvents and the resulting benzhydryl radicals dimerize to form III. It has been discovered that bis(acetylacetonato)-copper(II) (Cu(acac)$_2$) (IV) is an active catalyst for this decomposition and modifies the diphenylcarbene reactions as shown below.

Table 1 contains product distribution of thermal decomposition of I in the presence of copper catalysts. The observed formation of tetraphenylethylene (V) characterizes

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* For previous publications on copper chelates catalysing decomposition of diazo compounds see Ref. 3.

† This paragraph was partly published in a preliminary form.[4]

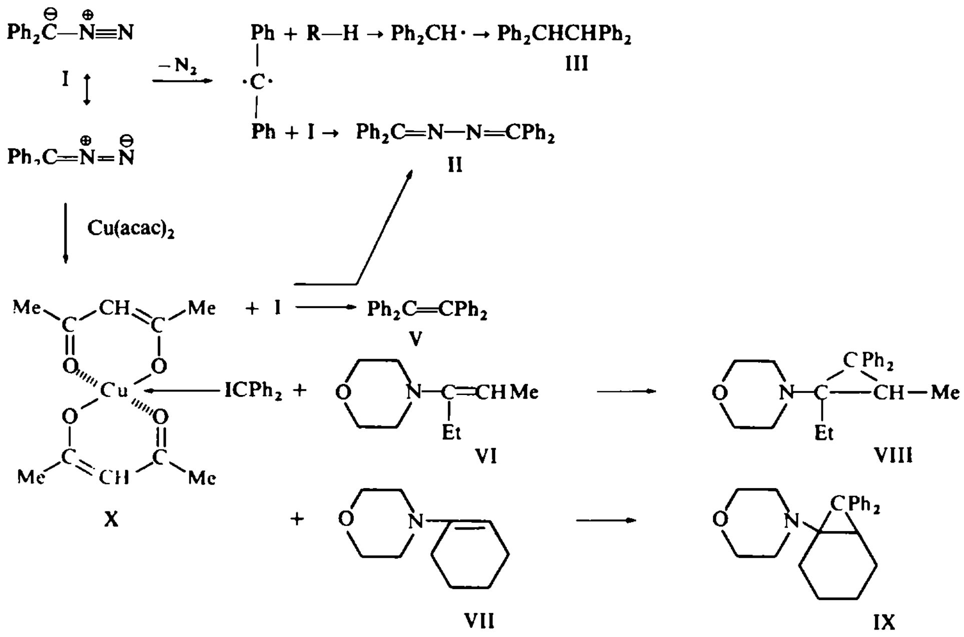

TABLE I. CATALYTIC DECOMPOSITION OF DIPHENYLDIAZOMETHANE

Catalyst	Solvent	Yield, % (ratio)[a] of		
		Azine II	Ethane III[b]	Ethylene V
Cu(acac)$_2$	benzene	30 (33)	0 (0)	60 (67)
	cyclohexane	51 (54)	0 (0)	43 (46)
	cyclohexene	40 (73)	0 (0)	15 (27)
	THF	65 (67)	12 (12)	20 (21)
Cu powder	benzene	97 (98)	1 (1)	1 (1)
	THF	84 (85)	15 (15)	0 (0)
CuSO$_4$	benzene	81 (83)	9 (9)	8 (8)
	THF	60 (61)	35 (35)	4 (4)

[a] Analyses by GLC on SE 30 (4%) with a hydrogen flame detector.

[b] Isolated as a $(Ph_2CH—)_2 \cdot (Ph_2C=N—)_2$ adduct (Ref. 5).

the decomposition catalyzed by the chelate IV. The ethane derivative III was practically absent among products in benzene, cyclohexane and even in cyclohexene solutions. In contrast, however, a fair amount of III was isolated when the reaction was carried out in ethereal solvents such as THF. The catalytic activity of IV was practically suppressed in pyridine possibly by its strong coordination.* Copper powder and anhydrous cupric sulphate were found to yield mainly II along with III and V.

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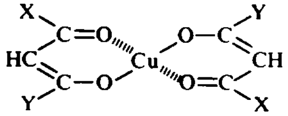
* The pyridine adducts of IV and related compounds have been described.[6]

No diphenylcarbene adducts were obtained in cyclohexene or ethyl vinyl ether. Enamines VI and VII afforded the corresponding cycloadducts[*] VIII and IX along with by-products II and V. The adducts were found homogeneous on TLC and the assigned structures were consistent with elemental analyses, mass, IR, UV and NMR spectra.[†]

The conclusion derived from these observations is the electrophilic nature of the diphenylcarbene carbon and the absence of free-radical reactions and this would tentatively be explained by assuming a carbene complex X, or an inverse ylide[9] presumably having a square-pyramidal structure analogous to that of known pyridine adduct.[‡, 6]

The ratio of azines : tetraphenylethylenes was found to be dependent on the nature of ligands of copper chelates, as summarized in Table 2. All runs were carried out in

TABLE 2. CATALYTIC DECOMPOSITION OF DIARYLDIAZOMETHANE (Ar_2CN_2) IN THE PRESENCE OF COPPER CHELATES



Ar	Catalyst		Yield, % (ratio) of[a]	
	X	Y	$(Ar_2C{=})_2$	$(Ar_2C{=}N{-})_2$
Ph	Me	Me	60 (67)	30 (33)
Ph	Ph	Me	47 (50)	46 (50)
Ph	Ph	Ph	41 (45)	50 (55)
Ph	OEt	Me	74 (100)	0 (0)
p-An	OEt	Me	48[b] (100)	0 (0)
Ph	CF_3	Me	84 (85)	15 (15)

[a] These values were obtained on the basis of GLC analysis on SE 30 (4%) with a hydrogen flame detector unless otherwise stated.

[b] An isolation yield.

[*] Addition of carbenes to enamines is known[7] and electrophilic attack of enamines by bis(iodomethyl)-zinc has been described.[8]

[†] Mass spectra were obtained on Hitachi RMU 6D spectrometer. The *m*/*e*, abundance in % and assignment of prominent peaks are given. VIII: 321 (8, molecular peak), 234 (7, M-87 (morpholine)), 167 (35, benzhydryl or rearranged peak(s)) and 154 (100, M-167). IX: 333 (7, molecular peak), 246 (6, M-87), 167 (25, benzhydryl or rearranged cation(s)) and 166 (100, M-167). The isotope abundances supported the formulae VIII and IX. In 99% EtOH both adducts showed no maximum above 220 mμ. Shoulders were observed for VIII at 259 mμ (log ε 3·10) and for IX at 260 (2·88), 266 (2·81) and 274 mμ (2·55).

