SN2 reactions are synchronous and have a single transition state. This is "looser" than either of the transition states for formation or decomposition of the SNAr intermediate.[7] In a loose transition state, entering and/or leaving groups have only weak covalent bonding interactions with carbon. The looser the SN2 transition state, the smaller the difference in reactivity between the strongest and weakest nucleophiles,[7] the tighter the transition state, the greater the difference in nucleophilicity. Thus the very tight SNAr transition state allows a wide range of reactivity for nucleophiles. There are other differences too between SN2 and SNAr reactions, associated with the two-step formation and decomposition of the SNAr intermediate and the steric consequences of a four- (SNAr) vs. a five- (SN2) coordinate transition state.[3]

A feature of Table IV is that methoxide, phenoxide, azide, and nitrite ions are $>10^5$ times more reactive than chloride ion in SNAr reactions, but these ions are of similar reactivity to chloride ion in SN2 reactions. In the SNAr reactions, the nucleophilicity is strongly influenced by the ability of the base to form strong bonds with carbon. Nitrite ion (N-attack) has a nucleophilicity which is comparable with azide ion toward 1-iodo-2,4-dinitrobenzene.

SNAr nucleophilicities toward 1-iodo-2,4-dinitrobenzene in methanol decrease in the order $PhS^- > Ar''S^- > MeO^- > PhO^- > N_3^- > NO_2^- > SCN^- > I^- > Br^- > ONO^- > Cl^- > F^-$. As one might expect from the substantial effects of different leaving groups and solvents on reactivity, SNAr nucleophilicity toward 1-fluoro-2,4-dinitrobenzene in DMF is very different,[13] i.e., PhS^-, $PhO^- > N_3^- \gg ONO^- > Ar''S^-$, NO_2^-, $F^- > Cl^- > SCN^-$, $SCN^- > Br^- > I^-$. SN2 nucleophilic tendencies toward methyl iodide in methanol decrease in yet a different order: $PhS^- \gg SCN^- > I^- > MeO^- > PhO^-$, $N_3^- > NO_2^-$, $Br^- > SNN^-$, Cl^-.

N- vs. O-Attack. It is now apparent (see preceding discussion) why the relative rates of N-attack vs. O-attack in SNAr reactions of the ambident nitrite ion change with the solvent, the leaving group, and substituents. The following examples highlight these interesting effects, which can be explained using the principles outlined herein.

An example of the solvent effect on this ambident ion is the reaction of NO_2^- with 1-chloro-2,4-dinitrobenzene, where N-attack is more than five times faster than O-attack in methanol, but in Me_2SO O-attack is faster than N-attack (Table I).

An example of the leaving group effect on ambident NO_2^- is the reaction of the 1-halo-2,4-dinitrobenzenes with nitrite ion in methanol. Here N-attack is more than ten times *slower* than O-attack on the fluoro compound but N-attack is more than five times *faster* than O-attack for reaction with the iodo compound (Table I).

An example of the substituent effect on reactions of the ambident nitrite ion are the reactions of *o*- and *p*-fluoronitrobenzene with nitrite ion in Me_2SO at 100°. Here N-attack is three times *slower* than O-attack on the ortho isomer, but N-attack is four times *faster* than O-attack on the para isomer.

Registry No.—Ar''F, 70-34-8; Ar''Cl, 97-00-7; Ar''I, 709-49-9; *o*-Ar'F, 1493-27-2; *o*-Ar'Cl, 88-73-3; *o*-Ar'I, 609-73-4; *p*-Ar'F, 350-46-9; *p*-Ar'Cl, 100-00-5; *p*-Ar'I, 636-98-6; PhS^-, 13133-62-5; $Ar''S^-$, 56437-88-8; SCN^-, 302-04-5; N_3^-, 14343-69-2; Pip, 26330-84-7; NO_2^-, 14797-65-0; MeO^-, 3315-60-4; Br^-, 24959-67-9; Cl^-, 16887-00-6; PhO^-, 3229-70-7; *p*-$Ar'O^-$, 14609-74-6; $Ar''O^-$, 20350-26-9; I^-, 20461-54-5; F^-, 16984-48-8.

