

Decomposition of diazonitrite might be either spontaneous or one step in a chain reaction, again by analogy with proposals of Buchholz and Powell.

Whatever the mechanism, our results demonstrate that a free-radical path for the decomposition of aliphatic diazonium salts (or diazohydroxides) is energetically accessible and may compete with the usual carbonium ion process whenever the latter is relatively unfavorable. The formation of triptycene in the deamination of 9-aminotriptycene with nitrosyl chloride in ether<sup>4b,c</sup> and the formation of unrearranged chloride in the deamination of 3'-amino-1,2-cyclopropanoacene<sup>15</sup> may be examples of such free-radical processes. We are investigating the latter possibility as well as continuing our study of the chemistry of amine 1.

(15) R. Pettit, *J. Am. Chem. Soc.*, **82**, 1972 (1960); see C. H. DePuy, L. G. Schnack, J. W. Hausser, and W. Wiedemann, *ibid.*, **87**, 4006 (1965), for an alternative explanation.

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### The Use of Aluminum Chloride-Nitromethane for the Production of Cation Radicals<sup>1</sup>

Sir:

Positive ion free radicals have been investigated with esr spectroscopy by Weissman,<sup>2</sup> Carrington,<sup>3</sup> and others, usually by dissolving the appropriate neutral substance in concentrated sulfuric acid. Although

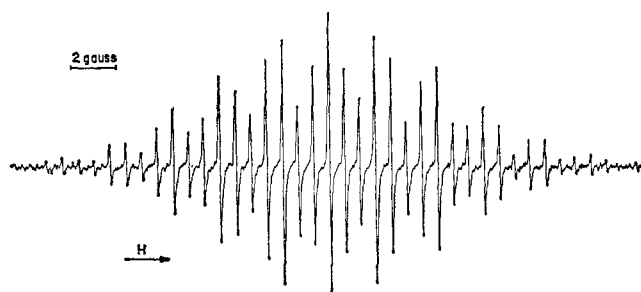


Figure 1. The esr spectrum of dimethoxydurene at  $-24^\circ$  in  $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ .

other chemical methods for producing cation radicals are known (e.g., ref 4), concentrated acid oxidation has become the most frequently used method. The purpose of this communication is to report on the use of aluminum

(1) This research was supported by the National Research Council of Canada.

(2) S. I. Weissman, E. De Boer, and J. J. Conradi, *J. Chem. Phys.*, **26**, 963 (1957).

(3) A. Carrington, F. Dravnieks, and M. C. R. Symons, *J. Chem. Soc.*, 947 (1959).

(4) I. C. Lewis and L. S. Singer, *J. Chem. Phys.*, **43**, 2712 (1965).

chloride-nitromethane ( $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ ), which was found more satisfactory than concentrated sulfuric acid for producing a number of cation radicals. Although  $\text{AlCl}_3\text{-CH}_3\text{NO}_2$  is known to produce cation radicals,<sup>5</sup> except for *p,p'*-dimethoxybiphenyl<sup>6</sup> the method does not appear to have been used for the investigation of hyperfine structure. Further, we have not been able to find any comparisons of the two systems in the literature.

For a number of radicals, such as the cation radicals of 1,4-dimethoxybenzene and 1,4-diethoxybenzene, the radical concentration obtained with  $\text{AlCl}_3\text{-CH}_3\text{NO}_2$  approximates to 100%, whereas the radical concentration obtained in concentrated sulfuric acid was considerably less than 1%.<sup>7</sup> Sometimes, the low radical concentration obtained in sulfuric acid solution does not permit analysis of the hyperfine structure. This was found to be the case for 1,4-di-*n*-butoxybenzene, where again the  $\text{AlCl}_3\text{-CH}_3\text{NO}_2$  system gave a satisfactory spectrum. The increased radical concentration of these compounds permits a spectral analysis to be made in terms of *cis* and *trans* isomerism.<sup>7</sup> For these and other compounds,  $\text{AlCl}_3\text{-CH}_3\text{NO}_2$  was therefore found to be an oxidizing agent superior to sulfuric acid.