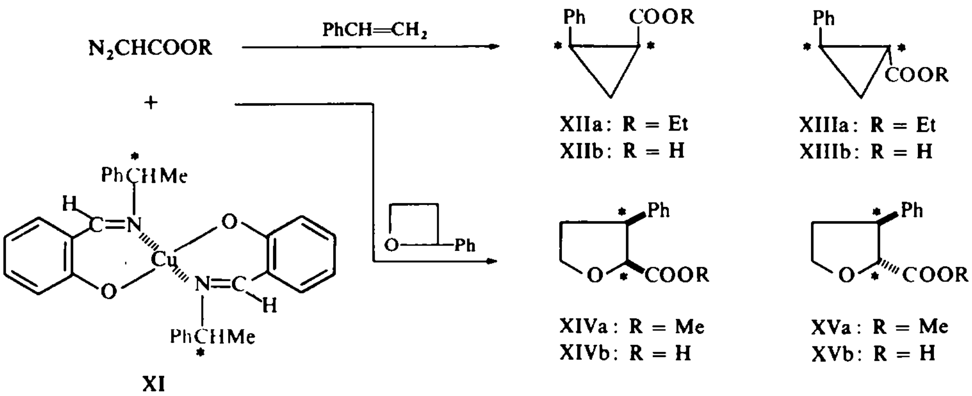
NMR spectra were taken on Varian A-60 and chemical shifts are given in ppm from internal TMS standard. The adduct VIII showed a multiplet of methylene protons adjacent to nitrogen at 2·59 (4H), a multiplet due to methylene protons of ethyl group at 2·30–1·65 (2H), a complex multiplet arising both from methine proton of the cyclopropane ring and from Me protons of Et group at 1·27–0·70 (4H) and a doublet (J = 6·5 c/s) of methyl group attached to the cyclopropane ring at 1·00 (3H). The adduct IX showed a multiplet at 3·29 (4H) and a triplet (J = 4·8 c/s) at 2·37 (4H) both originating from morpholino group, besides two broad signals centring at 1·9 (4H) and at 0·9 (5H) and arising from cyclohexane ring protons. Any signals due to olefinic proton(s) were not observed in each spectrum.

[‡] Thermal decomposition of I in the presence of ZnI_2 produces a small amount of V, although the major product is II. The formation of an organozinc compound has been postulated.[10]

boiling benzene (ca. 0·08 M) in the presence of 0·18 equivalent of the copper chelates. Remarkably diminished yields of azines were obtained with chelates having ethoxyl and trifluoromethyl substituents.* Further investigations are required for explaining such an effect of these electron-attracting substituents.

Partial asymmetric syntheses by means of chiral carbenoids produced from alkyl diazoacetates †

An independent evidence has been obtained in support of the above proposed explanation which involves intermediary occurrence of a copper carbenoid. Partial asymmetric synthesis has been attained with diazoacetates in two kinds of carbenoid reactions, *viz.*, addition to C═C bond and insertion to C—O bond, under homogeneous catalysis by a chiral copper chelate.



Ethyl diazoacetate was smoothly decomposed in styrene in the presence of bis[N-(*R*)-α-phenethylsalicylaldiminato]copper(II) ((*R*)-XI).‡ The reaction gave an optically active mixture of *cis* and *trans* isomers of ethyl 2-phenylcyclopropanecarboxylate (XIIa and XIIIa). The mixture was separated by GLC into the pure components, which were hydrolyzed to corresponding optically active acids XIIb and XIIIb, respectively. These reactions were repeated with the copper chelate XI having N-(*S*)-α-phenethyl group ((*S*)-XI), and the optical data of all products were listed in Table 3. Based on the recorded rotations and absolute configurations of XIIIb,[14] the optical yields of 1*R*,2*R*- and 1*S*,2*S*-acids produced in excess are calculated to be 6%.

The reaction of ethyl diazoacetate with 2-phenyloxetane results in a ring-enlargement yielding a *cis-trans* mixture of ethyl 3-phenyltetrahydrofuran-2-carboxylate.[15] It has been discovered that catalytic decomposition of methyl diazoacetate in the presence of the chelate (*R*)-XI modifies the reaction so as to yield an optically active

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* Electron-attracting substituents stabilizes base-chelate complex.[6b]

† This paragraph was partly communicated in a preliminary form.[11]

‡ Both (*R*)-XI and (*S*)-XI were obtained by the published method.[12] The possibility of racemization under the reaction conditions was excluded, as careful hydrolysis of recovered XI afforded the Schiff base of unchanged rotation. cf. Ref. 13.

TABLE 3. PARTIAL ASYMMETRIC SYNTHESIS WITH DIAZOACETATE

Product	M.p., °C (B.p., °C/mm)	α^{25a} obsd.	c g/100 ml	$[\alpha]_D^{25}$ deg.
Catalyst: (*R*)-XI[b]				
XIIa + XIIIa	(90–95/2)	+0·656	10·1	+13·0
XIIa	(94–96/2)	+0·065	7·00	+1·86
XIIIa	36–38	+0·644	7·14	+18·0
XIIb	98–101	+0·075	5·10	+2·94
XIIIb	88·5–89·5	+0·800	6·98	+22·9
XIVa + XVa	(92–93/0·08)	+0·253	10·2	+4·96
XIVa	(90–92/0·08)	+0·054	2·02	+5·35
XVa	(93–95/0·08)	+0·098	4·14	+4·73
XIVb	140–143	+0·050	2·06	+4·85
XVb·H_2O	69–71	+0·082	4·10	+4·00
Catalyst: (*S*)-XI[b]				
XIIa + XIIIa	(90–92/2)	−0·682	10·5	−13·0
XIIa	(95–96/2)	−0·064	6·78	−1·89
XIIIa	36–38	−0·636	6·92	−18·4
XIIb	97–101	−0·071	5·05	−2·81
XIIIb	88–89	−0·798	7·02	−22·8
XIVa + XVa	(92–93/0·08)	−0·241	10·0	−4·82
XIVa	(91–92/0·08)	−0·058	2·04	−5·69
XVa	(92–94/0·08)	−0·092	4·04	−4·55
XIVb	140–143	−0·052	2·10	−4·95
XVb·H_2O	68–70	−0·083	4·20	−3·95

[a] Measured in chloroform solutions with cells of 5 cm length.

