520–570 cm^{-1} (Sn–CH$_3$ asymmetrical stretch), and 506–525 cm^{-1} (Sn–CH$_3$ symmetrical stretch) as limits for these absorptions.

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Halomethyl–Metal Compounds. XII.[1] The Action of Sodium Iodide on Phenyl(trihalomethyl)mercury Compounds. A New Method of Dihalocarbene Generation

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Abstract: The action of sodium iodide in acetone or in 1,2-dimethoxyethane (DME) on phenyl(trihalomethyl)mercury compounds results in displacement of trihalomethyl anion from mercury with formation of phenylmercuric iodide. In acetone the CX_3^- species is intercepted by the solvent and the products formed are haloform, dimethyl(trihalomethyl)carbinol, and 3,3,3-trihalo-*t*-butyl isobutyrate. The action of sodium iodide in DME on phenyl(trihalomethyl)mercurials in the presence of olefins provides a new route to *gem*-dihalocyclopropanes. With $C_6H_5HgCCl_3$ these reactions are rapid at 83–85° and slow at room temperature; with $C_6H_5HgCCl_2Br$ they are rapid at room temperature and slow at −15°. As yet unknown side reactions limit the product yields when relatively unreactive olefins are used (*e.g.*, tetrachloroethylene, triethylvinylsilane, vinyl acetate), but very good product yields are obtained with the more reactive (toward CCl_2) olefins such as cyclohexene and cyclooctene. A study of the relative reactivities of olefins toward the $C_6H_5HgCCl_3$ + NaI (at 80°) and the $C_6H_5HgCCl_2Br$ + NaI (at −15°) systems was carried out. The k_{rel} values obtained at 80° were virtually identical with those obtained at 80° using $C_6H_5HgCCl_2Br$ in benzene (or DME) and CCl_3CO_2Na in DME, and the values obtained at −15° were virtually identical with those obtained at this temperature using $CHCl_3$ + *t*-BuOK as the CCl_2 source.

We have described in some detail the reactions of $C_6H_5HgCCl_2Br$, $C_6H_5HgCClBr_2$, $C_6H_5HgCBr_3$, and $C_6H_5HgCCl_3$ with olefins, in which CX_2 is transferred from the mercurial reagent to the olefin to produce *gem*-dihalocyclopropanes in high yield.[3–6] As noted, such reactions proceed rapidly in refluxing benzene when $C_6H_5HgCCl_2Br$ is used as the CCl_2 source, but much longer reaction times (36–48 hr) are required for $C_6H_5HgCCl_3$. This marked difference in reactivity was attributed to a more favorable elimination of phenylmercuric bromide, as compared with phenylmercuric chloride, owing mainly to steric effects.[6] Since phenyl(trichloromethyl)mercury is cheaper and somewhat more easily prepared than phenyl(bromodichloromethyl)mercury, we were quite interested in the possible "activation" of the former, either *via* a catalytic process or by its conversion, possibly *in situ*, to a more reactive species.

It was the report by Ledwith and Phillips[7] that ethyl(chloromethyl)mercury undergoes extremely rapid and quantitative displacement of Cl by iodide ion in acetone (eq 1) which suggested a possible activation of $C_6H_5HgCCl_3$ to us. If iodide ion would react in a

$$CH_3CH_2HgCH_2Cl + Na^+I^- \xrightarrow{\text{acetone}} CH_3CH_2HgCH_2I + NaCl(s) \quad (1)$$

similar fashion with the latter, then generation of $C_6H_5HgCCl_2I$ should be possible. This mercurial would be expected to be less stable, *i.e.*, a more reactive CCl_2 source, than $C_6H_5HgCCl_2Br$, and thus CCl_2 generation *in situ* by the action of iodide ion on $C_6H_5HgCCl_3$ in the presence of an olefin seemed a possibility worth investigating. However, an alternative mode of attack of iodide ion on phenyl(trichloromethyl)mercury had to be considered. Nucleophilic attack at mercury in RHgX compounds, *e.g.*, eq 2, is well known.[8] The

$$C_6H_5HgCl + Na^+I^- \xrightarrow{\text{acetone}} C_6H_5HgI + NaCl(s) \quad (2)$$

trichloromethyl group is quite electronegative[9] and the trichloromethyl anion is a relatively stable species;[10] furthermore, the presence of three chlorine substituents on the carbon atom introduces very severe steric

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[1] (a) Part XI: D. Seyferth, M. E. Gordon, and R. Damrauer, in press; (b) preliminary communication: D. Seyferth, J. Y.-P. Mui, M. E. Gordon, and J. M. Burlitch, *J. Am. Chem. Soc.*, 87, 681 (1965).

[2] (a) Alfred P. Sloan Foundation Fellow, 1962–1966; (b) National Institutes of Health Predoctoral Fellow, 1963–1966; (c) National Institutes of Health Postdoctoral Fellow, 1964–1965.

[3] D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D. Simmons, Jr., A. J.-H. Treiber, and S. R. Dowd, *J. Am. Chem. Soc.*, 87, 4259 (1965).

[4] D. Seyferth and J. M. Burlitch, U. S. Patent 3,265,745 (Aug 9, 1966).

[5] D. Seyferth and J. M. Burlitch, *J. Am. Chem. Soc.*, 86, 2730 (1964).

[6] D. Seyferth, in "Proceedings of the Robert A. Welch Foundation Conferences on Chemical Research. IX. Organometallic Compounds," Robert A. Welch Foundation, Houston, Tex., 1966, pp 89–135 (review).

[7] A. Ledwith and L. Phillips, *J. Chem. Soc.*, 3796 (1962).

[8] D. Seyferth and R. H. Towe, *Inorg. Chem.*, 1, 185 (1962).

[9] χ_{CCl_3} = 2.84 on the Pauling scale: J. E. Huheey, *J. Phys. Chem.*, 68, 3073 (1964).

[10] (a) J. Hine, N. W. Burske, M. Hine, and P. B. Langford, *J. Am. Chem. Soc.*, 79, 1406 (1957); (b) J. Hine, "Divalent Carbon," Ronald Press Co., New York, N. Y., 1964, pp 36–41.

hindrance to nucleophilic attack at carbon. Thus on the basis of these considerations, one might expect that a more favorable process would be attack by iodide ion at mercury (eq 3).

$$C_6H_5HgCCl_3 + Na^+I^- \longrightarrow C_6H_5HgI + Na^+CCl_3^- \quad (3)$$

When equimolar amounts of phenyl(trichloromethyl)-mercury and sodium iodide were allowed to react in anhydrous acetone at 25°, a voluminous, white precipitate was formed, and the solution turned faintly yellow. Filtration, followed by a water wash of the residue, afforded phenylmercuric iodide in 93% yield. Gas–liquid partition chromatography (glpc) of the filtrate demonstrated the presence of chloroform (34%), dimethyl(trichloromethyl)carbinol (henceforth chloretone) (26%), and 2,2,2-trichloro-*t*-butyl isobutyrate, $(CH_3)_2CHCO_2C(CH_3)_2CCl_3$ (10%). Under identical conditions equimolar amounts of phenyl(bromodichloromethyl)mercury and sodium iodide reacted in acetone solution to give bromodichloromethane (43%), dimethyl(bromodichloromethyl)carbinol, $(CH_3)_2(CCl_2Br)COH$ (15%), 2-bromo-2,2-dichloro-*t*-butyl isobutyrate, $(CH_3)_2CHCO_2C(CH_3)_2CCl_2Br$ (3%), and phenylmercuric iodide (85%). In both cases traces of elemental mercury, mercuric iodide, iodoform, and iodobenzene were formed.

