(11) For example, see R. A. Benkeser, R. F. Cunico, S. Dunny, P. R. Jones, and P. G. Nerlekar, *J. Org. Chem.*, **32**, 2634 (1967).
(12) Hydrosilylations of ethynylsilanes (SiC≡CR, R = H) are well-known and generally give *trans*-1,2-disilylethylenes. A few hydrosilylations of other silylacetylenes are known: (a) (R = Me, Ph; $(PhCO_2)_2$ and Pt/C catalysts used; 1,1-disilyl products obtained) L. L. Shchukovskaya, A. D. Petrov, and Yu. P. Egorov, *Zh. Obshch. Khim.*, **26**, 3338 (1956); *Chem. Abstr.*, **51**, 9474g (1957); (b) (R = vinyl and isopropenyl; 1,2 and 1,4 addition observed; stereochemistry not indicated) M. D. Stadnichuk and A. A. Petrov, *J. Gen. Chem. USSR (Engl. Transl.)*, **32**, 3449 (1962); *ibid.*, **33**, 2796 (1963); (c) (R = *t*-Bu, Me_3Si; 1,1-disilyl products obtained) H. Bock and H. Seidl, *J. Organomet. Chem.*, **13**, 87 (1968); (d) (R = Me_3Si) L. C. Quass, R. West, and R. G. Husk, *ibid.*, **21**, 65 (1970).
(13) (a) A. Hassner and J. A. Soderquist, *J. Organomet. Chem.*, **131**, C1 (1977); (b) G. Zweifel and S. J. Backlund, *J. Am. Chem. Soc.*, **99**, 3184 (1977); see also ref 6d and 6i.
(14) (a) J. J. Eisch and M. W. Foxton, *J. Org. Chem.*, **36**, 3520 (1971); (b) J. J. Eisch and S.-G. Rhee, *J. Am. Chem. Soc.*, **97**, 4673 (1975); see also ref 6b and 6c.
(15) The stereochemical assignment is based on the reported *Z* values for alkyl [U. E. Matter, C. Pascual, E. Pretsch, A. Pross, W. Simon, and S. Sternhell, *Tetrahedron*, **25**, 691 (1969)] and Me_3Si groups [T. H. Chan, W. Mychajlowskij, and R. Amouroux, *Tetrahedron Lett.*, 1605 (1977)].
(16) Protiodesilylation reactions of vinylsilanes generally take place with retention of configuration. See (a) E. Rosenberg and J. J. Zuckerman, *J. Organomet. Chem.*, **33**, 321 (1971); (b) K. E. Koenig and W. P. Weber, *J. Am. Chem. Soc.*, **95**, 3416 (1973); (c) K. Utimoto, M. Kitai, and H. Nozaki, *Tetrahedron Lett.*, 2825 (1975). For exceptions, see ref 4e.
(17) For discussions of the mechanism of electrophilic substitution reactions of vinylsilanes, see ref 4b, 4c, and 16b.
(18) Some other methods for the synthesis of bis silylated alkenes are described in ref 9, 12, and 19 and K. Tamao, N. Miyake, Y. Kiso, and M. Kumada, *J. Am. Chem. Soc.*, **97**, 5603 (1975).
(19) B.-T. Grobel and D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **13**, 83 (1974).
(20) The following columns were used for VPC analysis: (a) 3% SE-30 on Varaport 30, 5 ft × 0.25 in. stainless steel; (b) 20% Carbowax 20M on Chromosorb W, 10 ft × 0.25 in. stainless steel; (c) 10% DC-550 on Chromosorb W, 10 ft × 0.25 in. aluminum.
(21) Compound **3** (R = *n*-C_8H_{13}) has been recently prepared by Chamberlin, Stemke, and Bond.[7c]
(22) This spectrum was taken of the product from a separate but similar experiment.
(23) Acetic-*d* acid was prepared from acetic anhydride and D_2O. This method has been reported to give AcOD in 87–93% isotopic purity: R. Renaud and L. C. Leitch, *Can. J. Chem.*, **34**, 98 (1956).
(24) R. Misra, unpublished work at Rutgers University.

