

257 (1983).

4. (a) M. Mikolajczak, P. Balczewski and S. Grzejszczak, *Synthesis*, 127 (1980).
 5. D.Y. Kim and D.Y. Oh, *Synthetic Commun.*, 859 (1986).
 6. R.T. Reetz and H. Muller-Strake, *Tetrahedron Lett.*,

3301 (1984).

7. (a) M. Sekine, K. Okimoto, K. Yamada and T. Hata, *J. Org. Chem.*, **46**, 2097 (1981); (b) D. Seebach, K.H. Geiss, A.K. Beck, B. Graf and H. Daum, *Chem. Ber.*, **105**, 3280 (1972).

Formation of *p*-Cymene from the Catalytic Reactions of Unsaturated Aldehydes and Alcohols with a Rhodium(I) Complex

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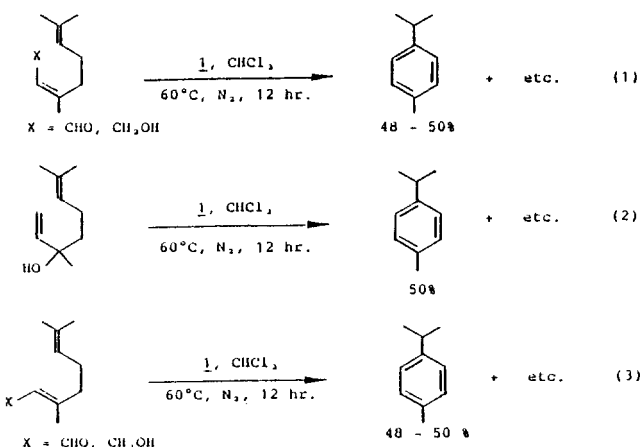
Received, August 13, 1986

Catalytic cyclization of unsaturated aldehydes to give cycloketones^{1,5} and unsaturated cycloalcohols⁶ with various transition metal complexes has been observed. Aromatization of olefin substituted cyclohexenones by a transition metal complex has been also reported.⁷ In the presence of transition metal catalyst, alcohols and ketones undergo the hydrogenation reaction to give hydrocarbons under H₂,^{8,11} in the presence of hydrogen donor,¹² or simply under N₂ (bimolecular disproportionation reaction, 2R₂CHOH → R₂CH₂ + R₂CO + H₂O).¹³ Dehydrogenation of cyclohexanes with transition metal complexes has been known.^{14,15}

NMR spectra. The reactions also yield some other products (besides *p*-cymene) which have not been fully characterized. It should, however, be mentioned that *p*-isopropenyl toluene (ca. 12%) has been found in the reactions of unsaturated aldehydes, and H₂O in all reactions (eqs. 1-3). It is noticed in eqs. 1-3 that the yield is always close to 50%. Accordingly, it may be suggested that the catalytic reactions (eqs. 1-3) involve a bimolecular disproportionation reaction such as 2R₂CHOH → R₂CH₂ + R₂CO + H₂O as previously reported.¹³

Acknowledgement. We wish to thank the Korea Science and Engineering Foundation and the Ministry of Education for their financial supports.

References



During our investigation on the catalytic activities of M(ClO₄)(CO)(PPh₃)₂ (M = Rh, Ir) for the reactions of unsaturated nitriles,^{16,17} aldehydes¹⁸ and alcohols,¹⁹ we have found the formation of *p*-cymene from the catalytic reactions of the unsaturated aldehydes (neral and geranial) and alcohols (nerol, geraniol and linalool) with Rh(ClO₄)(CO)(PPh₃)₂ (**1**) (eqs. 1-3). In all experiments, 0.7 mmole of **1** and 14 mmoles of the corresponding aldehyde or alcohol were used in 5 ml of CHCl₃ to produce ca. 7.0 mmoles of *p*-cymene. The product, *p*-cymene was identified by GC, mass (m/e = 134) and ¹H-

1. B.R. James and C.G. Young, *J. Organomet. Chem.*, **285**, 321 (1985).
2. R.E. Campbell, Jr., C.F. Lochow, K.P. Vora, and R.G. Miller, *J. Am. Chem. Soc.*, **102**, 5824 (1980).
3. R.C. Larock, K. Oertle, and G.F. Potter, *J. Am. Chem. Soc.*, **102**, 190 (1980).
4. C.F. Lochow and R.G. Miller, *J. Am. Chem. Soc.*, **98**, 1281 (1976).
5. K. Sakai, J. Ide, O. Oda, and N. Nakamura, *Tetrahedron Lett.*, 1287 (1972).
6. K. Sakai and O. Oda, *Tetrahedron Lett.*, 4375 (1976).
7. P.A. Grieco and N. Marinovic, *Tetrahedron Lett.*, 2454 (1978).
8. R. Durand, P. Geneste, C. Moreau, and J.L. Pirat, *J. Catal.*, **90**, 147 (1984).
9. R.K.M.R. Kallury, T.T. Tidwell, D.G.B. Boocock, and D.H.L. Chow, *Can. J. Chem.*, **62**, 2540 (1984).
10. D.J. Drury, M.J. Green, D.J.M. Ray, and A.J. Stevenson, *J. Organomet. Chem.*, **236**, C23 (1982).
11. W.F. Marier, K. Bergman, W. Bleicher, and P.V.R. Schleyer, *Tetrahedron Lett.*, 4227 (1981).
12. G.A. Olah and G.K.S. Prakash, *Synthesis*, 397 (1978).
13. J. Blum, *J. Mol. Catal.*, **3**, 33 (1978).
14. R.H. Crabtree, *J. C. S. Chem. Commun.*, 1829 (1985).
15. D. Brady, M. Ephritikhine, H. Felkin, and R. Homes-Smith, *J. C. S. Chem. Commun.*, 789 (1983).