The above results are in agreement with iodide ion attack at mercury, as illustrated in eq 3. Compared with $C_6H_5HgCCl_3$, phenyl(bromodichloromethyl)mercury reacted more rapidly and more cleanly with sodium iodide. This is in line with expectation on the basis of Hine's studies,[10] which showed that the rate of formation of CCl_2Br^- is roughly six times greater than that of CCl_3^- in the base-catalyzed hydrolysis of the respective haloforms. The trihalomethyl anion formed by displacement at mercury then could abstract a proton from the acetone solvent to give haloform or add to the C=O bond[11] of acetone to give the carbinol. Although the mechanism of formation of the isobutyrate esters was not studied, it is possible that a dichloroepoxide intermediate may be involved.

Sodium thiocyanate was shown to effect a similar displacement of trihalomethyl anion from phenyl(trihalomethyl)mercury compounds in acetone. These reactions appeared to be much more facile than those of sodium iodide, and only two volatile products were formed, the corresponding dimethyl(trihalomethyl)-carbinol and haloform. Thus, treatment of 10 mmoles of phenyl(trichloromethyl)mercury with 12 mmoles of sodium thiocyanate in acetone afforded chloroform (68%), chloretone (26%), and diphenylmercury (37%). Neither phenylmercuric thiocyanate nor the isobutyrate ester were detected. The absence of phenylmercuric thiocyanate is not surprising, since it is known that thiocyanate ion in excess can cause its disproportionation to diphenylmercury and $Hg(SCN)_4^{2-}$.[12]

If the reaction between phenyl(trihalomethyl)mercurials and sodium iodide were to be carried out in the absence of a reagent or solvent capable of trapping the intermediate trihalomethyl anion, then the latter should form dihalocarbene ($CX_3^- \rightarrow CX_2 + X^-$). Such a reagent system would represent a novel procedure for dihalocarbene generation and one that could be effected under mild conditions without the use of a basic reagent. It thus appeared that our original goal of "activating" $C_6H_5HgCCl_3$ as a CCl_2 source by reaction with sodium iodide could be realized, although the mechanism originally conceived was not followed. Such was the case.

When a solution of 7 mmoles each of phenyl(trichloromethyl)mercury and sodium iodide and 21 mmoles of cyclohexene in 1,2-dimethoxyethane (henceforth DME)—in which sodium iodide is soluble—was heated at reflux (83–85°) for 3 hr, phenylmercuric iodide and sodium chloride precipitated. Glpc analysis of the filtrate showed that chloroform (5%) and 7,7-dichloronorcarane (78%) had been formed. A blank run carried out under identical conditions, but without sodium iodide, gave 7,7-dichloronorcarane in 15.5% yield and only a trace of chloroform, thus showing the marked effect of the sodium iodide. This effect was even more pronounced at room temperature. A reaction of phenyl(trichloromethyl)mercury (7 mmoles), sodium iodide (7 mmoles), and cyclohexene (21 mmoles) in DME at room temperature (35°) for 48 hr gave 7,7-dichloronorcarane in 66% yield and some chloroform (10%). A blank run, with the only difference being the absence of sodium iodide, failed to produce any 7,7-dichloronorcarane. Similar experiments were carried out with phenyl(bromodichloromethyl)mercury. Reaction of this mercurial with an equimolar quantity of sodium iodide in the presence of a tenfold excess of cyclohexene in DME at 30° for 4 hr gave 7,7-dichloronorcarane in 75% yield. In contrast, the room-temperature reaction of this mercurial with excess of cyclohexene in DME for 4 hr in the absence of sodium iodide produced the norcarane in only 1.5% yield. The $C_6H_5HgCCl_2Br$ + NaI reagent is an effective CCl_2 transfer agent even at −15°, as the results of low-temperature competition experiments discussed below indicate. To cite one example, reaction of 10 mmoles of $C_6H_5HgCCl_2Br$ and 11 mmoles of sodium iodide with a mixture of 53.5 mmoles of cyclohexene and 49.8 mmoles of 2,3-dimethyl-2-pentene for 15 hr at −15° gave a combined *gem*-dichlorocyclopropane yield of 49.6%. Longer reaction times should give higher product yields.

The phenyl(trihalomethyl)mercury + sodium iodide system does, however, appear to have some limitations. These are illustrated in Table I, which lists results of the reactions of various olefins with this reagent pair. It will be noted that high yields of *gem*-dichlorocyclopropanes were obtained with cyclohexene and cyclooctene, both of which are quite reactive toward CCl_2 derived from other sources.[13] However, with olefins known to be quite unreactive toward CCl_2, such as tetrachloroethylene, triethylvinylsilane, and vinyl acetate, the product yields were low. Since the latter three olefins could be converted to the corresponding *gem*-dichlorocyclopropanes in high yield by reaction with $C_6H_5HgCCl_2Br$ in benzene at 80°,[3] it would appear that side reaction(s) do complicate matters in the case of the $C_6H_5HgCX_3$ + NaI system. What these are is

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[11] Addition of CCl_3^- to C=O bonds has been reported previously: *e.g.*, (a) C. Weizmann, E. Bergmann, and M. Sulzbacher, *J. Am. Chem. Soc.*, **70**, 1189 (1948), and prior references cited therein; (b) E. Kaspar and R. Wiechert, *Chem. Ber.*, **91**, 2664 (1958). Note also the addition of $LiCCl_3$ to ketones: (c) G. Köbrich, K. Flory, and R. H. Fischer, *ibid.*, **99**, 1793 (1966).

[12] F. C. Whitmore, "Organic Compounds of Mercury," Chemical Catalog Co., New York, N. Y., 1921, pp 60–61.

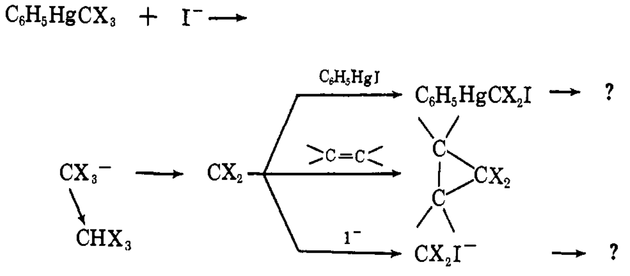
[13] W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, p 166.

Table I. Reactions of the $C_6H_5HgCCl_3$ + NaI System with Olefins

Olefin[a]	Reaction time, hr (temp, °C)	Product (yield, %)	C_6H_5HgI yield, %
Cyclohexene	3 (85) and 14 (25)	7,7-Dichloronorcarane (91)	89
Cyclohexene	48 (30)	7,7-Dichloronorcarane (74)	
Cyclohexene (using $C_6H_5HgCCl_2Br$)	21 (32)	7,7-Dichloronorcarane (83)	88
Cyclooctene	3 (85) and 20 (25)	9,9-Dichlorobicyclo[6.1.0]nonane (98)	86
trans-Stilbene	1 (85)	*trans*-1,1-Dichloro-2,3-diphenylcyclopropane (88)	81
Allyl bromide[b]	8 (80)	1,1-Dichloro-2-bromomethylcyclopropane (59)	70[c]
Triethylvinylsilane	3 (85)	1,1-Dichloro-2-triethylsilylcyclopropane (18)	61
Tetrachloroethylene[d]	2 (85) and 10 (25)	Hexachlorocyclopropane (29)	47
Tetrachloroethylene[d]	19 (27)	Hexachlorocyclopropane (10)	60
Vinyl acetate	3 (85)	1,1-Dichloro-2-cyanocyclopropane (14) and $CH_3CH(CCl_3)O_2CCH_3$ (7)	79

[a] Mercurial:NaI:olefin = 1:1.1:3 in 25 ml of DME unless otherwise specified. [b] 1:1 mixture of allyl bromide and DME was used. [c] Also HgI_2 in 24% yield. [d] 1:1 mixture of tetrachloroethylene and DME was used.

not known with certainty, but two possibilities may be mentioned: interception of CCl_2 by phenylmercuric iodide and (or) by iodide ion when only poorly reactive olefins are present. We have demonstrated that dihalocarbene insertion into the mercury–halogen bond is possible[14] and, more specifically, have obtained evidence from kinetic studies that CCl_2 will insert into the Hg–I linkage of phenylmercuric iodide.[15] Thus phenyl(iododichloromethyl)mercury may actually be formed during these reactions and may in fact contribute to the *gem*-dichlorocyclopropane yield in a simple thermal reaction.[16] However, our experience with $C_6H_5HgCHBrI$ and $C_6H_5HgCHI_2$ has shown these to be rather poor CHBr and CHI transfer agents, apparently because of competing homolytic decomposition pathways,[17] and so there exists the possibility that any CCl_2 diverted to producing $C_6H_5HgCCl_2I$ is lost as far as *gem*-dichlorocyclopropane formation is concerned. Further consideration of this question will require synthesis of this as yet unknown mercurial. Hine and Dowell[18] have demonstrated that halide ions react with CCl_2 ($\rightarrow CCl_2X^-$) and that the rates of such reactions are the most rapid when $X^- = I^-$, so iodide ion could intercept CCl_2 in our systems to produce ultimately products other than those desired. The situation obtaining in the $C_6H_5HgCX_3$ + NaI + olefin systems therefore can be summarized as follows.



