isomers in any case. Also, syntheses of the hydrazones in dioxane at 0-10 °C gave results similar to those obtained by using ethanol at elevated temperatures.

**Hydrazone Rearrangement Using Commercial Nitrosyl Sulfate.** As a preliminary experiment, the benzophenone hydrazone rearrangement[3] was repeated with substitution of the equivalent quantity of nitrosylsulfuric acid for the $NaNO_2$. The crude yield of benzanilide (mp 159.7-161.1 °C) was 97%. This method, which reduced the reaction time to about half and produced a purer product, was then used in the following work with the diketone monohydrazones.

Concentrated $H_2SO_4$ (6.3 ml) was added to a 30-mL beaker equipped with a ball stirrer and cooled in an ice bath. Nitrosylsulfuric acid (1.3 mL, 0.0073 mol of Du Pont nitrosyl sulfate, 40% in 87% $H_2SO_4$) was added with stirring. The powdered diketone monohydrazone **2** (0.0050 mol) was added over a 20-min period, with gas being evolved upon each addition. Stirring and cooling were continued for 10 min longer. The reaction mixture was poured into a mixture of ice and NaOH solution (12.5 g of NaOH in 50 mL of $H_2O$). The remainder of the product isolation and identification procedure was then carried out as in the Beckmann rearrangement above.

**Identification of Rearrangement Products.** All solids were identified by melting point (corrected) and mixture melting point with authentic samples. The trace amounts of liquid amines and the nitriles were identified by infrared spectrophotometry, and the nitriles were hydrolyzed to the corresponding acids. In addition, **6c** was converted to the anilide.

A number of runs were made in some cases, and typical melting points of unrecrystallized product obtained at various points in the rearrangement procedures were as follows (literature[13] values in parentheses): **3a**, 121.5-123 °C (122 °C); **3b**, 179.0-180.5 °C (181 °C); **3c**, 183.0-184.0 °C (184 °C); **5a**, 126.0-128.5 °C (130 °C); **5b**, 159.0-160.0 °C (155 or 165 °C); **5c**, 166.0-167.2 °C (163 °C); **6c**, 53-56 °C (57 °C); benzanilide, 159.7-161.1 °C (163 °C); 4-methoxyacetanilide, 128.0-129.0 °C (130-132 °C).

**Registry No. 1a**, 134-81-6; **1b**, 3457-48-5; **1c**, 1226-42-2; **2a**, 5344-88-7; **2b**, 40030-78-2; **2c**, 40030-79-3; **3a**, 65-85-0; **3b**, 99-94-5; **3c**, 100-09-4; **4a**, 100-47-0; **4b**, 104-85-8; **4c**, 874-90-8; **5a**, 55-21-0; **5b**, 619-55-6; **5c**, 3424-93-9; **6c**, 104-94-9; **6c** benzanilide, 7472-54-0; **6c** 4-methoxyacetanilide, 51-66-1.

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# Preparation of Spiro[cyclopropane-1,3'-[3*H*]indol]ones from Isatin in a Novel One-Step Process. A Study of Long-Range Chiral Recognition

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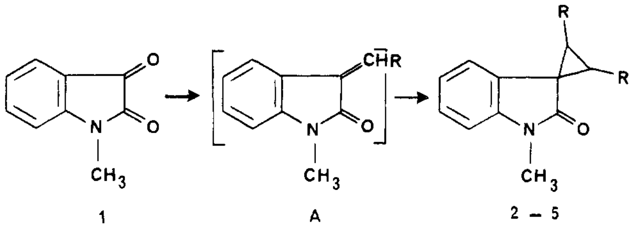
The spiro[cycyopropane-1,3'-[3*H*]indol]-2'(1'*H*)-one ring system has been prepared by the addition of diazomethanes[1] and stabilized sulfur ylides[2] to (2-oxindolin-3-ylidene)acetic esters. We have observed that Wittig reagents add to 1-methylisatin (**1**) to give this ring system in a single operation. Treatment of **1** with 1 equiv of the ylide prepared from 5-bromopentene and triphenylphosphine[3] in ether gave 15% of **2**, triphenylphosphine, and its oxide. The yield was increased to 74% by extraction of **1** from a Soxhlet with refluxing toluene into 2 equiv of the ylide. The trans isomer was isolated in pure form as indicated by the $^{13}C$ NMR spectrum with all the carbons accounted for by individual signals. Nonequivalency for the diastereotopic[4] carbons removed by four bond lengths from the nearest center of asymmetry was detected. In the proton-coupled spectrum of **2** the methine carbons of the cyclopropane ring (39.8 and 40.1 ppm) gave rise to a doublet with a coupling constant of 160 Hz, characteristic for this ring system.[5]

