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Conformational and Related Studies of α-Mercuricyclohexanones by ^{1}H, ^{13}C, and ^{199}Hg Nuclear Magnetic Resonance

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Two series of α-mercuricyclohexanones (RHgCl and R_2Hg) have been prepared, in which R is based on cyclohexanone and its 4-methyl, 4-*tert*-butyl, and 4,4-dimethyl derivatives. The parent systems (in which R is cyclohexanone) are concluded on several grounds to favor strongly a conformation in which the mercuri group is axial. An estimate of the stabilizing interaction of an axially disposed HgCl with the carbonyl system is given. The ^{13}C, ^{1}H, and ^{199}Hg spectra have been interpreted in terms of favored conformations and the effects of interaction of the polarized C–Hg bond and the π C=O system. A syn-axial ($CH_3 \leftrightarrow HgCl$) interaction is concluded to be unfavorable by >1.5 kcal/mol in 4,4-dimethyl-2-chloromercuricyclohexanone and supported by studies of 3,3-dimethylcyclohexylmercuric bromide.

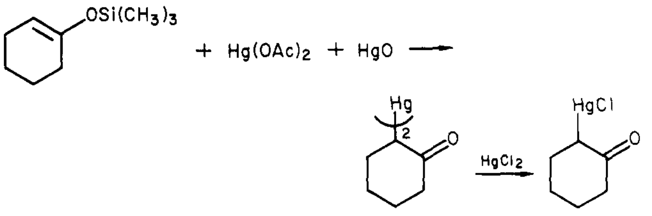
Introduction

α-Mercurated aldehydes and ketones exhibit high reactivity toward a variety of reagents, and Russian workers developed an interpretation of their chemistry based on interaction of the (polarized) C–Hg bond with the adjacent carbonyl π system (σ–π conjugation).[1] That a "conjugative" effect was in action was indicated to the Russian workers by the quite different chemistry of α-(chloromercuri)camphenylone in which the Hg–C bond was located essentially in the nodal plane of the C=O system, but which nevertheless was a bridgehead mercurial![2,3] More recently, Nesmeyanov[4] employed a variety of spectroscopic techniques to reflect behavioral differences in compounds in which σ–π interaction was possible, or largely prohibited. In connection with our studies of the conformational preferences of metallo groups in cyclohexyl systems,[5-7] and our studies of carbon–metal hyperconjugation by NMR techniques,[8,9] we have synthesized a number of α-mercuricyclohexanones and obtained their ^{1}H, ^{13}C, and ^{199}Hg spectra. Aspects of these data are utilized to define the conformational preference of the Hg groups in cyclohexanone and to indicate how these parameters respond when σ–π interaction is favored or disfavored. It is our view that study of conformationally defined α-mercuricyclohexanones provides data which are amenable to more direct interpretation than some of the systems utilized by the Russian workers.[4] Indeed, we demonstrate that some of the changes in spectroscopic parameters, regarded as characterizing σ–π interactions in these α-mercuri ketones, are based on faulty models.

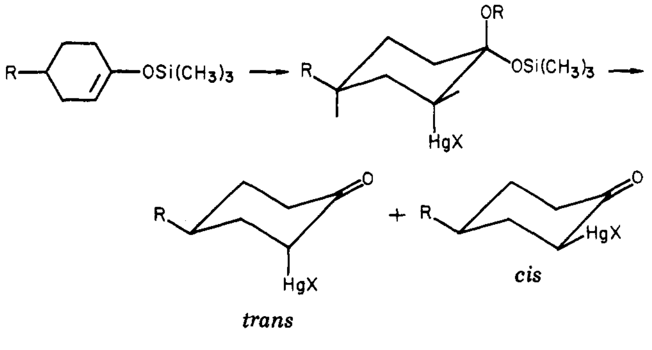
Results and Discussion

Synthesis of Compounds. In the first tactical approach to synthesis of α-mercuri aldehydes and ketones, e.g., (chloromercuri)acetaldehyde, (chloromercuri)acetone, etc., Russian workers[1] utilized the oxymercuration reaction with the highly reactive vinyl ethers, followed by conversion of the acetal or hemiacetal intermediate to the carbonyl compound as shown below. Enol acetates can also be employed with considerable success. House and coworkers[10] reported the use of silyl enol ethers, and reaction with a mixture of mercuric acetate and mercuric oxide (0.5 equiv of Hg(II)) in aqueous ethanol produces the bismercurials in good yield. Cleavage of these with $HgCl_2$ in tetrahydrofuran produces the α-chloromercuri derivative. We have generally employed this procedure and good yields of nicely crystalline compounds were obtained.

$$CH_2{=}CHOR + Hg(OAc)_2 + H_2O \longrightarrow AcOHgCH_2CH(OH)OR + HOAc \longrightarrow AcOHgCH_2CHO \xrightarrow{KCl} ClHgCH_2CHO$$



Reaction of the 4-methyl- or 4-*tert*-butylcyclohexanone enol ethers affords largely one chloromercuri isomer, and assuming the normal stereoelectronic constraint for an anti-periplanar addition of HgX and OR to the double bond, the trans mercurial (with axial Hg) would result. However, it is clear from the NMR spectra that while the trans isomer predominates, significant amounts (~10%) of cis mercurial also form.



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(1) For a collection of relevant papers see A. N. Nesmeyanov, "Selected Works in Organic Chemistry" (translated from the Russian by Dr. A. Birron and Z. S. Cole), Pergamon Press, London, 1963.

(2) A. N. Nesmeyanov and I. I. Kritskaya, *Dokl. Akad. Nauk SSSR*, **121**, 477 (1958) (reprinted (English) in ref 1, p 499).

(3) A. N. Nesmeyanov, V. A. Blinova, E. I. Fedin, I. I. Kritskaya, and L. A. Fedorov, *Dokl. Akad. Nauk SSSR*, **220**, 1336 (1975).

(4) A. N. Nesmeyanov, V. T. Aleksanyan, L. I. Denisovich, Yu. S. Nekrasov, E. I. Fedin, V. I. Khvostenko, and I. I. Kritskaya, *J. Organomet. Chem.*, **172**, 133 (1979).

(5) W. Kitching, D. Doddrell, and J. B. Grutzner, *J. Organomet. Chem.*, **107**, C5 (1976).

(6) F. A. L. Anet, J. Krane, W. Kitching, D. Doddrell, and D. Praeger, *Tetrahedron Lett.*, 3255 (1974).

(7) P. R. Barron, D. Doddrell, and W. Kitching, *J. Organomet. Chem.*, **132**, 339 (1977).

(8) W. Adcock, B. D. Gupta, W. Kitching, and D. Doddrell, *J. Organomet. Chem.*, **102**, 297 (1975).

(9) W. Kitching, G. Drew, W. Adcock, and A. N. Abeywickrema, *J. Org. Chem.*, submitted.

(10) H. O. House, R. A. Auerbach, M. Gall, and N. P. Peet, *J. Org. Chem.*, **38**, 514 (1973).

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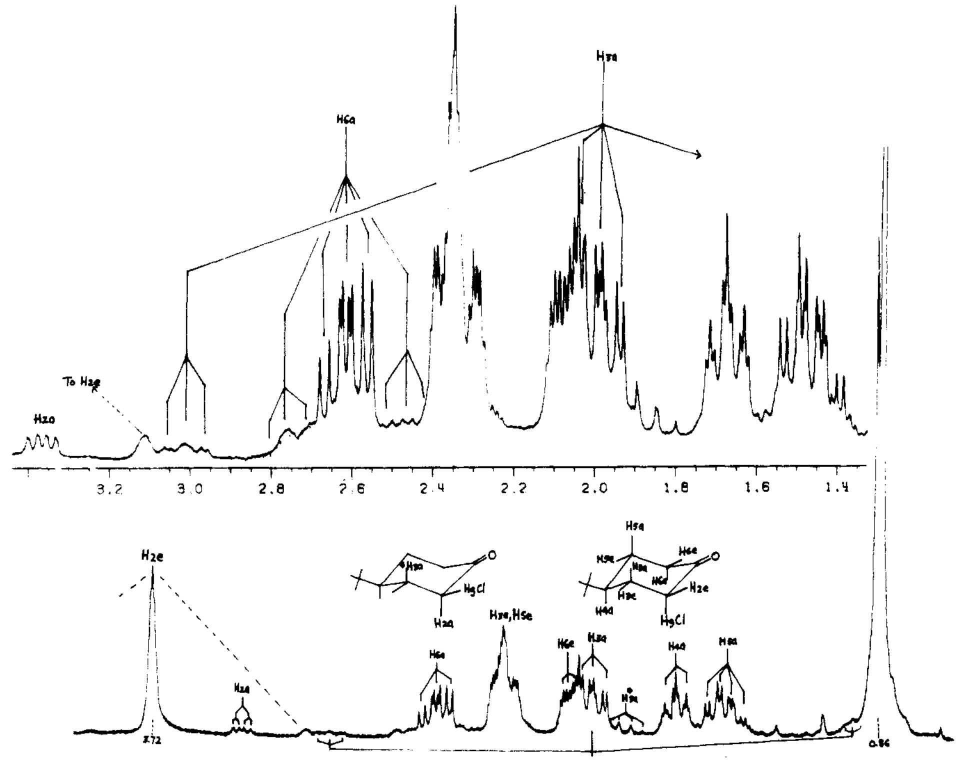
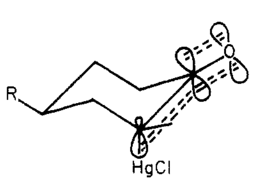
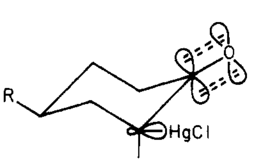


Figure 1. Lower: 270-MHz ^{1}H spectrum of an ca. 90:10 trans–cis mixture of 4-*tert*-butyl-2-(chloromercuri)cyclohexanone (solvent 80:20 $CDCl_3$–pyridine). Assignments for the major trans isomer are indicated, while H_{2a} and H_{3a}* represent the minor cis isomer. Two *tert*-butyl resonances at 0.86 ppm are evident. Upper: Amplified and expanded version of the 1.3–3.4-ppm region of the lower trace, with ^{199}Hg–^{1}H couplings indicated.