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The Nucleophilic Step of the Ring Opening Reactions of Cyclopropanes with Electrophiles. Mechanism and Stereochemistry. I. Reaction of 1-Phenylbicyclo[4.1.0]heptane with Mercuric Salts

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The regio- and stereoselectivity of the cyclopropane ring opening reactions of 1-phenylbicyclo[4.1.0]heptane (1) with mercuric salts has been investigated. The stereoselectivity of the mercuration of 1 is highly variable, ranging from a syn:anti ratio of 13.5:86.5 to one of 82.5:17.5, and it is influenced by the type of mercuric salt and by the solvent. The observed results can be accounted for by a mechanism implying transition states or intermediates with high degree of development of positive charge on the benzylic carbon, in analogy with what was found in the case of the ring opening of aryl-substituted oxiranes and oxetanes in acidic media.

The ring opening reactions of cyclopropanes with electrophiles have been the subject of many recent investigations,[1–4] and in most cases a regiospecificity in accordance with the Markovnikov rule has been observed, with some exceptions.[5,6]

As to the stereochemistry of the ring opening it has been found that the electrophilic attack can occur with either retention or inversion of configuration depending on the nature and configuration of the ring substituents, whereas the nucleophilic step is highly stereoselective with complete or

Table I
Stereochemistry of the Nucleophilic Step of the Mercuration of 1

Mercuric salt	Added nucleophile	Solvent	% 5	% 6
$Hg(OOCCH_3)_2$		H_2O	13.5	86.5
$Hg(OOCCF_3)_2$		H_2O	19.5	80.5
$HgSO_4$		H_2O	22.5	77.5
$Hg(NO_3)_2$		H_2O	22.5	77.5
$Hg(ClO_4)_2$		H_2O	23.0	77.0
$Hg(OOCCH_3)_2$		$THF-H_2O$ (1:1)	25.5	74.5
$Hg(OOCCF_3)_2$		$THF-H_2O$ (1:1)	28.5	71.5
$Hg(OOCCH_3)_2$		CH_3COOH	45.0	55.0
$Hg(OOCCH_3)_2$		CH_2Cl_2	58.0	42.0
$Hg(OOCCH_3)_2$	1 *M* CH_3COOH	CH_2Cl_2	54.5	45.5
$Hg(OOCCF_3)_2$		Cyclohexane	69.5	30.5
$Hg(OOCCF_3)_2$	H_2O (satd)	Cyclohexane	69.0	31.0
$Hg(OOCCF_3)_2$		CCl_4	62.0	38.0
$Hg(OOCCF_3)_2$		$CHCl_3$	82.5	17.5
$Hg(OOCCF_3)_2$		CH_2Cl_2	75.0	25.0
$Hg(OOCCF_3)_2$	H_2O (satd)	CH_2Cl_2	73.0	27.0
$Hg(OOCCF_3)_2$		Benzene	71.0	29.0
$Hg(OOCCF_3)_2$	H_2O (satd)	Benzene	68.5	31.5
$Hg(OOCCF_3)_2$		CH_3NO_2	72.0	28.0

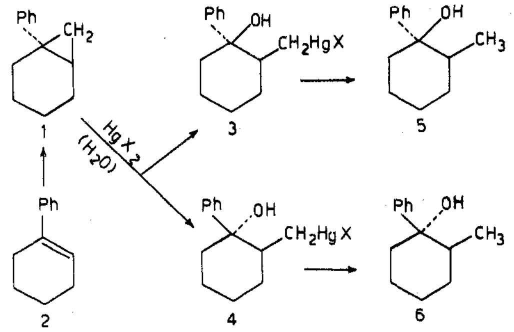
strongly predominant inversion of configuration in the majority of the reported cases.[1-4]

Mercuric salts and protic acids (H^+ and D^+) have been the most studied electrophiles in these reactions, but the latter afford very often significant amounts of elimination and/or rearrangement products.[1]

Previous work in our laboratory on the steric course of the ring opening reactions in acidic media of small ring heterocycles such as oxiranes,[7] aziridines,[8] and oxetanes[9] bearing aryl substituents on the ring has shown that the regio- and stereochemistry of these reactions are strongly influenced by the structure of the heterocycle, the nature of the substituents, the reaction condition, etc., the attack by the nucleophile taking place with courses ranging from complete retention to complete inversion of configuration.[7-9]

In connection with these studies we started an investigation on the ring opening reactions of cyclopropanes in order to establish possible correlations between the steric course of the nucleophilic stage of these reactions and that of the ring opening of small ring heterocycles in acid media. We wanted in particular to find out what analogies, if any, exist between the latter reactions, involving oxygen or nitrogen as the leaving atom, and the former ones, in which carbon exerts this function. We are reporting here the results of the ring opening reactions with mercuric salts of 1-phenylbicyclo[4.1.0]heptane (1), an analog of heterocycles[7a-c,8,9] that have previously been extensively investigated by our group.