Different spectra are sometimes obtained for the two systems as illustrated by the spectrum of dimethoxydurene.<sup>8</sup> The esr signal in  $\text{AlCl}_3\text{-CH}_3\text{NO}_2$  (Figure 1) affords narrow lines (half-width ca. 70 mgauss) and analyses for  $a_{\text{CH}_3} = 2.11$  gauss and  $a_{\text{OCH}_3} = 2.76$  gauss at  $+14^\circ$ . Moreover, the dimethoxydurene cation radical showed a marked temperature dependence of the  $-\text{OCH}_3$  splitting constant, which is being further investigated. In sulfuric acid solution an esr signal was obtained which was identical with that observed on dissolving duroquinol in sulfuric acid.<sup>9</sup> Hence in this case only the  $\text{AlCl}_3\text{-CH}_3\text{NO}_2$  system gives rise to the appropriate cation radical without further chemical reaction.

Since  $\text{AlCl}_3\text{-CH}_3\text{NO}_2$  is less viscous than concentrated sulfuric acid, effects due to the anisotropic dipolar  $g$  tensor interaction terms of the line-width equations<sup>10</sup> are of little importance. For example, the duroquinol cation radical can be studied to  $-95^\circ$  in the former, whereas in the latter system determinations below  $0^\circ$  are marred by line-width variations. Studies at  $-95^\circ$  allow observation of the *cis* and *trans* isomers of the duroquinol cation radical.

Sometimes,  $\text{AlCl}_3\text{-CH}_3\text{NO}_2$  permits oxidation beyond the one-electron stage. For example, *p,p'*-biphenol gave a blue paramagnetic solution which analyzed as  $a_{4\text{H}} = 1.95$  gauss,  $a_{2\text{H}} = 1.64$  gauss, and  $a_{4\text{H}} = 0.73$  gauss. Using excess  $\text{AlCl}_3$ , the solution became yellow in color and was diamagnetic. This further oxidation was reversed by diluting or by adding more starting material.

Experimentally, the chemicals used were Fisher

(5) H. M. Buck, W. Bloemhoff, and L. J. Oosterhoff, *Tetrahedron Letters*, No. 9, 5 (1960).

(6) D. L. Allara, B. C. Gilbert, and R. O. C. Norman, *Chem. Commun.*, 1, 319 (1965).

(7) W. F. Forbes and P. D. Sullivan, *Can. J. Chem.*, in press, and unpublished information.

(8) We are indebted to Drs. H. G. Cassidy and M. Hashimoto for a sample of this compound.

(9) J. R. Bolton and A. Carrington, *Mol. Phys.*, **5**, 161 (1962).

(10) J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 326 (1963).

reagent grade. Nitromethane was dried over calcium hydride and deoxygenated by passing dry nitrogen gas through the solution, followed by degassing under vacuum. The oxidation was carried out in an inverted U-tube, one arm of which was filled with anhydrous aluminum chloride and the compound to be oxidized (ca. 20 and 5 mg, respectively). This U-tube was connected to a vacuum line and nitromethane (1 ml) was distilled into the reaction mixture. The reaction proceeded at room temperature and the solution was subsequently transferred under vacuum into the capillary tube, which was then placed in the esr cavity.

The spectra were run on a JES-3BX spectrometer using a field-selector unit. Values of splitting constants are believed accurate to  $\pm 0.5\%$ .

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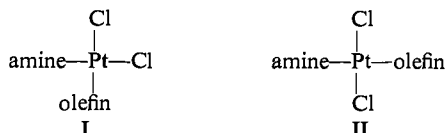
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### Induction of Asymmetry in *cis*-Dichloro(olefin)(amine)platinum(II) Complexes

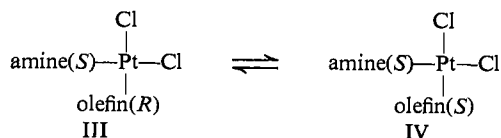
Sir:

In previous publications<sup>1</sup> we have described a number of platinum(II) complexes of olefins, containing a dissymmetric amine [(*R*)- or (*S*)- $\alpha$ -phenethylamine], *trans* or *cis* coordinated with respect to the olefin, of the general types I and II.



If the ethylene complex is allowed to equilibrate with an olefin having a symmetry different from  $C_{2v}$  or  $D_{2h}$ , two diastereoisomers are formed. For the *trans*-coordinated complexes no evidence has been found for the induction of asymmetry during the course of the exchange reaction.

For the *cis*-coordinated complexes we now report data showing that the equilibrium constant of the reaction



is generally different from unity.

