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Synthesis and Thermolysis of Poly(2,2-dimethyltrimethylene phenylphosphinate)

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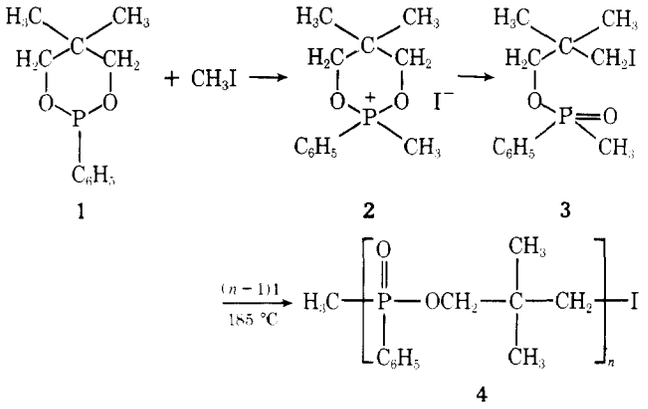
Poly(2,2-dimethyltrimethylene phenylphosphinate) has been synthesized through the ring-opening polymerization of 2,2-dimethyltrimethylene phenylphosphonite using CH_3I as an initiator. The structure of the polymer has been established by NMR spectroscopy, and its thermal and other properties are reported. Its thermolysis at 300 °C gave cyclic 2,2-dimethyltrimethylene phenylphosphinate, whose conformational analysis has been conducted from ^1H NMR spectral data.

Ring-opening polymerization of cyclic phosphonites to polyphosphinates has been reported in literature. For example, Petrov[2] and Mukaiyama[3] and their co-workers prepared poly(trimethylene phenylphosphinate) from the corresponding cyclic phosphonite at 120–200 °C using CH_3I as an initiator. However, only low molecular weight polymer ($\leq$3200) was obtained,[2] presumably due to decomposition at these temperatures. Assuming that the low molecular weight polymer resulted due to β-elimination, $>P(=O)OCH_2CH_2- \rightarrow >P(=O)OH + CH_2=CH-$, we have prepared poly(2,2-dimethyltrimethylene phenylphosphinate) in which both of the β-hydrogens are substituted by methyl groups. This paper describes the thermolysis of poly(2,2-dimethyltrimethylene phenylphosphinate) and compares it with that of poly(trimethylene phenylphosphinate).

Results and Discussion

Poly(2,2-dimethyltrimethylene phenylphosphinate) was prepared by the reaction shown in Scheme I.

Scheme I



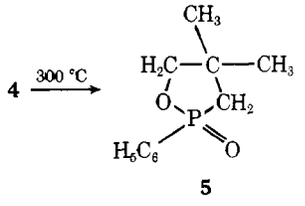
The reaction of the cyclic phosphonite **1** with CH_3I proceeds via the phosphonium salt intermediate **2**, which undergoes Arbuzov rearrangement to give phosphinate **3**. Both **2** and **3** were isolated and identified by their NMR spectra (Figure 1). The rearrangement of the phosphonium salt to the phosphinate is quite facile as it occurred even when running the NMR spectrum. The spectrum of **3** shows the OCH_2 protons to be magnetically nonequivalent. Heating to 100 °C in toluene did not change its spectrum, suggesting that the nonequivalence of the methylene protons is due to chiral phosphorus and not to restricted rotation around the P–O bond.

Phosphonite **1** is known to exist in the chair conformation,[4,5] but different configurations have been assigned at the phosphorus atom. Gagnaire et al.[4] originally assigned the phenyl substituent to the equatorial position on steric grounds. However, from NMR studies of cyclic phosphonites, Verkade and Bentrude and their co-workers[5,6] assigned the phenyl group to the axial position in **1**. Bentrude et al.[6] showed that $^3J_{POCH}$ depends on the dihedral angle POCH and the orientation of the lone pair on phosphorus. If the substituent is axial, $^3J_{PH_a} \approx 2$ Hz and $^3J_{PH_e} \approx 10$ Hz; and if the substituent is equatorial, $^3J_{PH_a} \approx 2$ Hz and $^3J_{PH_e} \approx 20$ Hz. In phosphonite **1** the $^3J_{POCH}$ couplings are 3 and 10.2 Hz for the axial and equatorial protons, respectively, which are consistent with the structure in which the phenyl group is in the axial arrangement.

