phenyl groups are *cis*, and the observation of constancy of product suggests thermodynamic control. If compound **3** contained *trans*-phenyl groups, the nmr spectrum might be expected to show nonequivalence of the hydrogen atoms at the 2 and 5 positions. Since the methynyl hydrogens appear as only one singlet[12] (at δ 6.07), it seems most likely that they are *cis*, for the S-methyl group would provide a different chemical environment for a *trans* pair. An unfavorable interaction between the S-methyl group and an adjacent phenyl group also leads to the tentative conclusion that a *cis*-diphenyl array is thermodynamically favored over the opposite configuration.

The production of the same product from each of the isomeric compounds **2a**, **2b**, and **2c** is inconsistent with a concerted 1,4 addition[13] of the methanesulfenyl group, CH_3S^+, to the diene. In such a reaction, **2b** should yield a product that is stereoisomeric with that obtained from either **2a** or **2c**. A concerted, stereospecific addition has been observed, for example, in the reaction of sulfur dioxide with 1,3-dienes.[14,15] Thus, the reaction of **1** with **2a**, **2b**, or **2c** probably proceeds *via* 1,2 addition followed by rearrangement, even though it has been impossible to detect any primary product under a variety of reaction conditions and with different isolation techniques. Our results show direct agreement with the conclusions of Mueller and Butler[4,5] that addition of sulfenyl compounds to conjugated dienes occurs in a 1,2 manner.

Experimental Section

Micoanalyses on the dihydrothiophene products were carried out by Elek Microanalytical Laboratories, Torrance, Calif., and Galbraith Laboratories, Knoxville, Tenn. All solvents were reagent grade and were dried over Linde 4A Molecular Sieves before use. **2a** was prepared by the method described by Fieser;[16] **2b** was prepared from the Wittig reaction of triphenylcinnamylphosphonium bromide with benzaldehyde;[17] and **2c** was prepared by catalytic hydrogenation of 1,4-diphenylbutadiyne as described by Lindlar.[18] The 2,3-diphenylbutadiene was prepared from acetophenone pinacol by the prodedure of Alder and Hayden.[19] All melting points are uncorrected.

2,5-Dihydro-2,5-diphenyl-S-methylthiophenonium 2,4,6-Trinitrobenzenesulfonate.—On the fritted disk of a modified Schlenk tube apparatus as previously described[11] was placed a solution of 5.23 g (0.01 mol) of silver 2,4,6-trinitrobenzenesulfonate (acetonitrile complex)[10] in 20 ml of dry nitromethane. Dry nitrogen was passed upward through the fritted disk to keep the reaction mixture blanketed with an inert atmosphere. A solution of 0.01 mol of methanesulfenyl bromide in 35 ml of dichloromethane (solution prepared *in situ* from bromine and dimethyl disulfide) was added to the silver salt solution, with immediate formation of a silver bromide precipitate. The solution was stirred for 30 min, then filtered free of silver bromide by forcing the mixture through the fritted disk with positive nitrogen pressure above and a partial vacuum below. The solution of methanesulfenyl 2,4,6-trinitrobenzenesulfonate was mixed with 2.06 g (0.01 mol) of one of the isomeric 1,4-diphenylbutadienes in 35 ml of dichloromethane. The color of the reaction mixture immediately turned a deep purple. The product was isolated by the addition of about 650 ml of anhydrous ether to the stirred solution. The precipitate was dissolved in acetone and crystallized from warm acetone–ether to yield crystals of the thio phenonium salt, mp 132–135.5° dec. The yields from the three isomers of 1,4-diphenylbutadiene were as follows: *trans,trans*, 49%; *cis,trans*, 15%; *cis,cis*, 29%.

Anal. Calcd for $C_{23}H_{19}N_3O_9S_2$: C, 50.64; H, 3.51; N, 7.70; S, 11.75; mol wt, 546. Found: C, 50.90; H, 3.72; N, 7.08; S, 11.37; mol wt, 565 (by vapor pressure osmometry).

