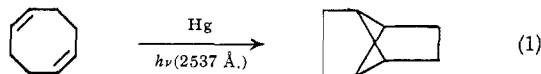from 1,5-cycloöctadiene according to reaction 1 are worth commenting about.

(1)

One of these is the fact that although the starting material has the *cis,cis* conformation, the tricyclic product is derived from the *trans,trans* conformation. Since the over-all yield of tricycloöctane was less than 1% (the major product being a non-volatile oil) this may mean that either both the double bonds in 1,5-cyclo-octadiene have to twist to a *trans* conformation in the excited state before the molecule can close to form the tricycloöctane, or only a small fraction of 1,5-cyclo-octadiene molecules that may be in the *cis,trans* conformation may participate in reaction 1. A second interesting fact is that in the *cis,cis* conformation, the formation of IV could be expected to be favored. Failure to observe any IV among the products suggests that it may decompose before it can get rid of its excess energy through collisions. In contrast, pyrolysis studies suggest that V may be more stable thermally than even bicyclo[2.1.1]hexane.

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RECEIVED FEBRUARY 12, 1963

CHLORINE MIGRATION IN EPOXIDE—CARBONYL REARRANGEMENT

Sir:

Recent investigations in our laboratories into the synthesis[1,2] and chemistry[3] of α-haloepoxides have led to the observation of the novel and preferential chlorine migration in certain epoxide–carbonyl rearrangements.[4] We wish to report some of our results in this communication.

Treatment of *trans*-α-chlorostilbene[5] (Ia) with trifluoroperacetic acid in methylene chloride solution with sodium carbonate as the insoluble base[6] did not give the expected α-chloroepoxide; instead the only isolable organic product was desyl chloride (IIa, 63%). Treatment of Ia with peracetic acid also gave only IIa (67%), as did perbenzoic acid (74%).

Since the formation of IIa can be explained by either chlorine or hydrogen migration from the α-chloroepoxide (or its protonated form), several experiments were carried out to check this point. 4-Methyl-α-phenylacetophenone was prepared by the Friedel–Crafts reaction of phenylacetyl chloride with toluene (82%, m.p. 109–111°). Treatment of this ketone with phosphorus pentachloride and heating to complete dehydrochlorination afforded *trans*-1-chloro-1-(*p*-tolyl)-2-phenylethylene[7] (Ib) (56%, m.p. 36–38°). When Ib was treated with trifluoroperacetic acid under the same conditions as mentioned above, a single product was isolated in 58% yield which was found to be p-methyl-α-chloro-α-phenylacetophenone (IIb, m.p. 73–74°), λ_{max} 258 mμ, ϵ 26,200. Also, when Ib was treated with

(1) Chlorination of epoxides has been reported by C. Walling and P. S. Fredericks, *J. Am. Chem. Soc.*, **84**, 3326 (1962), and H. Gross and A. Rieche, German Patent 1,084,707 (1960).

(2) M. Mousseron and R. Jaquier, *Bull. Soc. Chim. France*, 698 (1950), have converted 1-chlorocyclohexene to the corresponding epoxide with perbenzoic acid.

(3) A. A. Durgaryan, C. A. Testanyan and R. A. Kaeryan, *Akad. Nauk S.S.S.R., Izvest. Ser. Khim. Nauk*, **14**, 165 (1961).
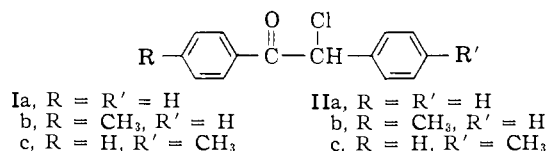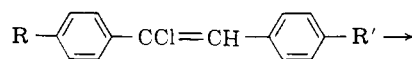
(4) Previous research on the epoxide–carbonyl rearrangement has been reviewed by R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959).

(5) T. W. J. Taylor and A. R. Murray, *J. Chem. Soc.*, 2078 (1938).

