followed. Similar rate expressions have been reported for related halogen cleavages or organotin compounds in other systems.[5]

This result requires uniquely the reactions shown in eq 5 and 6.

$$Br_3^- \overset{1/K}{\rightleftharpoons} Br^- + Br_2 \tag{5}$$

$$Br_2 + R_4Sn \xrightarrow{k_2} RBr + R_3SnBr \tag{6}$$

The effect of structure on reactivity is especially illuminating. These results are summarized in Table II and are compared with SE2 retention and SN2 inversion data. A close parallelism exists between these SN2 and SE2 inversion rates, but no relationship exists between the SE2 inversion and the "SE2" retention reaction rates. However, the tabulated "SE2" retention rates are similar to the rates of other "SE2" retention processes. *It is proposed that the stereochemical assignment of an* SE2 *process can be made by comparison of pertinent rate data with those of* SE2 *processes known to occur with retention of configuration and with inversion of configuration.*

Table II. Effect of Structure on the Relative Rates of Electrophilic and Nucleophilic Substitution on Carbon

R	Typical SN2 inversion[a]	SE2 inversion[b] ($Br_2 + RSnR_3'$)	SE2 retention[c,d] ($HCl + R_2Hg$)
CH_3-	1	1	1
CH_3CH_2-	0.03	0.144	5.95
$CH_3CH_2CH_2-$	0.013	0.0408	3.2
$(CH_3)_2CH-$	8×10^{-4}	7.53×10^{-3}	3.5
$(CH_3)_3CCH_2-$	3×10^{-7}	5.84×10^{-4}[e]	

[a] A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, p 13. [b] This work, obtained from rate constants. In methanol at 45.0°, [NaBr] = 0.366, R′ = neopentyl, $k_{methyl} = 16.6\ M^{-1}\ sec^{-1}$. [c] Rates in DMSO by R. E. Dessy and J. Y. Kim, *J. Amer. Chem. Soc.*, **83,** 1167 (1961). [d] Stereochemistry in dioxane is retention: L. H. Gale, J. Landgrebe, and F. R. Jensen, *Chem. Ind.* (*London*), 118 (1960). [e] Corrected for a statistical factor of four.

In Figure 1, the log k_{rel} for the SE2 inversion reaction is plotted *vs.* the log k_{rel} for the SN2 exchange reaction of bromide ion with alkyl chlorides.[6] This reaction was selected for comparison purposes because in both processes Br–C bonds are being formed. Clearly, a marked similarity between steric factors (and possibly electrical factors) must be present in the two very different processes. Also, the excellent agreement for the neopentyl derivatives strongly suggests that the bromodemetalation reaction for even this compound occurs highly preferentially with inversion of configuration. (In SE2 retention processes, neopentyl cleaves at about the same rate as other alkyl groups.[7])

The data presented herein demonstrate that in the transition state only bromine and tetraalkyltin are involved and that the reaction proceeds with inversion of configuration. These data uniquely require transition state III.

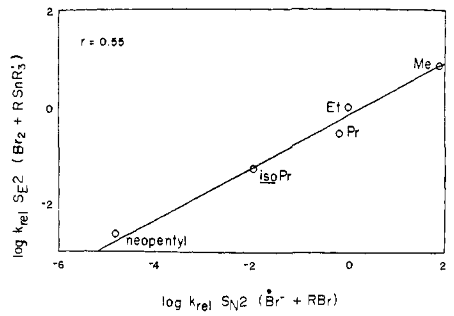

Figure 1. Comparison of the log k_{rel} for two inversion processes, exchange of bromide ion with alkyl bromides[6] and the bromodemetalation of organotin compounds (this work).

Two previous studies with optically active cyclopropyltin compounds have shown that halodemetalation of these materials occurs with retention of configuration.[8] Because of the very high resistance of cyclopropyl derivatives to react with inversion of configuration, these results are not surprising.

Acknowledgments. Grateful acknowledgment is made to the National Institutes of Health for partial support of this work under Grant No. 15373.

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(6) P. B. D. De la Mare, *J. Chem. Soc.*, 3180 (1955).

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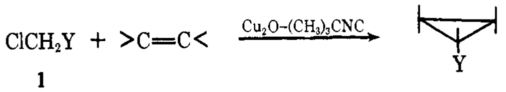
Received April 2, 1971

Synthetic Reactions by Complex Catalysts. XXIII. Cyclopropanes from α-Chloro Ketones, Esters, and Nitriles, Olefins, and a Copper(I) Oxide–Isonitrile Complex

Sir:

We wish to report a new synthesis of cyclopropane rings from an olefin, α-chloro compound **1**, and the copper(I) oxide–isonitrile system. Transient α-chloroorganocopper–isonitrile complexes[1] are assumed to be the key intermediates in these reactions; these constitute members of a new class of copper carbenoids. A typical experimental procedure is as follows. Under a nitrogen atmosphere, a mixture of Cu_2O (10 mmol), *tert*-butyl isonitrile (60 mmol), methyl monochloroacetate (20 mmol), and methyl acrylate (30 mmol) was stirred at 80° for 3 hr. The reaction mixture was extracted with ether, the extract was concentrated, and the residue was subjected to glpc analysis. Dimethyl cyclopropane-1,*trans*-2-dicarboxylate (**2**) was isolated by preparative glpc. The structure of the product was established by spectral data and elemental