New Method for the Preparation of Bismuth(III) Triesters

Timothy R. Koch and Peter P. Wickham*

Department of Chemistry, Coe College, Cedar Rapids, Iowa 52402

Received June 13, 1978

Bismuth(III) salts of organic acids have been shown to be useful in the catalysis of aromatic substitution,[1] in the catalysis of high temperature esterification of alcohols with organic acids or their derivatives,[2] and as mild oxidants for the conversion of acyloins to diketones.[3] We have recently shown they can be used in the acylation of amines, alcohols, amides, and esters.[4]

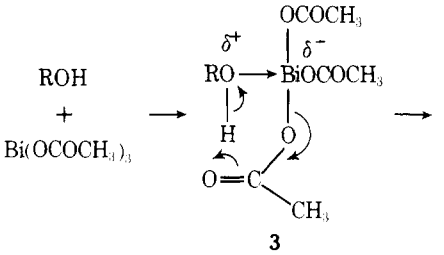
In our continuing study of the reactions of these compounds, we found it necessary to synthesize a wide variety of them. Previously reported methods for the synthesis of bismuth(III) triesters[5] were not widely applicable. We have therefore developed a new procedure which is useful for the preparation of bismuth(III) triesters that cannot be produced in high temperature reactions or which decompose easily in the presence of water.

Three general procedures have been claimed to be useful for the preparation of bismuth(III) triesters. Early workers prepared bismuth(III) compounds by a "decomposition reaction" of bismuth(III) nitrate with an organic acid[6–11] or with the salt of an organic acid.[12–18] Reactions of triarylbismuth compounds with some organic acids to yield such compounds have been reported.[19,20] The third procedure involves the reaction of bismuth(III) oxide (**2**) with an organic acid, usually at temperatures of 150 °C or greater.[21] None of these procedures are widely satisfactory for such syntheses. Analyses reported for the products indicate the presence of mixtures of various bismuth compounds. Thus, substantial confusion in the literature has resulted from a dearth of satisfactory widely applicable procedures for the preparation of bismuth(III) triesters and a lack of reliable information on methods for their characterization.

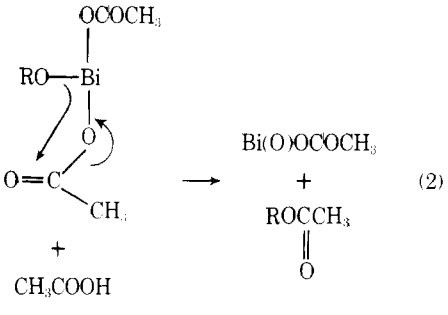
In an attempt to prepare such bismuth(III) triesters, it was discovered that reaction of bismuth(III) triacetate (**1**) with an organic acid yielded a mixture of acetic acid, the initial organic acid, and a new bismuth(III) triester. When the reaction was conducted in toluene, and acetic acid was removed by azeotropic distillation, **1** was smoothly converted into various bismuth(III) triesters in high yields (see eq 1). Table I summarizes the results obtained with a variety of carboxylic acids.

$$Bi(OCOCH_3)_3 + 3RCO_2H \xrightarrow[\text{reflux}]{\text{toluene}} Bi(OCOR)_3 + 3CH_3CO_2H \quad (1)$$

This transesterification reaction which compound **1** undergoes with organic acids appears to be very similar to the reaction of **1** with alcohols and amines.[4] For example, the reaction of **1** with an alcohol is thought to proceed through **3**, which decomposes to form bismuthyl acetate and an ester (eq 2).

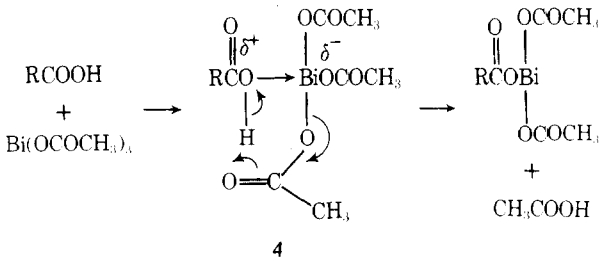


3



(2)

The ability of **1** to function as a Lewis acid is also essential in the proposed mechanism for the new reaction, shown in eq 3, which involves a similar attack on the electron-deficient



4

(3)

bismuth atom. The proposed intermediate **4** is similar to the $BiCl_3$–dimethylformamide complex reported by Kuhn and