Cyclopropane 1 has been obtained by the Simmons–Smith reaction of olefin 2, and has been purified by its treatment with ozone followed by chromatography. Levina and coworkers[10] reported that the ring opening reaction of 1 with mercuric acetate in water leads to 70% 1-phenyl-2-acetoxymercurimethylcyclohexanol, without giving any detail on the stereochemistry of the product. We have, therefore, reexamined this reaction and determined the composition and the stereochemistry of the products by reductive demercuration of the crude reaction mixture with sodium borohydride,[11] followed by GLC analysis. The known 1-phenyl-*cis*- (5) and -*trans*-2-methylcyclohexanol (6)[12] were thus obtained in a ratio of 13.5:86.5 (see Table I), indicating a similar ratio of the corresponding organomercurials 3a and 4a in the initial reaction mixture. Pure 4a was obtained through crystallization of the crude oxymercuration product.

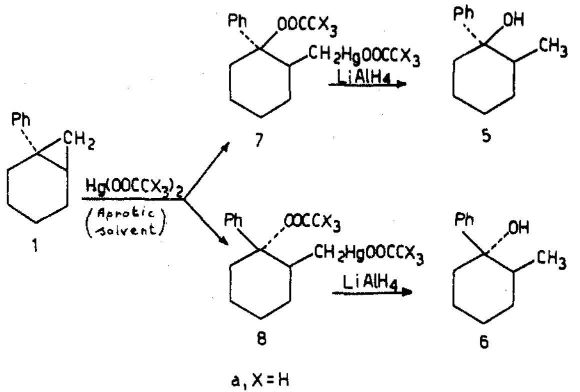


a, X=OOCCH3 ; b, X=OOCCF3 ; c, X=½SO4 ;
d, X=NO3 ; e, X=ClO4

The hydroxymercuration reactions were also carried out with other mercury salts (Table I) and it was found that the 3:4 ratio increased when salts of stronger acids were used. Pure 4b was obtained by crystallization of the crude oxymercuration products. Higher percentages of cis adducts were also formed when 1:1 THF–water was used as the solvent.

Cleavage of 1 with $Hg(OOCCH_3)_2$ in acetic acid gave a mixture of the cis (7a) and trans diacetate (8a) which was reduced by $LiAlH_4$ to the alcohols 5 and 6 in a ratio of 45:55; when this reaction was carried out in CH_2Cl_2 the amount of syn opening of the cyclopropane ring increased to 58.0%. The presence of free acetic acid in the reaction medium did not substantially modify the result (Table I).

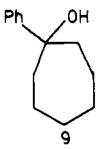
The use of mercury trifluoroacetate in aprotic solvents gave products 7b and 8b, with a high prevalence of the former, reaching 82.5% in $CHCl_3$ (Table I). From the reaction mixtures pure 7b was obtained by crystallization. The presence of water in the aprotic medium does not modify substantially the trend of the reactions, except for making them slightly less syn stereoselective.



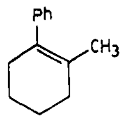
a, X=H
b, X=F

In all the mixtures obtained after reductive demercuration of the cleavage products of 1 with mercuric salts no trace was revealed of the alcohol 9, that should have been formed from the electrophilic attack of the mercuric salt on the secondary cyclopropylic carbon of 1 followed by the ring opening in the direction of the more stable benzylic cation.

