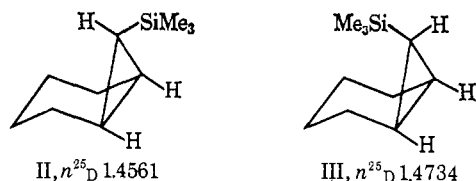


pounds by Chvalovský, *et al.*⁷ Such CuCl-catalyzed decomposition of $\text{Me}_3\text{SiCHN}_2$ in benzene in the presence of an excess of cyclohexene gave as the major product (in 65% yield) *anti*-7-trimethylsilylnorcarane (II). Three minor products were the other 7-trimethylsilylnorcarane isomer (III) (7%), *trans*-1,2-bis(trimethylsilyl)ethylene (13%), and the *cis* isomer (9%). All products were isolated as pure materials by glpc. The identification of the 7-trimethylsilylnorcarane iso-



mers was based on their analyses and their infrared and nmr spectra. Particularly the latter were of value: in the nmr spectrum (in CCl_4) of II, the Me_3Si group appeared as a singlet at τ 10.09 and the cyclopropane proton *gem* to the trimethylsilyl group as a triplet at τ 10.69 ($J = 7$ cps). In III these resonances were seen at τ 9.88 and 10.41 (triplet, $J = 10$ cps). In support of these assignments we may note that previous work has established that in norcaranes the 7-proton *syn* to the $-(\text{CH}_2)_4-$ bridge is more highly shielded than is the proton which is *anti* to the tetramethylene bridge and, furthermore, that the magnitude of *cis* coupling between vicinal protons in cyclopropanes is greater than that of *trans* coupling.⁸ The CuCl-catalyzed decomposition of trimethylsilyldiazomethane in the presence of an excess of *cis*-4-methyl-2-pentene gave, in addition to *trans*- and *cis*-1,2-bis(trimethylsilyl)ethylenes, the two isomers of 1-methyl-2-isopropyl-3-trimethylsilylcyclopropane. Further carbenoid reactions of trimethylsilyldiazomethane are under investigation.

In conclusion, it should be noted that trimethylsilylcarbene has been proposed as an intermediate previously: in the $\text{Me}_3\text{SiCHCl}_2 + \text{Na-K}$ gas phase reaction (which gave $\text{Me}_2\text{HSiCH}=\text{CH}_2$),⁹ in the rather complicated reaction of $\text{Me}_3\text{SiCH}_2\text{Cl}$ with lithium,¹⁰ and in the reaction of $\text{Me}_3\text{SiCH}_2\text{Cl}$ with *n*-butyllithium.¹¹ The latter reaction was carried out in the presence of cyclohexene, but no 7-trimethylsilylnorcarane was obtained. More recently, a brief report concerning trimethylsilylcarboethoxycarbene has appeared.¹²

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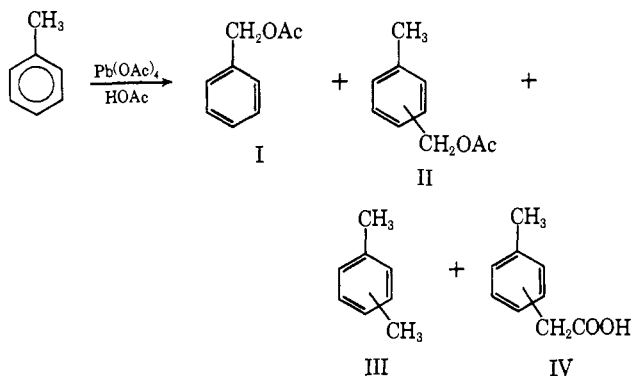
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Oxidation by Metal Salts. I. The Reaction of Lead Tetraacetate with Toluene

Sir:

Despite many investigations of the oxidation of alkylaromatics by lead tetraacetate, the mechanisms of these processes are not fully understood, and some conflicting theories and interpretations are current in the literature.¹ In particular, the formation of products in which the $-\text{CH}_2\text{OAc}$ group has been added to the aromatic ring has been observed in a few instances² and the mechanism of their formation has not been adequately explained. We wish to report our studies on the oxidation of toluene by lead tetraacetate and present a general mechanism which explains the production of these adducts and predicts the conditions conducive to their formation.