[b] More than 70% of the catalysts used in 0·009 mole ratio to diazoacetate were recovered unchanged.

mixture of XIVa and XVa.* GLC separation gave the pure stereoisomers, which were carefully hydrolyzed to yield *cis*- and *trans*-3-phenyltetrahydrofuran-2-carboxylic acid (XIVb and XVb), respectively, both in optically active form. Reaction in the presence of (*S*)-XI gave products of comparable magnitude but different sign of rotation also in this case (Table 3).

Partial asymmetric synthesis of cyclopropane hydrocarbons by means of the carbenoid reaction of diazomethane

Carbene as produced by thermal or photochemical decomposition of diazomethane itself shows nonselective, extremely high reactivity.[16] Catalytic decomposition proceeded smoothly in the presence of XI at 0°. The resulting species showed remarkable selectivity upon *cis*-cycloaddition to olefins to give optically active cyclopropane hydrocarbons as shown in Table 4.

The reaction with *trans*-propenylbenzene gave *trans*-1-methyl-2-phenylcyclopropane (XVI) in a 62% yield. Any trace of the *cis* isomer could not be detected. An

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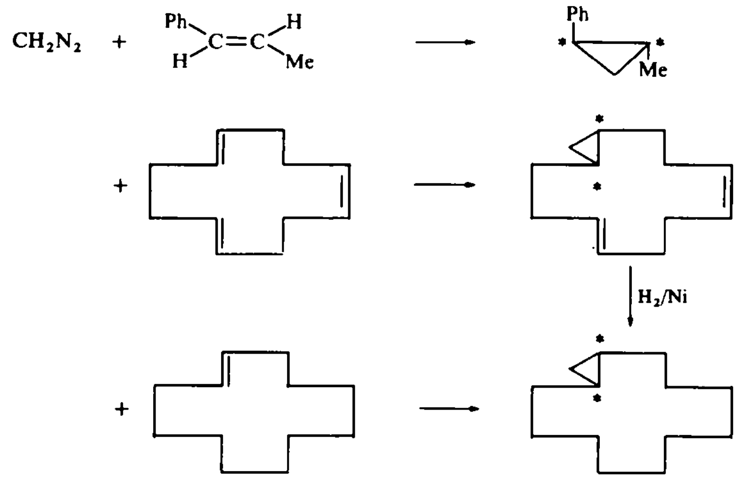
* Attempted GLC separation of *cis* and *trans* isomers of ethyl 3-phenyltetrahydrofuran-2-carboxylate was unsuccessful.



XVI

XVII

XVIII

TABLE 4. PARTIAL ASYMMETRIC SYNTHESIS OF CYCLOPROPANES WITH DIAZOMETHANE

Product	B.p., °C/mm	$\alpha_D^{25\,a}$ obsd.	*c* g/100 ml	$[\alpha]_D^{25}$ deg.
Catalyst: (*R*)-XI[b]				
XVI	73–76/20	+0·125	2·95	+8·48
XVII	69–71/2	+0·027	7·59	+0·71
XVIII	70–72/2	+0·060	11·8	+1·02
XVIII[c]	70–72/2	+0·018	13·8	+0·26
Catalyst: (*S*)-XI[b]				
XVI	74–76/20	−0·151	3·23	−9·35
XVII	70–71/2	−0·034	9·04	−0·75
XVIII	70–72/2	−0·047	7·98	−1·18
XVIII[c]	70–72/2	−0·016	10·9	−0·29

[a] Measured in chloroform solutions and with cells of 5 cm length.

[b] About 90–95% of the catalysts (used in 0·009 mole ratio to diazomethane) were recovered unchanged.

[c] Hydrogenation product of XVII.

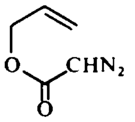
optically pure sample of 1*R*,2*R*-XVI was prepared from an optically pure sample of 1*R*,2*R*-XIIIb according to the published method.[17] The optical yield of the asymmetric synthesis was calculated to be ca. 8%.

Methylenation of *cis,trans,trans*-1,5,9-cyclododecatriene yielded mainly mono-adduct XVII, which was isolated by preparative GLC in a 36% yield and showed optical activity. Similarly, *trans*-cyclododecene gave a 51% yield of an optically active adduct XVIII, a hydrocarbon having C_2 symmetry. Hydrogenation of XVII also gave XVIII of lower specific rotation. The enantiomeric catalysts gave products of comparable magnitudes but different signs of rotation.

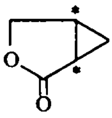
Pyridine destroyed the catalytic action of the copper chelate. Prolonged introduction of gaseous diazomethane into a solution of XI in pyridine resulted in formation of a dark tarry material.

Intramolecular asymmetric carbenoid reactions

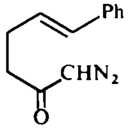
Decomposition of allyl diazoacetate (XIX) in the presence of cupric sulphate gives a cyclization product XX as a major product.[1b] Similar reaction of diazoketone XXI furnishes a bicyclic ketone XXII.[18] The copper chelate XI was found to be an effective catalyst in both reactions giving the cyclization products in partially resolved form as summarized in Table 5. The inactive lactone XX was converted to barium salt of the corresponding hydroxy acid XXIII. Resolution by means of quinine sulphate and lactonization of the resulting optically pure specimen gave XX, whose specific rotation indicated that the partial asymmetric synthesis of XX had proceeded with optical yields of 8% at most. The bicyclic ketone XXII has not been resolved yet.



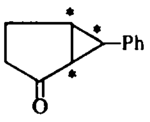
XIX



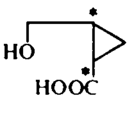
XX



XXI



XXII



XXIII

TABLE 5. INTRAMOLECULAR ASYMMETRIC CARBENOID REACTIONS

Product	M.p., °C (B.p., °C/mm)	α_D^{25}[a] obsd.	c g/100 ml	$[\alpha]_D^{25}$ deg.
Catalyst: (*R*)-XI[b]				
XX	(60–65/1)	+0·153	6·06	+5·05
XXII	71–73	+0·174	10·56	+3·30
Catalyst: (*S*)-XI[b]				
XX	(60–64/1)	−0·151	6·22	−4·86
XXII	71–73	−0·161	10·34	−3·12

[a] Measured in chloroform solutions and with cells of 5 cm length.