The nmr spectrum of the product in perdeuterionitromethane showed peaks at δ 3.40 (singlet, three protons assigned to S-methyl); 6.07 (singlet, two methynyl protons); 6.59 (singlet, two vinyl protons); 7.45 (broad singlet, ten phenyl protons); and 8.50 (singlet, two protons from the anion).

2,5-Dihydro-3,4-diphenyl-S-methylthiophenonium 2,4,6-Trinitrobenzenesulfonate.—In a manner exactly analogous to that described above, 0.01 mol of methanesulfenyl 2,4,6-trinitrobenzenesulfonate and 0.01 mol of 2,3-diphenylbutadiene yielded 3.40 g of an amorphous solid that melted with decomposition at about 110°. The desired product could be isolated only with great difficulty from this mixture. After many recrystallizations from acetone–ether, 30 mg of an analytically consistent sample of 2,5-dihydro-3,4-diphenyl-S-methylthiophenonium 2,4,6-trinitrobenzenesulfonate was isolated: mp 230.5–231.5°.

Anal. Calcd for $C_{23}H_{19}N_3O_9S_2$: C, 50.64; H, 3.51; N, 7.70; S, 11.75. Found: C, 50.75; H, 3.48; N, 7.75; S, 11.81.

Registry No.—**3**, 20178-09-0; **5**, 20178-10-3.

---

[12] The absence of splitting between the methynyl protons and the adjacent vinyl protons can be accounted for by a dihedral angle that may be as large as 80° owing to ring distortion from phenyl–phenyl interaction.

[13] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

[14] W. L. Mock, *J. Amer. Chem. Soc.*, **88**, 2857 (1966).

[15] S. D. McGregor and D. M. Lemal, *ibid.*, **88**, 2858 (1966).

[16] L. F. Fieser, "Organic Experiments," 2nd ed, Raytheon Education Co., Lexington, Mass., 1968, pp 121–123.

[17] H. Misumi and M. Nakagawa, *Bull. Chem. Soc. Jap.*, **36**, 399 (1963).

[18] H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

[19] K. Alder and J. Hayden, *Ann.*, **570**, 201 (1950).

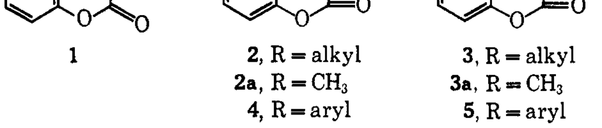
Concerning the Postulated Rearrangement of 4-Acyloxy- and 4-Aroyloxycoumarins to 5-Acyl- and 5-Aroyl-4-hydroxycoumarins

J. F. STEPHEN AND E. MARCUS

Research and Development Department,
Union Carbide Corporation, Chemicals and Plastics,
South Charleston, West Virginia

Received January 13, 1969

There have been a number of reports on the acylation of 4-hydroxycoumarin (**1**) with aliphatic and aromatic acid chlorides.[1-3] Eisenhauer and Link[2] studied the mechanism of the reaction of **1** with aliphatic acid chlorides in pyridine leading to 3-acyl-4-hydroxycoumarins (**3**), using acetyl chloride as representative of this class, and found that the initial product formed was 4-acetoxycoumarin (**2a**), which then rearranged to 3-acetyl-4-hydroxycoumarin (**3a**). These authors also investigated the reaction of **1** with various aromatic acid chlorides in pyridine and observed that the initially formed esters **4** did not rearrange to the corresponding 3-aroyl-4-hydroxycoumarins (**5**) as in the aliphatic series.[3] The ester **4a**, however, can be rearranged to 3-benzoyl-4-hydroxycoumarin (**5a**) with aluminum chloride.[4]



1

2, R = alkyl
2a, R = CH_3
4, R = aryl
4a, R = C_6H_5

3, R = alkyl
3a, R = CH_3
5, R = aryl
5a, R = C_6H_5

---

[1] T. Ukita, S. Nojima, and M. Matsumoto, *J. Amer. Chem. Soc.*, **72**, 5143 (1950).