(6) W. D. Emmons and A. S. Pageno, *J. Am. Chem. Soc.*, **77**, 89 (1955).

(7) All new compounds described have given satisfactory analyses. Melting points, mixture melting points and spectra have been used to conclude structural assignments. All are in agreement with the structures given.

either peracetic or perbenzoic acids, IIb was formed in 71% and 73% yields, respectively. IIb was synthesized independently in 83% yield by the treatment of *p*-methyl-α-phenylacetophenone with sulfuryl chloride.

Ia, R = R' = H   IIa, R = R' = H
b, R = CH₃, R' = H   b, R = CH₃, R' = H
c, R = H, R' = CH₃   c, R = H, R' = CH₃

In order to complete the investigation, the other vinyl chloride, *trans*-1-chloro-1-phenyl-2-(*p*-tolyl)-ethylene (Ic), was prepared. The monobromide of *p*-xylene, from *p*-xylene and bromine under ultraviolet conditions (55%, b.p. 94–96° (12 mm.)) was treated with sodium cyanide to give the corresponding nitrile (82%, b.p. 94–96° (3 mm.), which was hydrolyzed to the corresponding acid (92%, m.p. 91–92°). Treatment with phosphorus trichloride gave *p*-tolylacetyl chloride which underwent Friedel–Crafts reaction readily with benzene to give α-(*p*-tolyl)-acetophenone (83%, m.p. 93–95°). Reaction of this ketone with phosphorus pentachloride and heating gave Ic (61%, m.p. 47–48°).

Treatment of Ic with trifluoroperacetic acid, as above, gave a product which proved to be α-chloro-α-(*p*-tolyl)-acetophenone (IIc, 53%, m.p. 73–74°[8]), λ_{max} 247 mμ, ϵ 24,500. Also, when Ic was treated with either peracetic or perbenzoic acid, IIc was isolated in 67 and 71% yields, respectively. IIc was also prepared independently by reaction of sulfuryl chloride with α-(*p*-tolyl)-acetophenone in 83% yield.

As evident from the above experiments, in every instance only that α-chloroketone was isolated which necessarily involves chlorine migration. Also, no acid chlorides or aldehydes were found which would be the result of aryl migration. There appear to be several reasonable mechanisms[9] for this rearrangement dependent upon whether the α-chloroepoxide or the intermediate protonated species is involved. The breaking of the particular C–O bond of either the epoxide or protonated epoxide leading to rearrangement is readily explained by the following contributing structures to the possible resonance hybrid of III.[10] Carbonium ion III would be of greater stability than the
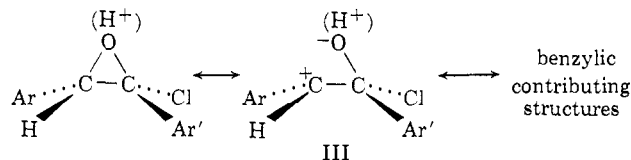
someric one formed by breaking the other C–O bond. Such stabilization also explains why no α-chloroepoxide is isolated in our examples, whereas such is the case with 1-chlorocyclohexene.[2] In this latter example only inductive and hyperconjugative stabilization could be involved in the stabilization of intermediates.

Experiments designed to elucidate the mechanism and the steric requirements of the rearrangement are

(8) Although the melting points of IIb and IIc are the same, their infrared spectra are quite different and their mixture melting point is appreciably depressed to 35–45°.

(9) Some of these possibilities involve chloronium ions as intermediates or transition states: J. Hine, "Physical Organic Chemistry," 2nd ed., McGraw-Hill, New York, N. Y., 1962, pp. 148–149, has reviewed the evidence for the intermediacy of halonium ions in organic reactions.

(10) Similar structures of a hybrid have been proposed to explain the nature of the epoxide ring system (see ref. 4, pp. 739–740). Such structures should be of greater importance in the protonated epoxide to enable distribution of the charge

being carried out. Studies into the generality of halogen and pseudo-halogen migration and their migratory apptitudes in this and other systems are also presently under investigation.

