introduced, as 3-phenylpropanol was obtained in quantitative yield. Coniferyl alcohol (3-methoxy-4-hydroxycinnamyl alcohol, **13**) gave the corresponding derivative of 3-phenylpropanol.

Simple allylic alcohols appear to be unaffected by the catalyst in the abence of of a hydrogen donor. Thus, hex-3-ene-2,5-diol (in admixture with the corresponding 3-yne) was recovered unchanged from a treatment with palladium/carbon in methanol. In the presence of formic acid, nevertheless, both the alkene and alkyne were readily hydrogenated to give hexane-2,5-diol.[7]

No reaction was observed with cinnamic acid (**14**) or it coniferyl analogue (**15**). However, it is noteworthy that *cis*-*p*-hydroxycinnamic acid (**16**) was converted quantitatively into its trans isomer by palladium/carbon in methanol at room temperature. Alkene isomerization with palladium salts or complexes is known,[8] although metallic palladium appears to require much higher temperatures.[9] Also, partial cis to trans isomerization may occur during catalytic hydrogenation over palladium/carbon, for example, as observed[10] with *cis*-cinnamic acid and *cis*-stilbene; in the absence of hydrogen, however, no isomerization of these two compounds was detected.[10] By contrast, we found that *cis*-stilbene (**17**) was isomerized completely to *trans*-stilbene.

Experimental Section

Solutions were evaporated below 40 °C under diminished pressure or, with highly volatile products, were distilled at atmospheric pressure. Eastman Chromagram sheets of silica gel with fluorescent indicator were used for thin-layer chromatography. Proton magnetic resonance spectra were recorded with a Varian T-60 or HA-100 spectrometer. Mass spectra were obtained with an LKB 9000 spectrometer, with an on-line GC component, at an ion source voltage of 70 eV. Palladium (10%) on activated charcoal and compounds **1** to **4** as well as **14–17** were obtained from Aldrich Chemical Co. Inc., whereas compounds **10** and **12** were obtained from Eastman Kodak. Compounds **7–9** were kindly provided by G. K. Hamer, and **13** was provided by B. I. Fleming.

Reaction of Aryl Alcohols on Palladium Charcoal. In a representative experiment, a solution of diphenylmethanol (**3**, 0.1 g) in methanol (5 mL) was added to a stirred suspension of 10% palladium on charcoal (0.5 g) in the same solvent (5 mL) maintained under a nitrogen atmosphere. After 16 h, the catalyst was filtered off and washed with methanol (in some instances, the catalyst also was washed with water), and the filtrates were combined and evaporated. The residue was found to be a mixture of diphenylmethane and benzophenone by comparison of its ^{1}H NMR spectrum with spectra of the known compounds.

Isomerization of *cis*-Stilbene to *trans*-Stilbene. Under the conditions described in the preceeding section, liquid *cis*-stilbene (0.1 g) in the presence of 10% palladium on charcoal (0.5 g) afforded *trans*-stilbene in quantitative yield (mp 122–124 °C) which was indistinguishable from an authentic specimen by ^{1}H NMR.

Catalytic Transfer Hydrogenation of Methyl 2,3-Di-*O*-benzyl-α-D-glucopyranoside. A solution of **5** (0.2 g) in methanol (5 mL) was added to a stirred suspension of 10% palladium on charcoal (1 g) in the same solvent (10 mL) maintained under a nitrogen atmosphere, followed by 1-phenylethanol (1 g) in methanol (5 mL). After 16 h when TLC examination indicated that the reaction was complete, the catalyst was filtered off and successively washed with methanol and water, and the filtrates were combined and evaporated. The residue, dissolved in deuterium oxide (99.5%, 0.5 mL) afforded a ^{1}H NMR spectrum indistinguishable from that of methyl α-D-glucopyranoside; no other products were detected.

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Registry No. **1**, 76-84-6; **2**, 100-51-6; **3**, 91-01-0; **4**, 98-85-1; **5**, 17791-36-5; **7**, 2415-09-0; **8**, 454-91-1; **9**, 79917-56-9; **10**, 93-56-1; **11**, 60-12-8; **12**, 104-54-1; **13**, 458-35-5; **14**, 140-10-3; **15**, 537-98-4; **16**, 4501-31-9; **17**, 645-49-8; Pd, 7440-05-3.