As noted previously,<sup>2</sup> the deviation of the molecular rotation of an olefin complex (I) from that of the corresponding ethylene complex affords an indication that asymmetric induction occurs in the coordination of the olefin. A probable origin of the effect is a steric interaction between the amine and the *cis*-coordinated olefin. In fact, the deviation is particularly marked in the case of the complexes with olefins of the type *trans*-R-CH=CH-R.

(1) (a) G. Paiaro, P. Corradini, R. Palumbo, and A. Panunzi, *Makromol. Chem.*, **71**, 184 (1964); (b) G. Paiaro and A. Panunzi, *J. Am. Chem. Soc.*, **86**, 5148 (1964).

(2) G. Paiaro and A. Panunzi, *Tetrahedron Letters*, **8**, 441 (1965).

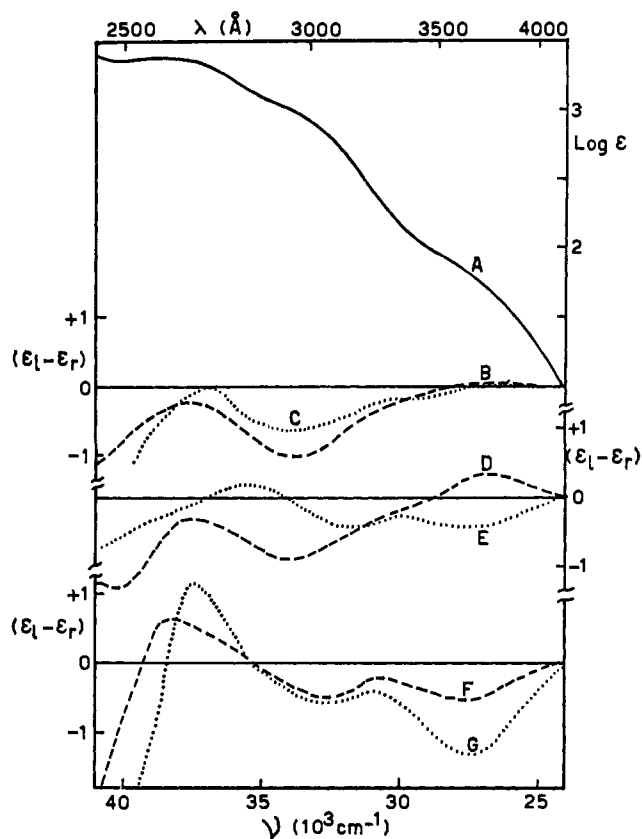


Figure 1. The electron absorption and circular dichroism spectra of *cis*-dichloroolefin-(*S*)- $\alpha$ -phenethylamineplatinum(II) complexes in ethanol solution: (A) the absorption spectrum, and (B) the circular dichroism spectrum of the ethylene complex; the circular dichroism spectra of (C) the *cis*-2-butene complex, (D) the (+) diastereoisomer and (E) the (-) diastereoisomers of the propylene complex, (F) the equilibrium mixture of diastereoisomers, and (G) the (-) diastereoisomer of the *trans*-2-butene complex.

The molecular rotations should indicate (Table I) that for the complexes with *trans*-2-butene, *trans*-3-hexene, and *trans*-1,4-dichlorobutene, there is a 25%

Table I.<sup>a</sup> Data of the Optical Activity<sup>b</sup> of *cis*-Dichloro(olefin)-(*S*)- $\alpha$ -phenethylamineplatinum(II) Complexes

Olefin	M <sub>D</sub> <sup>c</sup>	M <sub>D</sub> <sup>d</sup>
Ethylene	...	-226
(+) Propylene	+21	-238
(-) Propylene	-485	-238
(+) <i>t</i> -Butylethylene	-780	-197
(-) <i>t</i> -Butylethylene	+317	-197
(-) <i>trans</i> -2-Butene	-788	-365
(-) <i>trans</i> -3-Hexene	-675	-387
(-) <i>trans</i> -1,4-Dichloro-2-butene	-555	-394

<sup>a</sup> The reported data are average values. For the diastereoisomers the values are the maximum ones obtained after several recrystallizations. <sup>b</sup> In acetone at 25° (*c* 1.2-1.4). <sup>c</sup> Values for the pure diastereoisomers. <sup>d</sup> Values at equilibrium (after mutarotation) and values for the nonresolvable complexes.

or more excess of the (-) diastereoisomer in acetone solution at room temperature. Some deviation in the case of the *t*-butylethylene and propylene complexes, where both the (+) and the (-) diastereoisomers were isolated, was also found.