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Y = CO_2R, COR, CN

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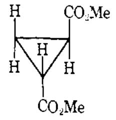
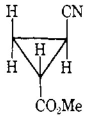
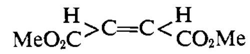
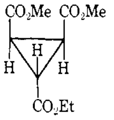
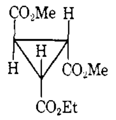
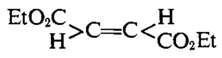
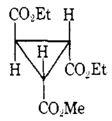
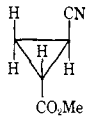
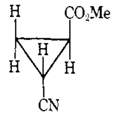
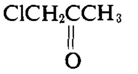
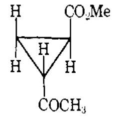
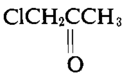
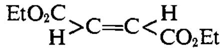
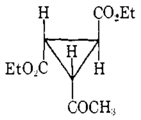
(1) For previous studies of reactions utilizing copper(I)–isonitrile complexes as intermediates, see (a) T. Saegusa, Y. Ito, S. Tomita, and H. Kinoshita, *J. Org. Chem.*, **35,** 670 (1970); (b) T. Saegusa, Y. Ito, H. Kinoshita, and S. Tomita, *Bull. Chem. Soc. Jap.*, **43,** 877 (1970).

Table I. Cyclopropane Synthesis from α-Chloro Compound, Olefin, and Copper(I) Oxide-Isonitrile[a]

α-Halo compd	Olefin	Product yield (%)
$\mathrm{ClCH_2CO_2Me}$	$\mathrm{CH_2{=}CHCO_2Me}$	 **2** (22)
$\mathrm{ClCH_2CO_2Me}$	$\mathrm{CH_2{=}CHCN}$	 **3** (31)
$\mathrm{ClCH_2CO_2Et}$	 $\mathrm{{}^{H}_{MeO_2C}\!>\!C{=}C\!<^{H}_{CO_2Me}}$	 **4a** +  **4b** total (29)
$\mathrm{ClCH_2CO_2Me}$	 $\mathrm{{}^{EtO_2C}_{H}\!>\!C{=}C\!<^{H}_{CO_2Et}}$	 **5** (53)
$\mathrm{BrCH_2CO_2Me}$	$\mathrm{CH_2{=}CHCN}$	 **3** (4)
$\mathrm{ClCH_2CN}$	$\mathrm{CH_2{=}CHCO_2Me}$	 **3** (10)
 $\mathrm{ClCH_2\underset{\underset{\displaystyle O}{\|}}{C}CH_3}$	$\mathrm{CH_2{=}CHCO_2Me}$	 **6** (21)
 $\mathrm{ClCH_2\underset{\underset{\displaystyle O}{\|}}{C}CH_3}$	 $\mathrm{{}^{EtO_2C}_{H}\!>\!C{=}C\!<^{H}_{CO_2Et}}$	 **7** (33)

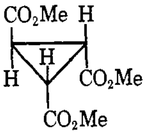
[a] A mixture of 20 mmol of an α-halo compound, 30 mmol of an olefin, 10 mmol of Cu_2O, and 60 mmol of *tert*-butyl isocyanide was stirred at 80° for 3 hr.

analysis: ir (neat) 3050, 1725, and 1025 cm^{-1}; nmr (in CCl_4) τ 6.30 (s, 6 H), 7.90 (m, 2 H), 8.62 (m, 2 H). The symmetric A_2B_2 pattern in the region between τ 7.7 and 8.7 was taken to indicate the trans dicarboxylate structure. Representative results obtained on application of these procedures to other substrates are shown in Table I. Spectral data and elemental analyses supported the assigned structures of all products. Especially, the structure of methyl cyclopropane-1,*trans*-2-cyanocarboxylate (**3**) was firmly determined by converting it into **2** by treatment with $HCl-CH_3OH$.

Monochloroacetate, monochloroacetonitrile, and monochloroacetone can be used as the α-chloro component. Monobromoacetate gave a lower yield than monochloroacetate. α,β-Unsaturated esters and nitriles can be used as the olefinic component. No reaction was observed with cyclohexene, with vinylic esters, or with vinylic ethers. No reaction occurred in the absence of isonitrile.

This cyclopropane synthesis is stereoselective. Except for the case of maleate, only one of the stereoisomers, in which ester, carbonyl, and nitrile groups from the two reaction components are oriented trans to each other, is produced. In the reaction of maleate, two stereoisomers **4a** and **4b** were formed. It has been assumed that the isomerization of maleate to fumarate occurred concurrently with cyclopropane formation, and **4a** and **4b** were produced, respectively, from maleate and fumarate. By glpc analysis, a considerable amount of dimethyl fumarate was actually detected in the reaction mixture. When fumarate was used as the olefin component, **5** was the sole cyclopropane product. This fact is taken to indicate the cis addition of the alkoxycarbonylmethine moiety to the olefin double bond.