(7) See footnote *c* of Table I.
(8) Reference 3, p 128.
(9) (a) S. Carra and V. Ragaini, *J. Catal.*, **10**, 230 (1968); (b) V. Ragaini, G. Somerzi, and S. Carra, *ibid.*, **13**, 20 (1969).
(10) G. Bellinzona and F. Bettinetti, *Gazz. Chim. Ital.*, **90**, 426 (1960).

Synthesis Using Allylidenedihydropyridines. 9.[1] First Preparation of Thiino[3,2-*a*]indolizine Derivatives

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Previous studies in our laboratory have demonstrated that indolizines and pyrazolo[1,5-*a*]pyridines substituted with both an amino and an electron-poor vinyl group on the five-membered ring were synthesized via an allylidenedihydropyridine route[2,3] and were converted into the corresponding pyridine-fused heterocycles under acidic and basic conditions.[4] The latter finding has opened a route to new condensed indolizines and pyrazolopyridines, and we are especially interested to extend it to other derivatives. We now describe the first preparations of some thiino[3,2-*a*]indolizine derivatives from acidic treatment of 2-(alkylthio)-1-(2-cyanovinyl)indolizines.

The key compounds, 2-(alkylthio)-1-(2-cyanovinyl)-indolizines **16–23**, were synthesized in moderate yields from pyridinium salts **1–5** according to known sequences (Scheme I),[2] and their structures were determined by physical and spectral comparison with known indolizines **16** and **18**. One possible method to prepare thiinoindolizine, the S-deprotection of these indolizines **16–23** was initially investigated by using bases[5] such as sodium/liquid NH_3, potassium hydroxide, and potassium *tert*-butoxide, but none of the expected 2-mercaptoindolizines or other significant products were obtained, perhaps because indolizines **16–23** have cyano and ester groups which are more sensitive to hydrolysis than the sulfide linkage. When indolizines **16–22** with an ethoxycarbonyl group in the 3-position were heated with strong acids, however, substances with extremely strong

(1) For part 8 of this series, see Kakehi, A.; Ito, S.; Watanabe, K. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1775.
(2) Kakehi, A.; Ito, S.; Uchiyama, K.; Kondo, K. *J. Org. Chem.* **1978**, *43* 2896.
(3) Kakehi, A.; Ito, S.; Maeda, T.; Takeda, R.; Nishimura, M.; Tamashima, M.; Yamaguchi, T. *ibid.* **1978**, *43*, 4837.
(4) (a) Kakehi, A.; Ito, S.; Watanabe, K.; Ono, T.; Miyajima, T. *Chem. Lett.* **1979**, 205 (b) *J. Chem. Res., Synop.* **1980**, 18; *J. Chem. Res., Miniprint* **1980**, 401–425.
(5) In general, simple alkyl substituents such as a methyl and an ethyl group are not appropriate for the deprotection of sulfides, but the formations of some thiol derivatives from alkyl aryl sulfides under basic conditions were reported. See (a) Field, L.; Grunwald, F. A. *J. Org. Chem.* **1951**, *16*, 946. (b) Overberger, C. G.; Biletch, H.; Orttung, F. W. *Ibid.* **1959**, *24*, 289.

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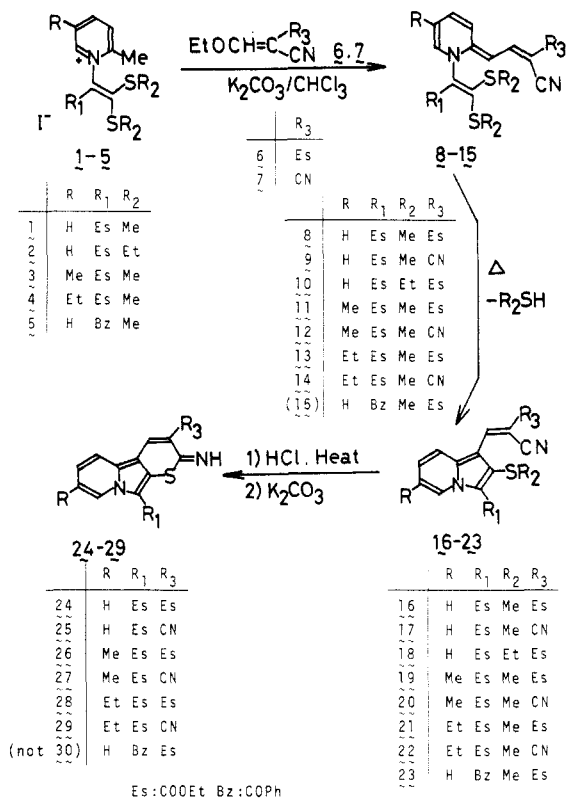
Table I. Some Data of Allylidenedihydropyridines and Indolizines

