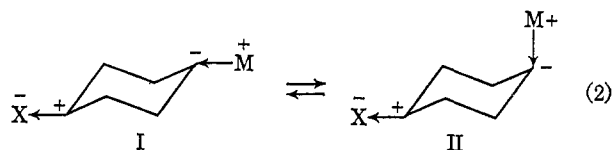
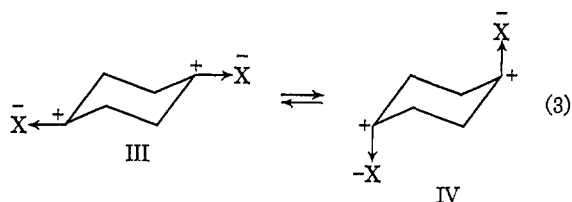


was carbonated at -78° . These acids were analyzed by glpc as the methyl esters,¹¹ and the isomer distribution of 83% *trans* and 17% *cis* was obtained. Identical results are obtained for reaction with mercuric bromide.¹¹ Assuming an *A* value for methyl of 1.8 kcal/mol² and utilizing the *A* value for the magnesium moiety at -83° (0.784 kcal/mol), a predicted isomer distribution of 79% *trans* and 21% *cis* is obtained. The observed isomer distribution is in accord with the distribution expected from the *A* value by low-temperature nmr spectroscopy.

In contrast, the 4-phenylcyclohexyl Grignard reagent¹² and the 4-*t*-butylcyclohexyl Grignard reagent yield only a very small amount (<4%) of *cis* acid upon carbonation at low temperature. Ring deformation¹³ by the large *t*-butyl and phenyl groups may affect the conformational preferences of the magnesium moieties. In addition, dipole interactions in the phenyl



compound with phenyl equatorial and magnesium axial, as compared to the diequatorial configuration (eq 2, structure I), is expected to be less favorable because of the increased interaction of the positive charges (eq 2, structure II). An analogy for this proposal is found in the well-known phenomenon that cyclohexanes containing two electron-withdrawing groups prefer diaxial configurations,¹⁴ presumably because of the favorable



interactions of the positive and negative charges in structure IV.

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A Reinvestigation of a Purported SH₂ Reaction. The Reaction of Trichloromethyl Radicals with Organomercury Compounds. A Novel Radical-Elimination Reaction

Sir:

The benzoyl peroxide induced reactions of dialkyl- and diarylmercury compounds in carbon tetrachloride

have been studied by Nesmeyanov, *et al.*¹ These authors report that this reaction follows the general path



The evidence presented consisted of the recovery of the alkyl- or arylmercuric chloride and the trichloromethyl compound or its corresponding carboxylic acid after alkaline hydrolysis. Significantly, no alkyl chlorides (RCl) were reported as products.

These workers suggested the formation of $RCCl_3$ arises from the reaction given by eq 2. Indeed, it is



difficult to conceive of a reaction mechanism to yield the reported products that does not proceed through an SH₂ (bimolecular homolytic displacement) reaction. However, no examples of radical displacements on sp³ carbon are known,² even though radical displacements have been reported in cyclopropane³ and "Dewar" anthracene⁴ systems where the hybridization is not truly sp³.

In connection with studies of possible SH₂ reactions, the reaction of dibutylmercury was investigated under conditions similar to those reported by Nesmeyanov, *et al.*¹ In contrast to the products expected on the basis of the earlier work, the major products found were 1,1,1,3-tetrachloropentane, 1-chlorobutane, chloroform, butylmercuric chloride, and mercury. No 1,1,1-trichloropentane, the expected product, was found. Furthermore, all attempts to repeat the reactions reported by Nesmeyanov, *et al.*, on dialkylmercury compounds failed.

In typical experiments the dialkylmercury compound (0.45 M), benzoyl peroxide (0.056 M), and carbon tetrachloride were degassed, sealed in ampoules, and heated for 7 hr at 100° or for 50 hr at 77°. In one case the reaction was carried out in a flask fitted with a Vigreux column, allowing removal of low-boiling gases. After completion of the reaction, the mercury was collected by filtration, and the alkylmercuric chloride was removed by extraction with aqueous sodium thiosulfate. Addition of potassium iodide allowed recovery of the original alkylmercuric chloride as the corresponding mercuric iodide. Analysis of the remaining solution was carried out by glpc. The 1,1,1,3-tetrachloropentane was identified by ir, nmr, and glpc comparison with known material synthesized by the free-radical addition of CCl₄ to 1-butene. The yields of the major products from the reaction of dibutylmercury are shown in Table I.