The fact that the trihalomethyl anion is an intermediate in these reactions also introduces complications in certain cases. Wagner and co-workers[19] reported that decarboxylation of sodium trichloroacetate in the presence of vinyl acetate in DME gave both the expected *gem*-dichlorocyclopropyl acetate (10%) and the CCl_3^- addition product, $CH_3CO_2CH(CCl_3)CH_3$ (10%). Our result with vinyl acetate (Table I) was quite similar. The reaction of $C_6H_5HgCCl_2Br$ and $C_6H_5HgCCl_3$ with sodium iodide in the presence of acrylonitrile (which is known to undergo base-catalyzed haloform addition[20]) provided another example of trihalomethyl anion interception by an olefin. Thus reaction of phenyl(bromodichloromethyl)mercury with sodium iodide in the presence of acrylonitrile (1:1.1:3 ratio) in benzene–DME for 4 hr at room temperature gave bromodichloromethane (28.5%), 1,1-dichloro-2-cyanocyclopropane (16%), and 4-bromo-4,4-dichlorobutyronitrile (2%). When this reaction was carried out using acrylonitrile as solvent, the $CHCl_2Br$ and $CCl_2BrCCH_2CH_2CN$ yields rose to 40 and 13.4%, respectively; no 1,1-dichloro-2-cyanocyclopropane was present and some polyacrylonitrile was formed. In contrast, the reaction of phenyl(bromodichloromethyl)mercury with acrylonitrile in benzene at 80° (in the absence of sodium iodide) gave *only* 1,1-dichloro-2-cyanocyclopropane in 78% yield.[3] The reaction between the $C_6H_5HgCCl_3$ + NaI system and acrylonitrile also was studied. In this case polymerization of the olefin is a more serious problem. When acrylonitrile was used as the reaction medium, the $C_6H_5HgCCl_3$ + NaI reaction caused a vigorous, exothermic polymerization of the solvent, giving, after removal of volatiles, a brown, resinous residue. When this reaction was repeated in benzene–DME ($C_6H_5HgCCl_3$:NaI:$CH_2{=}CHCN$, 1:1.5:10) at 80° for 4 hr, chloroform (22%) and 4,4,4-trichlorobutyronitrile (15%) were produced. At room temperature for 24 hr, such a reaction gave these products in yields of 10 and 7%, respectively. In both cases no 1,1-dichloro-2-cyanocyclopropane could be detected, and some polymer was formed. The source

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(14) M. E. Gordon, K. V. Darragh, and D. Seyferth, *J. Am. Chem. Soc.*, **88**, 1831 (1966).

(15) D. Seyferth and J. Y.-P. Mui, unpublished work.

(16) A suggestion first made by F. R. Jensen: *cf.* the discussion (p 129) following the review listed in ref 6.

(17) H. D. Simmons, Jr., Ph.D. Thesis, Massachusetts Institute of Technology, 1965.

(18) J. Hine and A. M. Dowell, *J. Am. Chem. Soc.*, **76**, 2688 (1954).

(19) W. M. Wagner, H. Kloosterziel, and S. Van der Ven, *Rec. Trav. Chim.*, **80**, 740 (1961).

(20) H. A. Bruson, W. Niederhauser, T. Riener, and W. F. Hester, *J. Am. Chem. Soc.*, **67**, 601 (1945).

of the protons appearing in the haloform and trihalobutyronitrile produced in these reactions is not known.

From the discussion above it is apparent that the $C_6H_5HgCCl_2Br$ + NaI reagent system (as compared to $C_6H_5HgCCl_2Br$ reacting alone) has one important advantage: it allows *gem*-dichlorocyclopropane synthesis from olefins at room temperature or even at lower temperatures in nonbasic medium. Also, it allows $C_6H_5HgCCl_3$ to react rapidly as a CCl_2 transfer agent at 80°. Its disadvantages are that some as yet undefined side reactions appear to divert CCl_2 from the more unreactive olefins and that CCl_3^- is an intermediate.

A few experiments were carried out to test the $C_6H_5HgCX_3$ + NaSCN reagent combination as a CCl_2 transfer system. When roughly equimolar amounts of $C_6H_5HgCCl_3$ and NaSCN (at 80°) or $C_6H_5HgCCl_2Br$ + NaSCN (at 30°) reagents were allowed to react in the presence of an excess of cyclohexene in DME or benzene–DME, 7,7-dichloronorcarane was formed, but the yields were only 5–10%.

While the evidence that the $C_6H_5HgCCl_3$ + NaI system reacted to give initially CCl_3^- was quite good, we sought further information concerning the reagent by means of competition studies. Such studies would be especially valuable, since competitions had been carried out previously with other CCl_2 transfer systems: with $C_6H_5HgCCl_2Br$ (thermal reaction),[5] with sodium trichloroacetate in DME,[5] and with the $CHCl_3$ + t-C_4H_9OK reagent system.[21] In all of these studies it was found that olefin reactivity toward the CCl_2 source increased with increasing nucleophilicity of the olefin, a result in agreement with Hine's conclusion, based on the fact that the rate of base-catalyzed chloroform hydrolysis is dependent upon the nucleophilicity of added salts and that dichlorocarbene is an electrophilic reagent.

In the present study tetra-, tri-, di-, and monoalkylolefins corresponding to those utilized by us in our previous work[5] were selected so that a direct comparison of olefin relative reactivities toward $C_6H_5HgCCl_2Br$ and CCl_3CO_2Na would be possible. Cyclohexene was used as the reference olefin. In the standard experiment, 50 mmoles each of olefin "A" and cyclohexene were allowed to compete (in DME at 80°) for the reagent generated from 10 mmoles of $C_6H_5HgCCl_3$ and 11 mmoles of sodium iodide. Glpc analysis of the products provided yield data which could be translated into relative reactivities.[21] Table II summarizes these results and compares them with the k_{rel} values of the same olefins toward $C_6H_5HgCCl_2Br$ in benzene (or DME) at 80° and CCl_3CO_2Na in DME at 80°.