The phosphonium salt intermediate **2** probably has the same stereochemistry as the cyclic phosphonite; that is, the phenyl group is in the axial position.

Poly(2,2-dimethyltrimethylene phenylphosphinate) (4). **4** is a colorless polymer. The low molecular weight polymer is a viscous liquid, but the high molecular weight polymer is usually a glassy solid. A typical polymer, $\overline{M}_n \approx 16\,000$, has $T_g = 4$ °C and $T_m = 160$ °C. Its structure has been established by its NMR spectrum (Figure 1), which shows multiplets of equal area for the CH_2 and CH_2O groups bonding to phosphorus. The polymer was shown by X-ray analysis to be mainly amorphous. The lack of crystallinity is attributed to the bulky groups on phosphorus and close proximity of the phosphorus moieties along the polymer chain.

The polymer is stable up to about 250 °C, but decomposes at higher temperatures to give cyclic 2,2-dimethyltrimethylene phenylphosphinate (**5**) in almost quantitative yield (eq 1). The



(1)

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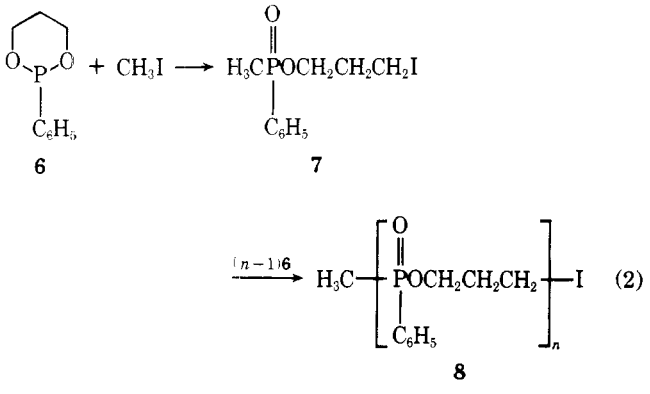
NMR spectrum of **5** (Figure 1) shows CH_2 and CH_2O groups attached to the phosphorus atom.

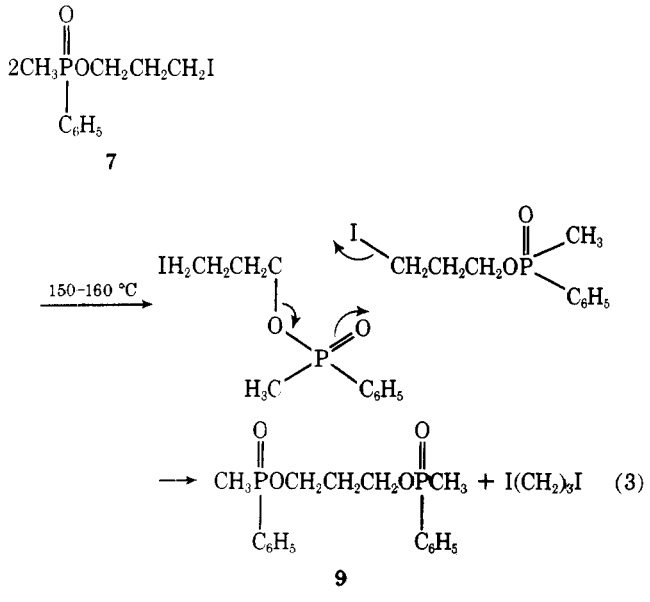
The decomposition of **4** to **5** does not appear to be an "unzipping" reaction involving an attack by the iodide carbon on the phosphorus atom because that would involve a highly sterically hindered transition state. Evidence against this mechanism is provided by the fact that the monomeric phosphinate **3**, on heating to 300 °C, did not decompose to give **5** and CH_3I. Instead, a dark brown, nondistillable product was formed. The decomposition of the polymer to **5** most probably occurs via homolytic cleavage of the P–C bond and subsequent closing of the ring.

We prepared poly(trimethylene phenylphosphinate) (**8**, eq 2) to compare its thermal stability with that of the sterically hindered polyphosphinate **4**.



