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

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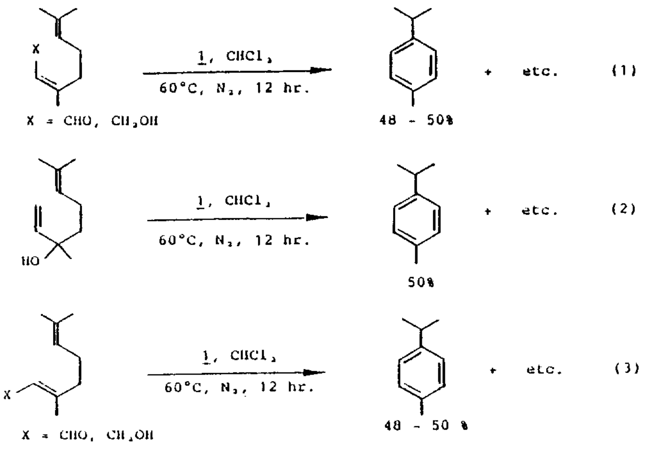
Catalytic cyclization of unsaturated aldehydes to give cycloketones[1-5] and unsaturated cycloalcohols[6] with various transition metal complexes has been observed. Aromatization of olefin substituted cyclohexenones by a transition metal conplex has been also reported.[7] In the presence of transition metal catalyst, alcohols and ketones undergo the hydrogenation reaction to give hydrocarbons under H_2,[8-11] in the presence of hydrogen donor,[12] or simply under N_2 (bimolecular disproportionation reaction, $2R_2CHOH \rightarrow R_2CH_2 + R_2CO + H_2O$).[13] Dehydrogenation of cyclohexanes with transition metal complexes has been known.[14,15]



During our investigation on the catalytic activities of $M(ClO_4)(CO)(PPh_3)_2$ (M = Rh, Ir) for the reactions of unsaturated nitriles,[16,17] aldehydes[18] 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 $Rh(ClO_4)(CO)(PPh_3)_2$ (**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 m*l* of $CHCl_3$ to produce *ca.* 7.0 mmoles of *p*-cymene. The product, *p*-cymene was identified by GC, mass (m/e = 134) and ^1H-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 H_2O 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 $2R_2CHOH \rightarrow R_2CH_2 + R_2CO + H_2O$ as previously reported.[13]

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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 value[1], $\chi_H/e = 0.088 \pm 0.015$. For example, the effective charge for the hydrogen atom in methane was observed to be[2] $\chi_H/e = 0.092$. However, it was found in our previous report[3] 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 report[3]. The normal coordinates were calculated by using the harmonic force field reported by Kirk and Wilt[7]. The transformation matrix between the internal coordinates and the Cartesian displacement coordinates was evaluated by using Wilson's method[8]. To calculate the elements of the "Atomic Polar Tensors" (APTs)[9,10], the numerical difference approximation $\partial P/\partial \sigma \cong \Delta P/\Delta \sigma$ is employed, with $\Delta\sigma = 0.02$ Å. 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 CNDO[11] and *ab initio* methods are presented in Table 1. The *ab initio* calculations were carried out with the GAUSSIAN-70 program[12] using a 6-31G basis set.

With regard to the intensities, we see that the *ab initio* results are somwthat in better agreement with the experimental values. Major discrepancy concerns the CF_2 bending modes (ν_3 and ν_6). The CNDO calculated intensity of the ν_5 band in CDF_3 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 CHF_3, 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 overping $\nu_2 + \nu_5$ 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, $\partial P/\partial Q_i$, 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 perdicted 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

$$P_x^H = P_x^H\,(\text{charge}) + P_x^H\,(\text{charge flux}) + P_x^H\,(\text{overlap}) \tag{1}$$

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

$$\partial P_x/\partial x_H = q_H + \sum_{\alpha} (\partial q_\alpha/\partial x_H)\, x_\alpha + (\partial p_x/\partial x_H)' \tag{2}$$

where q_H is the equilibrium net charge on the hydrogen atom, the summation represents the intramolecular charge transfer and $(\partial p_x/\partial x_H)'$ 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