These k_{rel} values could not be compared directly with the relative rate constants for the $CHCl_3$ + t-C_4H_9OK system, since the latter were measured at −15°. Such a comparison was, however, desirable, and use of the $C_6H_5HgCCl_2Br$ + NaI system at −15° made this possible. A series of competition experiments were carried out, with olefin "A" and cyclohexene competing for CCl_2 *via* reaction of phenyl(bromodichloromethyl)mercury with sodium iodide at −15 ± 5° (15-hr reaction time). As mentioned previously, a conversion to *gem*-dichlorocyclopropane products of 30–50% was obtained under these conditions. The results are presented in Table III. For comparison, the results (k_{rel} *vs.* cyclohexene) of Doering and Henderson's study[21] are given: $(CH_3)_2C{=}C(CH_3)_2$, 53.7; $(CH_3)_2C{=}CHCH_3$, 23.4; $(CH_3)_2C{=}CH_2$, 5.50; *cis*-$CH_3CH{=}CHC_2H_5$, 1.62; *trans*-$CH_3CH{=}CHC_2H_5$, 2.14; n-$C_3H_7CH{=}CH_2$, 0.186. The same trend is discernible; *i.e.*, the reactivity in both cases decreases in the order tetra- > tri- > 1,1-di- > monoalkylolefin. However, in our series $k_{\mathrm{rel}}(cis) > k_{\mathrm{rel}}(trans)$, while in the work of Doering and Henderson[21] it was reported that the reverse was the case. To check this apparent inconsistency, we determined the relative reactivities of *cis*- and *trans*-3-heptene toward the $CHCl_3$ + t-C_4H_9OK reagent and of *cis*- and *trans*-2-pentene toward both reagent systems. Table III gives the k_{rel} values determined. Good agreement between the k_{rel} values for both reagent systems is apparent, and it appears that *cis*-1,2-dialkylolefins are more reactive than the respective *trans*-1,2-dialkylolefins toward both reagents. We can offer no explanation for the data of Doering and Henderson cited above.

Table II. Relative Reactivities of Olefins toward the $C_6H_5HgCCl_3$ + NaI Reagent at 80°

Olefin	Total yield of cyclopropane products, % av	k_{rel}, k_A/k_1, av	k_{rel} for C_6H_5Hg-CCl_2Br at 80°[a]	k_{rel} for CCl_3CO_2-Na at 80°[a]
$Me_2C{=}CMeEt$	81.7	23.2	22.5	24.8
$Et_2C{=}CHMe$	47.7	3.13	3.54	3.52
Et(n-Bu)$C{=}CH_2$	60.0	2.30	2.31[b]	
Cyclohexene		1.0	1.0	1.0
cis-EtCH=CHPr-*n*	60.8	0.835	0.83	0.80
trans-EtCH=CHPr-*n*	75.3	0.537	0.52	0.52
n-$C_5H_{11}CH{=}CH_2$	66.7	0.218	0.24	0.22

[a] Data from ref 5. [b] Determined in this study.

Table III. Relative Reactivities of Olefins toward the $C_6H_5HgCCl_2Br$ + NaI Reagent at −15°

Olefin	Total yield of cyclopropane products, % av	k_{rel}, k_A/k_1, av	k_{rel} for t-BuOK + $CHCl_3$ system, av
$Me_2C{=}CMe_2$	45.9	43.6	53.7[a]
$Me_2C{=}CMeEt$	47.1	22.7	
$Et_2C{=}CHMe$	47.4	4.73	
cis-MeCH=CHEt[b]	39.8	1.44	1.52
Cyclohexene		1.0	1.0
trans-MeCH=CHEt[b]	39.8	0.834	0.86
cis-EtCH=CHPr-*n*[b]	38.7	0.81	0.89
trans-EtCH=CHPr-*n*[b]	38.7	0.435	0.435
n-$C_5H_{11}CH{=}CH_2$	27.7	0.11	

[a] Datum from ref 21. [b] The respective *cis* and *trans* isomers were allowed to compete directly with cyclohexene in the same experiment.

The finding that $k_{\mathrm{rel}}(Me_2C{=}CMe_2) > k_{\mathrm{rel}}(MeEtC{=}CMe_2)$, $k_{\mathrm{rel}}(MeCH{=}CHEt) > k_{\mathrm{rel}}(EtCH{=}CHPr\text{-}n)$, $k_{\mathrm{rel}}(Me_2C{=}CHMe) > k_{\mathrm{rel}}(Et_2C{=}CHMe)$, and $k_{\mathrm{rel}}(n\text{-}PrCH{=}CH_2) > k_{\mathrm{rel}}(n\text{-}C_5H_{11}CH{=}CH_2)$ for these CCl_2 transfer systems suggests that steric effects are of some importance, a fact not generally appreciated. The observation that Δ^5 double bonds of Δ^5 or $\Delta^{3,5}$

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[21] W. von E. Doering and W. A. Henderson, *J. Am. Chem. Soc.*, 80, 5274 (1958).

steroids bearing a 10β-methyl group are completely unreactive toward CCl_2 but reactive to a limited extent toward CF_2 and that such steroids without this methyl substituent do undergo CCl_2 addition at the Δ^5 double bond has been attributed to steric factors,[22] but, in general, steric effects in CX_2 addition to olefins have not yet been investigated.

The fact that the relative reactivities increase with increasing nucleophilic character of the olefin confirms the electrophilic nature of the reactive intermediate in the $C_6H_5HgCX_3$ + NaI system. More significant is the virtual identity of the k_{rel} values for all four CCl_2 transfer systems listed in Tables II and III. This suggests that the same intermediate (most likely CCl_2) is involved in all four systems compared. These data, of course, say nothing concerning the exact nature of the CCl_2 intermediate: is it "free" CCl_2 or is it complexed with NaCl or C_6H_5HgX?[23]

The application of the general procedure reported here (CX_3^- displacement from metal–trihalomethyl compounds by iodide ion) as a route to other useful carbene transfer systems is under active investigation. We already have noted that reaction of the $(CH_3)_3SnCF_3$ + NaI reagent system with olefins provides an excellent route to *gem*-difluorocyclopropanes.[1b]

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified nitrogen. Phenyl(trichloromethyl)mercury was prepared by the method of Schweizer and O'Neill,[24] but using high-speed stirring. The preparation of phenyl(bromodichloromethyl)mercury has been described in part I of this series.[25] Sodium iodide (analytical reagent) was dried at 110° (0.02 mm) for 24 hr. DME was purified by double distillation from potassium; it was used immediately after purification. The reaction of triethylchlorosilane with vinyllithium served in the preparation of triethylvinylsilane.[26]

Infrared spectra were recorded using a Perkin-Elmer Infracord 337 spectrophotometer. Proton magnetic resonance spectra were obtained with a Varian Associates A-60 nmr spectrometer. Reactions of phenyl(trihalomethyl)mercurials were monitored using thin layer chromatography: glass plates or microscope slides coated with Silica Gel G (Brinckman Instruments) or Eastman Chromagram Sheet, Type K301-R, with a mixture of benzene–cyclohexane (1:4) serving as eluent. The plates were developed in an iodine chamber and then sprayed with a 10% solution of sodium sulfide in 50% aqueous ethanol. Compounds containing mercury developed as black mercuric sulfide. Glpc was used for yield determination, for the collection of analytical samples, and for assessing the purity of volatile reagents. Three types of columns were used: (A) 8 ft × 12 mm glass column packed with 25% General Electric Co. SE-30 Silicone rubber gum on Chromosorb P; (B) 8 ft × 8 mm glass column packed with 20% SE-30 on Chromosorb P; (C) 12 ft × 6 mm aluminum column packed with either 20% SE-30 on Chromosorb P or 15% Carbowax 20-M on Chromosorb P. The first two were used in the MIT isothermal gas chromatograph, the last in an F & M Model 700 gas chromatograph.

Reaction of Phenyl(trichloromethyl)mercury with Sodium Iodide in Acetone. The mercurial (3.96 g, 10 mmoles) in 15 ml of anhydrous acetone under an atmosphere of dry nitrogen in a dry, 50-ml, three-necked flask equipped with reflux condenser topped with a nitrogen inlet tube, a magnetic stirring assembly, and a pressure-equalizing addition funnel was cooled to 0°. A solution of 1.65 g (11 mmoles) of anhydrous sodium iodide in 15 ml of dry acetone was added dropwise during 1 hr with stirring. Upon completion of the addition the reaction mixture was stirred at room temperature for 98 hr. At this time thin layer chromatography (tlc) indicated that the starting mercurial had been consumed. The reaction mixture was pale brown and a tan solid had precipitated. The volatile components were distilled at 0.02 mm (70° pot temperature) into a receiver at −78°, giving 19.82 g of clear distillate and 4.28 g of tan residue, mp 264–270° with residue. Glpc analysis of the distillate (column A) showed the presence of three major products, which were identified by comparison of their infrared spectra and glpc retention times with those of authentic samples, and where necessary by nmr, by elemental analysis, and by independent synthesis. These were chloroform (34%), chloretone (26%), and 2,2,2-trichloro-*t*-butyl isobutyrate (10%). The latter had $n^{25}D$ 1.4557 and was analyzed.

