the 865 observed intensities.[4] The fractional atomic coordinates relative to a twofold axis through the origin are given in Table I;[4] Figure 1 presents bond distances and agles in the solid-state molecular conformation.

Although no attempt was made to locate the hydrogen atoms, the positions of all but the methyl hydrogens may be defined within small limits. The molecular geometry clearly indicates that the methoxy group is α, or cis, to the hydrogen attached to C-6. The sulfur atom is displaced by 0.76 Å from the least-squares plane (P1) of the five other atoms of the dihydrothiazine ring (rms displacement of these five atoms 0.06 Å). The dihedral angle between P1 and the least-squares plane (P2) through the four atoms of the β-lactam ring (rms displacement 0.00 Å) is 30°. The least-squares plane (P3) of the exocyclic amide and benzylic carbon atoms, N-20, O-22, C-21, C-23, defines dihedral angles of 53 and 108° with P2 and the plane of the phenyl ring, respectively. The peptide-like hydrogen bonding between the exocyclic amide groups of neighboring molecules commonly found in crystal structures of cephalosporin derivatives[5] is not present in this crystal structure, nor is any other type of (N-20)–H···O hydrogen bonding evident. Instead, the (N-20)–H bond points directly toward the sulfur atom, S^1, of a (*b*) translationally related molecule (see Figure 1 for the intermolecular geometry of this approach), with S^1 displaced by only 0.67 Å from the exocyclic amide plane, P3.

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Registry No.—**1,** 36954-82-2; **2,** 37787-02-3; **3** (X = OAc), 37787-03-4; **4,** 51932-72-0; **5,** 51932-73-1; **6,** 37786-97-3.

Supplementary Material Available. Tables of fractional coordinates and isotropic temperature factors will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-74-2794.

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Oxidation–Reduction of 9-(*p*-Methoxyphenyl)-9-fluorenylacetaldehyde on Activated Alumina

Frederick A. Lamb, Philip N. Cote, Bruce Slutsky, and Bruno M. Vittimberga*[1]

Department of Chemistry, University of Rhode Island, Kingston, Rhode Island 02881

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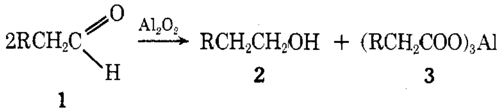
During a study of the alumina-catalyzed condensation reactions of aldehydes, we found that when 9-(*p*-methoxyphenyl)-9-fluorenylacetaldehyde (**1**) is chromatogrammed in the usual manner through a column prepared with activated alumina (Woelm neutral, activity grade I, pH 7.5), it undergoes an oxidation and a reduction reaction, reminiscent of the Cannizzaro reaction, yielding, in approximately equal amounts, the alcohol **2**, mp 107.5–109°, and a salt tentatively assigned the aluminum salt **3**.[2] The overall yield for the reaction was 90% based on converted aldehyde.



$$2RCH_2C(=O)H \xrightarrow{Al_2O_3} RCH_2CH_2OH + (RCH_2COO)_3Al$$

1 **2** **3**

R = [9-(*p*-methoxyphenyl)-9-fluorenyl]

Structure **2** was readily assigned on the basis of infrared and nmr analysis. The infrared spectrum of **3** is typical of a carboxylate salt. For identification purposes **3** was converted to the parent acid (**4**), mp 193–195°, by treatment with 5% sulfuric acid and extraction with ether. The parent acid was then identified by the usual spectral methods. Final confirmation of structure was obtained by synthesis. Reduction of **1** with sodium borohydride yields **2** (94%) while oxidation with silver oxide yields **4** (89%). The identity of these compounds with those obtained from the column was established by comparison of ir and nmr spectra and by mixture melting point determination.