We were somewhat surprised by the production of the cis isomer, in such amounts, and we did examine spectroscopically the initial crude bismercurial in the preparation of the 4-*tert*-butyl derivative, and the level of specificity was about 90:10. (This ratio is close to that expected considering the conformational preference of an α-mercuri group and presumed equilibration through an enolate.) Whatever the reasons for the coproduction of the isomers, the outcome is desirable as it allows comparison of spectral parameters within one system, differing only by the axial–equatorial orientation of the HgCl group, a situation not available to the Russian workers. The axially disposed HgCl is aligned for interaction with the adjacent carbonyl system (Hg–C–C–O dihedral angle of 120°), whereas the equatorial HgCl is nearly prohibited (dihedral angle of ~0°).

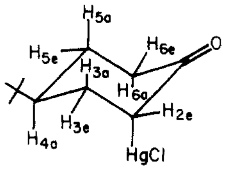




The following compounds were prepared and fully characterized. **Series A**: 2-(chloromercuri)cyclohexanone, 4-methyl-2-(chloromercuri)cyclohexanone and 4-*tert*-butyl-2-(chloromercuri)cyclohexanone (both as isomer mixtures), and 4,4-dimethyl-2-(chloromercuri)cyclohexanone. **Series B**: The bis compounds R_2Hg corresponding to those above. (Diastereoisomeric mixtures are now formed.)

^{1}H NMR Spectra. ^{1}H spectra (270 MHz) of the α-mercuricyclohexanones (usually employing a mixed solvent, $CDCl_3$–pyridine) were obtained. The main purpose was to determine the conformational preference of the mercuri group and any spectral regularities which could be attributed to C–Hg bond interaction with the carbonyl system. Understanding of the spectra of the parent cyclohexanone mercurials is facilitated by discussion of the conformationally biased 4-alkylcyclohexanone derivatives.

4-*tert*-Butyl-2-(chloromercuri)cyclohexanone provides a well-separated spectrum which in most respects is close to first order (Figure 1). That two isomers are present is indicated by the duality of signals in the HCHg (δ ~3.6) and *tert*-butyl regions (δ 0.85–0.9) in the ratio of ca. 90:10. The isomers I and II below are present. That I is the major isomer was indicated by the shapes of the H_2 resonances, the major one being a broadened singlet (δ 3.72, $W_{1/2}$ = 12–13 Hz) while the minor was clearly a doublet of doublets (δ 3.36, J = 11.9 and 7.5 Hz, $W_{1/2} \simeq$ 22 Hz) as appropriate for H_{2a} in II. H_{2e} (in I) is expected to be much narrower. The signal for H_{2e} in I provides definite indications of coupling to presumably H_{6e} and is also coupled to ^{199}Hg ($J \simeq$ 325 Hz) as expected. ^{199}Hg satellites about H_{2a} are also present in high-gain spectra, again with a similar J (~320 Hz). It is of considerable interest that H_{2e} in I is to lower field of H_{2a} in II, a sequence for α protons that is opposite to that in the *cis*- and *trans*-4-alkyl-2-bromocyclohexanones[11] and related sulfur or oxygen derivatives[12] and attributed primarily to the carbonyl dipole. The reversed sequence for the α-mercuri ketones can be understood when it is considered that the direction of the C—HgX dipole will be opposite from that



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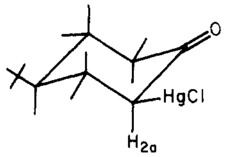

II

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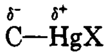
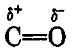
[11] K. M. Wellman and F. G. Bordwell, *Tetrahedron Lett.*, 1703 (1963).

[12] H. Özbal and W. W. Zajac, *Tetrahedron Lett.*, 4821 (1979).



$$\overset{\delta^-}{C}-\overset{\delta^+}{Hg}X$$

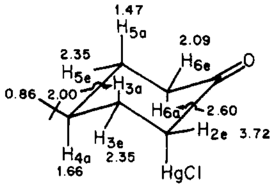
for electronegative α atoms and hence will oppose the C=O dipole when HgX is equatorial, and also σ–π inter-



$$\overset{\delta^+}{C}=\overset{\delta^-}{O}$$

action may become quite important when HgX is axial. These factors could reasonably be expected to cause a reversal in the H_{ax}–H_{eq} sequence when the α atom is changed from Br, O, or S to HgX. It would be of interest to see if this sequence applies to other α-metallocyclohexanones, and studies underway will determine this. In any event, the generalized final statement of Bordwell[11] does not apply.

The ring proton region of the 4-*tert*-butyl derivative can be readily interpreted in terms of the dominance of I. The assignments are indicated in Figure 1 and arrived at on the basis of the usual observations regarding vicinal ^1H–^1H couplings in rigid cyclohexyl systems. Geminal ^1H–^1H coupling is very similar to the vicinal trans diaxial couplings, being on the order of 11.5–13 Hz. Coupling between axial–equatorial and equatorial–equatorial protons ranges from 4.5–6.5 Hz. The chemical shifts are summarized below (I and II), and all are in agreement with decoupling experiments. A "quartet" of appropriate intensity at δ 1.87 is assigned to H_{3a} in II, but other ring proton resonances for II are presumably hidden by the major signals of I.



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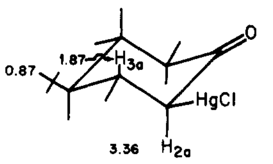
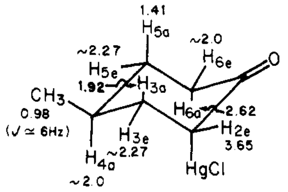
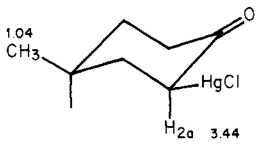


II

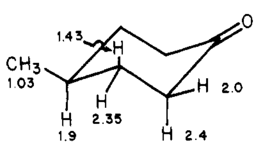
The assignments and spin-coupling patterns for the 4-*tert*-butyl derivative are fully consistent with the spectrum of the 4-CH_3 compound, and the chemical shifts are assigned below (III and IV). Again a minor proportion of isomer IV is observed.



III

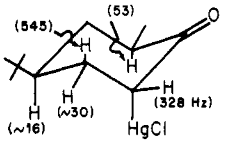


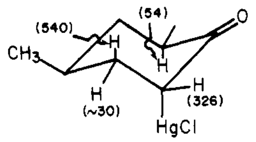
IV

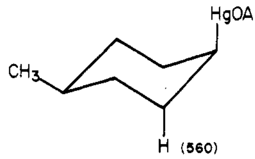


The above shifts may be compared with those determined for 4-methylcyclohexanone itself, by introducing ^2H selectively α-axial ([^2H]acid reaction with the trimethylsilyl enol ether)[13] to the carbonyl and obtaining the ^2H NMR spectrum.[14] Comparisons were than made with the 270-MHz spectrum of the ketone. Recognizing that the effect of the HgCl substituent will be greatest in the H_2, H_3 region, the assignments are seen to be in excellent agreement. The most significant interaction attributable to the axial C–Hg bond in III is a deshielding of the vicinal H_{3a} (by ca. 0.5 ppm), whereas H_{3e} is hardly affected. This interaction with an adjacent axial C–H bond may be associated with the definite axial preference ($A \simeq -0.2$ kcal/mol) of HgX in cyclohexane.[6,7]

^{199}Hg–^1H Spin Coupling in I and III. Spin coupling between ^{199}Hg (16.86% natural abundance; $I = 0.5$) and certain protons can be identified in the spectra of the conformationally rigid I and III and provides useful "base data" for the subsequent discussion of the conformationally inhomogeneous 2-(chloromercuri)cyclohexanone and 4,4-dimethyl-2-(chloromercuri)cyclohexanone. Two-bond coupling (^2J) is measured as 328 Hz in I and 326 Hz in III, significantly larger than ^2J in cyclohexylmercury halides (~180–190 Hz). This increase may be associated with increased polarization of the C–Hg bond due to interaction with the carbonyl group, or simply due to σ bond polarization by the carbonyl, affecting the nuclear charge and hybridization at C_2. This seems to be indicated by an exalted value of $^1J_{C-H}$ of ~140 Hz for the C_2–H_{2e} interaction,[15] compared with that of the ketone (~130 Hz). We did anticipate a significant difference in the $^2J_{^{199}Hg-H_2}$ in I and II, but these values are quite similar. Vicinal coupling (^3J) between ^{199}Hg and H_{3a} ($\theta \simeq 180°$) is expected to be very large for I and III, and values of ca. 540 Hz are observed, but much smaller to H_{3e}, with a relatively unfavorable dihedral angle.[16] Coupling to other protons could also be discerned (and is shown below) and is reasonable on the grounds of geometrical requirements for four-bond coupling.[16,17]

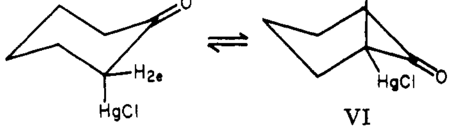






The large vicinal couplings in I and III incidentally require the indicated structures and resemble the vicinal coupling of 560 Hz observed for *cis*-4-methylcyclohexylmercuric acetate, with the HgX group very largely axially directed. The main purpose in identifying the vicinal couplings was their presumed utility in calculating an equilibrium position for the conformationally mobile (parent) 2-(chloromercuri)cyclohexanone. This is done below.

2-(Chloromercuri)cyclohexanone (at 270 MHz) provides a well-separated spectrum indicative of a conformationally biased system. The H_2 signal at δ 3.67 ($W_{1/2} \simeq 14$ Hz, $^2J = 317$ Hz) is very similar in shape and position to that of the H_{2e} signals in I (δ 3.72) and III (δ 3.65), but much narrower than H_{2a} in II (δ 3.36) or IV (δ 3.44), with $W_{1/2} \simeq 22$ Hz. This confirms V, with an axial HgCl, as



V VI

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[13] H. O. House, B. A. Tefertiller, and H. D. Olmstead, *J. Org. Chem.*, **33**, 935 (1968).

