Table II. ^{13}C NMR Chemical Shift[a] Data

compd	Ar-CH_3	C_4-CH_3	$C_{1,7}$	C_4	$C_{3,5}$	C_{14}	$C_{12,20}$[b]	$C_{10,16}$[b]	$C_{13,19}$[b]	$C_{11,15}$[b]	$C_{9,17}$[b]	$C_{8,18}$[b]
3a	19.4	23.9	33.2	35.7	40.4	43.2	(125.6)	(129.7)	(132.2)	(132.9)	(138.2)	(144.7)
3b	19.1	21.4, 25.1	34.7	35.7	40.4	43.2	(124.6)	(130.7)	(132.4)	(132.6)	(138.2)	(144.9)
3c	19.4	26.7	36.5	36.9	44.5	41.6	(126.6)	(130.2)	(131.4)	(134.7)	(137.3)	(140.8)
4a	20.1	26.3	62.6	35.6	60.1	42.2	(126.9)	(130.6)	(131.7)	(125.8)	(138.8)	(146.7)
4b	20.0	27.3, 25.6	62.1	35.6	60.3	43.4	(126.3)	(131.2)	(131.2)	(125.9)	(138.9)	(146.8)

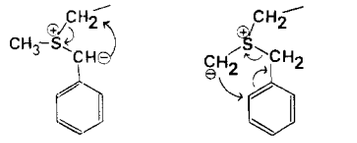
[a] Chemical shifts are quoted in ppm downfield from Me_4Si and are considered to be within ±0.1 ppm. [b] Assignments of aromatic ring carbons are tentative.

by 1.7 ppm. In the case of **3b**, the chemical shift difference of 3.7 ppm indicates the presence of a strong shielding effect on the ^{13}C nucleus above the aromatic rings.

The chemical shifts for most of the other ^{13}C nuclei in **3a** and **3b** are very similar (see Table II), but a number of changes are observed in the spectrum of **3c**. These changes may very well be the result of the relief of steric strain and similar effects have previously been noted in thia derivatives of [2.2]metacyclophane.[13]

One of the more curious facets of this problem is the facile formation of the 2,6-dithia[7.1]paracyclophane, a very rigid molecule which takes considerable time before it eventually gains some degrees of freedom, rather than the relatively strain-free [5.1]metacyclophane. Finch[1] has suggested that the proposed radical pair mechanism for the Stevens rearrangement[14] would disfavor the [5.1]metacyclophane route.

An alternative way of viewing this reaction is via Baldwin's rules for ring closure.[15] The Stevens rearrangement to yield the [5.1]metacyclophane can be classified as the disfavored 3-endo-tetrahedral process, see below, while the Sommelet rearrangement can be viewed as a 5-endo-trigonal process



which, while normally not a favored process, is facilitated by the presence of a second row element such as sulfur.[16]

Experimental Section

The samples for this investigation were kindly provided by Dr. Neville Finch of the Pharmaceuticals Division, CIBA-GEIGY Corp., Summit, N.J. ^1H and ^{13}C NMR spectra were obtained on a Bruker WH90 spectrometer operating in the FT mode at 90 MHz (+25 °C) and 22.62 MHz (+30 °C), respectively. Concentrations of 0.2 to 0.3 M in methylene chloride were used throughout and Me_4Si was used as the internal standard.

Carbon-13 chemical shift assignments, except for aromatic ring carbons, were essentially straightforward (see Table II) and any ambiguities were resolved by selective proton decoupling. Unequivocal assignment of the aromatic ring carbons was not attempted in this study; however, proton-bearing carbons ($C_{10,16}$, $C_{12,20}$, $C_{13,19}$) were readily distinguished from non-proton-bearing carbons; proposed ring carbon chemical shift assignments were based on substituent effects.

As noted by Finch,[1] the equilibration of the anti and syn forms of **3** occurred over a several-hour period at room temperature. The appearance of peaks attributable to **3c** was observed only after 2 days at 50 °C or after several weeks at room temperature.