6 **7** **8** (2)

Surprisingly, **8** did not decompose even when heated at 300 °C for 20 min. On the other hand, its monomeric species 3-iodopropyl methylphenylphosphinate (**7**) decomposed at 150–160 °C to give trimethylene bis(methylphenylphosphinate) (**9**) and 1,3-diiodopropane presumably via a bimolecular reaction (eq 3).



7 **9** (3)

Equation 3 would explain why only low molecular weight (≤3200) poly(trimethylene phenylphosphinate) was obtained by the earlier workers.[2] The internally generated 1,3-diiodopropane would react with the polymer to give low molecular weight species.

Conformational Analysis of 5. Theoretically, phosphinate **5** can exist in two conforms (**5a** and **5b**). Its NMR spectrum showed only two types of CH_3's, indicating that either there is rapid equilibrium between **5a** and **5b** or the compound exists exclusively in one conformation. However, the possibility of equilibrium was tentatively excluded on the basis that the spectrum showed no change at −80 °C (CD_2Cl_2).

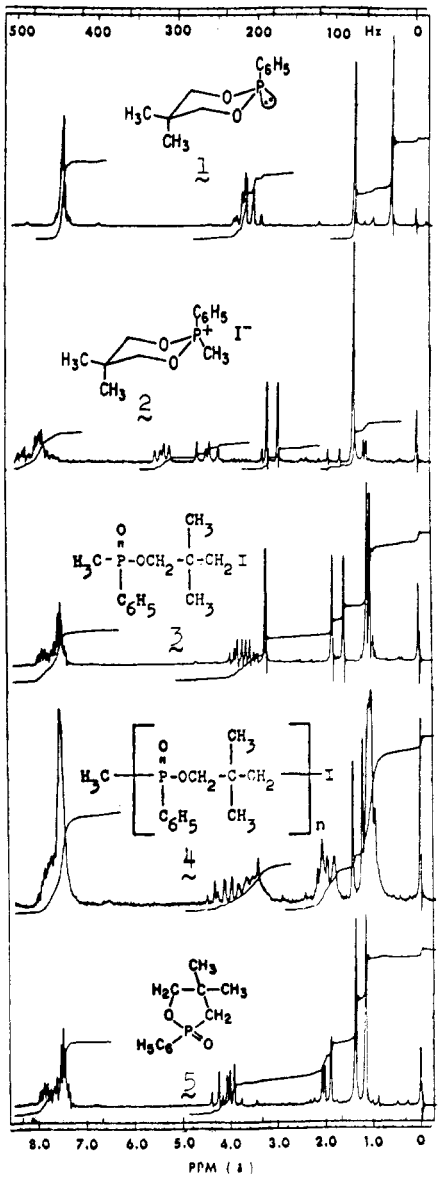
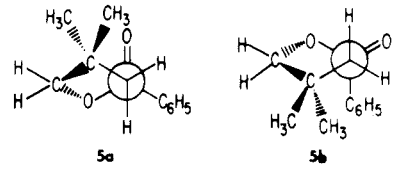


Figure 1. ^1H NMR spectra of phosphorus compounds.



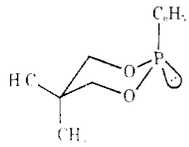
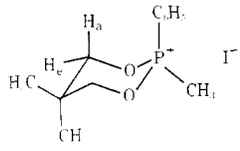
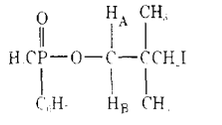
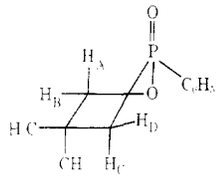
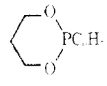
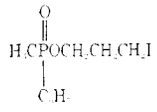
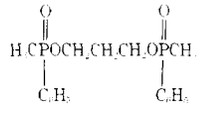
5a **5b**

In the previous paper, we showed that $^2J_{PCH}$ depends strongly on the OPCH dihedral angle.[7] Protons trans to P=O couple more strongly with phosphorus than the gauche protons. For example, in dineopentylphenylphosphine oxide, in which the neopentyl groups are fixed in the trans position because of the steric hindrance and their methylene protons are trans and gauche to P=O, $^2J_{PCH(trans)}$ = 12.8 Hz and $^2J_{PCH(gauche)}$ = 7.8 Hz.