The results were found to be reproducible. The length of the column and the amount of alumina used did not affect the course of the reaction.[3] Elution was carried out with mixtures of hexane, benzene, chloroform, ether, and methanol in increasing polarity and finally with 5% acetic acid–methanol solution. Unreacted aldehyde was eluted in early chloroform fractions followed by **2**. The compound **3** was isolated from the column with 5% acetic acid–methanol elution. Apparently the alumina surface serves a unique role in this conversion, since the base-catalyzed reaction of **1** under the usual Cannizzaro reaction conditions gave no reaction.[4]

The alumina oxidation of alcohols to carboxylic acids at elevated temperatures[5,6] and the reduction of benzaldehydes to benzyl alcohols[7] have previously been reported in the literature. Very recently, Kuiper, *et al.*,[8] reported a spectral study of benzaldehyde adsorbed on alumina. They observed bands in the infrared and Raman spectra which they attributed to benzoate and benzyl alcoholate bonds formed on the alumina surface. Products were not isolated, though benzyl alcohol was detected by gas chromatography.

The present study reports the first instance in which both oxidation and reduction products have been isolated from a column reaction.

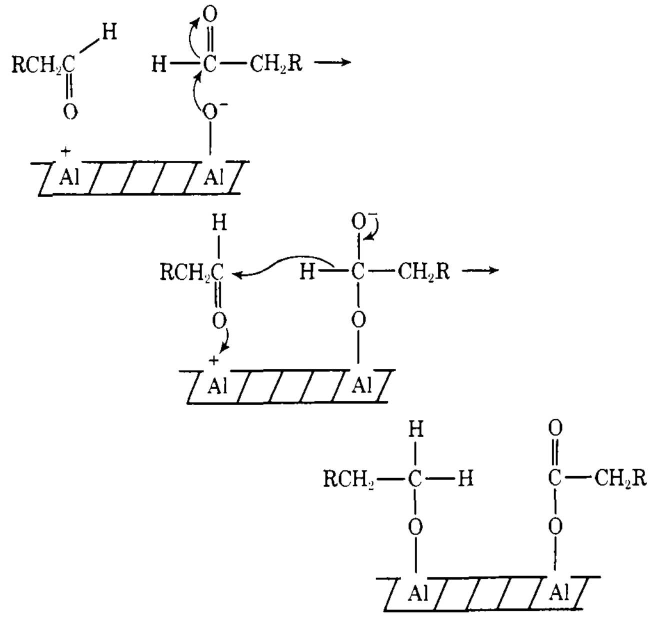
It would be rather premature to attempt to describe a precise mechanism at this time without additional information. However, a general mechanism can be postulated using Peri's description of the γ-alumina catalyst.[9] According to this description, the alumina surface is composed of exposed aluminum ions, oxide groups, and hydroxide groups of various basicity.

If one aldehyde group reacts with an oxide group while a second molecule reacts at a neighboring exposed aluminum ion site, hydride transfer would occur as shown in Scheme I.[10,11] Upon elution, the catalyst surface undergoes an exchange reaction, releasing **2** and **3**.

It is interesting to note that 9-carbazolylacetaldehyde, which is substituted with a less bulky group at the α carbon, undergoes an alumina-catalyzed condensation reaction instead.[12] The condensation may require enol formation, which is more favorable in the carbazole compound than in **1**.[13]

The mechanism of this reaction is under investigation and results will be reported at a later time.

Scheme I



Experimental Section[14]

Melting points are uncorrected and were determined on a Mel-Temp melting point apparatus. The nuclear magnetic resonance (nmr) spectra were recorded on a Jeolco C-60HL spectrometer at 60 MHz using tetramethylsilane as an internal standard. Infrared spectra were determined in potassium bromide on a Perkin-Elmer Model 700 spectrophotometer.