Furthermore, it was thought suitable to ascertain whether the results obtained in the cleavage of 1 with mercuric salts were due entirely to a direct opening of the cyclopropane or to a more complex sequence of reactions,[13] such as intermediate formation of the unsaturated organomercurials 12 and 13, followed by reaction with further mercuric salt affording products which, on reductive demercuration, should have given mixtures of alcohols 5 and 6. We there-



9



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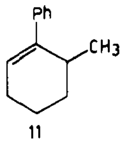

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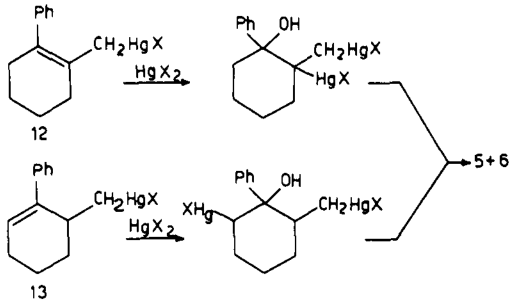


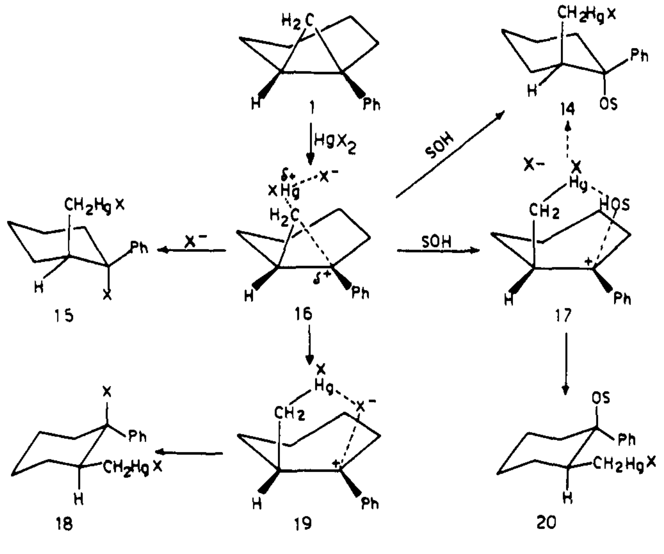
fore tested the reactivity of olefins **10** and **11**, structurally analogous to **12** and **13**, with mercuric acetate. It was found that **10** and **11**, when treated with $Hg(OOCCH_3)_2$ in water under the same conditions used for the ring opening of **1**, were recovered practically unreacted. These results agree with the very low reactivity of 1-phenylcyclohexene (**5**) with $Hg(OOCCH_3)_2$ in THF–H_2O reported by Brown.[11]

The main point of interest in our results is in the highly variable stereoselectivity ranging from a syn:anti ratio of 13.5:86.5 to one of 82.5:17.5, in contrast with what would be expected on the basis of previous results[1,2,4] indicating that in the mercuration of cyclopropanes the nucleophile attacks exclusively, or nearly so, with inversion of configuration. On the other hand, the complete regiospecificity of the ring cleavage is in accordance with expectations.[1,2,4,14]

As for the stereochemistry of the nucleophilic step, the fact that the stereoselectivity is influenced by the type of mercuric salt and by the solvent and that high percentages of syn adducts are obtained when the mercurations are effected in aprotic media points to a mechanism (Scheme I) implying transition states or intermediates with a high degree of development of positive charge on carbon, in which electron release by the phenyl probably plays an important role. Similar explanations were given in order to rationalize the steric course of the ring opening of phenyl-substituted oxiranes and oxetanes in acidic media.[7,9]

In aprotic solvents, the corner-mercurated intermediate,[1,2,4] obtained by the attack of the mercury (as HgX_2)[14] on the least hindered carbon of **1**, can evolve through an incipient carbenium ion **16** to an intimate ion pair (like **19**) in which the anion of the mercuric salt and the benzylic carbenium ion are probably held together by electrostatic interactions.[7,9] Because of the low degree of bond breaking of the C–C bond in the incipient carbocation **16**, the attack of the nucleophile at this stage occurs from the trans side leading to the anti adduct **15**. On the contrary, for the ion pair **19** direct collapse to the cis product **18** would be particularly favorable.

Scheme I



When the reactions are carried out in protic solvent, the benzylic carbenium ion formed can be selectively solvated to intermediates like **17** in which the mercury is coordinated with the solvent and the solvent itself is the effective nucleophilic agent because of the higher availability. Also, in the present case, combination of the solvated ion **17** should cause the preferential formation of the syn adduct **20**, whereas the attack of the solvent on **16** should give the anti adduct **14**. The higher trans stereoselectivity obtained in the reactions carried out in protic solvents, that has been observed also in the reactions of aryl-substituted small ring heterocycles in acidic media,[7-9,15] may be due to the attack by the protic solvent on the incipient carbenium ion **16** from the anti side before the complete rupture of the C–C bond which is favored by the high availability of nucleophilic molecules.