Conclusions

^1H and ^{13}C NMR studies show that 4,4,9,17-tetramethyl-2,6-dithia[7.1]paracyclophane, which is initially produced as the anti atropisomer, **3a**, rearranges via the syn atropisomer, **3b**, in which one C_4-methyl group is held in close proximity to both of the aromatic rings. Eventually, the relatively unstrained conformation **3c** is obtained in which the C_4-dimethyl group is no longer confined within the central molecular cavity. The ^{13}C nuclei positioned directly above the arene rings exhibit modest upfield chemical shifts.

Acknowledgments. It is a pleasure to thank Dr. Neville Finch of the Pharmaceuticals Division of the CIBA-GEIGY Corp., not only for generous gifts of compounds, but also for many helpful discussions. We thank the National Research Council of Canada for financial support.

Registry No.—**3**, 66514-08-7; **4**, 66514-09-8.

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Diphenylamino Isocyanate Dimers

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The thermolysis of N,N-disubstituted carbamoyl azides has been extensively investigated by Stolle and his co-workers.[1,2] These authors had shown that *N,N*-diaryl and *N*-alkyl-*N*-aryl carbamoyl azides yield 1-substituted 3-hydroxy-1*H*-indazoles as major products as evidenced by independent synthesis. Occasionally small amounts of by-products

were isolated which were assumed to be dimers of the corresponding amino isocyanates. Although the thermolysis and photolysis of carbamoyl azides has been reinvestigated extensively in recent years,[3-9] the structures of the dimers were not elucidated. They were generally referred to as 1,3-diazetidinediones based on analogy to the well-known aryl isocyanate dimerization.[10] This structural assignment is highly doubtful, especially since N,N-dialkyl and other *N*-alkyl-*N*-arylamino isocyanates were shown not to form any four-membered ring heterocycles on dimerization. We therefore decided to reinvestigate the thermolysis of *N,N*-diphenyl carbamoyl azide (**1**) in order to elucidate the structure of the reaction products.

Heating of *N,N*-diphenyl carbamoyl azide (**1**) in chlorobenzene at 120–135 °C caused rapid formation of nitrogen. Work-up of the deeply colored reaction mixtures yielded three compounds, of which 1-phenyl-3-hydroxy-1*H*-indazole (**3**) was the major product. The remaining two compounds, **4** and **5**, proved to be dimers of *N,N*-diphenylamino isocyanate (**2**) or its nitrene precursor, as evidenced by elemental analysis and molecular weight determination.

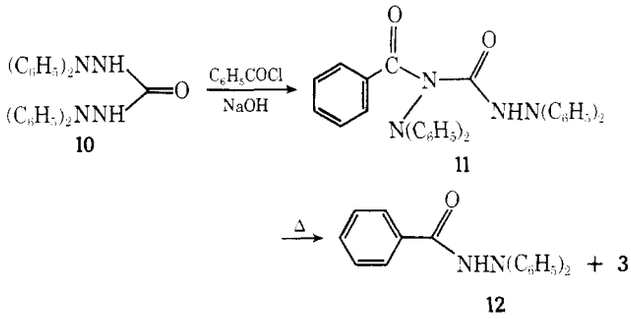
Clues for the structural assignment of the dimers as being carbazoylated derivatives of **3** were provided by thermal and chemical degradation reactions. Thus heating of the dimers in chlorobenzene gave almost quantitative yields of the indazole **3**. On following the reaction by thin-layer chromatography, it would be seen that **4** as well as **5** produce initially a mixture of both carbazoylated compounds **4** and **5**, which was slowly converted to **3**. Treatment of **4** and **5** with methanolic potassium hydroxide gave high yields of **3** and 3,3-diphenyl carbazate (**8**) in each case. The experimental data support the conclusion that the "dimers" are formed by O and N attack on *3*, giving 1-phenyl-2-(3,3-diphenylcarbazoyl)-1*H*-indazolin-3-one (**4**) and (1-phenyl-1*H*-indazol-3-yl)- 3,3-diphenylcarbazate (**5**).