compd[a]	reactants		% yield	appearance	mp, °C	IR (KBr) ν, cm⁻¹ CO		CN
9	1	7	56	red prisms	108-110	1702		2193
11	3	6	44	red amorphous				
12	3	7	39	red prisms	112-114	1700		2192
13	4	6	40	red amorphous				
14	4	7	40	red prisms	121-123	1688		2190
17	9		88	yellow needles	175-177	1670		2210
19	11		70	yellow needles	111-112	1724	1677	2220
20	12		85	yellow needles	144-146	1680		2218
21	13		90	yellow needles	118-119	1720	1683	2216
22	14		98	yellow needles	118-120	1690		2219
23	5	6	42	orange needles	168-169	1705		2222

[a] Satisfactory analytical values were reported for all compounds except 11 and 13, which were not obtained in pure form.

Scheme I



fluorescence were formed. For example, the treatment of **16** with concentrated hydrochloric acid followed by neutralization with base gave an orange product **24**, mp 142–145 °C, in 67% yield. The same compound **24** was also formed by the reaction of **18** in which only the 2-alkylthio group was different from that of **16**. Similar treatment of indolizines **17** and **19–22** yielded compounds **25–29** in 40–63% yields, respectively. On the other hand, acidic treatment of 3-benzoylindolizine **23** gave only a complex mixture and the expected product **30** could not be separated. Furthermore, the application of this reaction to its 3-aza homologue, 2-(alkylthio)-3-(2-cyanovinyl)-pyrazolo[1,5-*a*]pyridine,[1] was also unsuccessful.

The assignment of thiino[3,2-*a*]indolizine structure to compounds **24–29** was accomplished by the inspection of their physical and spectral data and by mechanistic considerations. The elementary analyses of **24–29** were in good accord with the proposed compositions, and the IR spectra showed the disappearance of an absorption band at near 2200 cm^{-1} due to the cyano group and the new appearance of a secondary amino absorption band at 3250–3260 cm^{-1}. The NMR spectra of **24**, **26**, and **28**[6] clearly showed the absence of the *S*-alkyl group derived from the sulfide moiety in indolizines **16–22**, together with proton signals characteristic for the thiinoindolizine structure; this agreed well with the experimental result that the same product **24** was obtained both from the reactions of 2-(methylthio)- and 2-(ethylthio)indolizines **16** and **18**. The retention of the ester group(s) in these thiinoindolizines was also supported by their NMR spectra, although the conditions employed here might have been drastic enough to hydrolyze or to deacylate it.[7] The IR and NMR spectral data were very similar to those of pyrido[3,2-*a*]indolizines prepared earlier by us.[3] Mechanistically, this reaction involves sterically favorable six-membered ring formation between a cyano and an alkylthio group in **16–22**. Thus, the following two possible routes are available: path a, a nucleophilic attack of the S lone pair on the cyano carbon activated by the protonation followed by the elimination of methyl or ethyl chloride from the cyclized intermediate **31**; and path b, the hydrolysis of the 2-alkylthio group followed by the cyclization of the resulting 2-mercaptoindolizine **32** (Scheme II). Path a is more reasonable than path b, because the hydrolysis of the sulfide linkage generally does not occur under such acidic conditions and the high nucleophilicity of the sulfur atom in sulfides is well-known.[8]

Although this cyclization is restricted largely by the substituents and heterocyclic skeletons, the utility for the synthesis of thiinoindolizines is still high because of the unavailavility of other methods and of the simplicity of the reaction.