The 1,1,1,3-tetrachloropentane must arise *via* the addition of carbon tetrachloride to 1-butene under the reaction conditions, a reaction for which there is ample precedent.⁵ Consequently, 1-butene was expected to be a major product. Indeed, when the low-boiling gases were allowed to escape, not only is 1,1,1,3-tetrachloropentane obtained in greatly decreased yield, but also 1-butene was trapped at -78° in 50% yield. It is also

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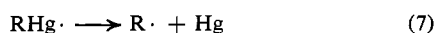
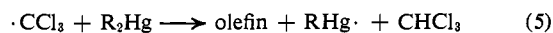
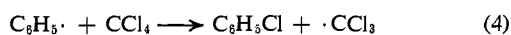
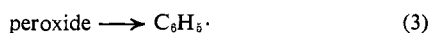
Table I. Yields of Products from Reaction of Dibutylmercury in Carbon Tetrachloride^a

Run	Hg, % ^c	BuHgCl, % ^c	TCP, ^b % ^c	BuCl, % ^c	CHCl ₃ , % ^c	Temp, °C	Conditions
1	63	25	52	51	64	100	<i>d</i>
2	63	24	54	53	64	100	<i>e</i>
3	65	25	49	54	69	100	<i>e</i>
4	2	0	0	0	0	100	<i>f</i>
5	69	13	12			77	<i>g</i>
6	73	16	53			77	<i>d</i>

^a [Bu₂Hg] = 0.45 M, [benzoyl peroxide] = 0.056 M. ^b TCP = 1,1,1,3-tetrachloropentane. ^c Mol %. ^d Ampoule sealed in air. ^e Ampoule degassed. ^f No peroxide. ^g Allowing removal of the gases by fractionation.

significant that 1-chlorobutane is produced in large amounts, whereas previous workers made no mention of this product.

Consideration of the major products solely allows formulation of a tentative chain mechanism (eq 3–9).



This sequence is consistent with the products in Table I, and, as expected, small amounts of chlorobenzene and hexachloroethane were identified by glpc.

In view of the weak bond (<6 kcal) in R–Hg·,⁶ a large yield of mercury is expected from RHg·, and considerable quantities of mercury were recovered. However, by the same reasoning the yield of RHgCl should be negligible. The proposed mechanism requires that the lifetime of RHg· is sufficiently long for chlorine abstraction to occur. Since the bond-energy measurements were carried out in the gas phase, the unexpected stability of RHg· in solution likely arises from complexation of RHg· with Lewis bases.

The 1-butene produced could not have resulted from disproportionation of butyl radicals since no butane is formed, nor is it likely that another process which is second order in radicals, such as disproportionation between butyl and trichloromethyl radicals, is occurring. Also, on the basis of previous studies on the reaction of radicals with mercurials,⁷ phenyl radicals prefer to attack mercury. In this light the reaction of eq 5, a free-radical elimination, with trichloromethyl radicals as the chain-carrying species, is postulated to explain olefin production. Although a similar radical elimination has been reported with phenyl radicals and *t*-butyl sulfide to give isobutylene,⁸ the reaction of eq 5 represents a novel reaction of radicals with dialkylmercurials. Furthermore it is very likely that this elimination is a concerted process because otherwise there is no reason to expect any special reactivity of the hydrogens β to mercury. This concerted process may involve either the loss of an alkylmercury radical or the formation of a bridged mercury radical. The bridged species could be similar to that suggested by Thaler⁹ to account for the enhanced

reactivity of the β hydrogens of alkyl bromides toward Br·. Further study of the generality, stereochemistry, and mechanism of this reaction is in progress.

Attempts were made to duplicate the reactions reported by Nesmeyanov, *et al.*, with butylethylmercury, butylcyclohexylmercury, and benzylcyclohexylmercury. In no case could more than a trace of the reported trichloride be detected, but instead products arising from olefins were found. However, the peroxide-induced decomposition of diphenylmercury in carbon tetrachloride under the same conditions as run 1 of Table I did yield phenylmercuric chloride (31%) and α,α,α-trichlorotoluene (25%), as previously reported by Borisov.¹⁰

We conclude that, although diarylmercurials are cleaved by trichloromethyl radicals to produce arylmercuric chloride and a trichloromethylaryl compound as originally reported,^{1,10} dialkylmercurials are not cleaved according to eq 1 but undergo a radical β-elimination reaction (eq 5).

Acknowledgment. This work was supported by the National Science Foundation under Grant GP-6350X.

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The Nuclear Magnetic Resonance Chemical Shift Method of Calculating Conformational Preferences in Cyclohexyl Derivatives

Sir:

Recently much work has appeared in which the conformational preferences, *A* values,¹ of a number of substituents have been calculated using the method of Eliel and coworkers which assumes that the chemical shifts of the axial and equatorial methine proton peaks of a cyclohexyl derivative are identical with those of the corresponding peaks of the 4-*t*-butylcyclohexyl derivative at room temperature.² In fact, in a recent review of the subject half of the *A* values tabulated for the cyclohexyl halides had been calculated by this procedure, and those obtained by this method were considered by the author of the article to be the best values.³ Although, many *A* values have been determined by this method, no con-

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