Interestingly, trimethyl cyclopropane-1,*cis*-2,*trans*-3-tricarboxylate (**8**) was produced in 34% yield when methylmonochloroacetate was treated with the copper (I) oxide–isonitrile system in the absence of olefin under the conditions of Table I. Probably fumarate was first formed from monochloroacetate and then fumarate participated in the formation of cyclopropanetricarboxylate.



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Comparison of this reaction with the synthesis of cyclopropanes from α-halo ester and α,β-unsaturated ester in the presence of a strong base such as sodium alkoxide and sodium hydride[2] suggests two prominent differences. First, the reaction with strong base is not stereoselective; for example, the reaction of ethyl monochloroacetate and methyl acrylate with sodium methoxide yields 26% cis and 22% trans isomers.[2] The basic reactions carried out in dimethylformamide or in hexamethylphosphoramide–benzene mixtures gave predominantly the more stable isomer, usually the trans isomer. However, the stereoselectivity was not high. Second, the reaction utilizing strong base is not applicable to maleate and fumarate, whereas that with the copper(I) oxide–isonitrile system can successfully be applied to these olefin 1,2-dicarboxylates to produce cyclopropanetricarboxylic esters.

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Received May 3, 1971

Spin State of Photogenerated Phenylnitrene

Sir:

The decomposition of organic azides results in the elimination of nitrogen and the formation of a nitrene. In the thermal reactions of azides the nitrene appears at first in an excited singlet state (spin conservation) which may either react with the solvent or decay by spin inversion to the triplet ground state.[1,2] In photolysis, nitrenes can be formed from both the singlet and the triplet excited states of the azide and may therefore appear either as singlets or as triplets.[3] Hydrazoic acid has been shown to produce exclusively the singlet-excited-state $HN\ (c\,^1\Pi)$ of the imino radical on irradiation in the vacuum uv,[4,5] and cyano azide, N_3CN, behaves in a similar way.[6,7] In contrast, irradiation of ethyl azidoformate results in a mixture of singlet and triplet ethoxycarbonylnitrene[8] in the approximate ratio 2:1. In the present communication an attempt is made to establish the spin state of photogenerated phenylnitrene, using its reactions with CH bonds to distinguish between the singlet and the triplet species.

Singlet nitrenes insert into CH bonds producing secondary amines; triplet nitrenes abstract hydrogen and may produce both primary and secondary amines, the first by successive hydrogen abstraction, the second by hydrogen abstraction and subsequent radical coupling.[9] If the radical concentration is kept low (low azide concentrations, low intensity of photolytic radiation), the formation of secondary amines from triplet nitrene can be minimized. Under these conditions the yield of primary and secondary amine is indicative of the spin state of the nitrene intermediate. Finally, it is recalled that both singlet and triplet nitrenes will react with lone electron pairs, an important reaction of this kind being the attack of nitrenes on azido groups with the formation of azo compounds and nitrogen.[10]

Dilute solutions ($10^{-2}\ M$) of phenyl azide in degassed solvents were irradiated with the 313-nm mercury line. Photolysis was stopped at an azide conversion of 2% and the products were analyzed by a combination of thin-layer chromatography, vpc, solvent extraction, and fluorescence spectrophotometry. The results are summarized in Table I. It can be seen that in hydrocarbon solvents the main reaction products are azobenzene and a polymer. Small amounts of aniline are obtained, but no insertion into the solvent is observed. The polymers obtained in different hydrocarbons appear to be identical. Their infrared spectra indicate only the presence of aromatic CH groups and -NH linkages, but no aliphatic CH and no unreacted azide. It is thought that the polymer arises by insertion of the singlet nitrene into the aromatic ring of phenyl azide, followed by decomposition of the azido group, further insertion, etc. This view is in complete agreement with recent work by Abramovitch and Scriven,[11] who observed the insertion of (we believe, singlet) 4-cyanophenylnitrene into the para position of dimethylaniline. It is also

Table I. Product Distribution in the Photolysis of Phenyl Azide

	Mol % product			
Solvent	Azobenzene	Aniline	Insertion into solvent	Polymer
Benzene[a]	50 ± 3	5 ± 2	<3	50 ± 7
b	97 ± 3	3 ± 2	<3	0
Cyclohexane[a]	51 ± 3	4 ± 2	<3	48 ± 7
2,2,4-Trimethylpentane[a]	46 ± 3	8 ± 2	<3	48 ± 7
Methanol[a]	5 ± 3	7 ± 2	~80	0
b	55 ± 3	12 ± 2	0	0
2-Propanol[a]	3 ± 3	12 ± 2	~80	0
b	45 ± 10	27 ± 2	0	0
tert-Butyl alcohol[a]	55 ± 5	5 ± 2	0	30 ± 10

[a] Direct photolysis of a $10^{-2}\ M$ solution of azide; irradiation with the 313-nm mercury line. [b] Sensitized photolysis with acetophenone; irradiation with the 365-nm mercury line.

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