Anal. Calcd for $C_8H_{13}Cl_3O_2$: C, 38.81; H, 5.29; Cl, 42.97. Found: C, 38.50; H, 5.32; Cl, 43.34.

The residue from the trap-to-trap distillation was washed with water, filtered, dried, and sublimed at 120° (0.03 mm) to give 3.76 g (93%) of phenylmercuric iodide, mp 270–272°. A mixture melting point with authentic C_6H_5HgI was not depressed. Two minor products also were detected: mercuric iodide, identified by its tlc retention time and its characteristic red color (turning yellow on warming), and iodoform, mp 119–120°, which was identified by comparison of its infrared and nmr spectra with those of an authentic sample.

A similar experiment was performed by adding the sodium iodide solution dropwise to the $C_6H_5HgCCl_3$ solution in acetone at reflux, with a total reaction time at reflux of 98 hr. The products in this case were chloroform (59%), chloretone (12%), and $(CH_3)_2CHCO_2C(CH_3)_2CCl_3$ (7%), together with phenylmercuric iodide in 84% yield.

An authentic sample of 2,2,2-trichloro-*t*-butyl isobutyrate was prepared as follows. Into a dry test tube were placed 0.178 g (1 mmole) of chloretone[11a] and 0.106 g (1 mmole) of isobutyryl chloride. The mixture was heated for 10 min with shaking over a Bunsen burner. The resulting crude product was injected into a glpc unit (4-ft preparative column, 25% SE-30 on Chromosorb W), and the high-boiling component, $n^{25}D$ 1.4557, was collected. Its nmr spectrum (in CCl_4) showed a doublet centered at 1.19 ppm (J = 7.0 cps) (6 H), a singlet at 1.88 ppm (6 H), and a complex multiplet centered at 2.50 ppm (1 H) downfield from internal TMS. Its infrared spectrum (in CS_2) showed bands at 3010 (m), 2985 (s), 2940 (m), 2885 (m), 1750 (vs), 1470 (s), 1395 (s), 1370 (s), 1255 (m), 1200 (m), 1148 (s), 1074 (m), 1011 (w), 969 (w), 941 (w), 904 (m), 861 (m), 798 (s), and 745 (w) cm^{-1}.

Reaction of Phenyl(bromodichloromethyl)mercury with Sodium Iodide in Acetone. The same procedure was used in the reaction of 4.40 g (10 mmoles) of this mercurial with 11 mmoles of sodium iodide in anhydrous acetone at room temperature for 52 hr. The reaction mixture, at the end of this time, was pale yellow and contained a white precipitate. Glpc analysis of the distilled (under vacuum) filtrate showed the presence of bromodichloromethane (43%), dimethyl(bromodichloromethyl)carbinol (15%), and $(CH_3)_2CHCO_2C(CH_3)_2CCl_2Br$ (3%). Phenylmercuric iodide was isolated in 85% yield. The products were identified by comparison of their glpc retention times and spectra (infrared and/or nmr) with those of authentic samples.

An authentic sample of $CCl_2Br(CH_3)_2COH$ was prepared as follows. A mixture of 101 g (0.18 mole) of KOH and 50 ml of methylal (freshly distilled from sodium) was cooled to −4° in a dry, 250-ml, three-necked flask equipped with a high-speed stirrer and an addition funnel. A mixture of 29.5 g (0.18 mole) of bromodichloromethane and 11.6 g (0.20 mole) of anhydrous acetone was added dropwise over a period of 2 hr. Stirring was continued for another 2 hr at −4°. The reaction mixture was poured over crushed ice and dilute sulfuric acid. The methylal layer was separated, dried, and concentrated at reduced pressure. A viscous, yellow oil (*ca.* 4 g) remained. This was purified by preparative glpc (column A) to give the carbinol, mp 119–120°. Its nmr spectrum (CCl_4) showed a singlet at 1.67 ppm (6 H) and a singlet at 2.46 ppm (1 H). Its infrared spectrum showed absorptions at 3580 (s), 3000 (s), 2950 (m), 1395 (s), 1390 (s), 1190 (s), 1120 (s), 982 (m), 907 (m), 831 (s), 792 (s), 752 (s), and 550 (m) cm^{-1}.

Anal. Calcd for $C_4H_7Cl_2BrO$: C, 21.64; H, 3.18; AgX from a 3.367-mg sample, 7.198 mg. Found: C, 21.52; H, 3.24; AgX from a 3.367-mg sample, 7.166 mg.

An authentic sample of $(CH_3)_2CHCO_2C(CH_3)_2CCl_2Br$ was prepared from this carbinol and isobutyryl chloride. The product, a sweet-smelling liquid, $n^{25}D$ 1.4760, was isolated by pre-

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(22) L. H. Knox, E. Velarde, S. Berger, D. Cuadriello, P. W. Landis, and A. D. Cross, *J. Am. Chem. Soc.*, **85**, 1851 (1963).

(23) See the pertinent remarks by P. S. Skell in the discussion (pp 131–133) following the review listed as ref 6.

(24) E. E. Schweizer and G. J. O'Neill, *J. Org. Chem.*, 28, 851 (1963).

(25) D. Seyferth and J. M. Burlitch, *J. Organometal. Chem.* (Amsterdam), 4, 127 (1965).

(26) D. Seyferth and M. A. Weiner, *J. Am. Chem. Soc.*, 83, 3583 (1961).

parative glpc. Its infrared spectrum (in CS_2) showed the following absorptions: 3010 (m), 2980 (s), 2940 (m), 2880 (m), 1760 (vs), 1475 (s), 1395 (s), 1380 (s), 1262 (m), 1200 (m), 1155 (s), 1075 (m), 1011 (w), 970 (w), 941 (w), 898 (w), 798 (s), 759 (s) cm^{-1}.

Anal. Calcd for $C_8H_{13}Cl_2BrO_2$: C, 32.90; H, 4.49. Found: C, 33.09; H, 4.49.

Reactions of Phenyl(trihalomethyl)mercurials with Sodium Thiocyanate in Acetone. a. With Phenyl(trichloromethyl)mercury. To 10 mmoles of the mercurial in 10 ml of anhydrous acetone under nitrogen was added a solution of 12.5 mmoles of anhydrous sodium thiocyanate [dried at 110° (0.02 mm) for 80 hr] in 20 ml of acetone over a period of 1 hr. A voluminous white precipitate filled the flask. The reaction mixture was stirred at room temperature for 12 hr; at this time tlc showed that starting mercurial still was present. The mixture was stirred at reflux for another 32 hr. Work-up as in the sodium iodide reactions gave a filtrate containing chloroform (68%) and chloretone (26.5%), but none of the ester. The distillation residue (4.55 g of gray-white solid, mp 119–123° with residue) was washed with water to leave 1.93 g of tan solid, mp 119° with residue. This solid was dissolved in benzene; the resulting solution was filtered through neutral alumina and evaporated to give 1.30 g (37%) of diphenylmercury, mp 122–124°, identified by infrared spectrum and mixture melting point.

b. With Phenyl(bromodichloromethyl)mercury. A similar reaction was carried out using this mercurial. The orange reaction mixture, which contained tan solid, was stirred at room temperature for 12 hr, at the end of which time tlc showed the mercurial had been consumed. The volatile products were bromodichloromethane (39%) and dimethyl(bromodichloromethyl)carbinol (10%).