Experimental Section

Melting points were measured with a Yanagimoto micro-melting-point apparatus and are uncorrected. Microanalyses were carried out on a Perkin-Elmer 240 elemental analyzer. The NMR spectra were determined with a Varian EM360A spectrometer in deuteriochloroform with tetramethylsilane as an internal standard. The chemical shifts are expressed as δ values. The IR spectra were taken with a Hitachi 260-10 infrared spectrophotometer.

Preparation of 2-(Alkylthio)-1-(2-cyanovinyl)indolizines 16–23. Indolizines **16–22** were synthesized by the reactions of 1-[2,2-bis(alkylthio)vinyl]-2-picolinium iodides **1–4**[9] and ethyl

(6) The NMR spectra of 3-cyanothiinoindolizines **25**, **27**, **29** could not be taken owing to the low solubility of the compounds.

(7) Boekelheide, V.; Windgassen, R. J., Jr. *J. Am. Chem. Soc.* **1959**, *81*, 1456.

(8) For example, the preparation of sulfonium salts from sulfides and various alkylating agents is a typical one in this category.

Table II. Some Data of Thiinoindolizines

compd[a]	reactant	% yield[b]	mp, °C	IR (KBr) ν, cm⁻¹ NH	CN	CO
24	16	67	142-145 (204-205)[c]	3250		1670
	18	63	142-145			
25	17	43	268-270	3250	2213	1688
26	19	57	202-205 (184-188)[c]	3260		1680
27	20	56	264-267	3250	2218	1685
28	21	40	199-202 (192-196)[c]	3260		1680
29	22	63	192-195 (184-187)[c]	3260	2218	1687

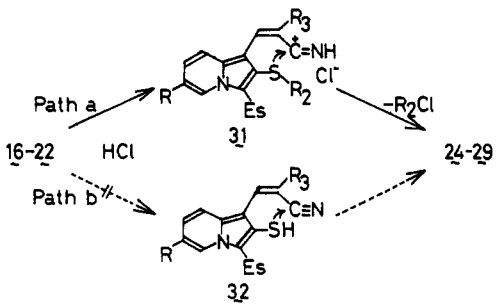
[a] Satisfactory analytical values were reported for all compounds in the table. [b] After recrystallization. [c] Its hydrochloride.

Table III. NMR Data of Thiinoindolizines

compd	C-4	C-5	C-6	C-7		C-8	NH	COOEt[a]
24	8.51 (s)	7.90 (br d)	7.50 (br t)	7.13 (dt)		9.71 (br d)	9.5-10.5 (br)	1.33 (t), 1.55 (t), 4.43 (q), 4.51 (q)
	$J_{5,6}$ = 9.0, $J_{6,7}$ = $J_{7,8}$ = 7.0, $J_{6,8}$ = 2.0 Hz							
26	8.78 (s)	7.65 (d)	7.23 (dd)	2.41 (s)		9.39 (br s)	9.5-10.5 (br)	1.41 (t), 1.47 (t), 4.34 (q), 4.40 (q)
		$J_{5,6}$ = 9.0, $J_{6,8}$ = 2.0 Hz						
28	8.45 (s)	7.81 (d)	7.48 (dd)	1.32 (t)	2.78 (q)	9.55 (br s)	9.0-10.0 (br)	1.42 (t), 1.49 (t), 4.41 (q), 4.49 (q)
		$J_{5,6}$ = 9.0, $J_{6,8}$ = 2.0 Hz						

[a] The coupling constants are 7.0 Hz.

Scheme II



path a, protonation-cyclization-elimination
path b, hydrolysis-cyclization

(ethoxymethylene)cyanoacetate **6** or (ethoxymethylene)malononitrile **7** in the presence of excess potassium carbonate in chloroform followed by the thermolyses in xylene or toluene of the resulting 2-allylidene-1,2-dihydropyridines **8-14**, according to the literature.[4] 3-Benzoylindolizine **23** was directly obtained without isolation of intermediate **15** from the reaction of picolinium salt **5**[9] with **6**. Some results and properties of new compounds **9**, **11-14**, **17**, and **19-23** are given in Table I.