[b] About 60–70% of the catalysts (0·01 mole ratio to diazo compounds) were recovered unchanged.

Inquiry into the nature of reactive species in the carbenoid reactions

These reactions of diazo compounds catalyzed by copper chelates have been explained on the assumption of an intermediary copper carbenoid as a reactive species. Additional evidences are summarized below in support of this postulation.

The electrophilic nature of the intermediate is clearly shown by the relative reactivity sequence of substrate olefins as listed in Table 6, which also contains the data of previous workers on other carbene or carbenoid reactions. The competition experiments were carried out by introducing diazomethane into cyclohexane solutions of appropriate pairs of olefins (each 2·8M) at −15 ~ −20° in the presence of racemic chelate XI (0·0056M). The reaction was intercepted before 10% conversion had been attained. The resulting mixture was analysed by GLC and each product was characterized by comparison with the authentic sample. An increase in substitution of the olefinic carbons with electron-releasing group such as alkyl or alkoxyl increases the relative rate, as seen in the case of other carbene or carbenoid reactions. Such a reactivity sequence of olefins is reconciled with the pi-basicity of these substrates and strongly points to the electron-seeking character of the attacking agent. The high reactivity of phenylated olefins may suggest that a significant factor is the over-all nucleophilicity of olefin including the polarizability factor as well as the basicity.[19] The smaller reactivity of propenylbenzene than styrene must be ascribed to the sizable steric effect of the β-methyl group in the transition state.

Table 6. Relative reactivities of olefins toward carbene or carbenoid

Olefin	CH_2—Cu(II)[a]	$:CCl_2$[b]	$:CCl_2$[c]	$LiCHCl_2$[d]	:CHCOOEt[e]
α-Methylstyrene	4·52	7·16	—	—	—
2,3-Dimethyl-2-butene	3·46	—	53·7	4·68	1·6
Styrene	3·32	1·23	—	—	—
2-Methyl-2-butene	3·32	—	23·4	2·97	1·6
Ethyl vinyl ether	3·06	—	1·9	—	—
trans-Propenylbenzene	2·79	—	—	—	—
Cyclohexene	1·00	1·00	1·0	1·00	1·0
1-Octene	0·60	—	—	—	—
1-Heptene	—	0·236	—	—	—

[a] Results obtained in this work.

[b] Pyrolysis of $PhHgCCl_2Br$; D. Seyferth and J. M. Burlitch, *J. Am. Chem. Soc.* **86**, 2730 (1964).

[c] $CHCl_3$—KOBu-*t* system; W. von E. Doering and Wm. A. Henderson, Jr., *Ibid.* **80**, 5274 (1958).

[d] G. L. Closs and L. E. Closs, *Ibid.* **82**, 5729 (1960).

[e] Cupric sulphate catalysis of ethyl diazoacetate; P. S. Skell and R. M. Etter, *Chem. & Ind.* 624 (1958).

The steric factor controlling the carbenoid reaction is also illustrated by the following fact. We cannot exclude *a priori* the possibility that the methylenation involves 1,3 dipolar addition of diazoalkane to olefin and the resulting labile pyrazoline or its chemical equivalent is converted to cyclopropane. The data listed in Table 7

Table 7. Stereoselective addition to cis,trans,trans-1,5,9-cyclododecatriene

Carbene or Carbenoid (method of generation)	Mono-adduct *trans/cis*	Bis-adduct *trans,cis/trans,trans*
$:CBr_2$ ($CHBr_3$—KOBu-*t*)[a]	89:11	84:16
$:CCl_2$ ($CHCl_3$—KOBu-*t*)[a]	91:9	87:13
$:CCl_2$ (CCl_3COONa)[a]	85:15	72:28
$(ICH_2)_2Zn \cdot ZnI_2$ (Simmons–Smith)[a]	97:3	81:19
CH_2—Cu(II)[b]	90:10	80:20

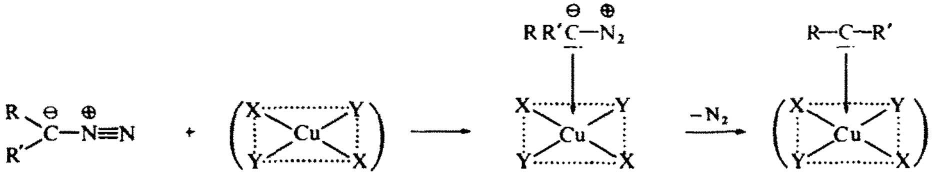
[a] The results in literature (Refs 20*a*, 21) are reproduced.

[b] Values obtained in the present work.

served also to eliminate this possibility and indicated that the cyclopropane formation was actually a three-centred reaction involving the carbenic carbon and olefinic ones. The results indicate that the carbenoid reaction with *cis,trans,trans*-1,5,9-cyclododecatriene proceeds with the same trend of stereoselectivity as observed with dihalocarbene[20] or with the Simmons–Smith reagent.[21] The cyclopropane formation occurs at one of the *trans* bonds first and then preferentially at the *cis* bond with less sharp selectivity. This general tendency is characteristic of three-centred *cis*-addition reactions and is also the case with epoxidation of the triene.[22]

Electronic spectra of the copper chelate XI have been examined under certain conditions. Any noticeable change was not observed in the presence of such reaction substrates as olefins of ethers, whereas pyridine did bring about remarkable change in light absorption due to its strong coordination to the copper atom.[6] The recovery of the copper chelates was no less than 50% in every case, and particularly the reaction of diazomethane gave a recovery of more than 90%. Thus each copper chelate should be a true catalyst.