The oxidation of toluene with lead tetraacetate in refluxing acetic acid containing anhydrous potassium acetate under a nitrogen atmosphere³ yielded two major products, benzyl acetate (I) and methylbenzyl acetate (II) (mixture of isomers, predominantly *ortho*), along with minor amounts of xylenes (III) and tolylacetic acids (IV).



In a typical experiment in which 21.7 mmoles of lead tetraacetate was added to a solution of toluene (15-fold excess) in acetic acid, the following product yields were obtained: benzyl acetate (7.04 mmoles), methylbenzyl acetates (4.95 mmoles), xylenes (1.91

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(3) In the presence of oxygen, the reaction times increased and the yields of products based on lead tetraacetate consumed decreased, as would be expected in a radical chain process. These observations are in accord with those reported by Davidson and Triggs.^{2d}

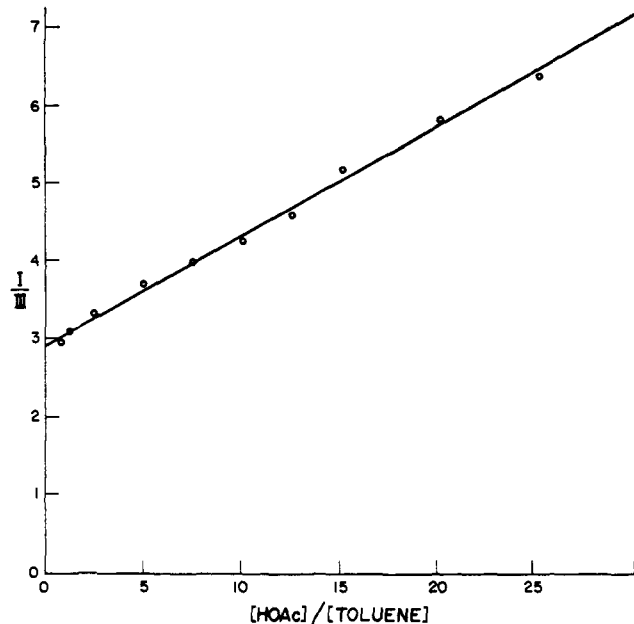


Figure 1. Oxidation of toluene by lead tetraacetate. Ratio of benzyl acetate to xylene formed.

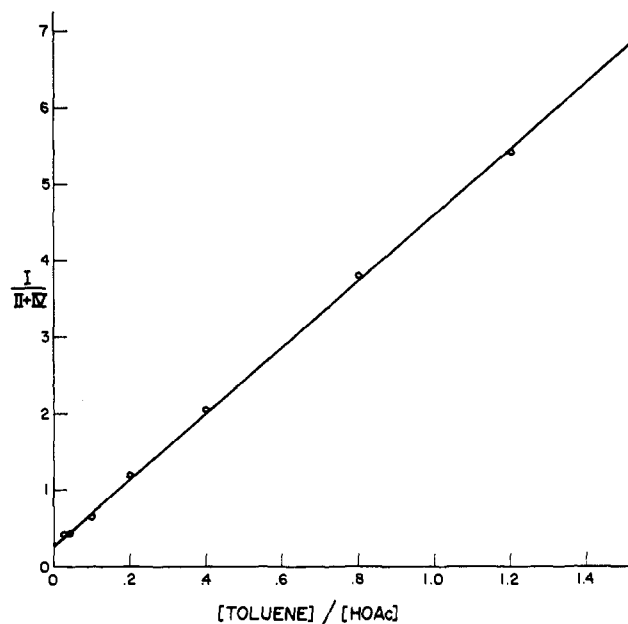
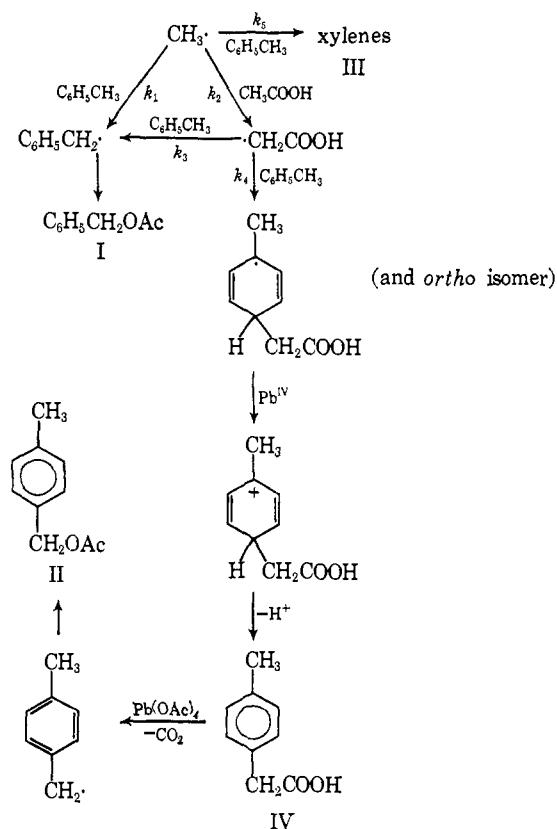
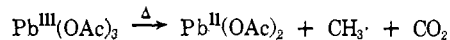
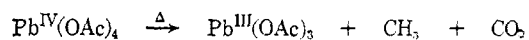