0022-3263/79/1944-0157$01.00/0

Table I. Bismuth(III) Triesters Prepared by Transesterification

$$3RCO_2H + Bi(OCOCH_3)_3 \rightarrow Bi(OCOR)_3 + 3CH_3CO_2H$$

compd	registry no.	R	registry no.	mp, °C[a]	yield, %	solvent[b]	IR carbonyl absorption[c]	elemental analysis C calcd	C found	H calcd	H found
6	67858-40-6	p-$CH_3C_6H_4$	99-94-5	286–290	91	toluene (VSS)	1520 (br)	46.92	46.89	3.44	3.66
7	29909-60-2	C_6H_5	65-85-0	293–295	95	toluene (I)	1524 (m)	44.07	42.89	2.64	2.59
8	67858-41-7	p-$NO_2C_6H_4$	62-23-7	335 (dec)	87	benzene (I)	1517 (s)	35.66	33.83	1.71	1.90
9	67858-42-8	Cl_3C	76-03-9	151 (dec)	60	benzene (S)	1626 (s)	45.83[f]	33.26[f]	30.02[g]	34.0[g]
10	67858-43-9	$CH_3(CH_2)_{14}$	57-10-3	91–92	70	benzene (S)	1520 (s)	59.11	56.71	9.61	9.09
11	67858-44-0	$C_6H_5CH_2$	103-82-2	95–98 (fus)	*d*	toluene (S)	1515 (br)	46.92	45.44	3.44	3.74
12	67858-45-1	$C_6H_5CONHCH_2$	495-69-2	136–138 (fus)	89	benzene (I)	*e*	43.61	46.29	3.25	3.90

[a] Dec = decomposes; fus = fused into an amorphous solid. [b] I = insoluble; VSS = very slightly soluble; and S = soluble. Solubilities were determined in the indicated solvent at its boiling point. [c] IR absorptions are reported in cm^{-1}: m = medium; s = strong; and br = broad. [d] Not obtained. [e] The IR spectrum of **12** was identical with that of an authentic sample of *N*-benzoylglycine. [f] Chlorine analysis. [g] Bismuth analysis.

McIntyre[22] and is also virtually identical with intermediate **3**. We propose that initial loss of acetic acid occurs in the same manner from **3** and **4**; the only real difference would be that the resultant product from eq 2 is unstable and decomposes to the ester and bismuthyl salt.

If the acidity constant of the organic acid which is added to a suspension of **1** is comparable with or less than that of acetic acid, it is necessary to remove acetic acid by azeotropic distillation to produce a high yield of pure bismuth(III) triester. However, upon addition of trichloroacetic acid to a suspension of **1** in benzene, a clear solution is obtained without heating. This result suggests that the strong acid very readily displaces acetic acid from **1** to form the new bismuth(III) triester. It seems reasonable that the strengths of the acids involved determine the position of equilibrium between reactants and products. The physical properties of these substances suggest that they do possess considerable covalent character. As shown in Table I, the compounds **9, 10,** and **11** are quite soluble in the nonpolar solvents benzene and toluene. Interestingly, all of the bismuth triesters either melt or decompose at relatively low temperatures, a fact unreported in the previous literature, aside from bismuth esters of very large aliphatic acids.[21b] These melting or decomposition points occur at much lower temperatures than those for the corresponding bismuthyl salts and appear to be a reliable means for indicating their purity.

Infrared spectra of these bismuth(III) triesters show a number of sharp peaks, in contrast to spectra of clearly ionic substances such as bismuth trioxide and bismuthyl compounds. The original carbonyl peak for the carboxylic acid from which each triester is made, which would normally be present at 1670–1710 cm^{-1}, is not present; its absence is a useful indicator of purity of these triesters. The new carbonyl peak in these compounds usually occurs at 1515–1520 cm^{-1}. This low frequency of absorption has previously been described and is thought to result from field distortions causing the lone pair of electrons to orient themselves across the C–O bond, weakening it and thereby lowering its frequency.[23] Thus, the low infrared C–O frequency of these bismuth compounds does not seem to be a good criterion for judging their ionic character.