Scheme I[a]



[a] **2**, R = $CH_2CH_2CH{=}CH_2$; **3**, R = $C_6H_5$; **4**, R = $CH_2CH_2C_6H_5$; **5a**, R = $CH_2CH_2CH_2OC_6H_5$; **5b**, R = $CH_2CH_2CH_2OC_6H_5$.

Cyclopropyl rings have been isolated from Wittig reactions starting with fluorenone[6] and in intramolecular additions to an unsaturated ketone.[7] While the reaction of a stabilized ylide to isatin stops after one addition,[8] we have observed a faster addition of a second mole of ylide to the presumed intermediate A (Scheme I). This parallels the addition of an ylide to an unsaturated ketone[9] to form a spirocyclopropane ring system.

Since the spectral data of **2** did not allow the observation of the cyclopropyl protons due to overlap with the methylene protons, it was decided to examine the reaction of benzyltriphenylphosphonium benzylide[10] with **1**. We obtained **3** in 53% yield which allowed the isolation of pure *trans*-**3** as a white solid. In the $^1H$ NMR spectrum of **3** an AB quartet was seen at $\delta$ 3.80 ($J$ = 9 Hz, $\Delta\nu$ = 24.5 Hz). This pattern is compatible with the presence of a cyclopropyl ring in **3**. One of the indole protons ($C_4$ H) was shifted upfield ($\delta$ 6.10, d, $J$ = 8 Hz) due to the shielding effect by the two phenyl groups. The addition of (3-phenylpropyl)triphenylphosphonium 3-phenylpropylide[11] to **1** proceeded in 22% yield to give **4**.

More informative was the reaction between **1** and the ylide from (4-phenoxybutyl)triphenylphosphonium bromide[12] which gave **5** in 56% yield. Two isomers were separated, and their proton NMR spectra allowed us to distinguish the trans isomer from one of the cis isomers. The phenoxy-substituted methylene groups were observed at $\delta$ 3.86 as a triplet ($J$ = 6 Hz) and as a multiplet for the cis and the trans isomers, respectively. The $^{13}C$ NMR spectra confirmed the assignments. For the trans product the carbons of the side chains appeared as two sets of signals. An interesting feature emerged from close inspection of

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the signals attributed to the aromatic carbons. A total of 11 peaks could be observed, three of them in the 120-ppm region. Two of these three signals were assigned to the para carbons of the phenoxy groups. This was verified with the aid of the fully proton-coupled spectrum. By expanding the 120-ppm region, it was possible to determine the presence of two doublets ($J$ = 160 Hz) of triplets ($J$ = 7.5 Hz) (see Chart I). It may, therefore, be concluded that the trans isomer **5a** represents an example of chiral recognition[13] that extends over a distance of eight bond lengths counting along the periphery of the phenyl groups or the equivalent of seven bond lengths when measured across the phenyl rings.

A much simpler $^{13}C$ NMR spectrum was obtained for the cis isomer **5b** which gave a total of 17 signals. A comparison of the spectra of the cis and the trans isomers revealed an upfield shift for the resonance of the cyclopropyl and $\alpha$ aliphatic carbons of 2–3 ppm in the cis isomer. A similar upfield shift of 3 ppm was also observed for the indole carbon C-4, which was recognized as a doublet ($J$ = 160 Hz) of doublets ($J \simeq$ 8 Hz) in the fully proton-coupled spectrum. From this we conclude that the indole phenyl ring and the two alkyl substituents are in an all-cis configuration.