[14] G. Wickham, unpublished results.

[15] See also R. Meyer, L. Gorrichon-Guigon, and P. Masoni, *J. Organomet. Chem.*, **188**, 11 (1980).

[16] M. M. Kreevoy and J. F. Schaeffer, *J. Organomet. Chem.*, **6**, 589 (1966).

[17] D. N. Ford, W. Kitching, and P. R. Wells, *Aust. J. Chem.*, **22**, 1157 (1969), and references therein.

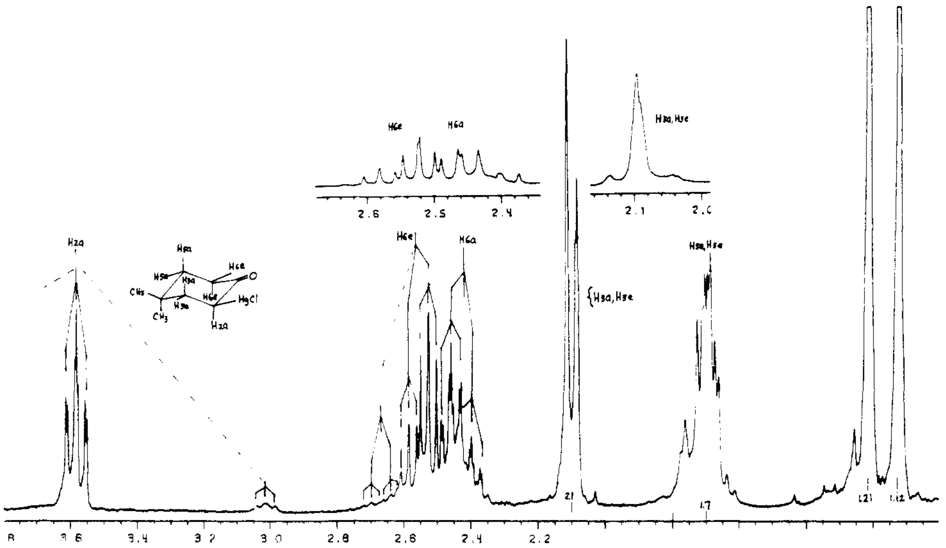
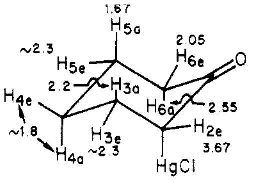


Figure 2. 270-MHz ^1H spectrum of 4,4-dimethyl-2-(chloromercuri)cyclohexanone (favored conformation drawn) with assignments and ^{199}Hg–^1H couplings. Insets show the effects on H_{6e}, H_{6a}, and $H_{3a,3e}$ of irradiation at H_2. (The ^{199}Hg satellites about H_{3a} are located within the multiplet of H_{6a} and on the low-field side of the $H_{5a,5e}$ multiplet.)

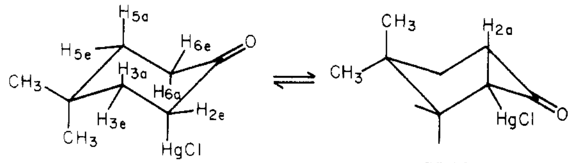
the dominant conformer. Chemical shifts of other ring protons show, where comparisons are valid, excellent agreement with the data for I and III. The ^1H shifts are shown below for V. (H_{4a}, H_{4e}, and H_{5a} have extremely similar shifts.)



V

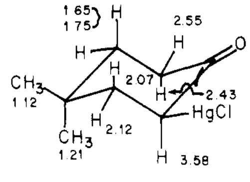
Values of ^{199}Hg–^1H coupling confirm V as being greatly favored. Thus, coupling to H_{3a} is 498 Hz, slightly lower than that to H_{3a} in the rigid I and III (540 Hz), thus indicating some VI in equilibrium in which such coupling would be ~30–40 Hz. These data permit calculation of K for the V $\rightleftharpoons$ VI equilibrium (at 298 K) to be 11.5 and $\Delta G°$ to be 1.45 kcal/mol. The substantial difference in the vicinal coupling constants in V and VI makes this calculation very meaningful, as even allowing the less precisely determined coupling for VI to be as large as 100 Hz leads to a value of K of ~10 and $\Delta G°$ of 1.37 kcal/mol. Allowing for the fact that HgCl prefers the axial disposition in cyclohexane ($A \simeq -0.2$ kcal/mol;[6,7] where interaction with two vicinal axial C–H bonds is possible), a value of ca. 1.30 kcal would closely describe the stabilizing effect when an axial C–HgCl bond is α to the carbonyl group.

4,4-Dimethyl-2-(chloromercuri)cyclohexanone represents an interesting case, as it is immediately clear from the ^1H spectrum that the equilibrium below (VII and VIII)



VII VIII

is more evenly balanced than that in the case of the parent, just discussed. The H_2 signal (J = 306 Hz) at δ 3.58 is now a well-defined doublet of doublets (J = 7 Hz and 8 Hz) with some longer range coupling ($J \simeq 1.5$ Hz) superimposed. These increased and similar couplings to the H_3 proton pair require comparable populations of VII and VIII in equilibrium. This conclusion is supported by the chemical shift trends (confirmed by double irradiation), as within the H_3, H_5, and H_6 pairs the shifts are quite similar (as shown in Figure 2), whereas in I and III (and even V) geminal proton pairs are well separated. The H_6 pair can be treated as an AB case with similar couplings to the H_5 pair, and the lower field component is coupled to ^{199}Hg ($J \simeq 60$ Hz), confirming it as cis to HgCl. This is consistent with the presence of additional coupling ($J \simeq 1$ Hz) to the higher field component (trans to HgCl), emanating from H_2, and quite clear in the H_2 signal. Examination of both 100- and 270-MHz spectra confirms that the vicinal ^{199}Hg coupling to H_3 (trans) is ca. 180 Hz, leading to $K \simeq 2.5$ (VIII/VII) ($\Delta G° \simeq 0.50$ kcal/mol) with HgCl now favoring the equatorial disposition. This reversal in conformational preference (from I) is presumably associated with a repulsive 1,3-CH_3,HgCl interaction in VII of ca. 1.8 kcal/mol and is supported by other data below.



Estimates of the magnitudes of methyl–halo 1,3-syn axial interactions have been provided by Lambert[18] and Allinger[19] and for iodo, bromo, and chloro are in excess of 1.5 kcal/mol, but 0.64 kcal/mol for fluoro. Because mercuri groups are not sterically demanding,[20] as judged by their slightly negative A values in cyclohexane (axial preference),[6,7] it appeared a worthwhile exercise to synthesize 3,3-dimethylcyclohexylmercuric bromide and determine the preferred conformation and hence the magnitude of the methyl–bromomercuri 1,3-syn axial interaction. The desired mercurial (which was obtained in a standard fashion from the Grignard reagent and mercuric bromide) exhibits ^1H and ^{13}C NMR spectra which require

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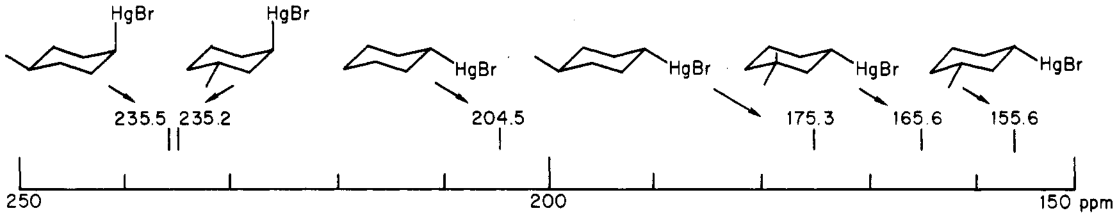
(18) D. S. Bailey, J. A. Walder, and J. B. Lambert, *J. Am. Chem. Soc.*, 94, 177 (1972).

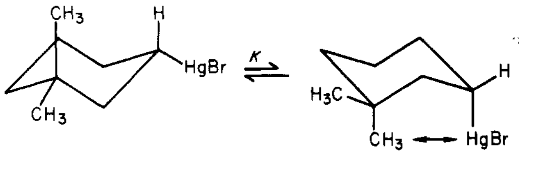
(19) N. L. Allinger, J. Allinger, L. W. Chow, and G. L. Wang, *J. Org. Chem.*, **32**, 522 (1967).

(20) F. R. Jensen and L. H. Gale, *J. Am. Chem. Soc.*, 81, 1261 (1959).

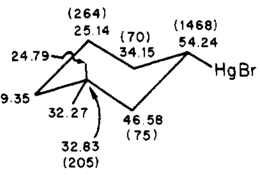
Chart I

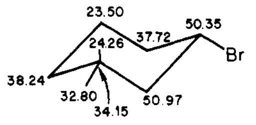


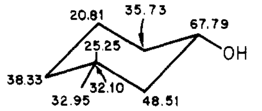
an overwhelming preference of HgBr for the equatorial disposition, resulting from a substantial energy-raising CH_3–HgBr interaction in the axial conformer.

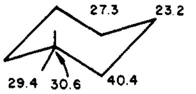


The ^1H chemical shift of CHHgBr (δ 3.0) is appropriate for an axial hydrogen (when comparisons are made with *trans*- and *cis*-4-methylcyclohexylmercuric bromides for which δ values of 2.7 and 3.4 have been measured)[21] when corrected (by 0.25 ppm) for the compressional deshielding, resulting from the 1,3-syn axial methyl–hydrogen interaction. Vicinal couplings (to CHHgBr) of ca. 12 and 4 Hz ($W_{1/2} \simeq$ 26 Hz) also require a large preference for the equatorial HgBr conformer. The most convincing aspect of the ^{13}C data shown below is the vicinal ^{199}Hg–^{13}C coupling of 264 Hz, which coincides with values for (alkylcyclohexyl)mercurials in which the HgX group is definitely predominantly equatorial.[22] This result indicated that low-temperature examination of the system, to accurately determine K (above), would be futile. Nevertheless, it can be concluded that the magnitude of the syn–axial CH_3–HgBr interaction is not less than 1.5 kcal/mol and supports the conclusion from the 4,4-dimethyl-2-(chloromercuri)cyclohexanone system. (Chemical shifts are for $CDCl_3$ solutions referenced to center of $CDCl_3$ triplet as 77.00 ppm; values in parentheses are ^{199}Hg–^{13}C coupling constants; values for 1,1-dimethylcyclohexane from ref 23.)