A proposed mechanism is given below. The open coordination site of the square-planar copper chelate would undergo electrophilic attack on carbon atom of diazoalkanes yielding a complex XXIV. The subsequent elimination of nitrogen molecule would furnish a carbene–copper complex (or an inverse ylide) (XXV),[23] in which the carbene moiety is coordinated to the copper atom as the fifth ligand. The possible back-donation from the metal atom to the vacant p_z orbital of the carbenic carbon may contribute to stabilize the complex.[23a,b,24] It should be noted that we cannot rule out an alternative possibility that the initially formed complex XXIV[25] directly reacts with the substrates.[*] Assuming that the term "copper carbenoid" involves both species XXIV and XXV, it may be safe to conclude that a *chiral carbenoid* is responsible for the accomplishment of asymmetric induction mentioned above.



X = O
Y = O or N

XXIV

XXV

The low optical yields in the asymmetric syntheses might be explained by assuming a certain (or major) fraction of the copper carbenoid could be dissociated into an optically inactive, free carbene to react with the substrates. This postulation is, however, excluded on the basis of results of dilution experiments. The partial asymmetric synthesis of 1-methyl-2-phenylcyclopropane (XVI) was repeatedly carried out under various degrees of dilution with n-hexane. The yields of XVI decreased appreciably upon dilution, the main by-product being polymethylene. Remarkably,

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[*] Such an argument may be analogous to the one concerning an ambiguous reactive intermediate in nitrous acid oxidation of aliphatic primary amine, *viz.*, carbonium ion or its precursory diazonium ion.[26]

the optical yield of XVI remained constant within an experimental error, and this cannot be explained by assuming the formation of a free carbene.

The configuration of asymmetric ligands of the copper chelate must be correlated to the one of products arising from the carbenoid reactions. Unfortunately, however, the optical yields are low and, in addition, the introduction of N-phenethyl substituents to the copper chelate is known to bring about considerable distortion from regular square-planar structure.[27] Under these circumstances the correlation becomes rather equivocal and is open to research in the future.

Finally, it should be added that the laevorotatory enantiomer of a *tetrahedral* copper(II) chelate, N,N'-(6,6'-dimethyl-2,2'-biphenylene)-bis(salicylaldiminato)copper(II) (XXVI),[28] was found to be an active catalyst in the reaction of ethyl diazoacetate with styrene giving XIIa ($[\alpha]_D^{25}$ $-1·17°$) and XIIIa ($[\alpha]_D^{25}$ $-3·20°$).

EXPERIMENTAL

All m.ps are corrected.

Catalytic decomposition of diphenyldiazomethane (I) *in certain solvents*

To a boiling soln of Cu(acac)$_2$ (55 mg, 0·21 mmole) in a solvent (50 ml) was added a soln of I[29] (500 mg, 2·6 mmoles) in the solvent (5 ml) under N_2 atm. After evolution of N_2 had ceased (ca. 3 hr), the mixture was washed successively with 1N HClaq, NaHCO$_3$aq and water, dried and concentrated. Product compositions and yields were obtained by GLC analyses, the results being listed in Table 1. In a green pyridine soln of the catalyst, only 15% of the theoretical amount of N_2 was evolved.

Similar decomposition of I (400 mg, 2·1 mmoles) was carried out by means of Cu powder[*] (100 mg) or anhyd CuSO$_4$ (120 mg).

Catalysis of diaryldiazomethanes with copper (II) chelates was performed in the similar manner. Employed are bis(benzoylacetonato)Cu (II),[6a] bis(dibenzoylmethano)Cu (II),[6a] bis(ethyl acetoacetato)Cu (II),[6a] and bis(trifluoroacetylacetonato)Cu (II).[30] A soln of I (1·1 g, 5·7 mmoles) or di-*p*-anisyldiazomethane[31] (1·4 g, 5·5 mmoles) in dry benzene (15 ml) was added dropwise to a boiling benzene soln containing the copper chelate (1·0 mmole) in the course of 2·5 hr under N_2 atm. The mixture was heated at reflux for an additional 0·5 hr. Workup in a usual manner followed by GLC analysis gave the results summarized in Table 2. Tetra-*p*-anisylethylene, m.p. 188–189° (lit.[31] 179–180°), was isolated in a 48% yield from the reaction of di-*p*-anisyldiazomethane.

Decomposition of diphenyldiazomethane (I) *in diethyl ketone morpholine enamine* (VI)

A soln of I (4·2 g, 22 mmoles) in enamine VI[32] (11·5 g, 74 mmoles) was added dropwise to a well-stirred homogeneous benzene soln (60 ml) of Cu(acac)$_2$ (500 mg, 1·9 mmoles) at 85–90° under N_2 atm in the course of 1 hr. The mixture was heated at reflux for an additional 1 hr. After cooling, the reaction mixture was concentrated *in vacuo*. Copper catalyst and benzophenone azine (II) precipitated were removed by filtration, and the unchanged VI (ca. 5 g) was recovered by distillation. The resulting residue was recrystallized from n-hexane to yield 1-*ethyl*-2-*methyl*-1-*morpholino*-3,3-*diphenylcyclopropane* (VIII) (0·78 g, 11% yield) as colourless crystals, m.p. 134–135°. IR (Nujol): 2980, 1605, 1505, 1455, 1273, 1104, 1000, 872, 758 and 703 cm^{-1}. (Found: C, 81·9; H, 8·6; N, 4·4. $C_{22}H_{27}NO$ requires: C, 82·1; H, 8·5; N, 4·4%).

Decomposition of diphenyldiazomethane (I) *in cyclohexanone morpholine enamine* (VII)

A soln of I (3·0 g, 15 mmoles) in cyclohexanone enamine VII[33] (35·0 g, 21 mmoles) was added to a boiling benzene soln (60 ml) of Cu(acac)$_2$ (500 mg, 1·9 mmoles) at 85–90° during 3 hr. Heating and stirring were continued for an additional 1 hr. After removal of the unchanged VII by distillation, the residual oil was dissolved in a small amount of hot EtOH. Upon 2 days standing, 1-*morpholino*-7,7-*diphenylbicyclo*-[4.1.0]heptane (IX) (3·1 g, 63% yield) was obtained as colourless prisms, m.p. 113–114°. IR (KBr): 2980, 2900, 1600, 1490, 1440, 1262, 1105, 1035, 873, 762, 750 and 710 cm^{-1}. (Found: C, 82·6; H, 8·3; N, 4·3. $C_{23}H_{27}NO$ requires: C, 82·8; H, 8·2; N, 4·2%).

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[*] Copper powder was washed with aqueous oxalic acid and water, and dried before use.