Clearly every factor which favors the development of positive charge on the benzylic carbon should increase the syn:anti ratio. As a matter of fact, when, in the mercuration of **1** in water, the mercuric salt is changed from mercuric acetate to more highly ionic salts, the higher electrophilicity of the mercury should make the rupture of the C–C bond more effective and therefore favor the path leading to the syn adduct **20** through carbenium ion **17**, in accordance with the observed increase of the cis adduct **3** on going from $Hg(OOCCH_3)_2$ to $Hg(ClO_4)_2$.[16] The same trend is observed in methylene dichloride, where the increase in syn adduct on going from $Hg(OOCCH_3)_2$ to $Hg(OOCCF_3)_2$ is considerably larger than in water or water–tetrahydrofuran. However, it should be pointed out that in the reactions carried out in methylene dichloride, the nucleophiles are different and the higher nucleophilicity of the acetate may make the attack at the stage **16**, affording the trans adduct **15**, more facile.

The high syn stereoselectivity in the reactions carried out in aprotic solvent is in agreement with our previous results on the ring opening of small ring heterocycles in acidic media.[7-9] The aprotic solvents should permit the ion-pair mechanism leading to the cis adduct to work efficiently. An added nucleophile (H_2O or CH_3COOH) affects only slightly the stereoselectivity of the mercuration reactions in aprotic solvents, showing that the ion pair **19** is sufficiently stable in the reaction conditions.

Further support for the existence of the mechanism proposed by us on the basis of the stereochemical results is given by the high negative ρ value (−3.2) found for a Hammett-type plot of the mercuration rates of arylcyclopropanes in acetic acid against the σ^+ constants.[14] In fact, the ρ value for the cleavage reactions approaches the ρ value for the solvolysis of aryldimethylcarbinyl chloride,[17] clearly a reaction with substantial carbenium ion character.

In conclusion, it is noteworthy that, in contrast with previous statements, the steric course of the nucleophilic step of the mercuration of cyclopropanes can change from complete trans stereoselectivity to nearly complete syn stereoselectivity depending on the substituents on the cyclopropanes, the reaction conditions, and the mercury salt which is used. The type of mercuric salt used may be of some importance in determining the steric course of mercuration reactions; therefore it ought to be stressed that the indiscriminate use of different mercuric salts may not be quite correct.

Experimental Section

All melting points were taken on a Kofler micro hot stage and are uncorrected. Infrared spectra were measured with a Perkin-Elmer Infracord Model 137 on paraffin oil mulls. The NMR spectra were determined on ca. 10% $CDCl_3$ solutions with a Jeol C-60 HL spectrometer using tetramethylsilane as internal standard. All GLC analyses were performed on a Perkin-Elmer apparatus Model F-11 using a glass column (2.5 mm × 2 m) packed with 15% Carbowax 20M on 80–100 mesh silanized Chromosorb W, temperatures column 200°, evaporator 230°, detector 230°, nitrogen flow 30 ml/min. The order of increasing retention times follows: **10, 11, 5, 6, 9.** The relative percentages of **5** and **6** were obtained from two or more separate runs on each experiment. All comparison between compounds were made on the basis of ir and NMR spectra and GLC. $MgSO_4$ was always used as drying agent. Evaporations were made in vacuo (rotating evaporator). Petroleum ether refers to the fraction boiling at 40–70°. Cyclohexane, benzene, CCl_4, and $CHCl_3$ were distilled from P_2O_5; CH_2Cl_2 was dried on P_2O_5 and CH_3NO_2 on molecular seives (3 Å).

1-Phenylbicyclo[4.1.0]heptane (1). A mixture of zinc dust (46.0 g, 0.70 g-atom) and cuprous chloride (6.88 g, 0.069 mol) in anhydrous ether (50 ml) was stirred rapidly and refluxed vigorously for 45 min in a nitrogen atmosphere.[18] After cooling, a few crystals of iodine and then 1-phenylcyclohexene (**2**,[19] 20.0 g, 0.12 mol) were added to the zinc–copper couple. The well-stirred mixture was then treated dropwise with methylene iodide (93.0 g, 0.35 mol) to maintain spontaneous refluxing. When the addition was complete the mixture was stirred and refluxed for an additional 24 hr. After cooling the ether layer was decanted from the unreacted couple, which was then washed with ether. The organic portion was washed with saturated NH_4Cl solution, 5% hydrochloric acid, and water and dried to yield crude **1** (18.3 g). The crude **1** was ozonized in $CHCl_3$ at 0° for 30 min in order to eliminate traces of olefinic products. Then the chloroformic solution was washed with 2 *N* Na_2CO_3 and water and evaporated to dryness and the residue was chromatographed on a 2.5 × 29 cm column of Al_2O_3 (activity I) using petroleum ether as the eluent and collecting 50-ml fractions. The second and the third fraction yielded pure **1** (14.0 g) (GLC), $n^{25}D$ 1.5404 (lit.[10] $n^{20}D$ 1.5425).