## Experimental Section

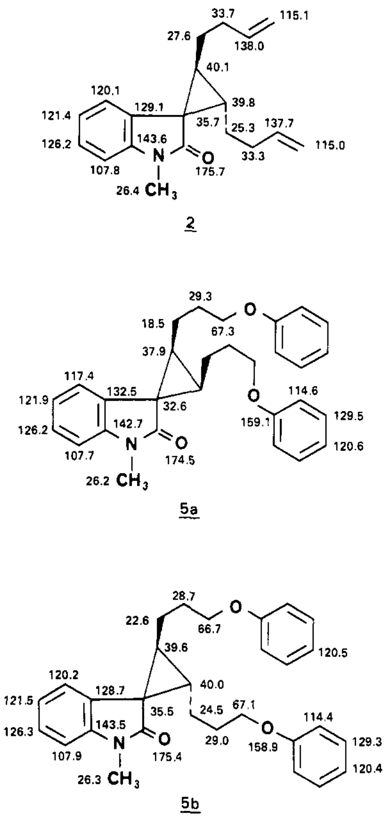
Natural-abundance $^{13}C$ NMR spectra were obtained at 25.2 MHz on a Varian XL-100 spectrometer system equipped with a 620/L 16K computer in the fourier transform mode with full proton decoupling. General spectral and instrumental parameters were as follows: internal deuterium lock to $CDCl_3$, spectral width of 5000 Hz, a pulse width $\mu$s (45°), normal pulse amplifier, a pulse repetition of 1.8 s.

Proton magnetic resonance spectra were obtained on a Varian Associates A-60 spectrometer and are recorded in $\delta$ values (parts per million) relative to $Me_4Si$ (tetramethylsilane) as an internal standard. Infrared spectra were recorded on a Perkin-Elmer spectrophotometer, Model 457. Thin-layer chromatography (TLC) was carried out on glass plates coated with silica gel HF-254 (E. Merck AG). Mass spectra were measured on a LKB 9000 mass spectrometer.

**2,3-Bis(3-butenyl)-1′-methylspiro[cyclopropane-1,3′-[3*H*]indol]-2′(1′*H*)-one (2).** An ice-cold suspension of 15.6 g (0.038 mol) of (4-pentenyl)-triphenylphosphonium bromide[3] in 150 mL of toluene was treated with 24 mL (0.038 mol) of 1.5 M *n*-butyllithium. After 1.5 h at room temperature the mixture was heated to reflux while 3.0 g (0.019 mol) of 1-methylisatin was extracted from a Soxhlet apparatus. After the mixture was heated for 2 h, it was worked up with methylene chloride, washed with water, dried over $MgSO_4$, and evaporated. The residue was chromatographed on silica gel to give 3.9 g (74%) of product, consisting of 2.7 g of pure trans product: mass spectrum, *m/e* 281 ($M^+$); NMR ($CDCl_3$) $\delta$ 0.6–2.4 (m, 10, 2 $CHCH_2CH_2$), 3.24 (s, 3, $CH_3$), 4.7–5.2 (m, 4, 2 $C{=}CH_2$), 5.3–6.2 (br, 2,2 $CH{=}$), 6.8–7.5 (m, 4, arom H). Anal. Calcd for $C_{19}H_{23}NO$ (mol wt 281.4): C, 81.1; H, 8.2; N, 5.0. Found: C, 80.8; H, 8.0; N, 5.0.