Synthesis of bis(N-*α-phenethylsalicylaldiminato*)*copper* (II) (XI)

(*S*)-(+)-N-Salicylidene-α-phenethylamine [(*S*)-XXVII] and its enantiomer [(*R*)-XXVII] were obtained from the respective enantiomeric α-phenethylamine[34] and salicylaldehyde in a usual manner.[35] (*S*)-XXVII: m.p. 75–76°, $[\alpha]_D^{25}$ +182° (*c*, 1·04, MeOH) (lit.[35] m.p. 75–76°, $[\alpha]_D^{25}$ +188°). (*R*)-XXVII: m.p. 73–74°, $[\alpha]_D^{25}$ −181° (*c*, 1·04, MeOH).

A soln of $Cu(OAc)_2 \cdot H_2O$ (2·5 g, 13 mmoles) in MeOH (200 ml) was added to a boiling soln of (*S*)-XXVII (4·3 g, 19 mmoles) in EtOAc (75 ml) to afford a deep brown soln. After treatment with water, the mixture was extracted with chloroform. The combined extracts were dried (Na_2SO_4) and concentrated *in vacuo*. The resulting deep brown solid was recrystallized from EtOH to give *bis*[N-(*S*)-*α-phenethylsalicylaldiminato*]*copper* (II) [(*S*)-XI] (3·1 g, 63%) as black needles, m.p. 142–143°. (Found: C, 70·2; H, 5·7; N, 5·3. $C_{30}H_{28}CuN_2O_2$ requires: C, 70·4; H, 5·5; N, 5·5%). *Bis*[N-(*R*)-*α-phenethylsalicylaldiminato*]*copper* (II) [(*R*)-XI], m.p. 143–144°, was obtained from (*R*)-XXVII in the same manner. Deep-brown colour of XI solns made measurement of the optical rotation impossible even in the diluted one.

Decomposition of ethyl diazoacetate in styrene in the presence of dissymmetric Cu (II) *chelates*

A mixture of ethyl diazoacetate (5·0 g, 44 mmoles) and styrene (5·0 g, 48 mmoles) was added to well-stirred styrene (10·0 g, 96 mmoles) containing (*R*)-XI [or (*S*)-XI] (202 mg, 0·40 mmole) at 58–60° in the course of 6 hr under N_2 atm. After N_2 evolution had ceased, the reaction mixture was distilled *in vacuo* to afford a crude mixture of ethyl *cis*- and *trans*-2-phenylcyclopropanecarboxylate (XIIa and XIIIa) (1:2·3 ratio) (6·0 g, 72% yield), b.p. 90–95°/2 mm. The mixture was dissolved in ether, washed successively with 0·1N HClaq and water, dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by passing through an alumina column and subjected to GLC separation (Apiezon L 30%, 2 m). Each pure stereoisomer isolated was hydrolyzed with alkaline soln (KOH (1·5 g, EtOH 20 ml, water 20 ml) at room temp during 24 hr. After neutralization with 1N HCl, the mixture was extracted with ether. The combined ethereal solns were washed, dried and concentrated to give *cis*- and *trans*-2-phenylcyclopropanecarboxylic acid (XIIb and XIIIb) as crystalline solids, respectively. All products showed optical activity and gave correct elemental analyses. The IR spectra (CCl_4 soln) were superimposable with those of authentic samples.[14] Optical data were summarized in Table 3.

Ethyl diazoacetate (5·0 g. 44 mmoles) was decomposed in styrene (5·4 g, 52 mmoles) in the presence of (−)-N,N'-(6,6'-dimethyl-2,2'-biphenylene)bis(salicylaldiminato)copper (II) (XXVI)[28] (207 mg, 0·40 mmole) at 58–60° to afford XII and XIII (a and b) in optically active form, respectively.

Decomposition of methyl diazoacetate in 2-phenyloxetane in the presence of Cu (II) *chelate* XI

A mixture of methyl diazoacetate (5·0 g, 50 mmoles) and 2-phenyloxetane[36] (5·0 g, 37 mmoles) was added dropwise to a soln of (*R*)-XI [or (*S*)-XI] (200 mg, 0·39 mmole) in the oxetane (40·0 g, 300 mmoles) maintained at 58–60° in the course of 6 hr under N_2 atm. After N_2 evolution had ceased, the reaction mixture was distilled *in vacuo* to yield a *cis-trans* mixture of methyl 3-phenyltetrahydrofuran-2-carboxylate (XIVa and XVa) (8·9 g, 87% yield), b.p. 92–93°/0·08 mm, in optically active form. The mixture was dissolved in ether and washed with 1N HClaq repeatedly. The ethereal soln was concentrated and passed through an alumina column. No change in optical rotation had taken place during these operations. GLC separation on Apiezon L (25%)–Silicone DC QF-1 (5%) column gave the respective pure stereoisomers. These were carefully hydrolysed with KOH at room temp to yield *cis*- and *trans*-3-phenyltetrahydrofuran-2-carboxylic acids (XIVb and XVb), respectively, both in optically active form. The *trans* acid was isolated as the monohydrate. All products gave correct analyses, and the IR spectra (CCl_4 soln) were completely identical with those of the authentic samples.[15] The optical values are given in Table 3.

Decomposition of diazomethane in the presence of Cu (II) *chelate* XI

Diazomethane was prepared separately by the modified Gaspar–Roth procedure[37] in a 300 ml, three-necked flask without ground glass joints. It was fitted with an inlet tube through which a stream of purified N_2 (50–100 ml/min) was introduced to the bottom of the flask. The flask was charged with 100 ml 50% KOH aq and purified decalin (25 ml), and the mixture was magnetically stirred. N-Methyl-N-nitrosourea was added in 1·0 g portions at 10-min intervals at 0–5°. Explosion in the generator occurred when the velocity of the stream of N_2 was too low (< 30 ml/min) and diazomethane accumulated in the generator. The generated gaseous diazomethane diluted with N_2 was dried by passing through a tube packed with KOH pellets and was introduced to a soln of copper chelate XI in a suitable olefinic solvent placed in a reaction vessel (100 ml volume), the side arm of which was connected with a reflux condenser. The top of the condenser (cooled at −70°) led to a trap containing an ethereal soln of acetic acid.