Spectral data support further the proposed structural formulas of both compounds: The IR spectrum (in $CHCl_3$) of the *O*-carbazoyl derivative **5** shows a broadened carbonyl band of only moderate intensity at 1775 cm^{-1} with a weaker shoulder at 1745 cm^{-1}, as well as a NH band at 3360 cm^{-1}. (No NH proton can be found in the H NMR spectrum of **5** [in $CDCl_3$].) Similar bands can be seen in the IR spectrum of methyl carbazate **8**. The NH band appears also at 3360 cm^{-1}, while the broad carbonyl band is shifted to 1745 with a shoulder at 1720 cm^{-1}. Here too the carbonyl band is only of moderate intensity. Missing from the H NMR spectrum is a signal for a NH proton which is here also hidden under the broad multiplet of the aromatic protons. The IR spectrum of *N*-carbazoyl derivative **4** shows two well-defined carbonyl bands at 1685 and 1740 cm^{-1}; the broadened NH band is centered at 3250 cm^{-1}.

The thermal convertibility of **4** and **5** into **3** explains why product ratios among **3**, **4**, and **5** depend upon the reaction duration. Sufficiently long reaction times will only give **3** and no evidence for dimers **4** and **5**.[11] The formation of both **4** and **5** during the thermolysis of **1** and on heating **4** or **5** alone points to an equilibrium between two tautomers of indazole **3a** and **3b**. Both tautomers undergo reaction with **2** to give *N*- and *O*-carbazoylation products **4** and **5**.

In order to provide further evidence for a solution tautomerization of **3**, its reaction with phenyl isocyanate was investigated. Heating a chloroform solution of **3** with equimolar amounts of phenyl isocyanate for 3 h produces a mixture of the *N*- and *O*-carbamoylated products **6** and **7** in a ratio of 9:1. Both acylation products are readily cleaved by methanolic potassium hydroxide, affording **3** and methyl *N*-phenylcarbamate **9** in high yields. Heating of **6** in chloroform under conditions similar to those at which **6** and **7** are produced leads to formation of 10% **7** (97% material recovery), indicating here also the lability of the carbamoyl group and an equilibrium between **3a** and **3b**.

A compound structurally related to **4** is 1,1,5,5-tetraphenyl-2-benzoyl carbohydrazide (**11**) which was prepared from the parent tetraphenyl carbohydrazide (**10**) and benzoyl chloride. **11** differs from **4** only in the missing C–N linkage forming the indazole nucleus. It is remarkable that, despite the absence of a 1-phenylpyrazolone-3 ring, the IR spectrum of **11** shows carbonyl bands at 1740 and 1670 cm^{-1}, in the shape and intensity very similar to those of **4** and **6**. As expected, **11** is thermolabile and dissociates on heating at 150 °C in chlorobenzene solution giving *N,N*-diphenyl-*N'*-benzoylhydrazine (**12**) and via the amino isocyanate **2** the indazole



10 **11** **12**

3.[12] This observation not only supports the proposed structure of **4** but also the one of **11**. A *O*-benzoylated product formed instead of **11** during benzoylation of **10** is not capable of dissociating in the observed manner.

Additional verification of the proposed structures was obtained by a single-crystal X-ray structure determination on compound **4**. The molecule crystallized with two symmetry-independent molecules in space group $P2_1/c$, with a = 12.937 (3) Å, b = 19.332 (4) Å, c = 17.237 (3) Å, and β = 103.37 (2)°. Three-dimensional intensity data (7138 reflections) were measured at low temperature (ca. −150 °C) using Cu Kα radiation. The structure, including all hydrogen atoms, has been refined to an agreement index, R, of 0.057. Further details will be published later when refinement is complete. The results of this determination leave no doubt as to the structure of **4**. The two symmetry independent molecules differ conformationally in the orientation of the phenyl groups. The amide-like nitrogen in the diphenylcarbazoyl moiety forms an intramolecular hydrogen bond (2.77 and 2.78 Å for the N–O distances) with the indazolinone oxygen in each of the symmetry independent molecules.

