and Schmidt to be E_a = 50.2 ± 0.2 kcal/mol and log A = 14.09, measured over a 50° temperature range.[3] The disparity between the reported activation parameters for cyclopropylallene and its methyl derivative implies either that the methyl group exerts an 8.7 kcal/mol activation energy lowering effect or that one of the sets of activation parameters is in error.

The MINDO/3 calculations are of especial importance as the first application of this procedure to a sigmatropic process,[1] and therefore an instructive test case for the validity of this method as a technique for probing mechanism. The calculations[1] predict that the reaction is a "forbidden" process "in which a biradical intermediate is the transition state"; the "allowed" *si* process should be truly forbidden; the favored path should involve retention of configuration of the migrating group; and the calculated results explain why rearrangements of vinylcyclopropanes take place with almost complete loss of configuration.

For the one vinylcyclopropane rearrangement of fully known stereochemistry,[5] the conversion proceeds 73% by allowed stereochemical paths; the "allowed" *si* process amounts to 65% of the four stereochemically distinct routes; the two paths with inversion of configuration at the migrating carbon account for 70% of the four; the rearrangement certainly does not take place with almost complete loss of configuration. Similarly, the vinylcyclopropane rearrangement of *trans*-2-isopropenyl-1-cyanocyclopropane proceeds with 69% inversion of configuration at the migrating carbon.[6] Thus, the MINDO/3 model calculations for the vinylcyclopropane rearrangement are directly contrary to experimental fact.

The authors of the work[7] cited to support the generalization that vinylcyclopropanes rearrange "with almost complete loss of configuration"[1] recognized the great experimental difficulty associated with separating the geometrical isomerizations of vinylcyclopropyl substrates from the structural isomerizations leading to cyclopentenes. They made no careless claims regarding the manner in which overall loss of configuration occurs.[7]

While the MINDO/3 model may have merit in some applications,[8] the inaccurate description it gives of the vinylcyclopropane rearrangement reemphasizes the need for skepticism when confronted with its predictions on the stereochemical course and mechanism of reactions. A considerable amount of difficult experimental work has been expended in efforts to determine the stereochemical courses of [1,3] sigmatropic shifts and other thermal hydrocarbon rearrangements. It seems inappropriate to supersede cautious mechanistic speculation based on recognition of experimentally determined facts with mechanistic generalization based on calculations which do not even account for the gross stereochemical preferences observed in these reactions.

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Received January 5, 1976

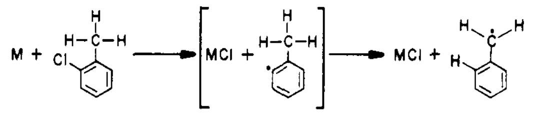
Rearrangement of the *o*-Tolyl Radical to the Benzyl Radical at Zero Pressure

Sir:

The high reactivity of free radical intermediates places stringent requirements on methods for their direct detection, but allows indirect observation by chemical trapping. Thus rearrangement of the *o*-tolyl radical to the benzyl radical was first detected by CIDNP measurements[1] in benzyl chloride, produced by the thermal decomposition of *o,o'*-dimethylbenzoyl peroxide in the presence of hexachloroacetone. Recently, the development of laser-induced fluorescence[2] has provided an experimental probe for measuring the vibrational energy distribution in products of gas-phase chemical reactions under conditions of very low concentration (10^{-15} M). Because of this extreme sensitivity, we are able to obtain the excitation spectrum of the benzyl radical resulting from the following reactions:

(1)

and



(2)

where M is a barium or sodium atom, providing direct evidence for the rearrangement of the *o*-tolyl radical.

Preliminary experiments showed that reactions of barium with various aryl chlorides under single collisions could be monitored by detecting BaCl fluorescence, excited by a tunable dye laser. The impetus for these studies was to determine substitutent effects on the BaCl spectrum, and hence to learn about the dynamics of the reactions.

Figure 1 shows the BaCl excitation spectra for the reactions of barium with benzyl chloride and with *o*-, *m*-, and *p*-chlorotoluene. The relative vibrational populations are calculated from the peak intensities using Franck–Condon factors tabulated elsewhere.[3] Relative rotational populations (assuming a Boltzmann distribution) are calculated by fitting computer-simulated spectra, using the known spectroscopic constants, to the observed spectra. Within experimental error, the BaCl product from each of the four reactions has the same average vibrational energy (~1.5 kcal/mol) and rotational energy (~1.5 kcal/mol). Since the exoergicity of these reactions[4] varies from ~40 kcal/mol for reaction 1 to ~25 kcal/mol for reaction 2, a substantial amount of energy must be released into translation and/or internal excitation of the resulting organic radical.[5]

Benzylic-type radicals are well-known reaction intermediates and have been detected in the condensed phase by ESR,[6] and in absorption following flash photolysis.[7] The latter technique also permitted Porter and co-workers[8] to observe the benzyl radical in the gas phase. Since then, extensive spectroscopic studies have been carried out by observing emission resulting from photon excitation in the solid phase[9a–c] and electron impact excitation in the gas phase.[9d,e] We report here the first gas-phase excitation spectrum of the benzyl radical (Figure 2a) obtained using a pulsed dye laser. The benzyl radical is produced from reaction 1 at a pressure of 2 × 10^{-4} Torr of benzyl chloride (barium oven temperature is approximately 1150 K). Under these conditions, no vibrational relaxation of the radical occurs, since the relative intensities in the corresponding BaCl spectrum are the same as at a pressure of 5 × 10^{-5} Torr.