16. M.K. Lee, I.B. Kim, and C.S. Chin, *J. Organomet. Chem.*, **290**, 115 (1985).
 17. S.H. Park, H.-K. Park, and C.S. Chin, *Inorg. Chem.*, **24**,

- 1120 (1985).
 18. I.B. Kim and C.S. Chin, *Polyhedron*, **3**, 1151 (1984).
 19. In preparation for publication.

Theoretical Analysis of Dipole Moment Derivatives in Fluoromethanes. (I) Fluoroform

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The analysis of the integrated infrared intensities of a variety of hydrocarbons and fluorocarbons revealed that the effective charge of hydrogen atom (χ_H) fell within the range of value¹, $\chi_H/e = 0.088 \pm 0.015$. For example, the effective charge for the hydrogen atom in methane was observed to be² $\chi_H/e = 0.092$. However, it was found in our previous report³ that the effective hydrogen atom charge in fluoroform is $\chi_H/e = 0.049 \pm 0.006$. Although this value is somewhat close to that in most hydrocarbons, the value is, strictly speaking, outside of the range of values common to other fluorocarbons.⁴ Consequently, it should be worthwhile to perform a theoretical analysis on the dipole moment derivatives and IR intensities of fluoroform. In this work, the quantum mechanical results are analyzed for the charge-charge flux-overlap (CCFO) electronic contributions to the dipole derivatives^{5,6}.

The equilibrium structural data, and the definition of the internal and symmetry coordinates are taken from the previous report³. The normal coordinates were calculated by using the harmonic force field reported by Kirk and Wilt⁷. The transformation matrix between the internal coordinates and the Cartesian displacement coordinates was evaluated by using Wilson's method⁸. To calculate the elements of the "Atomic Polar Tensors" (APT)^{9,10}, the numerical difference approximation $\partial P/\partial \sigma \cong \Delta P/\Delta \sigma$ is employed, with $\Delta \sigma = 0.02 \text{ \AA}$. Experimental values are used both for the molecular geometry and for the force field. The C-H bond was defined as the positive Z-axis.

The absolute intensities calculated by the CNDO¹¹ and *ab initio* methods are presented in Table 1. The *ab initio* calculations were carried out with the GAUSSIAN-70 program¹² using a 6-31G basis set.

With regard to the intensities, we see that the *ab initio* results are somewhat in better agreement with the experimental values. Major discrepancy concerns the CF₂ bending modes (ν_3 and ν_6). The CNDO calculated intensity of the ν_3 band in CDF₃ is too small. In general, the agreement between prediction and experimental data is better than a factor of two. It is not possible to separate experimentally the two intense and strongly overlapping CF stretching modes ν_2 and ν_5 of CHF₃, so Table 1 lists the sum of these two intensities. The CNDO and *ab initio* calculations have resulted in the 28 and 23% contributions of the ν_2 mode, respectively, to the intensity of the overlapping $\nu_2 + \nu_5$ band. On the other hand it was found that the directions (signs) of the dipole moment derivatives with respect

to the normal coordinates of fluoroform, $\partial P/\partial Q_n$, calculated by both methods were in good agreement.

The effective charge (χ)¹³, mean dipole derivative (\bar{P})¹³, and atom anisotropy (β)¹³ of the hydrogen atom are summarized in Table 2. The *ab initio* effective charge of the hydrogen atom in fluoroform is in good agreement with the experimental value. The CNDO calculated value is about two times larger than the experimental value. On the other hand, in methane the CNDO calculated value is 20% smaller than the experimental value while the *ab initio* value is about 35% larger than the observed one.

It can be seen from Table 2 that the atom anisotropy is nearly twice larger than the effective charge in both molecules, fluoroform and methane. Nevertheless, the CNDO calculations predicted the relative value of atom anisotropy in fluoroform too small rendering the mean dipole derivative to be relatively large.

According to the "charge-charge flux-overlap" (CCFO) model^{5,6}, the atomic polar tensor of the hydrogen atom, P_X^H , obtained from a MO calculation may be written as a sum of three contributions

$$P_X^H = P_X^H(\text{charge}) + P_X^H(\text{charge flux}) + P_X^H(\text{overlap}) \quad (1)$$

The first two terms on the right-hand side may be associated with the classical charge-charge flux model,^{14,15} whereas the third term represents a quantum-mechanical "interference" term,⁵ which is not amenable to a classical visualization. Considering a specific APT element of the hydrogen atom we may write eq. (1) as

$$\partial P_X^H/\partial x_H = q_H + \sum_{\alpha} (\partial q_{\alpha}/\partial x_H) x_{\alpha} + \{\partial p_{\alpha}/\partial x_H\}' \quad (2)$$

where q_H is the equilibrium net charge on the hydrogen atom, the summation represents the intramolecular charge transfer and $\{\partial p_{\alpha}/\partial x_H\}'$ denotes the non-classical contribution.

Table 3 shows the atomic polar tensor of the hydrogen atom in fluoroform. According to the *ab initio* calculation, the charge and overlap contributions are dominant. The charge-flux contribution is about one half of the other two terms. Nevertheless, it can be seen that all three of the constituent parts of the polar tensor defined in equation (1) are significant. On the other hand, the CNDO calculations represent that the