In neither experiment was phenylmercuric thiocyanate detected. An authentic sample, prepared *via* $(C_6H_5)_2Hg + Hg(SCN)_2$ in benzene–THF at room temperature, was available for comparison.

Reaction of the $C_6H_5HgCCl_3$ + NaI Reagent with Cyclohexene. a. At Reflux in DME. Into a 50-ml, three-necked flask equipped with a reflux condenser topped with a nitrogen inlet tube, a thermometer, a magnetic stirring assembly, and an addition funnel were charged 2.77 g (7 mmoles) of phenyl(trichloromethyl)mercury, 1.72 g (21 mmoles) of cyclohexene, and 10 ml of DME. To this mixture was added with stirring a solution of 1.05 g (7 mmoles) of sodium iodide in 10 ml of DME. The resulting yellow reaction mixture was heated at reflux (83–85°) for 3 hr. Filtration to remove 2.88 g of white solid (mp 268–271° with residue) was followed by distillation of the filtrate at 0.02 mm (pot temperature to 70°) into a receiver at −78° (standard trap-to-trap distillation). The distillation residue, 0.79 g of yellow solid, melted and turned black at 254–260°. The filtrate was analyzed by glpc (SE-30 on Chromosorb P, 165°, *n*-butylbenzene internal standard). It was determined that 7,7-dichloronorcarane had been formed in 78% yield. Another analysis carried out at 70° showed chloroform to be present in 5% yield.

Reaction of 7 mmoles of $C_6H_5HgCCl_3$ with 21 mmoles of cyclohexene in 20 ml of DME at reflux for 3 hr (in the absence of sodium iodide) produced 7,7-dichloronorcarane in 15.5% yield and only a trace (<1%) of chloroform.

Another experiment in which 10 mmoles of the mercurial, 11 mmoles of sodium iodide, and 30 mmoles of cyclohexene in 20 ml of DME were allowed to react for 3 hr at reflux and 14 hr at room temperature produced 7,7-dichloronorcarane in 91% yield. In this case the solids produced in the reaction (4.89 g) were washed with water and dried to leave 4.17 g of white solid, mp 266–270°. This was extracted with benzene using a Soxhlet extractor. Evaporation of the benzene solution gave 3.60 g (89%) of phenylmercuric iodide, mp 271–272°.

A mixed DME–benzene solvent system also was used with equally good results. For instance, a reaction of 7 mmoles each of mercurial and sodium iodide with 70 mmoles of cyclohexene in 25 ml of benzene and 5.5 ml of DME at reflux for 3 hr produced 7,7-dichloronorcarane in 72% yield.

The reactions of the $C_6H_5HgCCl_3$ + NaI reagent with the other olefins listed in Table I were carried out using the procedure described in this section. The *gem*-dichlorocyclopropane products were identified by comparing their glpc retention times, their infrared spectra, and at times the refractive indices with those of authentic samples available from a previous study.[3,27]

b. At Room Temperature in DME. A mixture of 7 mmoles each of $C_6H_5HgCCl_3$ and sodium iodide and 21 mmoles of cyclohexene in 20 ml of DME was stirred at 35° for 48 hr. The solution turned pale yellow and a white solid precipitated. A work-up identical with that described in the previous section gave 3.50 g of white solid, 7,7-dichloronorcarane (66%) and chloroform (10%). Another reaction, carried out at 31° for 68 hr, gave 7,7-dichloronorcarane in a yield of 71%, together with phenylmercuric iodide in 75% yield.

No 7,7-dichloronorcarane was produced when 7 mmoles of phenyl(trichloromethyl)mercury and 21 mmoles of cyclohexene in 20 ml of DME were stirred at room temperature for 48 hr. In another experiment 10 mmoles of mercurial and 30 mmoles of cyclohexene in 25 ml of DME were left to stand for 26 days; the yield of 7,7-dichloronorcarane produced was 12%.

Reaction of the $C_6H_5HgCCl_2Br$ + NaI Reagent with Cyclohexene. A solution of the mercurial (10 mmoles), sodium iodide (10 mmoles), and cyclohexene (100 mmoles) in 20 ml of DME was stirred for 4 hr at 30°. Tlc analysis at the end of this time showed that less than 3% of the starting mercurial remained unconverted. Solid residue, 4.12 g, mp 275–280° with residue, was filtered. Trap-to-trap distillation left 0.95 g of brown, solid residue. The filtrate was analyzed by glpc. It was determined that 7,7-dichloronorcarane had been formed in 75% yield. A trace (<1%) of 7-bromo-7-chloronorcarane also was detected, but this possibly was due to some $CHClBr_2$ contaminant in the $CHCl_2Br$ used in mercurial preparation. Another experiment was carried out in which 10 mmoles of mercurial, 11 mmoles of sodium iodide, and 30 mmoles of cyclohexene in 30 ml of DME were stirred at 31° for 21 hr. 7,7-Dichloronorcarane was produced in 83% yield; in this case phenylmercuric iodide (88%) was isolated also.

7,7-Dichloronorcarane was formed in only 1.5% yield when 7 mmoles of $C_6H_5HgCCl_2Br$ and 70 mmoles of cyclohexene in 14 ml of DME were stirred at 30° for 4 hr.

Reaction of Bromodichloromethane with Potassium *t*-Butoxide in the Presence of Cyclohexene. This experiment was performed in order to compare the results of the previous experiment with the results of another cyclopropanation of cyclohexene in which CCl_2Br^- is an intermediate. The procedure of Doering and Hoffmann[29] was used.

Into a 1-l., three-necked flask equipped with mechanical stirrer, nitrogen inlet tube, and a rubber connector to a *t*-BuOK storage flask were charged 83.3 g (0.507 mole) of bromodichloromethane, 333 ml of cyclohexene, and 100 ml of pentane. The contents were cooled to 0° under an atmosphere of dry nitrogen and then 0.62 mole of *t*-BuOK (the monosolvate[30]) was added in small portions over a period of 30 min. The reaction mixture was stirred for 30 min while the flask was allowed to warm slowly to room temperature and subsequently was hydrolyzed by addition of water. The dried organic layer was analyzed by glpc and shown to contain 7,7-dichloronorcarane (76%) and 7-bromo-7-chloronorcarane (1.2%). The organic layer then was distilled to give 72.3 g of mixed dihalonorcaranes (98% pure).

The same reaction was repeated using DME as solvent in place of pentane (30 mmoles each of $CHCl_2Br$ and *t*-BuOK, 200 mmoles of cyclohexene, and 40 ml of DME). The products were 7,7-dichloronorcarane (48%) and 7-bromo-7-chloronorcarane (<1%). A variation of the Doering–Hoffmann procedure[31] in which a deficiency of the olefin is used gave 7,7-dichloronorcarane and 7-bromo-7-chloronorcarane in yields of 66 and 1.1%, respectively. These results, that $CHCl_2Br$ + base produces only CCl_2 for all practical purposes, contradict the conclusions of Parham and Twelves[32] which suggested that significant amounts of CClBr also were formed.

Reaction of the $C_6H_5HgCCl_2Br$ + NaI Reagent with Acrylonitrile. a. In DME. Solutions of 10 mmoles of the mercurial and 30 mmoles of acrylonitrile in 20 ml of benzene and of 11 moles of sodium iodide in 17 ml of DME were mixed and stirred at room temperature for 4 hr. The resulting deep brown reaction mixture

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[27] Authentic 9,9-dichlorobicyclo[6.1.0]nonane, $n^{25}\text{D}$ 1.5037, was prepared by reaction of ethyl trichloroacetate, sodium methoxide, and cyclooctene[28] in hexane solution: bp 45° (0.3 mm); infrared spectrum showed 2970 (m), 2930 (s), 2860 (s), 1475 (s), 1450 (m), 1360 (w), 1238 (w), 1173 (m), 1070 (m), 1041 (w), 869 (s), 838 (s), and 808 (s) cm^{-1}.