Phosphinates are not much different from tertiary phosphine oxides in terms of bonding around phosphorus. Therefore, the $^2J_{PCH}$ values of 13.0 and 6.0 Hz observed for phosphinate **5** suggest that it exists in the less sterically hindered conformation **5a**, in which the strongly coupled proton is trans to P=O and the second proton is gauche to P=O.

The $^3J_{POCH}$ coupling constants in **5a** have been assigned in accordance with the POCH dihedral angle. In other words,

Table I. ^1H and ^{31}P NMR Data

no.	compd	proton chemical shifts, ppm[a]	coupling constants, Hz	^{31}P, ppm[b]
1		CH_3, CH_3 = 0.53, 1.30 C_6H_5 = 7.27–7.63		145.1
2		CH_3, CH_3 = 1.29 PCH_3 = 3.00 H_a = 4.38, H_e = 5.52 C_6H_6 = 7.48–8.35	$^2J_{PCH}$ = 14.0 $^3J_{POCH_a}$ = 6.6, $^3J_{POCH_e}$ = 15.4 $^2J_{H_aH_e}$ = 10.9	
3		CH_3, CH_3 = 1.00, 1.06 PCH_3 = 1.67 CH_2 = 3.19 H_A = 3.50, H_B = 3.83 C_6H_5 = 7.43–8.05	$^2J_{PCH}$ = 14.2 $^3J_{POCH_A}$ = 5.0, $^3J_{POCH_B}$ = 6.2	42.0
5a		CH_3, CH_3 = 1.15, 1.35 H_A = 3.95, H_B = 4.25 H_C = 2.07, H_D = 1.98 C_6H_6 = 7.33–8.00	$^3J_{POCH_A}$ = 9.5, $^3J_{POCH_B}$ = 13.5 $^2J_{H_AH_B}$ = 9.5 $^2J_{PH_C}$ = 13.0, $^3J_{PH_D}$ = 6.0	58.6
6				152.8
7		PCH_3 = 1.68 OCH_2 = 3.75–3.89 (m) 4.00–4.11 (m) CH_2 = 2.00–2.23 (m) CH_2I = 3.23 (t) C_6H_5 = 7.43–7.83 (m)	$^2J_{PCH}$ = 14.6 $^3J_{HH}$ = 7.0	42.3
9		CH_3, CH_3 = 1.61, 1.64 OCH_2 = 3.77–3.93 (m) 4.05–4.18 (m) CH_2 = 1.86–2.07 (m) C_6H_5 = 7.36–7.84 (m)	$^2J_{PH}$ = 14.5, 14.5	42.6

[a] Downfield from internal standard of Me_4Si; m = multiplet, t = triplet. [b] Downfield from external standard of 85% H_3PO_4.

the larger coupling is assigned to the equatorial proton and the smaller coupling to the axial proton (Table I).

Experimental Section

Analytical Methods. Proton and ^{31}P magnetic resonance spectra were run as described in the preceding paper.[7] The spectra were run in $CDCl_3$ unless mentioned otherwise. Infrared spectra were determined on neat samples using a Perkin-Elmer 221 spectrometer equipped with sodium chloride optics. A Norelco X-ray diffractometer with crystal monochromatized Cu Kα radiation was used to examine the polymer morphology.

2,2-Dimethyltrimethylene Phenylphosphonite (1). An ice-cold solution of 31.2 g (0.30 mol) of 2,2-dimethyl-1,3-propanediol and 65 g (0.64 mol) of triethylamine in 400 mL of anhydrous benzene was stirred in a 1-L creased flask fitted with a mechanical stirrer, a reflux condenser, and a dropping funnel. A solution of 53.7 g (0.30 mol) of phenylphosphonous dichloride was added dropwise. After the addition of phenylphosphonous dichloride was complete, anhydrous ether (300 mL) was added to complete the precipitation of triethylammonium chloride. The mixture was filtered and the solid washed with 100 mL of anhydrous ether. The filtrate was distilled, leaving white solid 61.8 g (91.8%). It was purified by sublimation at 80–90 °C (2–3 mm), mp 75 °C (DTA).