(a) *Decomposition in* trans-*propenylbenzene*. The mixture of diazomethane and N_2 generated from N-methyl-N-nitrosourea (15·0 g, 15 mmoles) as above was introduced into a soln of (*R*)-XI (212 mg, 0·41 mmole) in *trans*-propenylbenzene (16 g, 130 mmoles) maintained at 0°. After the last addition of N-methyl-N-nitrosourea, N_2 stream was bubbled into the mixture for an additional 1 hr. The reaction mixture was fractionated *in vacuo* to afford a volatile fraction (15·4 g), b.p. 70–80°/20 mm, which consisted of mainly *trans*-1-methyl-2-phenylcyclopropane (XVI) and some starting olefin. This fraction was washed with 1N HCl repeatedly, dried (Na_2SO_4) and passed through a short alumina column. Preparative GLC (Apiezon L 30%, 2 m) gave an analytical sample of XVI in optically active form. The yield of XVI (62%) was obtained by GLC analysis. Any products which might be attributed to the reaction of methylene with the C—H bond or the aromatic ring could not be detected. The IR spectrum was superimposable with the one of authentic sample.[38]

(b) *Decomposition in* cis,trans,trans-*1,5,9-cyclododecatriene*. A soln of (*R*)-XI [or (*S*)-XI] (230 mg, 0·45 mmole) in the triene (23·6 g, 150 mmoles) was treated at 0° with N_2 diluted diazomethane generated from N-methyl-N-nitrosourea (15·0 g, 150 mmoles). The reaction mixture was distilled to give a volatile fraction (17·6 g), b.p. 60–68°/2 mm, which was purified as above. Subsequent GLC separation gave optically active *trans*-bicyclo[10.1.0]trideca-*cis*-4,*trans*-8-diene (XVII). Analytical GLC of the reaction mixture indicated the formation of XVII (36% yield), *cis*-bicyclo[10.1.0]trideca-*trans*-4,*trans*-8-diene (4%), tricyclo[11.1.0-(*cis*).-$0^{4,6}$(*trans*)]tetradec-*trans*-9-ene (2·4%), tricyclo[11.1.0(*trans*).$0^{4,6}$(*trans*)]tetradec-*cis*-9-ene (0·6%) and trace amount of tetracyclo[12.1.0(*cis*).$0^{4,6}$(*trans*).$0^{9,11}$(*trans*)]pentadecane. These products were identified by comparison of IR spectra and GLC retention times with those of the authentic specimens.[20a] Elemental analyses gave correct values.

(c) *Decomposition in* trans-*cyclododecene*. *trans*-Cyclododecene[39] (6·0 g, 36 mmoles) containing (*R*)-XI [or (*S*)-XI] (220 mg, 0·43 mmole) was treated with N_2 diluted diazomethane (prepared from N-methyl-N-nitrosourea (6·0 g, 58 mmoles)). The fraction (5·3 g) boiling at 70–72°/2 mm was treated as mentioned above. Upon preparative GLC, pure trans-*bicyclo*[10.1.0]*tridecane* (XVIII) was obtained in optically active form (51% yield). (Found: C, 86·5; H, 13·2. $C_{13}H_{24}$ requires: C, 86·6; H, 13·4%).

A soln of XVII (0·75 g, 4·3 mmoles) in EtOH (50 ml) was stirred with Raney Ni (W-2 grade) in an atmospheric pressure of H_2 at room temp to afford optically active XVIII in a 76% yield. The results were summarized in Table 4.

Preparation of 1R,2R-trans-1-*methyl-2-phenylcyclopropane*

(a) 1R,2R-trans-1-*hydroxymethyl-2-phenylcyclopropane.*A soln of 1*R*,2*R*-XIIIb,[40] $[\alpha]_D^{27}$ −359° (*c*, 2·10, $CHCl_3$) (lit.[40] $[\alpha]_D^{24}$ −368°), (7·6 g, 47 mmoles) in dry ether (150 ml) was added dropwise to a well-stirred, ice-cooled mixture of LAH (7·0 g, 190 mmoles) and ether (125 ml). The mixture was stirred for 12 hr at room temp and heated at reflux for another 1 hr. Excess of LAH was destroyed with 10% NH_4Claq (150 ml), and the product was extracted with ether. The combined extracts were washed, dried and concentrated *in vacuo*. Distillation of the residue gave 1*R*,2*R*-*trans*-1-hydroxymethyl-2-phenylcyclopropane (XXVIII) (6·1 g, 88%), b.p. 104–106°/3 mm, $[\alpha]_D^{27}$ −88·7° (*c*, 2·06, $CHCl_3$), as a colourless oil. (Found: C, 80·9; H, 8·2. Calc. for $C_{10}H_{12}O$: C, 81·0; H, 8·2%).

(b) 1R,2R-trans-1-*methyl-2-phenylcyclopropane*. To a soln of *p*-toluenesulphonyl chloride (10·3 g, 54 mmoles) in 2,6-lutidine (6·0 ml) was added a soln of XXVIII (4·0 g, 27 mmoles) in lutidine (5·5 ml) at 0°. The mixture was allowed to stand at 20° for 2 hr with occasional cooling. After treatment with water, the mixture was extracted with ether. The extracts were washed with dil. HClaq and water, dried (Na_2SO_4) and concentrated *in vacuo* to yield the crude tosylate of XXVIII as a solid mass (10·5 g). Because of the instability of the tosylate at room temp, this was subjected to reduction without further purification.

A soln of the tosylate (8·0 g, 26 mmoles) in dry ether (50 ml) was added to a well-stirred slurry of LAH (10·0 g, 260 mmoles) in ether (150 ml) at 0°. After standing at 25° for 4 hr, THF (25 ml) was added, and stirring was continued for an additional 12 hr at 29°. Workup followed by vacuum distillation gave a volatile fraction (1·8 g, 53%), b.p. 85°/20 mm (bath temp). GLC purification on Apiezon L (30%) gave an analytical sample of 1*R*,2*R*-*trans*-1-methyl-2-phenylcyclopropane (XVI), $[\alpha]_D^{26}$ −114·9° (*c*, 2·12, $CHCl_3$). (Found: C, 91·0; O, 9·3. Calc. for $C_{10}H_{12}$: C, 90·9; H, 9·1%).