Figure 2. Oxidation of toluene by lead tetraacetate. Ratio of products.

mmoles), and tolylacetic acids (1.05 mmoles), thereby accounting for 92% of the lead tetraacetate used.⁴

It was found that the ratio of these products varied with the acetic acid:toluene ratio used in the reaction

Scheme I



(4) This calculation is based on the stoichiometry of 1 mole of lead tetraacetate used per mole of I, III, and IV produced and 2 moles of lead tetraacetate per mole of II obtained.

(Figures 1 and 2). The formation of II under our conditions cannot derive from the oxidation of xylenes produced in the course of the reaction in view of the high molar ratio of toluene to lead tetraacetate employed (greater than 15:1) and the reactivity of xylenes relative to toluene determined by competitive techniques (relative reactivity of toluene, 1; *m*-xylene, 2.3; *p*-xylene, 3.1).

To account for the formation of methylbenzyl acetates and the dependence of the product ratio on the acetic acid:toluene ratio used, we propose the mechanism given in Scheme I.

The facile decarboxylation of tolylacetic acid (IV) ultimately yielding methylbenzyl acetates (III) is quite consistent with the known mechanism of the oxidation of carboxylic acids by lead tetraacetate.⁵

Applying a steady-state kinetic treatment to the mechanistic scheme shown, one can derive the following relationships

$$\frac{d[\text{II}]}{d[\text{II} + \text{IV}]} = \frac{k_1}{k_2}(\alpha + 1) \frac{[\text{toluene}]}{[\text{HOAc}]} + \alpha$$

$$\frac{d[\text{I}]}{d[\text{III}]} = \frac{k_2}{k_5} \left(\frac{\alpha}{\alpha + 1} \right) \frac{[\text{HOAc}]}{[\text{toluene}]} + \frac{k_1}{k_5}$$

where $\alpha = k_3/k_4$. This would predict a linear relationship between the product ratio and the proper ratio of toluene and acetic acid used. Figures 1 and 2 show that the experimental results agree quite well with the expected linear relationship.

Relative rate constants were obtained from the slopes and intercepts of the two lines. From the intercept of Figure 1, k_1/k_5 was found to be equal to 2.9, *i.e.*, side-chain hydrogen abstraction by the $\cdot\text{CH}_3$ radical from toluene occurs approximately three times faster than its addition to the aromatic nucleus.

Our value appears to be somewhat lower than the reported values⁶ of 4 and 5; however, this could be due

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to the difference in conditions employed. A possible explanation is that the addition of methyl radical to the aromatic ring is reversible but in our system the presence of lead tetraacetate intercepts the radical intermediate very rapidly by electron transfer and hence decreases the over-all reversibility of addition. This could also explain the high percentage of the *o*-xylene isomer produced in our system, 64%, compared with the reported value of 56% using acetyl peroxide.⁷

From the intercept of Figure 2 the ratio k_3/k_4 was found to be 0.27; *i.e.*, the $\cdot\text{CH}_2\text{COOH}$ radical, unlike the more reactive methyl radical, adds to toluene faster than it abstracts the benzylic hydrogen atom. The difference in behavior between this radical and methyl radical can be attributed to the electrophilicity of the $\cdot\text{CH}_2\text{COOH}$ radical and/or its greater stability, as indicated by its ready formation in competition with the resonance stabilized benzyl radical. The more stable radical would be expected to favor the reaction of lower activation energy, which in this case is addition to the ring.⁸