Purification of these substances still represents a difficult problem that we have not yet wholly solved, as the analyses in Table I clearly indicate. Since these esters are unstable in the presence of water and a variety of protonic solvents, only relatively few solvents can be used for attempted recrystallization. The maintenance of an inert atmosphere over the pure solids is necessary, and failure to do so probably accounted for some of the poor analyses in this work. In difficult cases, it may be that a means other than recrystallization will be required to prepare solid samples of analytical purity. However, in many instances these triesters may be desired only for synthetic purposes; in such instances, rather than isolating it, the triester might be used in situ in solution for the necessary reaction.

Experimental Section[24]

General Procedure for the Synthesis of Bismuth(III) Organic Esters by the Transesterification Reaction. A mixture of **1** (1.93 g, 5.00×10^{-3} mol) and the organic acid (1.50×10^{-2} mol) suspended in 100 mL of solvent was heated at reflux in either toluene or benzene, and the azeotropic acetic acid–solvent mixture was distilled. When ~20 mL of solvent remained, the mixture was allowed to cool. Suction filtration afforded crystals of the new bismuth(III) organic ester.

Acknowledgment. The financial support of this work by the Research Corporation is gratefully acknowledged.

Registry No.—**1**, 22306-37-2.

References and Notes

(1) T. R. Koch, T. A. Potter, and P. P. Wickham, manuscript in preparation.
(2) J. R. Leebrick, W. J. Considine, and N. Kudisch, British Patent 1 010 175, 1965; *Chem. Abstr.*, **64**, 9645e (1966).
(3) W. Rigby, *J. Chem. Soc.*, 793 (1951).
(4) A. L. Reese, K. McMartin, D. Miller, and P. P. Wickham, *J. Org. Chem.*, **38**, 764 (1973).
(5) We refer to substances of general structure $Bi(OCOR)_3$ as tricarboxylic acid esters of $Bi(OH)_3$ because their reactions with amines, alcohols, and carboxylic acids afford the same products as those which result from reaction of the latter with typical carboxylic acid esters.
(6) M. Picon, *J. Pharm. Chim.*, **8**, III, 145 (1926).
(7) F. W. Adams, *Chem. Drug.*, **101**, 136 (1924).
(8) A. Firth, *Pharm. J.*, **154**, 5 (1945).
(9) L. Cuny, *Bull. Sci. Pharmacol.*, **34**, 65 (1927).
(10) L. Vanino and F. Hartyl, *J. Prakt. Chem.*, **74**, 142 (1906).
(11) M. Picon, *J. Pharm. Chim.*, **8**, IV, 529 (1926).
(12) P. Godfrin, *J. Pharm. Chim.*, **7**, II, 385 (1910).
(13) P. Godfrin, *J. Pharm. Chim.*, **8**, VI, 49 (1927).
(14) J. Dequidt and M. Delecroix, *Bull. Soc. Pharm. Lille*, 11 (1949); *Chem Abstr.*, **45**, 5627d (1951).
(15) F. Chemnitius, *Pharm. Zentralhalle Dtschl.*, **68**, 513 (1927).
(16) M. Picon, *J. Pharm. Chim.*, **8**, 206 (1928).
(17) E. A. Mauersberger, *Chem. Weekbl.*, **27**, 337 (1930).
(18) W. M. Lauter, A. E. Jurist, and W. G. Christiansen, *J. Am. Pharm. Assoc.*, **21**, 1277 (1932).
(19) M. M. Koton, *Zh. Obshch. Khim.*, **9**, 2283 (1939); *Chem. Abstr.*, **34**, 5049[2] (1940).
(20) M. M. Koton, *Zh. Obshch. Khim.*, **11**, 379 (1941). Note that the citation in Chemical Abstracts [*Chem. Abstr.*, **35**, 5870[4] (1941)] is seriously misleading on the reported results of these experiments.
(21) See, for example, (a) M. Picon, *Bull. Soc. Chim. Fr.*, **45**, 1056 (1929); (b) L. Polo Friz, *Boll. Chim. Farm.*, **100**, 692 (1961); *Chem. Abstr.*, **57**, 5792c (1962); (c) W. Rigby, *J. Chem. Soc.*, 793 (1951).
(22) S. J. Kuhn and J. S. McIntyre, *Can. J. Chem.*, **43**, 375 (1965).
(23) J. D. Donaldson, J. F. Knifton, and S. D. Ross, *Spectrochim. Acta*, **20**, 847 (1964).