1-Phenyl-*cis*- (5) and -*trans*-2-methylcyclohexanol (6). A 94:6 mixture of **5** and **6** was obtained by the Grignard reaction of 2-methylcyclohexanone and phenylmagnesium bromide according to Luderer,[12a] bp 113–118° (2.5 mm) [lit.[12b] bp 93–96° (0.38 mm)]. The carbinol mixture (10 g) was chromatographed on a 2.9 × 60 cm silica gel column, eluting in succession with petroleum ether (6.0 l.), 98:2 petroleum ether–ether (6.0 l.) and 97:3 petroleum ether–ether (6.0 l.). Elution with 98:2 petroleum ether–ether afforded pure **5** (5.8 g), $n^{25}D$ 1.5333 (lit.[12a] $n^{22}D$ 1.5331), and with 97:3 petroleum ether–ether gave mixtures of **5** and **6**.

1-Phenyl-2-methylcyclohexene (10) and 1-Phenyl-6-methylcyclohexene (11). A mixture of **10** and **11** in a ratio of 59:41 was obtained in a modification of the method of Garbisch.[20] The 94:6 mixture of **5** and **6** (2.0 g) was stirred for 60 sec with a 20% sulfuric acid–acetic acid solution and then processed as described by Garbisch.[20]

10 and **11** were separated by preparative GLC (Carbowax 20M) and their physical and NMR data agreed with those reported by Garbisch.[20]

1-Phenylcycloheptanol (9) was obtained by Grignard reaction of cycloheptanone with phenylmagnesium bromide, mp 32–34° (from petroleum ether) (lit.[21] mp 23°).

1-Phenyl-*trans*-2-acetoxymercurimethylcyclohexanol (4a). A suspension of **1** (1.0 g, 5.8 mmol) in water (100 ml) was treated with mercuric acetate (1.85 g, 5.8 mmol) and then stirred at room temperature for 48 hr. After this time the reaction mixture was extracted with CH_2Cl_2 and the extracts, washed with water, were evaporated to dryness. The solid residue (2.1 g) on recrystallization from ethyl acetate yielded **4a** (1.5 g), mp 150–151°, λ_{OH} 2.98, λ_{CO} 6.40 μ (lit.[10] mp 143–146°).

1-Phenyl-*trans*-2-trifluoroacetoxymercurimethylcyclohexanol (4b). Mercuric trifluoroacetate[22] (1.24 g, 2.9 mmol) was added to a suspension of **1** (0.5 g, 0.29 mmol) in water (50 ml). The mixture was stirred for 48 hr at room temperature and then extracted with CH_2Cl_2. Evaporation of the washed (water) organic extracts yielded a solid residue (1.3 g) which, on crystallization from petroleum ether (bp 80–100°), gave **4b** (0.6 g), mp 105–107°, λ_{OH} 2.91, λ_{CO} 5.97 μ. Anal. Calcd for $C_{15}H_{17}F_3HgO_3$: C 35.81; H, 3.38. Found: C, 36.90; H, 3.40.

1-Phenyl-*cis*-2-trifluoroacetoxymercurimethyl-1-trifluoroacetoxycyclohexane (7b). A solution of **1** (0.300 g, 1.74 mmol) in anhydrous benzene (30 ml) was treated with mercuric trifluoroacetate (0.665 g, 1.56 mmol) and then stirred for 24 hr at room temperature. The reaction mixture was washed (water, saturated $NaHCO_3$, and water) and evaporated to yield a solid residue (0.68 g) which on crystallization from hexane afforded **7b** (0.27 g), mp 114–116°, λ_{CO} 5.61, 5.96 μ. Anal. Calcd for $C_{17}H_{16}F_6HgO_4$: C, 34.07; H, 2.67. Found: C, 34.21; H, 2.54.