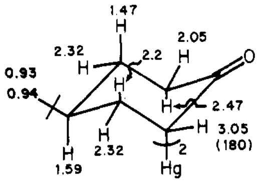


^{13}C chemical shifts for the related bromo and hydroxy (and the parent dimethylcyclohexane) precursors are also presented, and the CCH_3 shifts are so similar for the three substituted compounds that all must overwhelmingly prefer the equatorial disposition, established in the bromo case by low-temperature ^1H examination.[18] (No axial conformer was detectable.) Lambert[18] established that replacement of the 4-methylene group with the *gem*-dimethyl arrangement had quite minor effects on the conformational preferences for a number of groups, so that significant ring deformations were not a complication.

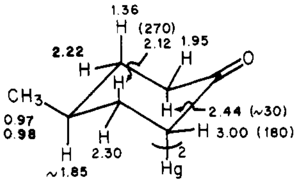
We have obtained the ^{199}Hg shifts[7] (solutions 0.4 M in 80% $CDCl_3$, 20% pyridine) of various (alkylcyclohexyl)mercuric bromides of established structures, as well as of cyclohexyl- and 3,3-dimethylcyclohexylmercuric bromides. The shifts are shown in Chart I on an arbitrary scale.

The strongly conformationally biased *cis*-4-methyl- and *trans*-3-methylcyclohexyl derivatives establish that axial HgBr resonate substantially to lower field (~60–70 ppm) than equatorial HgBr, as present in *cis*-3-methylcyclohexyl, or less satisfactorily in *trans*-4-methylcyclohexyl (where some diaxial conformer would be present). Notice that 3,3-dimethylcyclohexyl resonates in the region appropriate for a predominantly equatorial HgBr, in agreement with our conclusions above. As expected, cyclohexylmercuric bromide, with comparable populations of axial and equatorial HgBr,[6,7,20] resonates at the expected position, intermediate between the extremes for axial (~235 ppm) and equatorial (~165 ppm) bromomercuric groups. These findings illustrate the potential importance of ^{199}Hg and metal NMR shifts, generally, in conformational analysis.

The ^1H spectra of the bismercurials (R_2Hg) (series B) were not examined in great detail, as we anticipated more spectral complexity from the presence of additional stereoisomers. Nevertheless, the intelligence available from the RHgCl compounds (series A) greatly facilitated assignments (summarized below, IX and X) which are consistent with the spin-coupling patterns and chemical shifts.



IX



X

IX and X are diastereomeric mixtures (ca. 50:50) as judged by the equiintense *tert*-butyl signals at δ 0.93 and 0.94 and the CH_3 doublets (in X) at δ 0.97 and 0.98 ($J \simeq$ 6 Hz). A minor set of diastereomers is also anticipated for these systems (with Hg equatorial) and indicated (~10%) by a broad *tert*-butyl resonance at δ 0.88 and a (broad) minor methyl doublet at δ 1.09. These minor stereoisomers are probably responsible for the low-intensity broad signals at δ 2.7 (*tert*-butyl system) and 2.75 (CH_3 system) corresponding to H_2 (axial). (The diastereomers are more clearly evidenced in the ^{13}C and ^{199}Hg spectra to be described later.) By comparison of the ^1H data above for IX with I and that for X with III, the chief features are the higher field resonance position for H_{2e} (by ca. 0.6 ppm) and the reduced (by a factor of ca. 0.5) ^{199}Hg couplings to H_{2e} (180 Hz) and also H_{3a} (270 Hz). These changes are not only expected for the RHgCl → R_2Hg structural alteration[24] but also require a strong axial preference for the mercuri group.

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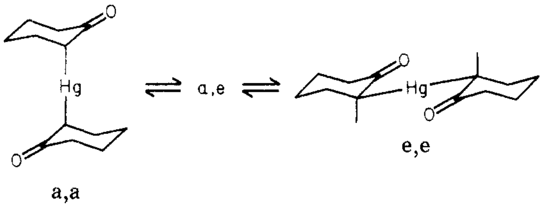
[21] W. Kitching, A. Atkins, G. Wickham, and V. Alberts, *J. Org. Chem.*, **46**, 563 (1981).

[22] W. Kitching, D. Praeger, D. Doddrell, F. A. L. Anet, and J. Krane, *Tetrahedron Lett.*, 759 (1975).

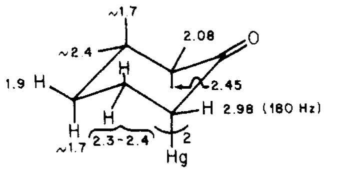
[23] D. K. Dalling and D. M. Grant, *J. Am. Chem. Soc.*, **89**, 6612 (1967).

[24] P. R. Wells, W. Kitching, and R. F. Henzell, *Tetrahedron Lett.*, 1029 (1964).

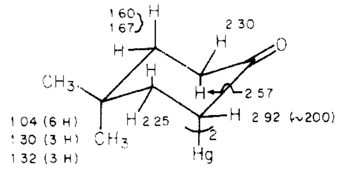
The **parent bismercurial** could adopt a number of conformations as illustrated below. In the light of the data



for the HgCl, the e,e conformation would be suspected to be least populated, with the a,a most stable. The shape of the H_2 resonance ($W_{1/2} \simeq$ 8–10 Hz), if anything, narrower than the corresponding signal in the mercuric chloride (for which an accurate estimate of $\Delta G°$ was available from ^{199}Hg coupling constants), would require the a,a conformation to be heavily populated. The 270-MHz ^{1}H spectrum still exhibits much signal overlapping and H_{3a} (and its ^{199}Hg coupling) could not be identified with precision. The assignments that were possible are shown below.



The **bismercurial based on 4,4-dimethylcyclohexanone** does not appear to favor the equatorial Hg disposition as much as the corresponding mercuric chloride. Thus, the H_2 signal is narrower ($W_{1/2} \simeq$ 13 Hz), indicating a predominance of a,a and a,e arrangements, and the ^{199}Hg coupling (~120 Hz) about the vicinal proton trans to Hg supports this. The likelihood that the axial and equatorial dispositions are nearly equally favored means a substantial proportion of the a,e form will be present, as it is favored statistically. The shifts are summarized below.



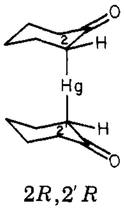
The apparently greater preference for the axial disposition in the above bismercurial compared with the mercuric chloride may be associated with the greater level of $\sigma-\pi$ (C–Hg $\rightarrow$ $\pi_{C=O}$) interaction sustainable in a bismercurial, which can operate effectively only in the axial arrangement.

^{13}C NMR Spectra. To assess the effects of conformational preferences and possible $\sigma-\pi$ interactions on the ^{13}C spectra in these systems, we have obtained the spectra at both 25.00 and 67.89 MHz for $CDCl_3$ and $CDCl_3$–pyridine solvents. Assignments were based on chemical-shift comparisons, ^{199}Hg couplings, and other routine techniques. Again, our approach was to assign the spectra of the conformationally "rigid" 4-*tert*-butyl and 4-CH_3 compounds and then examine the parent systems. The data for the mercuric chlorides are assembled in Table I.

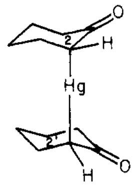
Comparison of the data for I, II, III, and IV indicates that axially oriented HgCl are responsible for an upfield shift (compared with the parent ketone) of the carbonyl resonance of ca. 2.5–3 ppm, whereas the effect for equatorially oriented HgCl is negligible. This small effect may be associated with a bond-order change about carbon when $\sigma-\pi$ effects operate. This effect is paralleled by the resonance position of C_2 (i.e., bearing HgCl) which is to higher field in I and II (δ 61.05 and 60.21), compared with II and IV (δ 63.33 and 62.40) for the same solvent (e.g., $CDCl_3$) by about 2.5 ppm. This again is consistent with C–Hg bond electron transfer to the carbonyl system from the polarized C–Hg bond. Regarding ^{13}C–^{199}Hg coupling, it was unfortunate that the low abundance of II and IV prevented observation of most of the ^{199}Hg satellites in their spectra (but see later). The one- and two-bond couplings are unexceptional but the vicinal couplings to C_4 and C_6 in I and III of ca. 40 and 30 Hz are consistent with the axial disposition of HgCl and the Karplus-type dependence[22] of this vicinal coupling. The vicinal coupling of ca. 65 Hz in the parent derivative is in line with V (with axial HgCl) given that C_4 in V is secondary, but tertiary in I and III, with a slightly depressed coupling in the latter. A more convincing comparison that illustrates the overwhelming axial preference of HgCl in V $\rightleftharpoons$ VI, concerns vicinal coupling to C_6—the values are 30.4 and 31.5 for III, 33.3 for I, and 33.3 for the mobile VI. (The upfield shift of $\delta_{C=O}$ by ca. 2.00 ppm for the parent is also indicative of axial HgCl.) With respect to 2-(chloromercuri)-4,4-dimethylcyclohexanone, the ^{13}C data contain trends that are consistent with our conclusion that axial and equatorial conformers are comparable. Thus, $\Delta\delta_{C=O}$ of ca. 1.3 ppm is between the extremes noted above of ca. 2.5–3.0 and ~0 for axial and equatorial HgCl.

The α, β, and γ effects of axial and equatorial HgCl are contained in Table II and several aspects deserve emphasis. (1) Carbon atoms bearing equatorial HgCl resonate at lower field. (2) β effects are negative to the carbonyl carbon but positive to the saturated C_3. (3) While γ effects are positive to C_4 for both orientations of HgCl as found previously in other systems, they are close to zero (to C_6) for equatorial HgCl but slightly negative for axial HgCl. These generalizations allow the conclusion, consistent with more rigorous arguments, that HgCl in 2-(chloromercuri)cyclohexanone is predominantly axial but displays a slight preference for equatorial in the 4,4-dimethyl compound. It is also of interest to note, that whereas in axial and equatorial cyclohexylmercuric acetate and cyanide, for example, the carbon bearing mercury is to lower field for axial, by ca. 4.3 ppm, the reverse is true for the α-(chloromercuri)cyclohexanones by ca. 2 ppm. Preferential electron release from the axial C–Hg bond in the ketones would result in a greater shift of that carbon to higher field.