Anal. Calcd for $C_9H_{14}Cl_2$: C, 55.97; H, 7.31; Cl, 36.72. Found: C, 56.06; H, 7.40; Cl, 36.63.

[28] W. E. Parham and E. E. Schweizer, *J. Org. Chem.*, 24, 1733 (1959).

[29] W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

[30] A. J. Speziale and K. W. Ratts, *ibid.*, **84**, 854 (1962).

[31] H. Komrsova and J. Farkas, *Collection Czech. Chem. Commun.*, **25**, 1977 (1960).

[32] W. E. Parham and R. R. Twelves, *J. Org. Chem.*, 22, 730 (1957).

Table IV. Competition of Olefins for the **$C_6H_5HgCCl_3$ + NaI Reagent at 80°**[a]

Olefin "A," mmoles	Cyclohexene, mmoles	Cyclopropane from olefin "A," %	7,7-Dichloronorcarane, %	k_{rel}	k_{rel}, av
$Me_2C{=}CMeEt$ 47.7	50.1	78.4	3.44	23.95	23.2
(47.5)	(49.4)	(78.0)	(3.63)	(22.4)	
$Et_2C{=}CHMe$ 50.5	50.0	36.3	11.85	3.05	3.13
(48.2)	(46.3)	(36.4)	(10.9)	(3.21)	
n-Bu(Et)C=CH_2 49.9	50.0	41.3	18.4	2.34	2.30
(50.1)	(50.2)	(42.3)	(18.05)	(2.26)	
cis-n-PrCH=CHEt 24.4	24.8	27.6	33.8	0.830	0.835
(24.35)	(24.20)	(27.6)	(32.6)	(0.841)	
trans-n-PrCH=CHEt 46.9	50.5	25.5	51.4	0.535	0.537
(48.0)	(48.2)	(25.7)	(48.0)	(0.539)	
n-$C_5H_{11}CH{=}CH_2$ 48.4	51.8	13.5	65.6	0.220	0.218
(49.6)	(49.5)	(11.25)	(53.0)	(0.216)	

[a] Values in parentheses are those obtained in duplicate runs.

was filtered to remove 5.76 g of brown solid and the filtrate was trap-to-trap distilled [80° (0.05 mm)]. Glpc analysis of the filtrate showed the presence of bromodichloromethane (28.5%), 1,1-dichloro-2-cyanocyclopropane[8] (16%), and 4-bromo-4,4-dichlorobutyronitrile (2%), mp 53–54.5°. The latter was identified by means of its analysis and spectra.

Anal. Calcd for $C_4H_4BrCl_2N$: C, 22.15; H, 1.85. Found: C, 22.08; H, 1.77.

The nmr spectrum of $CCl_2BrCH_2CH_2CN$ is very similar to that of $CCl_3CH_2CH_2CN$. The methylene protons constitute an A_2B_2 system producing a large number of splittings at 2.6–3.3 ppm. The infrared spectrum showed $\nu_{C\equiv N}$ at 2240 cm^{-1} and showed other bands at 2970 (w), 1440 (w), 1380 (w), 1268 (m), 1196 (m), 1062 (w), 1035 (s), 1012 (m), 1000 (sh), 948 (w), 888 (w), 828 (w), 792 (s), 776 (s), 731 (s), 696 (s), 669 (s), 596 (w), and 577 (m) cm^{-1}.

In another experiment in which the sodium iodide solution was added dropwise over 45 min to the solution of mercurial and acrylonitrile in DME and the resulting mixture was stirred at room temperature for 14 hr, the yields obtained were: $CHCl_2Br$, 17%; 1,1-dichloro-2-cyanocyclopropane, 26%; $CCl_2BrCH_2CH_2CN$, 5%.

b. In Acrylonitrile. Mercurial (15 mmoles) and sodium iodide (16 mmoles) were added to 40 ml of acrylonitrile, and the resulting mixture was stirred at room temperature for 4 hr. The filtrate contained bromodichloromethane (40%) and $CCl_2BrCH_2CH_2CN$ (13.4%), but no 1,1-dichloro-2-cyanocyclopropane could be detected. The solid residue appeared to contain polymeric material.

Reaction of the $C_6H_5HgCCl_3$ + NaI Reagent with Acrylonitrile. The mercury reagent (10 mmoles), 15 mmoles of sodium iodide, and 100 mmoles of acrylonitrile in 30 ml of 1:1 DME–benzene were heated at reflux for 4 hr. The brown reaction mixture was filtered, and the filtrate was trap-to-trap distilled [80° (0.05 mm)]. The distillate was shown by glpc to contain $CCl_3CH_2CH_2CN$ (15% yield) (analysis at 165°) and chloroform (22%) (analysis at 90°). 4,4,4-Trichlorobutyronitrile was identified by its melting point of 39.5–40.5° (lit.[20] mp 40°) and elemental analysis. Its infrared spectrum showed $\nu_{C\equiv N}$ at 2240 cm^{-1}.

Anal. Calcd for $C_4H_4Cl_3C$: C, 27.85; H, 2.34. Found: C, 28.18; H, 2.44.

This reaction was repeated, but with the amount of acrylonitrile reduced to 10.5 mmoles. It gave chloroform (19%), 4,4,4-trichlorobutyronitrile (7%), and 1,1-dichloro-2-cyanocyclopropane (5%). A further experiment in which acrylonitrile (25 ml) was used as solvent and the reaction temperature was 80° resulted in extensive polymerization. Distillation of the dark brown reaction mixture at reduced pressure left 8 g of resinous residue. The only volatile product which could be detected in the filtrate was chloroform (5%).

Competition of Olefins for Phenyl(trichloromethyl)mercury + Sodium Iodide at 80°. A typical experiment—the competition of cyclohexene with 3-ethyl-2-pentene—is described. A dry, 50-ml, three-necked flask equipped with a reflux condenser topped with a nitrogen inlet tube, an internal thermometer, a 60-ml pressure-equalizing dropping funnel, and a magnetic stirring assembly was charged with 10 mmoles of $C_6H_5HgCCl_3$, 50 mmoles of cyclohexene, 50.5 mmoles of 3-ethyl-2-pentene, and 10 ml of doubly distilled (from potassium) DME. A solution of 11 mmoles of dry sodium iodide in 10 ml of DME was transferred to the addition funnel. The reaction mixture was immersed in a preheated (80 ± 2°) oil bath and the sodium iodide solution was added at *ca.* 10–15 drops per min over a 35-min period. During this time the reaction mixture turned pale yellow and a white precipitate appeared. The reaction mixture was heated for 2 hr and then distilled under vacuum directly in two stages: first the solvent was removed in a closed system at 0.1 mm with pot temperature from −70 to 25°; then a straight vacuum adapter was placed between the distillation apparatus and the receiver flask, and the remaining high-boiling liquids were distilled directly (through a heated path) at 80° (0.02 mm) for 5 hr. The distillate weighed 34.38 g and the residue 4.81 g. Into a 0.5-oz vial were weighed 0.0942 g of *n*-butyrophenone and a 5.24-g aliquot of the distillate and this mixture was analyzed by glpc. The quantities of components were calculated from the measured areas according to the internal standard method. The validity of this scheme had been demonstrated by Burlitch.[33] The yield of 7,7-dichloronorcarane was 11.85% and that of 1,1-dichloro-2,2-diethyl-3-methylcyclopropane was 36.3%. The ratio of rate constants

$$k_{rel} = \frac{k_{3\text{-Et-2-pentene}}}{k_{\text{cyclohexene}}} = \frac{k_A}{k_1}$$

was calculated according to the formula[21]

$$\frac{k_A}{k_1} = \frac{(PM_A)(IMO_1)}{(PM_1)(IMO_A)}$$

where k_A is the rate constant of the reaction of olefin A with the reactive intermediate, k_1 is the rate constant of the reference olefin (cyclohexene), PM_A and PM_1 are the moles of products derived from olefin A and cyclohexene, respectively, whose initial moles are represented by IMO_A and IMO_1. Substitution of the appropriate values for the present experiment gave k_{rel} = 3.05. A duplicate reaction gave k_{rel} = 3.21. (In all cases the *gem*-dichlorocyclopropanes were identified by comparison of their glpc retention times, their refractive indices, and their infrared spectra with those of authentic samples.[3,33])

In the present experiment the distillation residue was washed with water, dried, and extracted with benzene (Soxhlet extractor). White, crystalline C_6H_5HgI, 2.91 g (72%), mp 269–271°, was obtained from the benzene solution.