1-Phenyl-*trans*-2-methylcyclohexanol (6). A. A suspension of **4a** (0.600 g, 1.33 mmol) in water (20 ml) and tetrahydrofuran (10 ml) was treated with 4 *N* NaOH (3 ml) and sodium borohydride (0.150 g, 3.8 mmol) and stirred at room temperature for 10 min. The reaction mixture was diluted with water and extracted with ether. Evaporation of the washed (water) and dried ether extracts yielded a solid residue (0.220 g) consisting of **6** (GLC) which on crystallization from petroleum ether (bp 30–50°) at −5° yielded pure **6** (0.150 g), mp 60–62° (lit.[12b] mp 61–63°).

B. Reduction of **4b** (0.300 g, 0.59 mmol) as described above for **4a** yielded a crude residue (0.070 g) consisting of **6** (GLC).

1-Phenyl-*cis*-2-methylcyclohexanol (5). A solution of **7b** (0.100 g, 0.17 mmol) in anhydrous ether (15 ml) was treated with lithium aluminum hydride (0.100 g, 2.63 mmol), stirred for 5 min at room temperature, and then refluxed for 15 min. After this time the excess of hydride was decomposed with the minimum amount of water and 2 *N* NaOH and the ether solution was dried and evaporated to yield an oily residue (0.025 g) which consisted of **5** (GLC).

Reaction of 1 with Several Mercuric Salts in Water. A suspension of **1** (0.100 g, 0.58 mmol) in water (10 ml) was treated under stirring with the appropriate mercuric salt (0.52 mmol) at room temperature. After 3 hr the mixture was treated with tetrahydrofuran (8 ml), 4 *N* NaOH (1 ml), and sodium borohydride (0.060 g, 1.58 mmol), left stirring for a further 10 min, diluted with water, and extracted with ether. Evaporation of the washed (water) and dried extracts gave a residue which was analyzed by GLC. The ratios of **5** to **6** are shown in Table I. Reactions of **1** carried out under the same reaction condition but reducting after 6 hr yielded the same product ratio within the experimental error. However, in the case of the reactions with mercuric salts of stronger acids, much longer contact times showed a slow epimerization of **6** into **5**. When olefins **10** and **11** were treated with mercuric acetate, as described above, they were recovered practically unchanged.

Reaction of 1 with Mercuric Acetate and Mercuric Trifluoroacetate in Tetrahydrofuran–Water. A solution of **1** (0.100 g, 0.58 mmol) in 1:1 (v/v) tetrahydrofuran–water mixture (10 ml) was treated with mercuric acetate or mercuric trifluoroacetate (0.52 mmol) and stirred at room temperature (6 hr for the reaction with the acetate and 1 hr for the reaction with the trifluoroacetate). Then 4 *N* NaOH (1 ml) and sodium borohydride (0.060 g, 1.58 mmol) were added and stirring was continued for 10 min. Work-up was carried out as in the case of the reactions in water and the residue obtained was analyzed by GLC (Table I). Reaction of **1** with each salt carried out under the same conditions but stopping after relatively longer contact times yielded the same product ratio within the experimental error.

Reaction of 1 with Mercuric Acetate in Acetic Acid. A solution of **1** (0.100 g, 0.58 mmol) in glacial acetic acid (10 ml) was treated under stirring with mercuric acetate (0.165 g, 0.52 mmol) for 1 hr. Then the reaction mixture was diluted with water and extracted with ether. The ether extracts were washed (water, saturated $NaHCO_3$, and water), dried, and evaporated to dryness. The residue (0.24 g) (λ_{CO} 5.78 and 6.17 μ) was dissolved in anhydrous ether (15 ml), treated with lithium aluminum hydride (0.100 g, 2.63 mmol), stirred for 5 min at room temperature, and then refluxed for 15 min. The excess of hydride was decomposed with the minimum amount of water and 2 *N* NaOH, and the dried ether layer was evaporated to dryness to yield a residue which was analyzed by GLC. The ratio of **5** to **6** is shown in Table I. Reactions of **1** carried out under the same reaction conditions but stopping after relatively longer contact times (2 hr) showed the same ratio of **5** to **6** within the experimental error.