In Table III, the ^{13}C data for the corresponding bismercurials are presented, and except for the chemical shift of C_2 (bearing Hg), the shifts are similar to those of the mercuric chlorides. The fact that the vicinal ^{13}C–^{199}Hg coupling to C_4 in the bis parent is about 0.6 that in the mercuric chloride strongly indicates a pronounced axial orientation in the bis series as well. It is also clear that duplication of many carbon resonances occurs, and this is expected for the cooccurrence of diastereomers. For example, in the case of the bis parent or bis 4,4-dimethyl compounds, equiintense signals corresponding to *RR*,*SS* and *RS*,*SR* enantiomeric sets are observed. Single enantiomers are represented below.



2*R*,2′*R*



2*R*,2′*S*

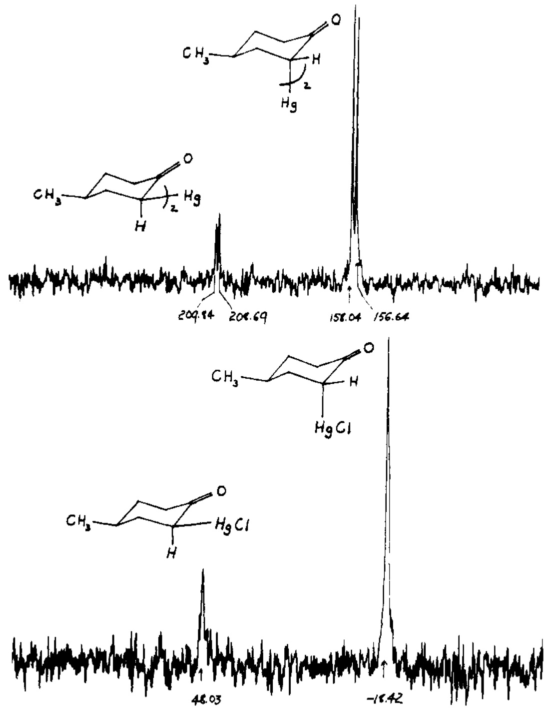
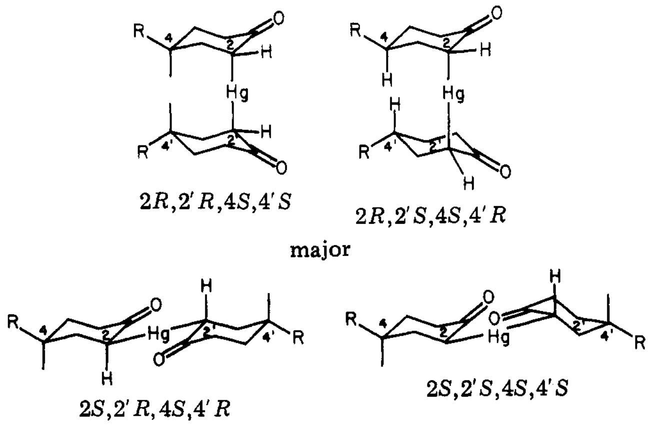


Figure 3. Upper: ^{199}Hg spectrum of the diastereomeric mixture of the bismercurial of 4-methylcyclohexanone, consisting of four signals of the four enantiomeric pairs (solvent $CDCl_3$). Lower: ^{199}Hg spectrum of the chloromercurials produced by ($HgCl_2$) cleavage of the bismercurial sample. ^{199}Hg shifts (and reference) are described fully in the text (solvent $CDCl_3$).

This conclusion is supported by the observation of two equiintense ^{199}Hg signals for the parent bismercurial and the bis 4,4-dimethyl compound (see below).

The bismercurials based on 4-methyl- or 4-*tert*-butylcyclohexanone provide a more complex stereochemical situation because of the presence of four chiral centers with the possible existence of eight enantiomeric pairs. The ^{13}C data above require the existence of four enantiomeric pairs only and the suggested ones are shown below.



2*R*,2′*R*,4*S*,4′*S*

2*R*,2′*S*,4*S*,4′*R*

major

2*S*,2′*R*,4*S*,4′*R*

2*S*,2′*S*,4*S*,4′*S*

minor

The dominant stereosets have both C–Hg bond axial, while the minor two are proposed to have both C–Hg bonds equatorial. (Single enantiomers of the pairs are represented.)

There appears to be no evidence to support the existence of diastereomers with one axial and one equatorial C–Hg bond (e.g., the (*SRSS*, *RSRR* set), for in such an isomer all carbon atoms are different. This conclusion is supported by the ^{199}Hg data below.

^{199}Hg Spectra. ^{199}Hg chemical shifts are particularly sensitive to environmental changes and seem capable of providing meaningful insights into conformational and substituent-effect questions.[7,9,25-27] We have obtained the ^{199}Hg chemical shifts for series A and series B, and these are summarized in Table IV. Series A were obtained with a resonating frequency of 17.8180 MHz and 17.8207 MHz was employed for series B. The quality of the spectra obtained is indicated in Figure 3.

The data reveal that the ^{199}Hg signal is to higher field for an axial orientation than for an equatorial one, in both series A and B, for 4-CH_3 and 4-*tert*-butyl derivatives. The ^{199}Hg nucleus is of interest, in that *lowered* electron density in the C–Hg bond results in a movement to higher field.[9] Hence, accepting that σ–π interaction between the polarized C–Hg bond and $\pi_{C=O}$ is more favored from the axial disposition, the higher field position of axial Hg is readily understandable, on the basis of comparatively greater electron denudation from the C–Hg bond. As expected, the shifts for the parent mercuric chloride and bis compound are between those for the corresponding conformationally biased axial and equatorial model compounds. Quantitative deductions from the shifts are possible but of dubious value, considering that the anchoring 4-alkyl groups may have slight but significant effects themselves.

The ^{199}Hg spectrum of the bis(5-methyl-2-oxocyclohexyl)- or bis(5-*tert*-butyl-2-oxocyclohexyl)mercury consists of four signals (Figure 3) appearing in two sets of two, with equal intensities within each set. We associate the dominant set with stereoisomers (indicated above) having both C–Hg bonds axial, and the minor set with those having both C–Hg bonds equatorial. The intensity ratio of ca. 90:10 (for the two sets) is retained in the product when these bismercurials are cleaved with mercuric chloride to yield the 4-alkyl-2-(chloromercuri)cyclohexanones, with a trans–cis ratio of 90:10. This is consistent with cleavage proceeding with retention of configuration at carbon, a result established in simpler two-alkyl mercury exchanges.[28]

The large positive shift (+36.52 ppm) for the 4,4-dimethyl mercuric chloride resembles those for II (+43.59 ppm) and IV (+48.03 ppm) with equatorial HgCl, rather than the values for I (−18.42 ppm) and III (−24.18 ppm) with axial HgCl. This reinforces the conclusion that a 1,3-($CH_3 \leftrightarrow Hg$) interaction operates in the axial HgCl conformer VII so that VIII is now favored. Similar considerations apply to the bis 4,4-dimethyl compound, which also is characterized by a large positive (δ 32.48) shift.

At this stage it is worthwhile summarizing the main findings of Nesmeyanov et al.[3,4] who reported that the contribution of σ,π conjugation to $^1J_{Hg-C}$ in α-mercuri carbonyl compounds was ca. 500 Hz for the mercuric chlorides and 300 Hz in the symmetrical series, i.e., a considerable reduction in the one-bond ^{199}Hg–^{13}C coupling.[3,4] Unfortunately, this type of comparison (below) between 2-(chloromercuri)cyclohexanone (where it was assumed[3,4] (but herein demonstrated) that σ–π interaction was operative) and the bridgehead mercurial is difficult, because of the structural features of the latter which may seriously influence ^1J. The very large coupling reported

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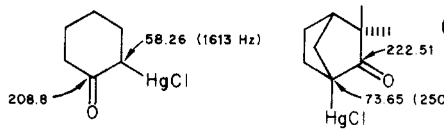
(25) M. Borzo and G. E. Maciel, *J. Magn. Reson.*, **19**, 279 (1975).

(26) M. A. Sens, N. K. Wilson, P. D. Ellis, and J. D. Odom, *J. Magn. Reson.*, **19**, 323 (1975).

(27) Yu. A. Strelenko, Yu. K. Grishin, M. A. Kazenkova, and Yu. A. Ustynyuk, *J. Organomet. Chem.*, **192**, 297 (1980).

(28) For a general discussion see: F. R. Jensen and B. Rickborn, "Electrophilic Substitution of Organomercurials", McGraw-Hill, New York, 1968, especially Chapter 5.

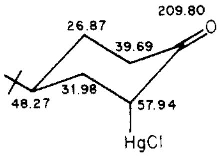


(from ref 3, 4)

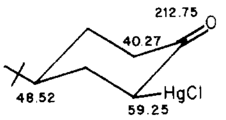
$\Delta^1 J$ = 894 Hz

(2507 Hz) almost certainly reflects the enhanced s character in the bridgehead carbon bonding orbital to mercury. (The $\Delta' J$ of 894 Hz was scaled down to 500 Hz to correct for "the polar effect of substituents and the decrease of ^1J when passing from rigid, sterically strained bicyclic systems to non-rigid systems".)

We considered it desirable to provide comparisons for more closely related systems. We obtained a ^{13}C spectrum (Figure 4) of the ca. 90:10 *trans-* and *cis*-4-*tert*-butyl-2-(chloromercuri)cyclohexanones (37K pulses) and located the ^{199}Hg satellites about C_2 in both isomers. The results are shown below (see also Table I).