Phosphonium Salt 2. A solution of 21.0 g (0.1 mol) of **1** and 28.4 g (0.2 mol) of CH_3I in 100 mL of anhydrous benzene was heated under N_2. As soon as the solution started to reflux, the phosphonium salt separated as white solid. The reaction mixture was cooled in ice, and the phosphonium salt was collected by filtration. It was quite unstable in air and turned brown. An analytical sample was prepared by recrystallization from chloroform/ethyl acetate. Anal. Calcd for $C_{12}H_{18}IO_2P$: C, 40.9; H, 5.1. Found: C, 41.2; H, 5.1.

3-Iodo-2,2-dimethylpropyl Methylphenylphosphinate (3). The phosphonium salt **2** redissolved in benzene when the reaction mixture was refluxed for 2 h. Benzene was distilled, leaving the phosphinate as colorless liquid in quantitative yield. It was distilled at 165–166 °C (1 mm), $n^{25}D$ 1.5522. Anal. Calcd for $C_{12}H_{18}IO_2P$: C, 40.9; H, 5.1. Found: C, 41.4; H, 5.3. Its IR spectrum showed P=O and P–O–C stretching absorptions at 1300 (m) and 1025 (s) cm^{-1}, respectively.

Poly(2,2-dimethyltrimethylene phenylphosphinate) (4). A mixture of 42.0 g (0.2 mol) of **1** and 1.32 g (0.0038 mol) of **3** was sealed under vacuum in a heavy-wall glass tube. It was heated at 185 °C for 24 h, during which time the contents had become quite viscous. The tube was broken, and the polymer was dried in a vacuum oven at 80 °C, $n^{25}D$ 1.5570. It had $\overline{M}_n \approx 16\,000$ (membrane osmometry in benzene). Its IR spectrum had two P=O absorptions at 1302 (w) and 1282 (w) cm^{-1} and P–O–C absorption at 1010 cm^{-1} (s).

Thermolysis of 4. The polyphosphinate (5 g) was heated at 300 °C under N_2 for 10 min. The polymer decomposed to cyclic 2,2-dimethyltrimethylene phenylphosphinate (**5**), which was distilled at 132 °C (0.2 mm) in almost quantitative yield. On cooling, it changed to white solid, mp 71 °C (DTA). Anal. Calcd for $C_{11}H_{15}O_2P$: C, 62.9; H, 7.1; P, 14.8. Found: C, 62.5; H, 7.3; P, 14.6. Its cryoscopic molecular weight in C_6H_6 was 213; calcd 210. Its IR spectrum showed the P–O–C stretch at 990 cm^{-1} (s) but showed no P=O absorption unless it was under a strong absorption centered at 1225 cm^{-1}.

Trimethylene Phenylphosphonite (6). This was prepared by the same procedure as phosphonite **1**. It is a colorless viscous liquid and

was used without purification for the preparation of phosphinate **7**.

3-Iodopropyl Methylphenylphosphinate (7). To 28.4 g (0.2 mol) of freshly distilled CH_3I was added dropwise 18.2 g (0.1 mol) of trimethylene phenylphosphonite (**6**) during stirring under N_2. The reaction was exothermic and the mixture started to reflux. After the addition of **6** was complete, the excess CH_3I was distilled in vacuo, leaving **7** as clear viscous liquid. During an attempted distillation at 150–160 °C (0.5 mm), it decomposed to give 12.3 g (83%) of 1,3-diiodopropane and 16.9 g (96%) of trimethylene bis(methylphenylphosphinate) (**9**). The structures of **7** and **9** were identified by NMR spectra. Their IR spectra showed P=O absorptions at 1295 cm^{-1} (m) and P–O–C absorptions at 1020 cm^{-1} (m).

Poly(propane phenylphosphinate) (8). A mixture of 18.2 g (0.1 mol) of **6** and 0.644 g (0.002 mol) of **7** was sealed in a heavy-wall glass tube under vacuum. The tube was heated at 160 °C for 6 h. The reaction mixture turned light brown and slightly viscous. It was cooled to room temperature, and the contents were isolated by breaking the tube. The polymer was dried at 100 °C (0.3 mm). Its thermolysis at 300 °C (0.5–1.0 mm) for 20 min gave essentially no volatile decomposition products.