(24) Melting points were determined using a Mel-Temp capillary melting point apparatus and are corrected. IR spectra were obtained from Nujol mulls using a Beckman Model IR-8 spectrophotometer. All chemical analyses were performed by M-H-W Laboratories, Garden City, Mich. Bismuth(III) triacetate (**1**) was prepared from bismuth oxide (**2**) following the procedure of Rigby[3] as modified by Wickham et al.[4] White crystals of **1** and all carboxylic acids used were dried under reduced pressure for 24 h prior to use. All solvents were distilled from $CaSO_4$ and then stored over "Linde" type molecular sieves (4–8 mesh).

Stereoselective Synthesis of (−)-Estafiatin[1]

Mark T. Edgar, Andrew E. Greene,* and Pierre Crabbé*

Laboratoire de Chimie Organique, C.E.R.M.O., Université Scientifique et Médicale, 38041 Grenoble, France

Received July 26, 1978

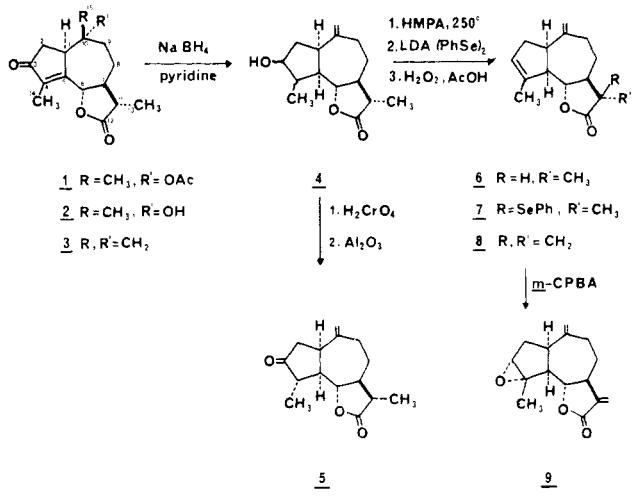
(−)-Estafiatin (**9**), a constituent of the medicinally useful bitter herb *Artemisia mexicana*, was isolated and structurally elucidated by Sanchez-Viesca and Romo.[2] We wish to report a short, stereoselective synthesis from α-santonin of (−)-estafiatin.

The key intermediate in the synthesis was the trisubstituted olefin **6**, which was secured as outlined below. α-Santonin was converted to *O*-acetylisophotosantonic lactone (**1**), which in turn was transformed via the alcohol **2** to the dienone lactone **3** using slightly modified literature procedures.[3] The introduction of the C-10 exocyclic methylene at this point was deemed necessary because it was felt that this conversion would be difficult to achieve later in the synthesis.[4] However, this in turn required a suitable method for reducing the enone function in **3** in the presence of the exocyclic methylene to give a cis-fused guaianolide. Of the reducing agents examined, the infrequently used combination of sodium borohydride in pyridine[5] proved to be by far the most effective in accomplishing this reduction, selectively producing alcohols **4**. This mixture of epimeric alcohols was converted for characterization by oxidation[6] and equilibration to ketone **5** (dihydroestafiatone[2,7]), which has been isolated from *Arctotis revoluta*.[7] Additional evidence that the hydride addition had produced the cis ring fusion was provided by the conversion of *O*-acetylisophotosantonic lactone (**1**) by the above sequence of reactions to the known acetoxy ketone (**5**, where

replaces the exocyclic methylene).[3c]

As had been expected from observations made in similar systems,[3c,8] conversion of alcohols **4** to the trisubstituted olefin **6** proved to be difficult. Several methods[3c,9] yielded only the disubstituted Δ^2-olefin; however, high-temperature dehydration in hexamethylphosphoric triamide[10] afforded a mixture of tri- and disubstituted olefins (ca. 1.4/1), which could be readily separated on silver nitrate impregnated silica gel. Although the spectral properties of trisubstituted olefin **6** closely resembled those of the known[11] isomeric trans-fused (1α, 5β) compound, obvious differences could be seen, especially in the C-6 hydrogen chemical shifts (3.82 and 4.27 ppm, respectively).