The data from other competition experiments are presented in Table IV.

2-Ethyl-1-hexene had not been used in our previous determinations of relative reactivities of olefins toward $C_6H_5HgCCl_2Br$ in benzene at 80°,[5] and for this reason the relative reactivity of this olefin (*vs.* cyclohexene) toward this mercurial was measured using the standard procedure.[5,33] The k_{rel} values for 2-ethyl-1-hexene determined in a duplicate experiment were 2.32 and 2.32. 1,1-Dichloro-2-ethyl-2-*n*-butylcyclopropane, the product derived from this olefin, is a new compound, $n^{24}D$ 1.4601. Its infrared spectrum (liquid film) showed bands at 2970 (s), 2940 (s), 2860 (m), 1465 (m), 1440 (w), 1390 (w), 1128 (w), 1096 (w), 1043 (m), and 762 (m) cm^{-1}.

Anal. Calcd for $C_9H_{16}Cl_2$: C, 55.39; H, 8.27; Cl, 36.34. Found: C, 55.50; H, 8.18; Cl, 36.21.

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(33) J. M Burlitch, Ph.D. Thesis, Massachusetts Institute of Technology, 1964.

Table V. Competition of Olefins for the $C_6H_5HgCCl_2Br$ + NaI Reagent at −15°[a]

Olefin "A," mmoles	Cyclohexene, mmoles	Cyclopropane from olefin "A," %	7,7-Dichloronorcarane, %	k_{rel}	k_{rel}, av
$Me_2C{=}CMe_2$ 50.4	53.0	44.7	1.25	44.1	43.6
(50.0)	(51.6)	(44.7)	(1.25)	(43.0)	
$Me_2C{=}CMeEt$ 49.8	53.5	47.5	2.14	23.9	22.7
(51.2)	(50.2)	(42.6)	(1.95)	(21.4)	
$Et_2C{=}CHMe$ 48.7	49.3	39.3	8.46	4.72	4.73
(52.2)	(49.2)	(39.1)	(7.78)	(4.75)	
cis-MeCH=CHEt 49.4	50.2	17.2	11.9	1.47	1.44
trans-MeCH=CHEt 50.9		9.96		0.827	0.834
(48.9)	(49.8)	(17.2)	(12.6)	(1.40)	
(50.4)		(10.7)		(0.840)	
cis-EtCH=CHPr-*n* 48.2	48.7	12.6	15.7	0.810	0.811
trans-EtCH=CHPr-*n* 50.8		7.16		0.437	0.435
(48.2)	(49.7)	(14.8)	(18.80)	(0.812)	
(50.7)		(8.32)		(0.433)	
n-$C_5H_{11}CH{=}CH_2$ 49.5	50.7	2.80	25.6	0.112	0.110
(46.5)	(49.3)	(2.50)	(24.)	0.108	

[a] Values in parentheses are those obtained in duplicate runs.

Competition of Olefins for Phenyl(bromodichloromethyl)mercury + Sodium Iodide at −15°. In a typical experiment a flask equipped as described in the previous experiment was charged with 48.7 mmoles of cyclohexene, 50.8 mmoles of *trans*-3-heptene, 48.2 mmoles of *cis*-3-heptene, 10 mmoles of $C_6H_5HgCCl_2Br$, and 10 ml of DME. The mixture was cooled to −15 ± 5° using Dry Ice in acetone and then 11 mmoles of sodium iodide in 10 ml of DME was added at 10–15 drops per min during 30 min. The reaction mixture turned pale yellow and a white solid precipitated. The reaction mixture was held at this temperature range and stirred for 15 hr. A work-up similar to that described in the previous experiment followed. The yields of product were: 7,7-dichloronorcarane, 15.7%; *cis*-1,1-dichloro-2-*n*-propyl-2-ethylcyclopropane, 12.6%; *trans*-1,1-dichloro-2-*n*-propyl-3-ethylcyclopropane, 7.16%, leading to $k_{rel}(cis)$ = 0.810 and $k_{rel}(trans)$ = 0.437. The yields obtained in a second experiment were 18.8, 14.8, and 8.32%, respectively, giving $k_{rel}(cis)$ = 0.812 and $k_{rel}(trans)$ = 0.433. The solid residue was washed with distilled water and dried, then extracted with benzene. Phenylmercuric iodide was obtained in 87.6% yield.

Pertinent experimental data for experiments with other olefins are given in Table V.

Competition of Olefins for Chloroform + Potassium *t*-Butoxide at −15°. a. *cis*- and *trans*-3-Heptene *vs.* Cyclohexene. A dry, 200-ml, three-necked flask fitted with a reflux condenser topped with a nitrogen inlet tube and a magnetic stirring assembly was charged with 100 ml of *t*-butyl alcohol (twice distilled from potassium) and 2.47 g (0.063 g-atom) of potassium. The potassium was consumed during a 2-hr reflux period. A Claisen distillation head was substituted for the condenser, and *t*-butyl alcohol was distilled off until a slurry remained. The residual *t*-butyl alcohol was removed by azeotropic distillation with about 300 ml of heptane. The resulting *t*-BuOK was dried under vacuum for 2 hr. To this was added 0.126 mole of *trans*-3-heptene, 0.120 mole of *cis*-3-heptene, 0.123 mole of cyclohexene, and 50 ml of pentane. By means of a syringe, 25.4 mmoles of chloroform was added dropwise over a 20-min period to this mixture which had been cooled to −15 ± 5°. During the addition the mixture turned deep orange. Sitrring was continued at this temperature for another 30 min. The reaction mixture then was hydrolyzed with 200 ml of distilled water. The water layer was washed with pentane. The combined organic layers were concentrated and then trap-to-trap distilled [pot temperature to 80° (0.02 mm)]. The weight of distillate was 28.74 g. It was analyzed by glpc using 1,2,4-trichlorobenzene as internal standard. The yields were: 7,7-dichloronorcarane, 37.7%; *cis*-1,1-dichloro-2-*n*-propyl-3-ethylcyclopropane, 32.7%; *trans*-1,1-dichloro-2-*n*-propyl-3-ethylcyclopropane, 16.8%, leading to $k_{rel}(cis)$ = 0.893 and $k_{rel}(trans)$ = 0.436. A second experiment gave values of 0.890 and 0.433, respectively.

b. *cis*- and *trans*-2-Pentene *vs.* Cyclohexene. A similar experiment was carried out using 125 mmoles of cyclohexene, 122.5 mmoles of *cis*-2-pentene, and 126.5 mmoles of *trans*-2-pentene. The yields obtained were: 7,7-dichloronorcarane, 23.2%; *cis*-1,1-dichloro-2-ethyl-3-methylcyclopropane, 34.6%; *trans*-1,1-dichloro-2-ethyl-3-methylcyclopropane, 20.45%, leading to $k_{rel}(cis)$ = 1.52 and $k_{rel}(trans)$ = 0.869. Authentic samples of the latter two products were obtained using the procedure of Parham and Schweizer.[28]

Anal. Calcd for $C_6H_{10}Cl_2$: C, 47.08; H, 6.59; Cl, 46.33. Found (*cis*): C, 47.18; H, 6.58; Cl, 45.43. Found (*trans*): C, 47.59; H, 6.70; Cl, 45.57.

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