^1J = 1544 Hz

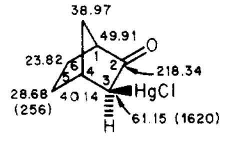


^1J = 1760 Hz

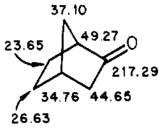
Considering that ^1J in normal cyclohexylmercuric acetates and chlorides is 1500–1600 Hz, it is difficult to attribute much to σ–π effects. ^1J in the cis isomer is somewhat larger but could be associated with enhanced s character in the C–Hg bond, resulting from C–H hyperconjugation.

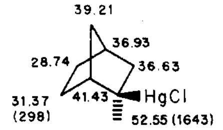
The Russian workers[3,4] also associated substantial changes in the chemical shifts of carbons bearing mercury (C_2) and carbonyl carbons (C_1) with the presence or absence of σ–π interactions. These changes were reported to be an increased shielding of ca. 15 ppm for the carbon-bearing mercury and ca. 13 ppm for the carbonyl group, for those cases (mercuric chloride series) where interaction can occur. However, these differences appear to have been obtained by direct comparison of the data for 2-(chloromercuri)cyclohexanone and (chloromercuri)-camphenilone (pyridine solvent) (see abstracted data of Nesmeyanov above), with no recognition of the fact that $\delta_{C=O}$ for camphenilone itself is reported to be 219.4 ppm,[29] significantly different from that for cyclohexanone (211.5 ppm, see Table I). It is clear that the variations in $\delta_{C=O}$ and $\delta_{C\text{-}Hg}$ are slight for the different orientations of a C–Hg bond with respect to an adjacent carbonyl system, but our careful comparisons (Table II) show that σ–π interaction may cause an upfield shift of ca. 2.5–3 ppm in $\delta_{C=O}$ and ca. 2.0 ppm in $\delta_{C\text{-}Hg}$. The β effects of both axially or equatorially disposed HgX in cyclohexane are ca. +5 ppm, so that in (minor) *cis*-4-methyl-2-(chloromercuri)cyclohexanone (where the β effect to C=O is ca. −0.20 ppm) a shielding effect quite unrelated to the operation of σ–π interactions must be operative, or the normal β effect is suppressed.

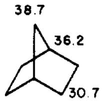
We have examined briefly some aspects of the NMR spectra of *exo*-3-(chloromercuri)-2-norbornanone obtained by oxidation of the 2-hydroxy-3-chloromercuri compound.[30] The exo nature of the chloromercuri group is confirmed[22] by the large (~250 Hz) vicinal ^{199}Hg–^{13}C coupling to C_5. The ^{13}C shifts for the oxo mercurial, 2-norbornylmercuric chloride, and 2-norbornanone (for 80:20 $CDCl_3$–pyridine solvent) are shown below.



$\delta_{^{199}Hg}$ 213 ppm







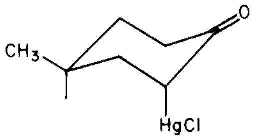
$\delta_{^{199}Hg}$ 233 (exo), 345 (endo)

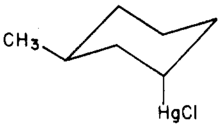
Considering that σ–π interaction between the C–Hg exo bond and the carbonyl system can in principle occur in the oxo mercurial (either exo or endo isomer; the O–C_2–C_3–Hg dihedral angle is ~60°), this is not reflected in any significant change in $^1J_{Hg\text{-}C}$, compared with 2-norbornylmercuric chloride. Compared with 2-norbornanone, $\delta_{C=O}$ is slightly (~1.00 ppm) to lower field in the oxo mercurial, in contrast to the small upfield effect (ca. −2.0 ppm) observed in the *trans*-4-alkylcyclohexanone series.

We also obtained the ^{199}Hg shifts of the oxo mercurial and both *exo*- and *endo*-2-norbornylmercuric chloride. The endo mercurial (345 ppm) is ca. 120 ppm to lower field of either of the *exo*-mercury compounds and implies greater polarization in the exo isomer. The effect of the carbonyl

$$\overset{\delta^-}{C}\text{—}\overset{\delta^+}{Hg}$$

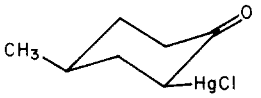
group is a modest 20-ppm shielding, which may be compared with the shifts below.

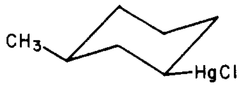




$\delta_{^{199}Hg}$ 174.26 285.16

Δ = −110.96 ppm





$\delta_{^{199}Hg}$ 190.79 203.75

Δ = −12.96 ppm

It follows that introduction of the carbonyl group in circumstances where σ–π is possible results in a substantial high-field shift (ca. −111 ppm) of the ^{199}Hg resonance, whereas a modest shift (ca. −13 ppm) characterizes the *cis*-3-methylcyclohexylmercury situation. Thus, the (upfield) 20-ppm difference between *exo*-2-(chloromercuri)-norbornane and *exo*-3-(chloromercuri)-2-norbornanone is consistent with a low level of σ–π interaction, which is probably associated with the inability of the norbornane skeleton to adjust or accommodate molecular changes associated with bonding and hybridization changes.

The present study establishes that in 2-mercuricyclohexanones, the mercury group is predominantly axial, and this preference could be associated with the operation of carbon–mercury (σ–π) hyperconjugative interaction with the adjacent carbonyl system. The magnitude of this interaction (ca. 1.3 kcal/mol) seems to render dubious a study (e.g., by NMR methods) of restricted rotation in mercury-substituted acetophenones, which we have plan-

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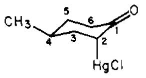
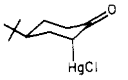
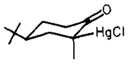
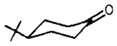
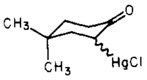
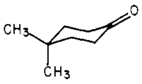
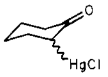
[29] J. B. Strothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, 1972, p 292.

[30] T. G. Traylor and A. W. Baker, *J. Am. Chem. Soc.*, 85, 2746 (1963).

Table I. ^{13}C Chemical Shifts[a] and ^{13}C–^{199}Hg Coupling Constants in 2-(Chloromercuri)cyclohexanones

compd	solvent	carbon no. 1	2	3	4	5	6	other
	$CDCl_3$ [c]	209.29	60.21 (1360.2)	38.69 (115.1)	32.77 (42.4)	33.85	40.12	21.19
	$CDCl_3$-pyridine [c]	209.49	57.93 (1500)	39.20 (125.3)	32.70 (38.5)	34.19	39.65 (30.4)	21.29
	$CDCl_3$-pyridine [d]	209.57	57.95 (1489)	39.17 (125.3)	32.76 (38.1)	34.17	39.67 (31.5)	21.30
	$CDCl_3$ [c]	n.o.[b]	62.40	40.81	33.55	33.11	40.92	21.00
	$CDCl_3$-pyridine [c]	n.o.	59.45	38.25*	33.01‡	32.10‡	40.12*	20.84
	$CDCl_3$-pyridine [d]	211.87	59.55	n.o.	33.08‡	32.15‡	40.19*	20.83
	$CDCl_3$ [d]	212.00	40.64	34.61	30.96	34.61	40.64	20.81
	$CDCl_3$ [d]	208.74 (1315)	61.05	31.39	48.67	26.47	40.36	27.64, 32.73
	$CDCl_3$-pyridine [c]	209.77	58.36 (1505)	31.90 (121.4)	48.27 (36.5)	26.83	39.78	27.63, 32.50
	$CDCl_3$-pyridine [d]	209.27 (109.2)	59.61 (1482)	31.68 (117.2)	48.53 (39.6)	26.68	40.07 (33.3)	27.64, 32.64
	$CDCl_3$ [d]	211.90	63.33	33.93	48.85	26.41	41.24	n.o., n.o.
	$CDCl_3$-pyridine [c]	212.65	60.10	32.94	48.48	25.56	40.47	27.46, 32.77
	$CDCl_3$-pyridine [d]	212.26	62.22	33.61	48.64	26.12	41.01	32.82, n.o.
	$CDCl_3$ [d]	212.29	41.17	27.48	46.58	27.48	41.17	27.48, 32.33
	$CDCl_3$ [d]	211.28	57.95 (1578)	43.97 (74.7)	30.68 (30.0)	37.71	37.85 (41.8)	28.96, 26.47
	$CDCl_3$ [c]	211.12	58.17 (1576)	44.09 (72)	30.79 (32)	37.75	37.88 (42)	29.14, 26.31
	$CDCl_3$-pyridine [d]	210.74	52.60 (1613)	42.95 (100)	28.85	36.57	37.16 (41.0)	28.20, 26.63
	$CDCl_3$ [c]	212.63	38.00	39.11	29.89	39.11	38.00	27.50
	$CDCl_3$-pyridine [d]	209.47	59.48 (1519)	31.05 (115.0)	25.93 (65.2)	25.58	40.26	
	$CDCl_3$-pyridine [c]	209.19	58.76 (1530)	30.83 (118.4)	25.64 (66.6)	25.38	39.87 (33.3)	
	$CDCl_3$ [d]	209.54	61.82 (1433)	31.34 (93.8)	26.23 (53.6)	25.63	41.05	
	$CDCl_3$ [d]	211.50	41.61	26.67	24.64	26.67	41.61	

[a] Chemical shifts relative to internal Me_4Si or center of triplet of $CDCl_3$ at 77.00 ppm. Values in parentheses are ^{199}Hg–^{13}C coupling constants. [b] n.o. = not observed. Shifts with asterisks and daggers are possibly interchanged. [c] Obtained at 67.89 MHz. [d] Obtained at 25.05 MHz.

ned. Syn 1,3-methyl–halomercury interactions are demonstrated to be substantial (>1.5 kcal/mol), in line with observations for methyl–bromo systems.[18,19] The spectroscopic characteristics of the α-mercuri ketones examined confirm the *C*-mercury structures.

Although we have not explored the chemistry of these mercurials in any depth, the possibility for regio- and stereospecific incorporation of deuterium by reduction of the C–Hg bond appears, while Pd(II)-induced transmetalation followed by loss of HPdX might produce 4-alkyl-α,β-unsaturated-cyclohexenones in acceptable yields.[31] Useful information might result from study of other α-metalated cycloalkanones, and activity in this area is continuing.