Conversion of the α-methyl lactone in **6** to the corresponding α-methylene lactone was readily accomplished by α-phenylselenenylation and oxidation.[12] Selective epoxidation of the resulting triene **8**[13] produced a major epoxide isomer **9** (ca. 80% by NMR), easily separated by crystallization, whose melting point, rotations, and spectral properties were in complete agreement with those of (−)-estafiatin.[2,14] The epoxide in estafiatin thus can be assigned the α configuration on the reasonable assumption that the major product in the



epoxidation of triene **8** is produced by approach of the peracid from the considerably less hindered α face.

Experimental Section

Solvents were redistilled prior to use. Tetrahydrofuran and diisopropylamine were distilled from lithium aluminum hydride, and hexamethylphosphoric triamide (HMPA) was distilled under vacuum from calcium hydride. Reaction products were isolated by addition of water followed by extraction with the solvent indicated and drying over anhydrous sodium sulfate.

Thin-layer chromatography was performed on Merck $60F_{254}$ (0.25 mm) sheets which were visualized with molybdatophosphoric acid in ethanol. Merck 230–400 mesh silica gel 60 was employed for column chromatography. A Beckman acculab 4 spectrophotometer was used to record IR spectra, and a Jeol PMX-60 spectrometer was used for the NMR spectra (Me_4Si as the internal reference). Mass spectra were obtained on an MS-30 AEI mass spectrometer (70 eV, direct insertion probe). Optical rotations were determined on a Perkin-Elmer 141 polarimeter ($CHCl_3$, *c* 1). Microanalyses were performed by the Central Service of the CNRS, Lyon.

Dienone Lactone 3. *O*-Acetylisophotosantonic lactone[3] (6.5 g, 21 mmol) was added to 1.2 L of 5% aqueous potassium hydroxide with stirring. After 1.25 h the reaction mixture was washed with ethyl acetate and acidified with 18% hydrochloric acid and the product was isolated with ethyl acetate, to provide 6.5 g of crude alcohol **2**. This material was dissolved in 20 mL of THF and cooled to −45 °C. A cold (−45 °C) solution of THF (20 mL), pyridine (20 mL), and thionyl chloride (20 mL) was added followed by stirring for 10 min. After addition to cold water–ether, the reaction mixture was thoroughly extracted with ether which was washed with aqueous sodium carbonate, water, and brine to furnish 4.5 g of an oil. This oil was chromatographed on silica gel using 30% ethyl acetate–hexane to afford 3.3 g of the dienone lactone **3**, whose properties were in accord with those reported in the literature.[3b]

Alcohols 4 and Dihydroestafiatone 5. Dienone lactone **3** (2.9 g, 12 mmol) in 50 mL of pyridine was added to a stirred solution of sodium borohydride (2.9 g, 76 mmol) dissolved in 37 mL of pyridine.[5] The resulting dark brown solution was stirred at 17 °C for 24 h followed by addition of 5 mL of water and an additional 1 h of stirring. The reaction mixture was slowly poured into 10% aqueous HCl–ether and the ether extract (concentrated to 250 mL) was added to a solution of 27 g of KIO_3 in 450 mL of water. After stirring for 15 h, the ether phase was washed successively with 5% sodium thiosulfate, water, 10% HCl, saturated sodium bicarbonate, and brine, dried over anhydrous sodium sulfate, and concentrated to give 2.0 g of brown oil.

The crude alcohol mixture (1.0 g, 4.0 mmol), dissolved in 50 mL of ether, was cooled to 0 °C and treated dropwise with a chromic acid solution[6] (540 drops, ~40 mmol). After 1 h at 0 °C and 1 h at 16 °C, the solution was extracted with ether, which was washed with saturated sodium bicarbonate and brine, dried, and concentrated. The resulting oil was stirred for 2 h with 6 g of activity I basic alumina in $CHCl_3$ and then chromatographed on silica gel using 30% ethyl acetate–hexane to afford 650 mg of dihydroestafiatone (**5**).[2,7] Recrystallization from ether–hexane gave colorless needles: mp 80–81 °C; $[\alpha]^{24}_D$ +139°; IR (Nujol) 3080, 1770, 1745, 1645, 995, 900 cm^{-1}; NMR ($CHCl_3$) δ 4.90 (s, 1 H), 4.59 (s, 1 H), 3.89 (broad t, *J* = 8 Hz, 1 H), 1.25 (d, *J* = 7 Hz, 6 H); mass spectrum *m/e* 248 (M^+).