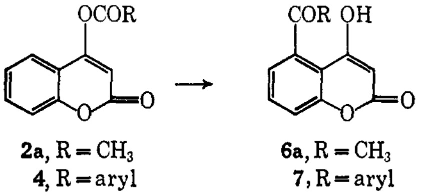
[2] H. R. Eisenhauer and K. P. Link, *ibid.*, **75**, 2044 (1953).

[3] H. R. Eisenhauer and K. P. Link, *ibid.*, **75**, 2046 (1953).

[4] K. Veres and V. Horak, *Coll. Czech. Chem. Commun.*, **20**, 371 (1955).

In view of these observations, the recent report of Woods[5] concerning the rearrangement of 4-acetoxycoumarin (**2a**) and various 4-aroyloxycoumarins (**4**) to 5-acetyl-4-hydroxycoumarin (**6a**) and the corresponding 5-aroyl-4-hydroxycoumarins (**7**) (Scheme I) was noted with considerable interest. However, these results were surprising, not only because of the unprecedented course of the rearrangements involved, but also because recent studies[6] in these laboratories have shown that the related 4-acetoxy-6-methyl-2-pyrone (**8a**) rearranges to dehydroacetic acid (**9a**) with some degradation to triacetic acid lactone (**10**) in refluxing trifluoroacetic acid (Scheme II). 4-Benzoyloxy-6-methyl-2-pyrone (**11a**), on the other hand, is rearranged only with difficulty[6] to 3-benzoyl-4-hydroxy-6-methyl-2-pyrone (**12a**) and suffers considerable degradation to **10** and benzoic acid, under similar conditions. It would be supposed *a priori* that analogous rearrangements would occur with 4-acetoxycoumarin (**2a**) and 4-benzoyloxycoumarin (**4a**) in trifluoroacetic acid. We wish to report at this time our observations concerning the fate of **2a** and **4a** upon treatment with trifluoroacetic acid.