Experimental Section

Compounds. The trimethylsilyl enol ethers of cyclohexanone, 4-methyl-, 4-*tert*-butyl-, and 4,4-dimethylcyclohexanone were synthesized in the standard way[32] and characterized by their boiling points and ^{1}H NMR spectra. The essential details are shown in Table V. The enol acetate of 4,4-dimethylcyclohexanone had bp 83–85 °C (17 mm) and that (mixture) of 4-methylcyclohexanone was 83–90 °C (25 mm).

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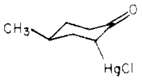
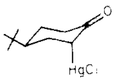
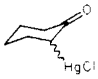
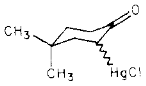
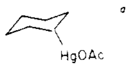
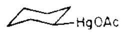
(31) R. F. Heck, "Organotransition Metal Chemistry", Academic Press, New York, 1974.

(32) H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, 34, 2324 (1969).

Table II. Substituent Effects of Axial and Equatorial HgCl in (Chloromercuri)cyclohexanones

compd	α	C=O	β	γ	
				C_4	C_6
	+19.57	−2.71	4.08	1.81	−0.53
	+21.76	~−0.20	+6.2	2.59	0.28
	+19.88	−3.85	+3.91	+2.09	−0.81
	+21.16	−0.39	+5.45	+2.27	+0.07
	+20.21	−1.96	+4.67	+1.59	−0.56
	+19.95	−1.35	+4.86	+0.79	−0.15
 [a]	+24.2		+5.8	+2.3	
	+19.9		+7.5	+2.3	

[a] C_2 to lower field in axial conformer.

These enol ethers were reacted with a mixture of mercuric oxide and mercuric acetate in aqueous ethanol, following a procedure developed by House.[10] The resulting bismercurials (series B) were cleaved (or redistributed) with 1 equiv of mercuric chloride in tetrahydrofuran to yield the corresponding mercuric chlorides (series A). The following procedure for the 4-*tert*-butyl compound is illustrative.

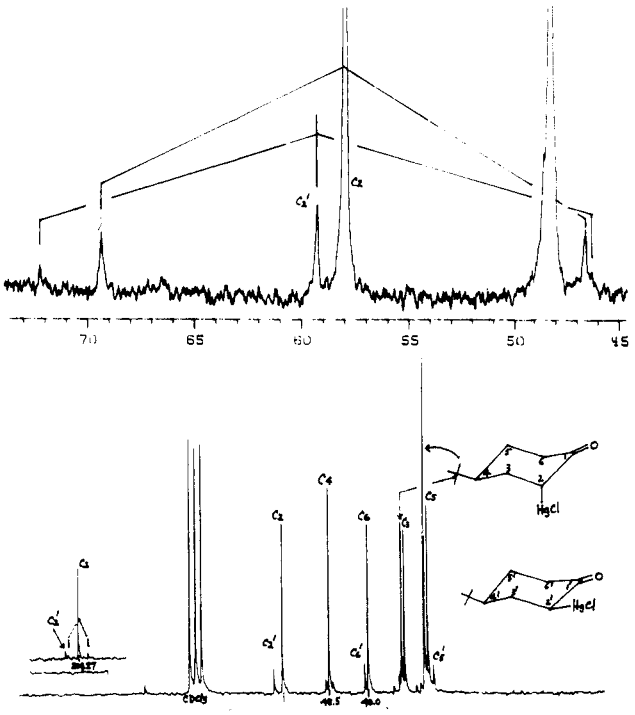
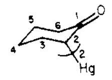
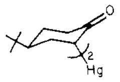
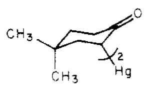


Figure 4. Lower: 25.05-MHz ^{13}C spectrum of the trans–cis mixture of 4-*tert*-butyl-2-(chloromercuri)cyclohexanone (solvent 80:20 $CDCl_3$ pyridine). Signals corresponding to the minor cis isomer are primed. (A full listing of chemical shifts and coupling constants is located in Table I.) Upper: 67.89-MHz spectrum (in part) showing ^{199}Hg coupling to C_2 and C_2'. Values are listed and discussed in the text.

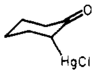
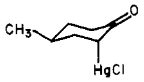
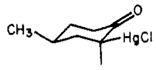
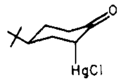
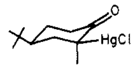
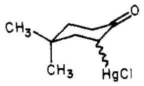
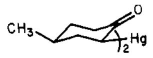
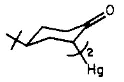
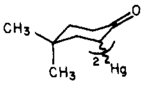
Mercuric oxide (5.4 g, 25 mmol), mercuric acetate (0.2 g, 0.6 mmol), water (1 mL), and ethanol (5 mL) were placed in a 250-mL flask and the trimethylsilyl enol ether of 4-*tert*-butylcyclohexanone (11.30 g, 50 mmol) was added, with stirring, over a period of 10 min. More ethanol (25 mL) was added to facilitate stirring, which

Table III. ^{13}C Chemical Shifts[a] and ^{13}C-^{199}Hg Coupling Constants in Bis(2-oxocyclohexyl)mercury Compounds

compd	solvent	carbon no.						other
		1	2	3	4	5	6	
	$CDCl_3$ [d]	210.44	67.81 (603.7)	29.37 (48.4)	26.30, 26.38 (37.4)	25.36	40.92	
	$CDCl_3$ [c]	210.43, 210.48	67.63, 67.59 (611.3)	29.43, 29.42 (49.0)	26.36, 26.31 (37.0)	25.38	40.86 (34.1)	
	$CDCl_3$ [d]	210.17, 210.11	67.45, 67.31 (603.3)	30.30 (50.6)	49.46, 49.58 (37.4)	26.38	40.57	27.73, 32.73
	$CDCl_3$ [c]	210.25, 210.21	67.26, 67.13 (604.8, 608.5)	30.36, 30.34 (50.9)	49.54, 49.41 (34.9, 34.6)	26.43	40.52 (35.4)	27.75, 32.73
	$CDCl_3$ [d]	n.o.[b]	65.79, 65.67	29.51	47.30, 47.12	25.41	40.19	27.35, 33.02
	$CDCl_3$ [c]	214.33, 214.26	65.65, 65.47	29.58, 29.38	47.40, 47.25	24.30, 24.23	40.12	27.39, 33.07
	$CDCl_3$ [d]	210.11	67.10 (584.7)	37.71 (51.3)	33.26, 33.26 (33.7)	33.81	40.45	21.62
	$CDCl_3$ [c]	210.06, 209.99	67.13, 67.10 (587.2)	37.75 (51.8)	33.27, 33.16 (38.7)	33.83	40.47	21.60
	$CDCl_3$ [d]	211.01	64.21	37.03	31.50	32.97	n.o.	20.88
	$CDCl_3$ [c]	213.21, 213.12	64.24, 64.14	36.97	31.59	n.o.	40.99	20.92
	$CDCl_3$ [d]	212.25 (61.7)	61.75, 61.66 (628.9)	42.09 (45.4)	30.36, 30.24	37.12	37.12	29.19, 26.91 30.0
	$CDCl_3$ [c]	212.16	61.90, 61.88 (630.0)	42.16, 42.15	29.25	37.17	37.17	30.17, 27.07

[a-d] See corresponding footnotes of Table I.

Table IV. ^{199}Hg Chemical Shifts[a] of 2-(Chloromercuri)cyclohexanones

compd	solvent	shift[b]	shift, ppm relative to 
	80% CDCl$_3$/ pyridine		−5.10
	CDCl$_3$		−18.42
	80% CDCl$_3$/ pyridine		+11.43
	CDCl$_3$		+48.03
	80% CDCl$_3$/ pyridine		−5.42
	CDCl$_3$		−24.18
	80% CDCl$_3$/ pyridine		+0.91
	CDCl$_3$		+43.59
	CDCl$_3$		+36.52
	80% CDCl$_3$/ pyridine	142.58, 143.07	−10.40[c]
	CDCl$_3$	156.64, 158.04	−13.90
	80% CDCl$_3$/ pyridine	186.90, 183.61	+32.03
	CDCl$_3$	209.84, 208.69	+38.03
	80% CDCl$_3$/ pyridine	142.83, 139.04	−12.29
	CDCl$_3$	156.97, 162.23	−11.64
	80% CDCl$_3$/ pyridine	166.18, 170.28	+15.25
	CDCl$_3$	193.30, 197.51	+24.17
	CDCl$_3$	199.56, 207.87	+32.48

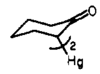
[a] See Experimental Section for details. [b] Arbitrarily referenced to end data point to indicate shifts for diastereomers. [c] Relative to  , the difference being between the average of the two signals of the compound and the two of the reference.

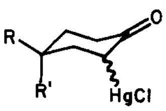
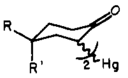
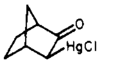
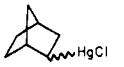
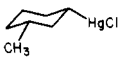
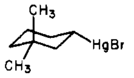
Table V

trimethylsilyl enol ether of	bp, °C (pressure, mm)	^{1}H NMR, δ
cyclohexanone	71–73 (18)	4.60 (=CH)
4-methylcyclohexanone	80 (17)	4.72
4-*tert*-butylcyclohexanone	68 (0.5)	4.76
4,4-dimethylcyclohexanone	80–84 (16)	4.68

continued for 1 h. The solution was diluted with warm chloroform (200 mL), filtered through Supercel, and dried (MgSO$_4$). The filtered solution was reduced in volume, and the residue crystallized from benzene/hexane. Fine white crystals (6.8 g, 54%) of the bismercurial were thus obtained (mp 136–137 °C).

2-(Chloromercuri)-4-*tert*-butylcyclohexanone was obtained as follows. The bismercurial (2.53 g, 5 mmol) was dissolved in tetrahydrofuran (40 mL) and added to mercuric chloride (1.36 g, 5 mmol) in tetrahydrofuran (15 mL). An immediate white precipitate formed, and the solution was stirred for 1 h. The solid material (after removal of THF) was recrystallized from chloroform, as soft white crystals (2.9 g, 75%, mp 187–188 °C).