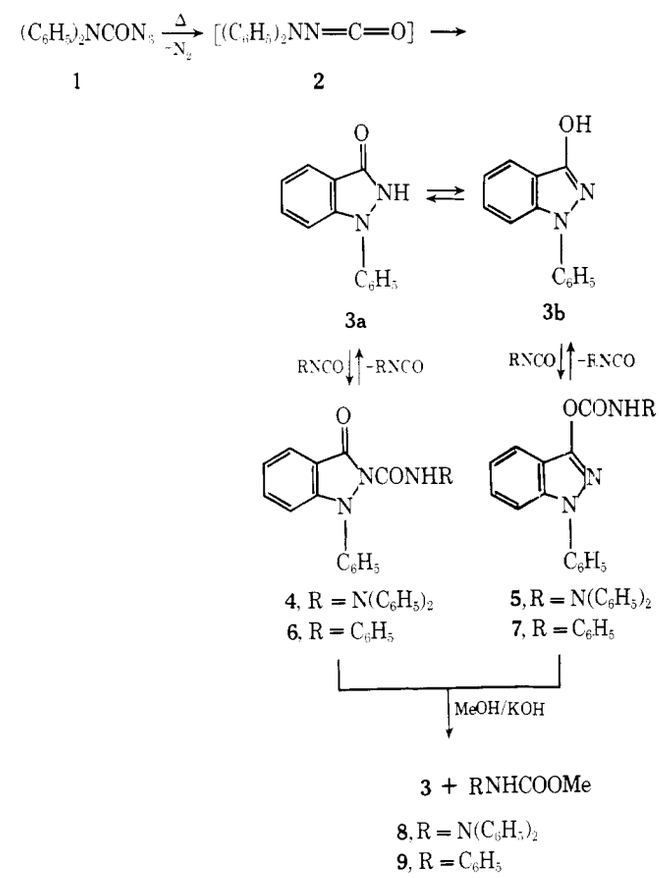
Our experiments have clearly shown that the formally "dimeric" products derived from *N,N*-diphenylamino isocyanate **2** are not actually isocyanate dimers but rather carbazoylation products of the indazole **3**, which is formed by intramolecular cyclization of the isocyanate **2**. The trapping of **2** by **3a** and **3b** apparently competes in a limited way with the irreversible conversion of **2** into **3**.

Experimental Section[13]

Thermolysis of *N,N*-Diphenylcarbamoyl Azide (1). A solution of 23.8 g (0.1 mol) of **1** in 55 mL of chlorobenzene is gradually heated to 135 °C. The nitrogen evolution, which starts at ca. 125 °C, is completed within 3 h, while the initially colorless solution turns first purple and finally dark brown. Cooling in an ice bath causes separation of colorless crystals which are filtered off and washed with methanol; 7.35 g (35%) of **1-phenyl-3-hydroxy-1*H*-indazole (3)**, mp 210–211 °C (lit.[1] mp 209 °C), identical in IR comparison with authentic material.

The filtrate is concentrated at reduced pressure, leaving a dark semisolid residue which is triturated with methanol; the remaining colorless crystals are filtered off and washed with methanol, giving 9.0 g of a mixture containing mainly **4** and **5**, as well as minor amounts of **3** (TLC analysis). Separation of the components by repeated recrystallization from benzene–hexane yields 3.0 g (14%) of **(1-phenyl-1*H*-indazol-3-yl) 3,3-diphenylcarbazate (5)**, colorless needles,

Scheme I



mp 177–178 °C dec. Anal. Calcd for $C_{26}H_{20}N_4O_2$: C, 74.27; H, 4.79; N, 13.33. Found: C, 74.61; H, 4.69; N, 13.34; mol wt 421 (vapor pressure osmometric in $CHCl_3$).

The combined benzene–hexane filtrate is evaporated to dryness, leaving a solid residue which is recrystallized from methanol, affording 4.0 g (19%) of **1-phenyl-2-(3,3-diphenylcarbazoyl)-1*H*-indazolin-3-one (4),** colorless needles, mp 152–153 °C. Anal. Calcd for $C_{26}H_{20}N_4O_2$: C, 74.27; H, 4.79; N, 13.33. Found: C, 74.28; H, 4.81; N, 13.32.