Reactions of 1 with Mercuric Salts in Several Aprotic Solvents. A solution of **1** (0.100 g, 0.58 mmol) in the appropriate solvent (10 ml) was treated with the mercuric salt (0.52 mmol) (see Table I), stirred at room temperature (15 min for the reactions with mercuric trifluoroacetate and 2 hr for the reactions with mercuric acetate), then diluted with CH_2Cl_2, washed immediately with water, dried, and evaporated. The residue [λ_{CO} 5.78, 6.17 μ for the reactions with $Hg(OOCCH_3)_2$ and λ_{CO} 5.61, 5.96 μ for the reactions with $Hg(OOCCF_3)_2$] was taken up in anhydrous ether (15 ml) and reduced with lithium aluminum hydride (0.100 g, 2.63 mmol) under the same conditions used for the mercuration reaction in acetic acid to give a residue which was analyzed by GLC. The ratios of 5 to 6 are reported in Table I. Reactions of 1 with each salt carried out for each solvent under the same conditions but stopping after relatively longer contact times (1 hr for the reactions with the trifluoroacetate and 4 hr for the reactions with the acetate) yielded the same product composition within the experimental error. However, much longer contact times showed changes in the ratios between 5 and 6.

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Registry No.—**1**, 2415-82-9; **2**, 771-98-2; **4a**, 56437-51-5; **4b**, 56437-52-6; **5**, 30689-79-3; **6**, 30689-80-6; **7b**, 56437-53-7; mercuric acetate, 1600-27-7; mercuric trifluoroacetate, 13257-51-7.

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Mercury in Organic Chemistry. VI.[1] A Convenient Stereospecific Synthesis of α,β-Unsaturated Carboxylic Acids and Esters via Carbonylation of Vinylmercurials

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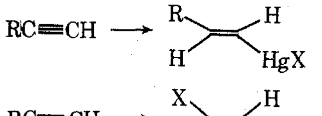
Vinylmercuric chlorides readily react with carbon monoxide (atmospheric pressure), lithium chloride, and palladium chloride in an alcohol solvent at low temperatures (<−20°) to give near-quantitative yields of α,β-unsaturated carboxylic esters in which the chloromercuri group is stereospecifically replaced by a carboalkoxy group. α,β-Unsaturated carboxylic acids may be obtained in an analogous fashion by employing 1–5% aqueous tetrahydrofuran as the solvent. The reaction accommodates a variety of functional groups and can also be effected using only catalytic amounts of palladium chloride or palladium on carbon if cupric chloride is used as a reoxidant. A mechanism involving vinyl- and acylpalladium intermediates is suggested.

The direct carbonylation of organomercurials is exceedingly difficult, requiring high temperatures and pressures and usually resulting in only very poor yields of carboxylic acids or their derivatives.[2,3] The addition of palladium salts generates organopalladium compounds[4] which are much more readily carbonylated.[5] Both the palladium exchange[6] and carbonylation[7] reactions have been determined to proceed with stereochemical retention of configuration. Unfortunately, the palladium-promoted carbonylation of alkyl-[6] and arylmercurials[8] gives poor yields of carboxylic acids or their derivatives and these reactions appear to be of rather limited synthetic utility. With the ready availability of a number of vinylmercurials through acetylene addition reactions (eq 1, 2)[9–11] and the ability of these reactions to accommodate a wide variety of functional groups, we were encouraged to examine some possible synthetic applications of these compounds. We wish to report now that the extremely facile palladium-promoted carbonylation of vinylmercurials provides an excellent new method for the preparation of α,β-unsaturated carboxylic acids and esters.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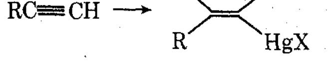
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Results and Discussion

α,β-Unsaturated Esters. In order to determine the best conditions for converting vinylmercurials into α,β-unsaturated carboxylic esters, we have examined the stoichiometry of this reaction. Both styrylmercuric chloride (1 mmol) and *trans*-1-hexenylmercuric chloride (1 mmol) were treated with varying amounts of palladium chloride, lithium chloride, and methanol or ethanol under 1 atm of carbon monoxide at low temperatures, and the yield of ester determined by GLC analysis (eq 3). The results are indicated in Table I.

Several points are obvious from this study. Although excellent yields are obtained in almost all reactions, the combination of 1 equiv of palladium chloride and 2 equiv of