The average ratio k_1/k_2 obtained from the slopes of Figures 1 and 2 was found to be 3.9 ± 0.5 ; *i.e.*, the $\cdot\text{CH}_3$ radical abstracts an α -hydrogen atom from toluene four times as fast as it does from acetic acid.⁹ The observed reactivity of acetic acid toward hydrogen abstraction by methyl radical, which is relatively insensitive to polar effects,¹⁰ suggests the existence of considerable resonance stabilization for the $\cdot\text{CH}_2\text{COOH}$ radical.

Our proposed mechanism serves to explain the conflicting observations in the literature and allows one to predict the conditions required to optimize the yield of any desired product, thereby increasing the synthetic utility of lead tetraacetate.

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Differences in the Reactivities of Trifluoromethyl and Methyl Radicals Produced by Photodissociation¹

Sir:

Laser emission from the $^2\text{P}_{1/2} \rightarrow ^2\text{P}_{3/2}$ iodine atom transition has been observed in the photodissociation of several alkyl iodides.^{2,3} The optical gain coefficient in a laser depends inversely on the Doppler width of the emitted line, and this in turn is related to the molecular dynamics of the photodissociation process.⁴ In this communication we report preliminary results of the photolysis of trifluoroiodomethane in the presence of

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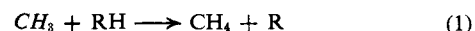
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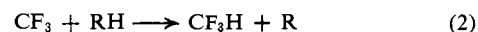
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hydrogen-containing substrates. The contrast in the behavior of these systems with the analogous methyl iodide systems is relevant to the question of energy distribution in photodissociation.

The near-ultraviolet absorption spectrum of CF_3I ⁵ is very similar to that of CH_3I ,⁶ as is the estimated C-I bond dissociation energy (54 kcal/mole).⁷ In both cases, the iodine atom from dissociation is excited to the $^2\text{P}_{1/2}$ state, 22 kcal/mole above the ground state. With 2537-Å radiation, this leaves 36 kcal/mole to be distributed among the radical and the iodine atom. If the energy is entirely translational, this division is determined by the conservation of momentum and energy; the CF_3 radical is produced with 23 kcal/mole of excess energy, whereas the CH_3 radical would have 32 kcal/mole. Methyl radicals produced in this way are capable of undergoing hydrogen abstraction reactions of the type⁸⁻¹³



where RH is methyl iodide or an added hydrogenic compound. Activation energies for such reactions are typically several kilocalories per mole. For analogous reactions of the CF_3 radical



the activation energy is 10–11 kcal/mole when RH is H_2 ¹⁴ or CH_4 .¹⁵ The similarity in the energetics of the $\text{CF}_3\text{I-RH}$ and $\text{CH}_3\text{I-RH}$ systems would lead one to expect a quantum yield for fluoroform in reaction 2 comparable to that for methane in reaction 1. The latter value is 3×10^{-3} for the photolysis of methyl iodide at 2537 Å and 1.5×10^{-4} for the photolysis of CD_3I at 3130 Å (13 kcal/mole of excess energy).

The data of Table I show that this is not the case. In

Table I. Photolysis of CF_3I by 2537-Å Radiation at Room Temperature

Reactant concn ^a		Product concn ^b		$\Phi_{\text{CF}_3\text{H}}$
CF_3I	Other	CF_3H	Other	
1.22	6.23 (H_2)	0.22		3×10^{-5}
0.19	0.82 (CH_4)	≤ 0.005		$\leq 5 \times 10^{-6}$
0.15	0.27 (CH_3I)	< 0.001	14.4 (CH_4) 0.12 (C_2H_6)	$< 5 \times 10^{-6}$
0.28	0.23 (NO)		220 (CF_3NO)	

^a In units of 10^{-3} M. ^b In units of 10^{-6} M.

particular, the experiment with a mixture of CH_3I and CF_3I shows that $\Phi_{\text{CF}_3\text{H}}/\Phi_{\text{CH}_4} \leq 3 \times 10^{-4}$. No C_2F_6 was detected in the reaction products from any of these

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