The excitation spectrum of the benzyl radical also is ob-

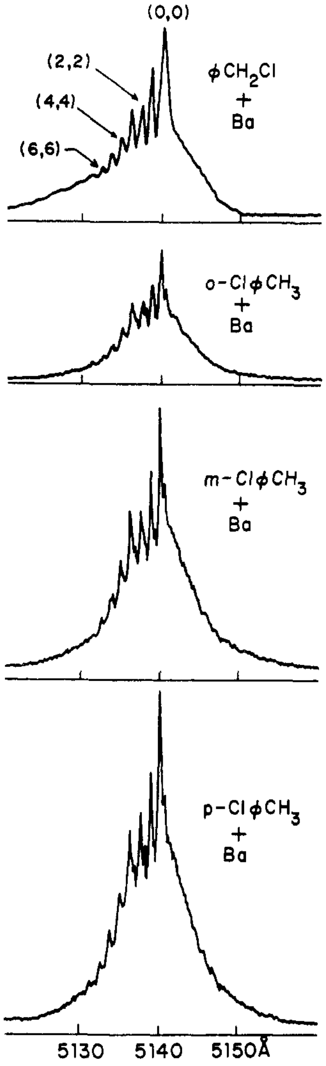


Figure 1. Laser-induced excitation spectra of BaCl ($C\ ^2\Pi_{3/2} - X\ ^2\Sigma^+$, $\Delta v = 0$ sequence) from reactions of Ba with various aromatic chlorides. Spectra, recorded at gas pressures of ~5×10^{-5} Torr are measured using a photomultiplier (extended S-20 cathode) detector and a gated boxcar integrator[2] (aperture duration 80 ns and time constant 1 μs).

served from reaction 2 (see Figure 2b). This result cannot be caused by secondary collisions because the collision frequency is much longer than the observation time (1-10 μs).[10] Therefore, detection of the benzyl radical from reaction 2 necessarily implies the occurrence of an intramolecular [1,3] hydrogen migration within the *o*-tolyl radical. No rearrangement was detected in reactions involving *m*- and *p*-chlorotoluene.[11,12]

A comparison of the rearranged and unrearranged benzyl spectra in Figure 2 shows that the relative intensities of these bands are nearly identical. Assuming that in each reaction the percent population of the ground-state vibrational levels in the A^1 transition is the same, the percent rearrangement is estimated from a comparison of the relative intensities of A^1 with the relative intensities of the (0,0) band of BaCl (at constant pressure). This gives an approximate value of 30% rearrangement, indicating the existence of an activation barrier for the rearrangement.

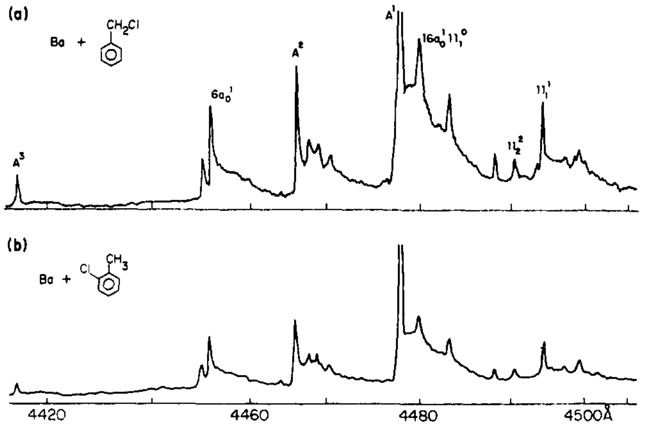


Figure 2. A portion of the benzyl excitation spectrum from (a) reaction 1 (gas pressure 2.2×10^{-4} Torr) and (b) reaction 2 (gas pressure 3×10^{-4} Torr). The visible spectrum spans the region 4300-4700 Å. Spectroscopic assignments are from the analysis of Cossart-Magos and Leach.[9e] In both spectra the A^1 peak is off scale. The ratio of the intensities of A^1:A^2 are ~2.5 in both cases. Relative intensities are reproducible to within 10%. Both spectra (resolution ±0.1 Å) are uncorrected for laser intensity. The boxcar integrator parameters are aperture duration 2 μs, aperture delay 100 ns, and time constant 100 μs.

Rearrangement of the *o*-tolyl radical may occur during the course of the collision with the metal atom (Ba or Na) or later as a unimolecular process. Analysis of the benzyl excitation spectrum may determine the actual energy distribution in several vibrational modes of the benzyl fragment itself. We are at present investigating further the nature of the rearrangement and the question of energy distribution in the benzyl radical by studying the thermolyses of *o,o'*-dimethylazobenzene and α,α'-azotoluene. These preliminary results demonstrate that it will be possible to study many other types of organic radicals by laser-induced-fluorescence detection.

Acknowledgments. We thank Professor Sydney Leach for providing us with unpublished spectroscopic data on the benzyl radical. Support by the National Science Foundation is gratefully acknowledged.

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Received May 14, 1976