**1′-Methyl-2,3-diphenylspiro[cyclopropane-1,3′-[3*H*]indol]-2′(1′*H*)-one (3).** An ice-cold suspension of 16.2 g (0.038 mol) of benzyltriphenylphosphonium bromide[10] in 150 mL of toluene was treated with 24 mL (0.038 mol) of 1.6 M *n*-butyllithium. After 2 h at room temperature the mixture was heated to reflux, thereby extracting 3.0 g (0.019 mol) of 1-methylisatin from a Soxhlet apparatus. Heating was continued for an additional 2 h. The mixture was worked up with methylene chloride, washed with water, and dried over $MgSO_4$. The residue was chromatographed on silica gel to give 2.2 g (36%) of pure product which was crystallized by the addition of ether: mp 165–166 °C; mass spectrum, *m/e* 325 ($M^+$); NMR ($CDCl_3$) $\delta$ 3.20 (s, 3, $CH_3$), 3.80 (q, 2, $J$ = 9 Hz, $\Delta\nu$ = 24.4 Hz), 6.10 (d, 1, $J$ = 7 Hz, $C_4$ H), 6.6–7.6 (m, 13, arom H). Anal. Calcd for $C_{23}H_{19}NO$ (mol wt 325.4): C, 84.9; H, 5.9; N, 4.3. Found: C, 84.9; H, 6.0; N, 4.2.

Chart I[a]



[a] Chemical shift assignments are given in parts per millions and those within 0.4 ppm may be interchangeable.

**1′-Methyl-2,3-bis(2-phenylethyl)spiro[cyclopropane-1,3′-[3*H*]indol]-2′(1′*H*)-one (4).** The ylide, prepared from 17.9 g (0.038 mol) of (3-phenylpropyl)triphenylphosphonium bromide[11] and 24 mL (0.038 mol) of 1.6 M *n*-butyllithium in 150 mL of toluene, was heated to reflux to extract 3.0 g (0.019 mol) of 1-methylisatin from a Soxhlet apparatus. The mixture was worked up with methylene chloride, washed with water, and dried over $MgSO_4$. The dark residue was chromatographed with Silica gel to give 1.5 g (21%) of the product: mass spectrum, *m/e* 381 ($M^+$); NMR ($CDCl_3$) $\delta$ 1.4–2.8 (m, 10, 2 $CHCH_2CH_2$), 3.13 (s, 3, $CH_3$), 6.7–7.5 (m, 14, arom H). Anal. Calcd for $C_{27}H_{27}NO$ (mol wt 381.5): C, 85.0; H, 7.1; N, 3.7. Found: C, 85.0; H, 7.1; N, 3.5.

**1′-Methyl-2,3-bis(3-phenoxypropyl)spiro[cyclopropane-1,3′-[3*H*]indol]-2′(1′*H*)-one (5).** To the suspension of 18.3 g (0.038 mol) of (4-phenoxybutyl)triphenylphosphonium bromide[12] in 150 mL of toluene which was cooled in an ice bath was added a solution of 24 mL of (0.038 mol) of 1.6 M *n*-butyllithium in hexane. After 1 h at room temperature the solution was heated to reflux, allowing the extraction of 3.0 g (0.019 mol) of 1-methylisatin from a Soxhlet apparatus. After the addition was complete the mixture was heated for an additional 2.5 h. The solvent was evaporated, and the crude residue was worked up in methylene chloride, washed with water, and dried over $MgSO_4$ to give 8.6 g of crude product. This was chromatographed on silica gel to give 4.6 g (56%) of a mixture of the two isomers besides 1.9 g of triphenylphosphine. The mixture of the two isomeric products was separated by a second chromatogram on silica gel. The cis isomer was obtained as a solid (ether): mp 111–112 °C; mass spectrum, *m/e* 441 ($M^+$); NMR ($CDCl_3$) $\delta$ 1.5–2.4 (m, 10, 2 $CHCH_2CH_2$), 3.07 (s, 3, $CH_3$), 3.86 (t, 4, $J$ = 6 Hz, 2 $OCH_2$), 6.7–7.5 (m, 14, arom H). Anal. Calcd for $C_{29}H_{31}NO_3$ (mol wt 441.6): C, 78.8; H, 7.1; N, 3.2. Found: C, 78.6; H, 7.1; N, 2.9.

The trans isomer was obtained as a liquid: mass spectrum, *m/e* 441 ($M^+$); NMR ($CDCl_3$) $\delta$ 1.4–2.4 (m, 10, 2 $CHCH_2CH_2$) 3.13 (s, 3, $CH_3$), 3.5–4.2 (m, 4, 2 $OCH_2$), 6.6–7.4 (m, 14, arom H). Anal. Calcd, as above. Found: C, 78.3; H, 7.0; N, 3.0.