Registry No.—**1**, 7526-31-0; **2** (charged form), 68900-51-6; **2** (uncharged form), 68900-56-1; **3**, 68900-52-7; **4**, 68900-57-2; **5**, 68900-53-8; **6**, 7526-32-1; **7**, 68900-54-9; **8**, 68900-58-3; **9**, 68900-55-0; 2,2-dimethyl-1,3-propanediol, 126-30-7; phenylphosphonous dichloride, 644-97-3.

References and Notes

(1) Address correspondence to E. I. du Pont de Nemours and Co., Kinston, N.C. 28501.
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Studies in Biomimetic Alkaloid Syntheses. 3. Syntheses of Ervinceine and Vincadifformine Analogues from Tetrahydro-γ-carbolines through Secodine Intermediates

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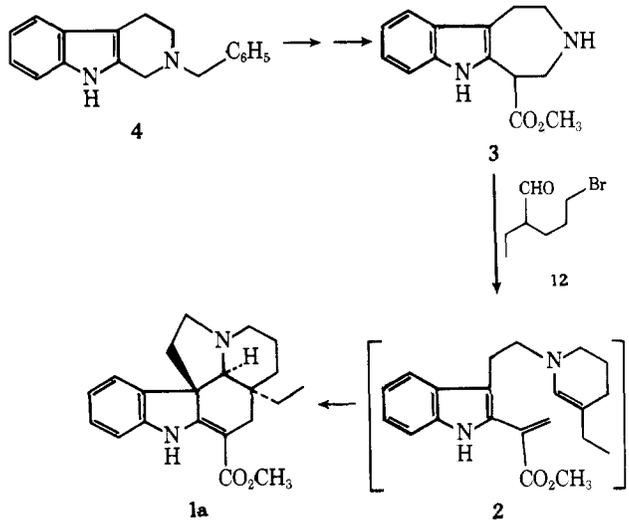
The chlorination of tetrahydro-γ-carbolines **10a–e** and reactions of the resultant chloroindolenines **11a–e** with thallium dimethyl malonate gave the indoloazepines **6b–f.** The 3-spiropyrrolidino-2-alkylideneindoline intermediate **7b** of this transformation could be isolated and characterized. Debenzylation of the indoloazepines **6b–f** to the secondary amines **14a–e** and reactions of the latter with halo aldehydes **12** or **15** yielded vincadifformine **1a** and its aryl-substituted analogues **1b–e.** The structure of ervinceine was established as 16-methoxyvincadifformine (**1e**). The spiroenammonium precursor **13b** of a secodine intermediate **2** was isolated and characterized.

A total synthesis of vincadifformine **1a,** recently reported from our laboratory,[1] proceeds by way of the biogenetically postulated[2,3] secodine intermediate **2** (Scheme I). This intermediate could be generated from an indoloazepine **3** through a spiroannelation and fragmentation sequence. The indoloazepine **3** was in turn obtained from a tetrahydro-β-carboline **4** by a biomimetic oxidative alkylation, followed by debenzylation and decarboxylation reactions. The present report describes an alternative approach to such indoloazepine precursors and their variations and reactions, which extend the scope of the synthesis to other alkaloids. These studies also substantiated mechanistic considerations in key steps of the vincadifformine synthesis.

Our earlier synthesis[1] of the indoloazepine **3** was based on chlorination of the tetrahydro-β-carboline **4** with *tert*-butyl hypochlorite, thus furnishing the chloroindolenine **5** (Scheme II). On reaction with thallium *tert*-butyl methyl malonate this chloride gave the indoloazepine **6a.** Formation of the seven-membered heterocycle was postulated to arise from rearrangement of an initial malonate to imine adduct, with generation of a 3-spiropyrrolidino-2-alkylideneindoline intermediate **7a.** It was proposed that such an intermediate would undergo fragmentation to a zwitterionic immonium malonate **8a,** with subsequent cyclization of the latter finally leading to formation of the indoloazepine ring system.

Since none of the reactive intermediates of the proposed

Scheme I



sequence were isolated during the transformation of the chloroindolenine **5** to the indoloazepine **6a,** it was of interest to see if intermediacy of the key 3-spiropyrrolidino-2-alkylideneindoline **7a** could be confirmed by an alternative synthesis such as by the chlorination and alkylation of the iso-

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