Preparation of Thiino[3,2-*a*]indolizines 24-29. General Method. To concentrated hydrochloric acid (20 mL) was added 2-(alkylthio)-1-(2-cyanovinyl)indolizine (1 mmol), and the suspended solution was heated on a water bath (70-80 °C) until the indolizine was completely dissolved (ca. 1-2 h). The fluorescent blue reaction solution was then evaporated to dryness at reduced pressure, and water (20 mL) was added. The resulting solution was neutralized carefully with aqueous potassium carbonate, and the yellow substance that separated was collected by suction. Recrystallizations from chloroform gave orange needles of a thiino[3,2-*a*]indolizine derivative. The hydrochlorides of these thiinoindolizines were obtained by recrystallizations of the residue from ethanol without alkaline treatment. However, treatment of 3-benzoylindolizine **23** and 3-[2-cyano-2-(ethoxycarbonyl)-vinyl]-2-(methylthio)pyrazolo[1,5-*a*]pyridine with hydrochloric acid afforded only complex mixtures, and any significant products could not be separated from them. These results and properties are given in Tables II and III.

Registry No. **1**, 59181-95-2; **2**, 67988-75-4; **3**, 79917-93-4; **4**, 79917-94-5; **5**, 59181-92-9; **6**, 94-05-3; **7**, 123-06-8; **8**, 67988-67-4; **9**, 79917-95-6; **10**, 67988-69-6; **11**, 79917-96-7; **12**, 79917-97-8; **13**, 79917-98-9; **14**, 79917-99-0; **16**, 67988-71-0; **17**, 79918-00-6; **18**, 67988-73-2; **19**, 79918-01-7; **20**, 79918-02-8; **21**, 79918-03-9; **22**, 79918-04-0; **23**, 79918-05-1; **24**, 79918-06-2; **24**·HCl, 79918-07-3; **25**, 79918-08-4; **26**, 79918-09-5; **26**·HCl, 79918-10-8; **27**, 79918-11-9; **28**, 79918-12-0; **28**·HCl, 79918-13-1; **29**, 79918-14-2; **29**·HCl, 79918-15-3; 3-[2-cyano-2-(ethoxycarbonyl)vinyl]-2-(methylthio)pyrazolo[1,5-*a*]-pyridine, 75619-88-4.

(9) Pyridinium salts **1-5** were prepared from 2-picoline, 2,5-lutidine, and 5-ethyl-2-methylpyridine according to the literature (Tominaga, Y.; Miyake, Y.; Fujito, H.; Matsuda, Y.; Kobayashi, G. *Yakugaku Zasshi* **1977**, *97*, 927), and some properties of new salts **3** and **4** are as follows. **3**: yellow needles (ethanol), mp 141-144 °C; IR (KBr) ν 1700 cm⁻¹ (CO). Anal. Calcd for $C_{14}H_{20}NO_2S_2I$: C, 39.53; H, 4.74; N, 3.29. Found: C, 39.43; H, 4.71; N, 3.32. **4**: yellow needles (ethanol), mp 146-147 C; IR (KBr) ν 1705 cm⁻¹. Anal. Calcd for $C_{15}H_{22}NO_2S_2I$: C, 41.00; H, 5.05; N, 3.19. Found: C, 41.03; H, 5.04; N, 3.19.

tert-Butylsilver-Induced 1,5-Substitution in Some 2,4-Pentadiynyl Methanesulfinates. A Novel Route to Di- and Trisubstituted Pentatetraenes

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Hitherto pentatetraenes are rather unexplored compounds. Up to 1976 only six pentatetraenes had been reported, all of them being tetrasubstituted.[1] In this year the parent hydrocarbon, C_5H_4, was prepared for the first time via a retro-Diels-Alder reaction.[2] The compound was substantially contaminated with 1,3-pentadiyne, however.

Because of their unique π system, pentatetraenes may exhibit chirality. An example of a chiral tetrasubstituted pentatetraene has recently been described.[3]

At the time this work was initiated, pentatetraenes had not been synthesized via an organometal-induced 1,5-substitution in appropriate 2,4-pentadiynyl esters. In view of the observed smooth alkylsilver induced 1,5-substitution in pentenynyl sulfinates (eq 1),[4] it was anticipated that

(1) Hopf, H. "The Chemistry of Ketenes, Allenes, and Related Compounds", Part 2; Patai, S., ed.; Wiley: New York, 1980; Chapter 20.
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