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**Registry No.** 1, 2058-74-4; **2**, 81276-65-5; **3**, 81276-66-6; **4**, 81276-67-7; **5a**, 81276-68-8; **5b**, 81339-49-3.

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# Polystyryl-Mercury Trifluoroacetate. A Convenient and Mild Reagent for Thioacetal and Thioketal Hydrolysis[1]

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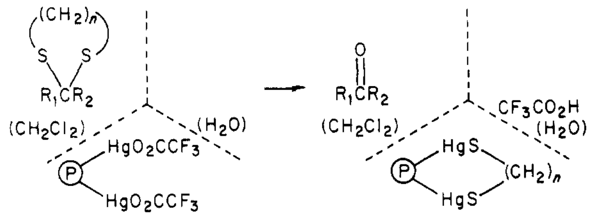
We describe herein a simple, mild, and effective technique for hydrolyzing thioacetals and thioketals, based on the use of a polystyryl–mercury trifluoroacetate reagent. Principal advantages of this new method over existing mercury(II) procedures are as follows:[3] (1) products are isolated by simple filtration and solvent evaporation, (2) spent and unused mercury is rendered innocuous by polymer attachment, (3) an inert atmosphere is not required for effective hydrolysis,[4] (4) acetal and ketal formation is avoided, and (5) the polymeric reagent is unreactive toward alkenes.

Scheme I illustrates the key features of this new desulfurization. A dithiane is dissolved in dichloromethane and then mixed with reagent 1 (ca. 2.1 mmol of Hg/mmol of dithiane) and water. Resinous trifluoroacetic acid is released into the water phase, aldehyde (or ketone) is expelled into the organic layer, and mercaptan is retained on the polymer in the form of a mercury salt.

The efficacy and convenience of this approach is demonstrated by the conversion of 2-phenyl-1,3-dithiacyclohexane to benzaldehyde. Thus, stirring a dichloromethane solution of the dithiane with 1 and water for 2 h at room temperature afforded a 92% yield of benzaldehyde (isolated from the dichloromethane layer by simple solvent evaporation). Titration of the aqueous phase also revealed quantitative formation of trifluoroacetic acid. Further examples of the use of 1 are presented in Table I.

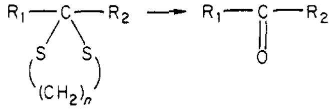
Two difficulties commonly associated with mercury(II) dithiane desulfurization procedures are (1) formation of acetals and ketals as side products and (2) reaction of double bonds within the substrate molecule.[3] Triphase hydrolysis avoids the former problem by virtue of the absence of alcoholic cosolvents. It is also interesting and significant to note that 1 shows no apparent reactivity toward alkenes under triphase conditions.[5] Like many mercury(II)-based reagents, however, 1 is unable to hydrolyze 1,2-dicarbonyl derivatives; e.g., 2-benzoyl-2-methyl-1,3-dithiacyclohexane is recovered quantitatively after attempted hydrolysis.

Scheme I. Triphase Hydrolysis of Dithianes



1, 50% ring substitution

Table I. Triphase Thioacetal and Thioketal Hydrolysis



| $R_1$ | $R_2$ | *n* | solvent | temp, °C | time, h | yield,[a] % |
|---|---|---|---|---|---|---|
| $n$-$C_5H_{11}$ | H | 2 | $CH_2Cl_2$ | 23 | 96 | 42 |
| $n$-$C_5H_{11}$ | H | 2 | $CHCl_3$ | 50 | 48 | 77 |
| $n$-$C_5H_{11}$ | H | 3 | $CHCl_3$ | 50 | 48 | 93 |
| $C_6H_5$ | H | 2 | $CH_2Cl_2$ | 23 | 2 | 95 |
| $C_6H_5$ | H | 3 | $CH_2Cl_2$ | 23 | 2 (3.5) | 82 (92) |
| $n$-$C_5H_{11}$ | $CH_3$ | 3 | $CH_2Cl_2$ | 23 | 4.5 (7) | 86 (79) |
| $n$-$C_6H_{13}$ | $(CH_2)_2CH_3$ | 3 | $CH_2Cl_2$ | 23 | 4.5 (5) | 96 (87) |
| $C_6H_5$ | $CH_3$ | 3 | $CH_2Cl_2$ | 23 | 5 (5) | 90 (65) |
| $-(CH_2)_5-$ | | 2 | $CHCl_3$ | 50 | 3.5 | 79 |
| $-(CH_2)_5-$ | | 3 | $CH_2Cl_2$ | 23 | 5 (5) | 90 (72) |
| 3-cholestanone | | 3 | $CHCl_3$ | 23 | (3.5) | (88) |
| $CH_3$ | $C_6H_5CO$ | 3 | $CHCl_3$ | 50 | 48 | 0[b] |