Decomposition of allyl diazoacetate (XIX) *in the presence of* XI

A cyclohexane (150 ml) soln of XIX[1b] (8·0 g, 64 mmoles) was added dropwise to a soln of (*R*)-XI [or

(*S*)-XI] (500 mg, 1·0 mmole) in cyclohexane (200 ml) at 60–62° with vigorous stirring under N_2 atm over a period of 15 to 18 hr. After N_2 evolution had ceased, the mixture was distilled *in vacuo* to give a volatile fraction (3·1 g), b.p. 50–70°/2 mm. This fraction was dissolved in ether and washed with dil. HCl repeatedly. After concentration *in vacuo*, the resulting oily products were dissolved in n-hexane and the soln was passed through an alumina column. The evaporation residue was subjected to GLC separation on PEG 3000 (5%). Along with diallyl maleate[1b] and fumarate[1b] (20–30%), pure 3-oxabicyclo[3.1.0]hexan-2-one (XX) (42% yield) was isolated in optically active form as shown in Table 5. The IR spectrum was identical with the one of authentic sample.[1b]

Optical resolution of 3-*oxabicyclo*[3.1.0]*hexan*-2-*one* (XX)

A soln of $Ba(OH)_2 \cdot 8H_2O$ (23·2 g, 74 mmoles) in MeOH (400 ml) was added to a mixture of racemic lactone XX[1b] (12·0 g, 120 mmoles) in one portion. The mixture was heated at reflux for 0·5 hr. After cooling, the excess of $Ba(OH)_2$ was neutralized by introduction of CO_2 gas and the resulting $BaCO_3$ ppts were removed by filtration. To this filtrate was added a soln of quinine sulphate (48·2 g, 62 mmoles) in MeOH (640 ml) at the reflux temp. The mixture was heated at reflux for an additional few min and cooled. The $BaSO_4$ ppts were removed centrifugally. The filtrate was concentrated to 500 ml and left in a refrigerator for 30 hr to yield crystalline solid (4·4 g), m.p. 179–181°. Concentration of the mother liquor was repeated to a volume of 150 ml and the resulting crystals (total 14·2 g) were collected. The solid was recrystallized seven times from EtOH to give *a quinine salt of* cis-2-*hydroxymethylcyclopropanecarboxylic acid* (XXIII) (salt A) (8·4 g, 16%), m.p. 184–185°, $[\alpha]_D^{20}$ −118° (*c*, 0·76, EtOH). (Found: C, 67·4; H, 7·6; N, 6·1. $C_{25}H_{32}N_2O_5$ requires: C, 68·2; H, 7·3; N, 6·4%). The mother liquor was concentrated to 60 ml and left at −15° for one week to give *another quinine salt of* XXIII (5·6 g), m.p. 120–124. Five recrystallizations from a mixture of benzene and acetone (1:4) gave a pure salt B (3·7 g, 7%), m.p. 132–133°, $[\alpha]_D^{20}$ −134° (*c*, 0·70, EtOH). (Found: C, 68·0; H, 7·5; N, 6·1. $C_{25}H_{32}N_2O_5$ requires: C, 68·2; H, 7·3; N, 6·4%).

A soln of $Ba(OH)_2 \cdot 8H_2O$ (3·5 g, 11 mmoles) in water (150 ml) was added to a boiling suspension of the salt A (7·5 g, 17 mmoles) in MeOH (120 ml). After concentration, free quinine was extracted with chloroform and then with ether repeatedly. The excess of $Ba(OH)_2$ in the aqueous layer was neutralized with CO_2 and resulting $BaCO_3$ ppts were removed by filtration. The filtrate was evporated to dryness to give barium salt of XXIII. This solid mass was macerated with EtOH (70 ml) and was acidified with ethanolic HCl (800 mg, 22 mmoles) soln (15 ml). The $BaCl_2$ precipitates were removed by filtration, and the filtrate was concentrated. Dehydration of the residual hydroxy acid was effected by successive azeotropic distillations of the benzene soln. Final distillation *in vacuo* gave optically pure lactone XX (953 mg, 57%) as a colourless oil, b.p. 88–91°/8 mm, $[\alpha]_D^{20}$ −65·9° (*c*, 6·14, $CHCl_3$). Similarly the salt B (3·5 g, 7·9 mmoles) afforded an enantiomeric lactone XX (486 mg, 63%), $[\alpha]_D^{20}$ +64·1° (*c*, 6·24, $CHCl_3$).

Decomposition of 1-*diazo*-6-*phenyl*-5-*hexen*-2-*one* (XXI) *in the presence of* XI

Diazoketone XXI[18] (10·0 g, 50 mmoles) was dissolved in cyclohexane (150 ml) and the soln was added dropwise to a soln of (*R*)-XI [or (*S*)-XI] (500 mg, 1·0 mmole) in cyclohexane (200 ml) at 53–55° in the course of 15 hr under N_2 atm. After N_2 evolution had ceased, the mixture was distilled *in vacuo* to yield crude 6-phenylbicyclo[3.1.0]hexan-2-one (XXII) (5·5 g, 64%), b.p. 95–100°/0·07 mm, which solidified upon standing, m.p. 68–72°. This solid was purified by treating with dil. HCl and passing through a short alumina column. Redistillation gave an analytical sample of XXII, m.p. 71–73°, in optically active form as shown in Table 5. The IR spectrum (CCl_4 soln) was superimposable with the one of authentic sample.[18]

Determination of relative reactivities of olefins in the carbenoid reaction

To a cyclohexane soln containing copper chelate XI (0·0056M) and an appropriate pair of olefins (each 2·8M) was introduced N_2 diluted diazomethane at −15 ~ −20°. The reaction was monitored by GLC and intercepted before 10% conversion had been attained. The product composition was determined by GLC (Apiezon L (30%) or dinonyl phthalate (17%)) of the reaction mixture without concentration. The results were summarized in Table 6. Following cyclopropanes were identified by comparison of the IR spectra and the GLC retention times with those of authentic samples; 1-methyl-1-phenylcyclopropane,[41] phenylcyclopropane,[41] cyclopropyl ethyl ether,* 1,1,2,2-tetramethylcyclopropane,[38] 1,1,2-trimethylcyclopropane,[38] *trans*-1-methyl-2-phenylcyclopropane,[38] norcarane,[38] and n-hexylcyclopropane.[42]

* Prepared by the method of Ref. 38.

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