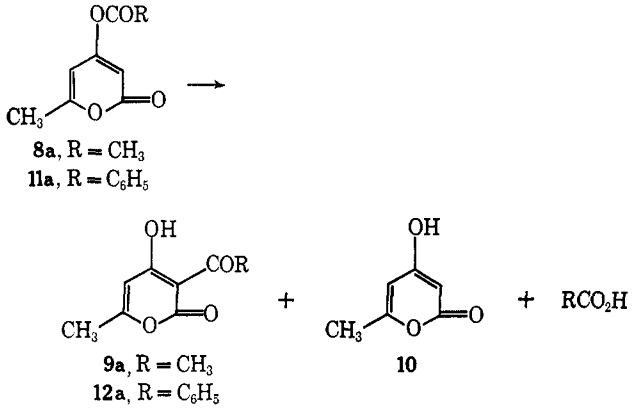
Scheme I



2a, R = CH_3
4, R = aryl

6a, R = CH_3
7, R = aryl

Scheme II



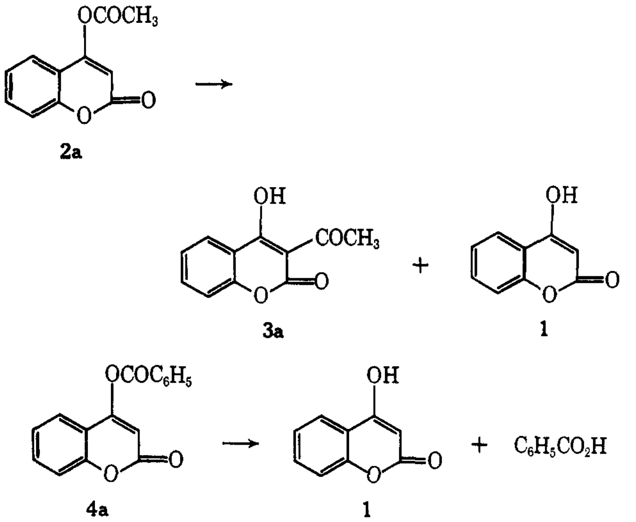
8a, R = CH_3
11a, R = C_6H_5

9a, R = CH_3
12a, R = C_6H_5

10

4-Acetoxycoumarin (**2a**) was treated with trifluoroacetic acid under reflux for 15.5 hr. Thin layer chromatography of the product mixture showed the presence of 4-hydroxycoumarin (**1**), 3-acetyl-4-hydroxycoumarin (**3a**), as well as unchanged **2a** (Scheme III). Nmr analysis (DMF-d_6) indicated that the mixture contained about 46 mol % of **1**, 43 mol % of **3a**, and 11 mol % of **2a**. Compounds **1** and **3a** were separated from unchanged **2a** by extraction into aqueous sodium carbonate. 3-Acetyl-4-hydroxycoumarin (**3a**) was isolated in 29% yield by acidification of the carbonate extract followed by fractional crystallization of the resulting solid from ethanol. 4-Hydroxycoumarin (**1**) was obtained in 40% yield[7] by evaporation of the ethanol mother liquor from the above crystallization, followed by recrystallization from water. The structures of **3a** and **1** were confirmed by comparison of their ir and nmr spectra and mixture melting point determinations with authentic **3a** and **1**, respectively. Structure **3a** was further substantiated when **3a** was converted into 2-methylchromone (**13**) upon refluxing with concentrated hydrochloric acid in ethanol solution.[8] No formation of 5-acetyl-4-hydroxycoumarin (**6a**) was observed in this reaction.

Scheme III



Treatment of 4-benzoyloxycoumarin (**4a**) with trifluoroacetic acid under reflux for 15 2/3 hr gave a mixture, thin layer chromatography of which indicated the presence of **1**, benzoic acid, and unchanged **4a**. Nmr analysis (DMF-d_6) showed that the mixture contained about 45 mol % of **1**, 31 mol % of benzoic acid, and 24 mol % of **4a**. The product mixture was easily separated from **4a** by extraction into aqueous sodium bicarbonate followed by acidification. 4-Hydroxycoumarin (**1**) and benzoic acid were then isolated in 48 and 26% yields, respectively, by fractional crystallization from water. The identity of these products was established by comparison of their respective ir and nmr spectra and mixture melting point determinations with authentic samples of **1** and benzoic acid. No rearrangement product, **5a** or **7a**, was detected in this reaction.

As mentioned above, in neither the reaction of 4-acetoxycoumarin (**2a**) nor the reaction of 4-benzoyloxycoumarin (**4a**) with trifluoroacetic acid did we detect the previously reported[5] rearrangement products, **6a** and **7a**, respectively. The reason for these differing results is not apparent to us.

---

(5) L. L. Woods and M. Fooladi, *J. Org. Chem.*, **33**, 2966 (1968).

(6) E. Marcus, J. F. Stephen, and J. K. Chan, *J. Heterocycl. Chem.*, **6**, 13 (1969).

(7) Such a high yield of 4-hydroxycoumarin (**1**) cannot be accounted for by hydrolysis of ester **2a** by traces of water in the solvent. The mechanism for the formation of **1** is uncertain. 4-Hydroxycoumarin could conceivably be formed by direct hydrolysis of **2a** with trifluoroacetic acid or by acidolysis and subsequent hydrolysis of the formed trifluoroacetic acid ester during work-up.

(8) C. Mentzer, J. Chopin, and M. Mercier, *C. R. Acad. Sci., (Paris)*, **242**, 1034 (1956).