Reaction of 1 with Alumina. 9-(*p*-Methoxyphenyl)-9-fluorenylacetaldehyde (**1**, 1.00 g) was dissolved in benzene-hexane (1:1) and placed on a column prepared with 100 g of activated alumina (Woelm neutral, activity grade I, pH 7.5). The column was eluted with benzene-hexane (1:1), benzene, benzene-chloroform (1:1), chloroform, chloroform-ether (9:1), chloroform-ether (3:1), ether, methanol, and 5% acetic acid in methanol. Unreacted aldehyde (0.474 g) was eluted in early chloroform fractions as determined by mixture melting point determination and infrared analysis. This was followed by elution of the alcohol **2** (0.254 g, 48%): mp 107.5-109° (tlc); ir 3330 cm^{-1} (OH); nmr ($CDCl_3$) δ 7.3 (m, 12, Ar), 3.7 (s, 3, CH_3O), 2.97 (t, 2, J = 6.0 Hz, $-CH_2-$), 2.87 (t, 2, J = 6.0 Hz, $-CH_2O$), and 1.27 (s, 1, OH). The band at δ 1.27 disappeared when the nmr spectrum was run in D_2O. The compound **3** was isolated from the column with 5% acetic acid-methanol elution.

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Registry No.—**1**, 31462-49-4; **2**, 50515-86-1; **3**, 50515-87-2; **4**, 50515-88-3.

Supplementary Material Available. A supplementary experimental section will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JOC-74-2796.

References and Notes

(1) To whom correspondence should be addressed.

(2) An acid-treated sample of the salt gave a positive aluminum lake test. No test was obtained prior to acid treatment.

(3) We have evidence, however, which suggests that there is a direct relationship between the amount of alumina used and the amount of reaction.

(4) Under more severe conditions (50% aqueous sodium hydroxide, 130°, 2.5 hr) a small amount of acid and alcohol formed, though the principal reaction was decarbonylation.

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(10) At this point the mechanism would be similar to that proposed for the base-catalyzed Cannizzaro reaction. See J. Hine, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1962, p 267, and references cited therein.

(11) A similar mechanism has recently been proposed by Kuiper, *et al.* (ref 8).

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(13) Preliminary studies indicate that aldehydes that are not substituted with large groups on the α carbon, such as hexanal or heptanal, undergo the aldol condensation on activated alumina.

(14) See paragraph at end of paper regarding supplementary material.

Calculation of Resonance Effect Reaction Parameters. I. Arylene, Vinylene, and Ethynylene Skeletal Groups

Marvin Charton

Department of Chemistry, School of Science, Pratt Institute, Brooklyn, New York 11205

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Consider a set of compounds, XGY, in which X represents a substituent, Y a reaction site, and G the skeletal group to which X and Y are bonded. We have previously shown that the Hammett ρ values for various groups G may be calculated in the case of the ionization constants of carboxylic acids[1,2] and rates of alkaline hydrolysis of ethyl carboxylates.[2,3]

Taft[4] has proposed an expanded form of the Hammett equation. The ρ values calculated for groups G may be

$$Q_X = \alpha\sigma_{IX} + \beta\sigma_{RX} + h \tag{1}$$

identified with the α values of eq 1, as α represents the magnitude of the localized electrical effect, and these ρ values were calculated from an equation derived by combining the Hammett and Kirkwood-Westheimer equations. It seemed of interest to develop a method for calculating the β parameters of eq 1 as a function of G.

Dewar and Grisdale,[5] in calculating new σ constants for substituted naphthalene and biphenyl sets, have proposed that the delocalized effect is proportional to the formal negative charge q (at the carbon atom of G which bears the reaction site) in the ion $^-CH_2GH$. When G is derived from an alternant hydrocarbon, q may be simply and easily calculated[6] by the method developed by Dewar. We have examined the relation

$$\beta_G = mq_G + c \tag{2}$$

Equation 2 has been studied for the ionization of carboxylic acids in water at 25°, in 50% v/v $EtOH-H_2O$ at 25°, and in 80% v/v methyl cellosolve-H_2O at 25°. Also studied were the rates of alkaline hydrolysis of ethyl carboxylates in 85-88.7% $EtOH-H_2O$ at 30° and the rates of reaction of carboxylic acids with diphenyldiazomethane at 30° in EtOH.

We have also examined the applicability of eq 2 to the ionization of azaarenes. The q values for the corresponding arene, G, have been used in the correlation on the assumption that q_N, the charge on the nitrogen, will be directly