[a] Glc yield; numbers in parentheses refer to 4-mmol-scale reactions and isolated yields. [b] 96% recovery of starting dithiane.

Polystyryl–mercury trifluoroacetate is very easy to prepare and provides the basis for an extremely simple method for hydrolyzing thioketals and thioacetals. It should find broad use.

## Experimental Section

**General Methods.** Unless stated otherwise, all reagents and chemicals were obtained commercially and were used without purification. One percent cross-linked polystyrene (gel type, 200–400 mesh) was purchased from Bio-Rad Laboratories, Richmond, CA. All $^1H$ NMR and IR spectra were recorded on Varian A-60 and Beckman Acculab 7 spectrometers, respectively. Product mixtures were analyzed by GLC on a Hewlett-Packard Model 5830 A flame-ionization instrument (2 ft × 0.125 in. UCW-982 on Chromosorb W column). Thioacetals and thioketals were prepared from the corresponding aldehydes and ketones, using procedures similar to those previously described.[6] 2-Benzoyl-2-methyl-1,3-dithiacyclohexane was synthesized from 2-methyl-1,3-dithiacyclohexane and benzonitrile.[7]

**Polystyryl–Mercury Trifluoroacetate (1).** To a solution of 6.40 g (15 mmol) of mercury trifluoroacetate dissolved in 220 mL of dichloromethane was added 3.12 g of 1% cross-linked polysytrene (30 mmol of $C_6H_5$), and the mixture was stirred for 48 h at room temperature. The polymer was filtered, washed with 6 × 50 mL of dichloromethane, and dried (23 °C, 24 h (0.1 mm)) to yield 7.69 g (98%) of 1: IR (Nujol) 1690, 1200, 860, 820 cm$^{-1}$. The absence of mercury in the filtrate confirmed that mercuration of the polymer was quantitative.

**Benzaldehyde.** To a mixture of 4.4 g (8.45 mmol of Hg) of 1 suspended in 10 mL of dichloromethane was added a solution of 0.784 g (4.0 mmol) of 2-phenyl-1,3-dithiacyclohexane dissolved in 10 mL of dichloromethane. After the mixture was stirred for 10 min, 10 mL of water was added and the three-phase mixture then stirred at room temperature for 3.5 h. The resin was removed by filtration and washed with 3 × 30 mL of dichloromethane, and the combined filtrate was dried ($Na_2SO_4$). Evaporation of solvent

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[1] Supported by the Division of Basic Energy Sciences of the Department of Energy (Contract EG-77-S-02-4446).

[2] On leave from the Institute of Macromolecular Chemistry of the Czechoslovak Academy of Sciences.

[3] For recent dithiane hydrolysis procedures, see: Grobel, B.-T.; Seebach, D. *Synthesis* **1977**, 357. Bates, G. S.; O'Doherty, J. *J. Org. Chem.* **1981**, *46*, 1745. Degani, I.; Fochi, R.; Regondi, V. *Synthesis* **1981**, 51.

[4] Vedejs, E.; Fuchs, P. L. *J. Org. Chem.* **1971**, *36*, 366.

[5] Heating a mixture of 0.22 g (0.42 mmol of Hg) of 1, 0.42 mmol of 1-octene in 1 mL of $CHCl_3$, and 1 mL of water for 2 weeks at 50 °C did not result in any loss of alkene.

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