Experimental Section[9]

4-Acetoxycoumarin (**2a**) was prepared from **1** and acetic anhydride in 10% aqueous sodium hydroxide as outlined by Eisenhauer and Link.[2] 4-Benzoyloxycoumarin (**4a**) was obtained from **1** and benzoyl chloride in pyridine.[3]

Treatment of 4-Acetoxycoumarin (2a) with Trifluoroacetic Acid.—A solution of **2a** (20 g, 0.098 mol) in 60 ml of trifluoroacetic acid was refluxed for 15.5 hr and then poured into 400 ml of water. The mixture was chilled in ice for several hours, and the precipitated solid of 17.5 g, mp 76–184°, was collected by filtration. Tlc of this material with benzene–ethanol (3:2) indicated the presence of **1**, **3a**, and some unchanged starting material. The solid was extracted with three 100-ml portions of 5% aqueous Na_2CO_3; the insoluble portion was crystallized from ethanol to give 1.33 g of **2a**, whose melting point and mixture melting point with authentic **2a** was 111–112°. The carbonate extract was acidified with concentrated hydrochloric acid, and the solid of 14.0 g, mp 130–185°, which precipitated was filtered off. Recrystallization from *ca.* 75 ml of ethanol afforded 5.18 g of **3a**, mp 137–138°. The ethanol mother liquor was chilled in ice to give a second crop of material, which upon recrystallization from ethanol furnished an additional 0.53 g of **3a**, mp 137–138°. The combined yield of **3a** (5.71 g) was 28.6%; ir (KBr) 3.25 (aromatic CH), 3.4 (CH_3), 4.0 (broad, weak, chelated OH), 5.8 (lactone C=O), 6.23 (chelated acetyl C=O and C=C), 6.5 and 6.68 (aromatic C=C), 7.34 (CH_3CO), 8.55 (lactone C—O), 9.66, 10.24, 11.14, and 13.1 μ (4 adjacent aromatic hydrogens); nmr ($CDCl_3$) δ 2.73 (s, 3, $COCH_3$), 7.51 (complex m, 2, H-6 and H-8), 7.64 (t split into d, 1, H-7), 7.96 (d split into d, 1, H-5), and 17.60 (broad s, 1, intramolecularly chelated OH).

Anal. Calcd for $C_{11}H_8O_4$: C, 64.70; H, 3.95. Found: C, 64.71; H, 4.00.

The ethanol mother liquors from the above crystallizations were combined and the ethanol was evaporated under reduced pressure. Recrystallization of the residue thus obtained from water furnished 6.31 g (39.7%) of **1**, mp 210–212°. The mixture melting point with authentic **1** was not depressed.

Conversion of 3-Acetyl-4-hydroxycoumarin (3a) into 2-Methylchromone (13).—A mixture of 3-acetyl-4-hydroxycoumarin (**3a**) (3 g, 0.0245 mol), 150 ml of concentrated hydrochloric acid, and 90 ml of ethanol was heated under reflux for 67 hr. The ethanol and most of the hydrochloric acid were removed under reduced pressure. The pH of the solution was adjusted to 7 by adding 30% sodium hydroxide solution, and the oil which separated was extracted with ether. The ether extract was washed with 5% sodium bicarbonate solution; the ether layer was dried ($MgSO_4$), and after evaporation *in vacuo*, a solid residue was obtained. Recrystallization from hexane gave 1.1 g (47%) of 2-methylchromone, mp 70–71°. This material was identical with authentic 2-methylchromone prepared from *o*-hydroxybenzoylacetone as described by Badcock, *et al.*[10]

Treatment of 4-Benzoyloxycoumarin (4a) with Trifluoroacetic acid.—A solution of **4a** (10 g, 0.038 mol) in 30 ml of trifluoroacetic acid was heated under reflux for 15 $^2/_3$ hr and then poured into 200 ml of water. After chilling in ice for several hours, the mixture was filtered to give 10.0 g of a solid, mp 74–184°, which according to tlc (with benzene–ethanol 3:2) contained **1**, benzoic acid, and unchanged **4a**. This solid was extracted with two 100-ml portions of 5% aqueous sodium bicarbonate; the insoluble solid was recrystallized from ethanol to afford 3.07 g of **4a**, whose melting point and mixture melting point with authentic **4a** was 125–127°. The bicarbonate solution was acidified with concentrated hydrochloric acid, and the precipitated solid was filtered off and recrystallized from water to give 2.93 g (48.1%) of **1**, mp 210–213°. A mixture melting point with authentic **1** was not depressed. Evaporation of the aqueous mother liquor to small volume under reduced pressure furnished 1.2 g (26.2%) of benzoic acid, mp 118–120°. Recrystallization from water followed by sublimation *in vacuo* raised the melting point to 121–122°. No depression in melting point was observed on admixture with authentic benzoic acid. The materials were spectrally identical.