Table VI. Analytical Data and Melting Points of 2-Mercuricyclohexanones

		C, H		
R	R′	found	calcd	mp, °C
H	H	20.90, 2.64	21.62, 2.70	135
CH$_3$	H	24.18, 3.22	24.20, 3.17	130–131
C(CH$_3$)$_3$	H	30.84, 4.53	30.84, 4.37	187–188
CH$_3$	CH$_3$	26.46, 3.76	26.59, 3.60	134
				
H	H	36.11, 4.56	36.49, 4.56	136–138
CH$_3$	H	39.24, 5.18	39.75, 5.21	131–132
C(CH$_3$)$_3$	H	47.61, 6.77	47.37, 6.71	136–137
CH$_3$	CH$_3$	42.42, 5.80	42.61, 5.77	108–109
		24.62, 2.92	24.34, 2.61	201–202[30]
		25.51, 3.43	25.37, 3.32	183
		25.63, 4.06	25.23, 3.90	88–89
		24.70, 3.99	24.51, 3.83	126.5–127.5

3-Methylcyclohexylmercuric chloride was obtained from the bromide by treatment with excess silver acetate (acetone solvent) and precipitation with aqueous sodium chloride, followed by recrystallization from ethanol (mp 88–89 °C).

3,3-Dimethylcyclohexylmercuric bromide was synthesized from the Grignard reagent (in ether) and mercuric bromide and was recrystallized from ethanol (mp 126.5–127.5 °C).

All mercurials provided satisfactory C, H analyses. The melting points of the (chloromercuri)cyclohexanones were in the range 130–135 °C, except for the 4-*tert*-butyl derivative (187–188 °C). The bis compounds melted in the range 131–138 °C, except for the 4,4-dimethyl compound (108–109 °C).

The analytical data and melting points of the mercurials are listed in Table VI.

NMR Spectra. ^{1}H spectra were recorded initially on a JEOL JNM MH-100 or JEOL PS-100 spectrometer in this Department and then obtained at 270 MHz (Bruker) at the National NMR Center, Canberra. Solvents employed were CDCl$_3$ or CDCl$_3$–pyridine (80:20) and chemical shifts are with respect to internal Me$_4$Si or residual CHCl$_3$ (δ 7.27).

^{13}C spectra were obtained on the JEOL FX-100 at 25.05 MHz or at 67.89 MHz (Bruker) again for the CDCl$_3$ or CDCl$_3$–pyridine solvent mentioned above. ^{199}Hg spectra were obtained on the FX-100 spectrometer modified (10-mm probe) for multinuclear observation.[9] Solutions were very close to 0.4 M in mercurial, and observation frequencies were 17.82 MHz for the bis series and 17.81 MHz for the mono series. Compared with diphenylmercury (0.1 M) in 50:50 CDCl$_3$–CH$_2$Cl$_2$, the resonance of 2-(chloromercuri)cyclohexanone (solvent CDCl$_3$, 0.4 M) is calculated to be 504 ppm upfield, and the bismercurial is 296 ppm upfield.

Calculations of substituent-induced shifts and other comparisons of spectral data refer to the same solvent system and concentrations.

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Registry No. Cyclohexanone trimethylsilyl enol ether, 6651-36-1; 4-methylcyclohexanone trimethylsilyl enol ether, 38671-78-2; 4-*tert*-butylcyclohexanone trimethylsilyl enol ether, 19980-19-9; 4,4-

dimethylcyclohexanone trimethylsilyl enol ether, 77172-48-6; 4,4-dimethylcyclohexanone enol acetate, 77172-49-7; 4-methylcyclohexanone enol acetate, 22422-17-9; *exo*-3-(chloromercuri)-2-norbornanone, 77172-50-0; *endo*-2-norbornylmercuric chloride, 52251-50-0; *exo*-2-norbornylmercuric chloride, 52251-51-1; *cis*-3-methylcyclohexylmercuric chloride, 77172-51-1; 3,3-dimethylcyclohexylmercuric bromide, 77172-52-2; *trans*-2-(chloromercuri)-4-methylcyclohexanone, 77172-53-3; *cis*-2-(chloromercuri)-4-methylcyclohexanone, 77172-54-4; 4-methylcyclohexanone, 589-92-4; *trans*-2-(chloromercuri)-4-*tert*-butylcyclohexanone, 77172-55-5; *cis*-2-(chloromercuri)-4-*tert*-butylcyclohexanone, 77172-56-6; 4-*tert*-butylcyclohexanone, 98-53-3; 2-(chloromercuri)-4,4-dimethylcyclohexanone, 77172-57-7; 4,4-dimethylcyclohexanone, 4255-62-3; 2-(chloromercuri)cyclohexanone, 14839-64-6; cyclohexanone, 108-94-1; cyclohexylmercuric acetate, 10341-90-9; (2R*,2′R*)-bis(2-oxocyclohexyl)mercury, 77172-58-8; (2R*,2′S*)-bis(2-oxocyclohexyl)mercury, 77172-59-9; (2R*,2′R*,4S*,4′S*)-bis(5-*tert*-butyl-2-oxocyclohexyl)mercury, 77172-60-2; (2R*,2′S*,4S*,4′R*)-bis(5-*tert*-butyl-2-oxocyclohexyl)mercury, 77255-04-0; (2S*,2′R*,4S*,4′R*)-bis(5-*tert*-butyl-2-oxocyclohexyl)mercury, 77255-05-1; (2S*,2′S*,4S*,4′S)-bis(5-*tert*-butyl-2-oxocyclohexyl)mercury, 77255-06-2; (2R*,2′R*,4S*,4′S*)-bis(5-methyl-2-oxocyclohexyl)mercury, 77172-61-3; (2R*,2′S*,4S*,4′R*)-bis(5-methyl-2-oxocyclohexyl)mercury, 77210-00-5; (2S*,2′R*,4S*,4′R*)-bis(5-methyl-2-oxocyclohexyl)mercury, 77210-01-6; (2S*,2′S*,4S*,4′S*)-bis(5-methyl-2-oxocyclohexyl)mercury, 77172-62-4; (2R*,2′R)-bis(5,5-dimethyl-2-oxocyclohexyl)mercury, 77172-63-5; (2R*,2′S*)-bis(5,5-dimethyl-2-oxocyclohexyl)mercury, 77172-64-6.

Aromatic Substitution. 47.[1] Acid-Catalyzed Transfer Nitration of Aromatics with *N*-Nitropyrazole, a Convenient New Nitrating Agent

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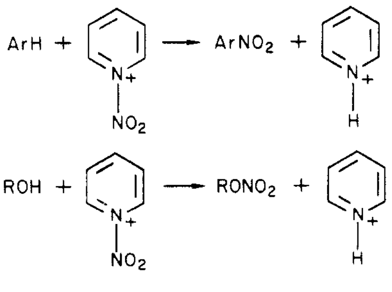
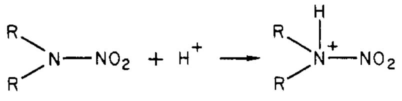
N-Nitropyrazole in the presence of Lewis or Bronsted acid catalysts was found to be an effective transfer nitrating agent for aromatic substrates. The nature of the acid catalyst affects both substrate and positional selectivities of the nitration of alkylbenzenes. No relationship was found between substrate and positional selectivities, which are considered to be determined in two separate steps.

The nitronium ion is usually the nitrating agent in electrophilic aromatic nitration. The nitronium ion is formed in situ from nitric acid, alkyl nitrates, acyl nitrates, etc., ($XONO_2$, X = H, R, RC(O)) in which it is bound to an oxygen atom.[2]

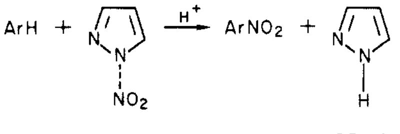
Even stable nitronium salts are utilized as nitrating agents. On the other hand, nitration with reagents in which the incipient nitronium ion is bound to nitrogen or other heteroatoms is rare. We have previously reported the nitration of aromatics and alcohols with *N*-nitropyridinium and *N*-nitroquinolinium salts, which undergo transfer nitration from nitrogen to π-donor and n-donor substrates.[3,4]



These nitrations take place readily at room temperature and the nitro aromatics and alkyl nitrates are obtained in excellent yields. One of the advantages in using *N*-nitropyridinium salts is the binding of the acid formed as a byproduct to the amine base, thus allowing the transfer nitrations to be carried out under essentially neutral conditions. *N*-Nitropyridinium salts are readily prepared from the corresponding pyridine and the nitronium salt. These salts are stable but require handling in a dry atmosphere because of their sensitivity to moisture. We have therefore been interested in developing suitable *N*-nitramines as nitrating agents, from which the *N*-nitrammonium salt can be generated in situ.



We report now on the use of *N*-nitropyrazole as a suitable new transfer nitrating agent.



X-ray structure determination of *N*-nitropyrazole showed that the nitro group is essentially coplanar with the heterocyclic ring.[5] The calculated angle between the ring plane and the plane of the nitro group is only 1.8°. On the other hand, the $N-NO_2$ bond length (1.399 Å) is considerably longer than in dimethylnitramine (1.30 Å) and other nitramines (average of 1.372 Å). This tends to indicate a greater lability of the $N-NO_2$ bond in *N*-nitro-

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[1] For part 46, see: Olah, G. A.; Bruce, M. R.; Clouet, F. L. *J. Org. Chem.* **1981**, *46*, 438.

[2] For a comprehensive listing of nitrating agents, see: Olah, J. A.; Lin, H. C.; Olah, G. A.; Narang, S. C. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 1045–1049.

[3] Olah, G. A.; Narang, S. C.; Olah, J. A.; Pearson, R. L.; Cupas, C. A. *J. Am. Chem. Soc.* **1980**, *102*, 3507–3510.

[4] Olah, G. A.; Narang, S. C.; Pearson, R. L.; Cupas, C. A. *Synthesis* **1978**, 452–453.

[5] Tarimci, C.; Schempp, E. *Acta Crystallogr., Sect. B* **1977**, *33*, 240–243.

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