The authors wish to thank the Research Corporation for financial assistance through a Frederick Gardner Cottrel grant-in-aid.

(11) A portion of a dissertation to be presented by P. A. Schwab to the Graduate School of Kansas State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

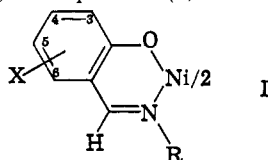DEPARTMENT OF CHEMISTRY
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RECEIVED DECEMBER 7, 1962

PROTON CONTACT SHIFTS IN DYNAMICAL NICKEL(II) COMPLEXES AND THE DETECTION OF DIASTEREOISOMERS BY NUCLEAR RESONANCE

Sir:

We have shown recently that bis(N-*sec*-alkylsalicyl-aldimine)–Ni(II) complexes (I, R = *i*-Pr, *sec*-Bu)

undergo a conformational equilibrium in solution involving planar (diamagnetic) and tetrahedral (paramagnetic) species.[1] Susceptibility measurements indicate ~ 40–50% paramagnetic form for most complexes examined in chloroform at 30°. This situation suggests that, like the bis(N,N'-disubstituted-aminotroponeimine)–Ni(II) complexes,[2–4] T_1^{-1} and/or T_e^{-1} might be sufficiently large to render isotropic hyperfine contact shifts observable[5] in the proton resonance spectra of these complexes. We are currently investigating n.m.r. spectra of complexes of the type I and have observed such contact shifts, similar in sign but not in magnitude to those detected[6] in the related bis(N-arylsalicylaldimine)–Ni(II) complexes, which attain paramagnetism by a different means at room temperature.[7]

A large variety of ring-substituted N-isopropyl and -*sec*-butyl complexes I have been examined, but discussion is confined to the X = 5-Me complexes. For R = *i*-Pr the following contact shifts[8] were observed (31°, CDCl₃, ~0.15 M): +825(3-H), −624(4-H), −138(6-H), −597(5-Me), −6059(C–H, *i*-Pr), −11570 (HC=N).[9] The solution equilibria are demonstrably temperature and solvent dependent. In particular, the nature of the inert solvent has a marked effect on the position of equilibrium. In CS₂ the equilibrium is displaced toward the diamagnetic species and first order spin–spin splitting is clearly resolved, verifying the above assignments. Under the above conditions, these shifts were observed in CS₂: +314(doublet, 3-H), −234(doublet, 4-H), −55.3(singlet, 6-H), −234 (5-Me), −2224(C–H, *i*-Pr), −4228(HC=N). The

(1) R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **2**, 181 (1963); similar conclusions have also been reached by others: *cf.* L. Sacconi, P. L. Orioli P. Paoletti and M. Ciampolini, *Proc. Chem. Soc.*, 255 (1962).

(2) D. R. Eaton, A. D. Josey, W. D. Phillips and R. E. Benson, *J. Chem. Phys.*, **37**, 347 (1962).

(3) D. R. Eaton, A. D. Josey, W. D. Phillips and R. E. Benson, *Mol. Phys.*, **5**, 407 (1962).

(4) D. R. Eaton, A. D. Josey, R. E. Benson, W. D. Phillips and T. L. Cairns, *J. Am. Chem. Soc.*, **84**, 4100 (1962).

(5) H. M. McConnell and D. B. Chesnut, *J. Chem. Phys.*, **28**, 107 (1958).

(6) E. A. LaLancette, D. R. Eaton, R. E. Benson and W. D. Phillips, *J. Am. Chem. Soc.*, **84**, 3968 (1962).

(7) R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **1**, 599 (1962).