Registry No.—**2a**, 15059-36-6; **3a**, 2555-37-5; **4a**, 16709-58-3; trifluoroacetic acid, 76-05-1.

---

[9] Melting points are uncorrected. Ir spectra were determined with a Baird-Atomic 4-55 spectrometer using potassium bromide pellets of the compounds. Nmr spectra were obtained with a Varian HA-100 spectrometer using tetramethylsilane as an internal standard. Elemental analyses were performed by Union Carbide Corporation, Analytical Department, South Charleston, West Virginia. Fluorescent silica gel (Eastman Chromatogram Sheet type K 301 R) was used for tlc. Visualization of spots was accomplished with uv light.

[10] G. G. Badcock, F. M. Dean, A. Robertson, and W. B. Whalley, *J. Chem. Soc.*, 903 (1950).

Silicon Tetrachloride as a Coupling Reagent for Amide Formation

T. H. CHAN[1] AND L. T. L. WONG[2]

Department of Chemistry, McGill University, Montreal, Canada

Received January 22, 1969

Even though silicon tetrachloride is known to react vigorously with water[3] and the silicon–oxygen–silicon bond is extremely stable thermodynamically as exemplified by silica and the silicones,[4] the use of halosilanes as dehydrating agents for organic synthesis has not been fully explored.[5,6]

We report the use of silicon tetrachloride in pyridine as a coupling reagent for the formation of an amide from a carboxylic acid and an amine.[7] Thus, to a solution of 2.5 g (0.04 mole) of acetic acid and 3.8 g (0.04 mol) of aniline in 50 ml of pyridine, 4.0 g (0.023 mol) of silicon tetrachloride was added. A white precipitate was formed instantaneously. The mixture was stirred at room temperature for 10 hr, and was poured onto crushed ice. The acetanilide was obtained in 60% yield after recrystallization from water. Under these conditions, aromatic amines reacted with both aliphatic and aromatic acids to give good to moderate yields of amides. Aliphatic amines, however, gave only poor yields of amides at room temperature. The yield could be substantially improved by raising the reaction temperature to reflux (Table I).

This method of effecting the formation of a carbon–nitrogen bond appears to be simple and efficient. It offers the advantage that the other product of this

---

[1] To whom inquiries should be addressed.

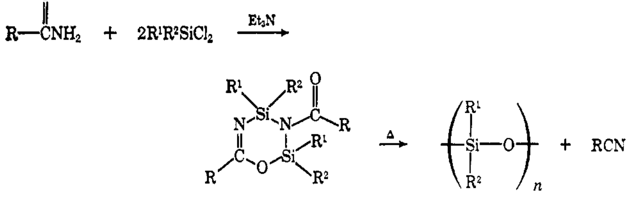
[2] Holder of National Research Council Studentship, 1968–1969.

[3] See for example, R. J. H. Voorhoeve, "Organohalosilanes," Elsevier Publishing Co., Amsterdam, 1967.

[4] See for example, E. G. Rochow, "An Introduction to the Chemistry of the Silicones," John Wiley & Sons, New York, N. Y., 1946; and also, G. Fritz, *Angew. Chem. Intern. Ed. Engl.*, **7**, 1 (1968).

[5] The use of silanes for organic reactions has been reviewed by R. Calas, *Pure Appl. Chem.*, **13**, 61 (1966).

[6] J. F. Klebe [*J. Amer. Chem. Soc.*, **90**, 5346 (1968)] reported the reaction of acetamide or benzamide with dichlorosilanes and found that nitrile was eliminated on heating



[7] For a summary of reagents for amide formation, see J. P. Greenstein and M. Winitz, "The Chemistry of the Amino Acids," Vol. 2, John Wiley & Sons, New York, 1961.