(8) Contact shifts, ΔH_i, are proportional to $ga_i[Te^{\Delta F/RT} + 3]^{-1}$ and are given as $\nu_{complex} - \nu_{ligand}$ in c.p.s. at 60 Mc. Both complex and ligand were referenced internally to tetramethylsilane.
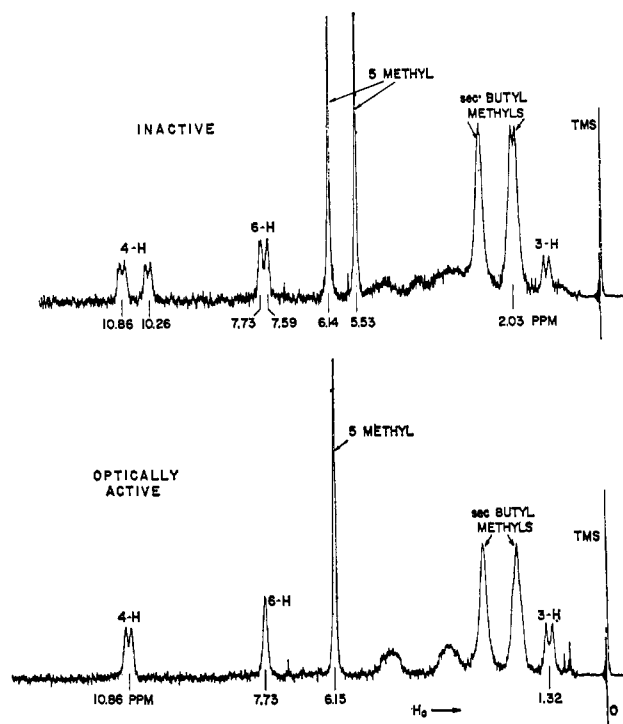
(9) Assignment verified by deuteration.

Fig. 1.—Proton resonance spectra of bis(5-methyl-N-*sec*-butylsalicylaldimine)–Ni(II) complexes in CS₂ at 31° and 60 Mc. Chemical shifts are in p.p.m; assignments are as shown; (a) optically inactive mixture of complexes: (+, +) and (−, −), (+, −); additional pairs of signals not shown are found at 35.3 and 41.8 p.p.m. (C−H, *sec*-Bu) and at 67.5 and 78.7 p.p.m. (HC=N); (b) optically active complex: (+, +) or (−, −); additional signals not shown are at 41.8 and 78.7 p.p.m.

signs of the contact shifts are in accord with a valence bond model for a non-alternant system inasmuch as structures can be written[6] for the paramagnetic form placing an unpaired spin at carbons 3 and 5 and nitrogen (positive spin densities). Remaining position acquire negative spin densities through electron correlation effects.[2]

The spectra of R = *sec*-Bu complexes are very similar to those of the corresponding *i*-Pr complexes in signs and magnitudes of contact shifts, but one striking difference is evident upon inspection of Figure 1a, *viz.*, that all signals related to a given proton occur in pairs. This effect is especially evident from the doubled signal of the 5-Me group. These doubled features imply two distinct averages of chemical shift over the planar and tetrahedral forms. The independence of the two sets of resonances was first established by proton double resonance[10] whereby it was possible (in CS₂) to decouple the outer set of doublets at 1.32 and 10.86 p.p.m. without disturbing the inner set at 2.03 and 10.26 p.p.m. The magnitude of contact shift differences for a given proton and for the 5-Me group strongly imply that these differences arise from two distinct paramagnetic tetrahedral configurations over which the chemical shifts are separately averaged.[11] Because contact shifts in equilibrium systems of this type can be at least in part dependent upon a free energy difference between the two conformers,[8] the results indicate two ΔF values for the planar ⇌ tetrahedral equilibrium correlated with two tetrahedral conformations of slightly different

(10) We thank Drs. J. D. Baldeschwieler and K. Kuhlmann of this department for these measurements and for helpful discussion.

(11) Evidence that conformation effects of the *sec*-butyl group in diamagnetic planar and tetrahedral configurations produce negligible chemical shift difference is afforded by the very similar spectra of the inactive (*vide supra*) bis(5-methyl-N-*sec*-butylsalicylaldimine) Pd(II) and Zn(II) complexes which show no evidence of doubling.