Thermal Conversion of 4 and 5 into 3. A. A suspension of 0.3 g (0.7 mmol) of **5** in 2 mL of chlorobenzene is heated to 150 °C (bath temperature) for 3.25 h while the progress of the rearrangement is followed by TLC. A mixture of **4** and **5** is formed which slowly disappears, leaving **3** as the sole product. Cooling of the dark purple reaction solution to 5 °C leads to separation of 0.23 g (76%) of colorless crystals of **3**.

B. A mixture of 0.8 g (1.9 mmol) of **4** and 4 mL of chlorobenzene is treated as described under A (the formation of **5** during the rearrangement is detected by TLC). Cooling and filtration yields 0.6 g (75%) of colorless crystals of **3**, identical in IR comparison with material obtained under A.

Methanolysis of 4 and 5. A. A sample of 0.2 g (0.47 mmol) of **4** is treated with 2 mL of 10% methanolic potassium hydroxide, resulting in formation of a yellow solution which turns colorless within 5 min. On diluting the solution with 5–7 mL of water, a colorless precipitate is formed; filtration and drying afford 0.1 g (86%) of **methyl 3,3-diphenylcarbazate (8),** mp 157 °C (lit.[8] mp 156–157 °C).

Colorless crystals of **3** are obtained on neutralizing the alkaline filtrate with concentrated hydrochloric acid; 0.09 g (90%), mp 210–211 °C, identical in IR comparison with authentic material.

B. A sample of 0.2 g (0.47 mmol) of **5** is treated with methanol/potassium hydroxide as described under A, giving 0.09 g (78%) of **8** and 0.07 g (70%) of **3**.

Formation of 1-Phenyl-2-(*N*-phenylcarbamoyl)-1*H*-indazolidin-3-one (6) and (1-Phenyl-1*H*-indazol-3-yl) *N*-Phenylcarbamate (7) from 3 and Phenyl Isocyanate. A solution of 4.2 g (0.02 mol) of **3** and 2.4 g (0.02 mol) of phenyl isocyanate in 40 mL of chloroform is heated to 70 °C for 3.5 h. After stopping the reaction, the solvent is distilled off, leaving a colorless solid which is triturated with 20 mL of methanol, filtered off, and washed with 20 mL of methanol; 5.34 g (81%) of **6,** mp 160 °C, resolidifies and melts again at 210–211 °C (mp of **3**) after losing phenyl isocyanate: IR ($CHCl_3$) 3350 (broad NH), 1735 and 1685 cm^{-1} (C=O). Anal. Calcd for $C_{20}H_{15}N_3O_2$: C, 72.93; H, 4.59; N, 12.76. Found: C, 72.78; H, 4.61; N, 12.89.

A semisolid material, obtained on evaporating the methanolic filtrate, is dissolved in benzene. Gradual addition of hexane causes the separation of 0.63 g (9.5%) of **7:** mp 130–131 °C dec; colorless needles; IR ($CHCl_3$) 3420 (NH) and 1760 cm^{-1} (C=O). Anal. Calcd for $C_{20}H_{15}N_3O_2$: C, 72.93; H, 4.59; N, 12.76. Found: C, 72.84; H, 4.55; N, 12.68.

Thermal Rearrangement of 6 to 7. A solution of 5.0 g (0.015 mol) of **6** in 30 mL of chloroform is kept at 70 °C for 4.5 h, while the gradual formation of **7** is followed by TLC. After stopping the reaction the solvent is distilled off, leaving a colorless residue which is triturated with 20 mL of methanol, filtered off, and washed with 20 mL of methanol; 4.36 g (87%) of unchanged **6** are recovered. The semisolid, obtained on concentrating the methanolic filtrate, is dissolved in benzene. Diluting the solution with hexane leads to separation of 0.5 g (10%) of **7,** mp 130–131 °C (benzene–hexane), identical in IR comparison with material obtained following the preceding procedure.

Methanolysis of 6 and 7. A. A solution of 8.8 g (0.027 mol) of **6** in 20 mL of 10% methanolic potassium hydroxide is kept at room temperature for 5–10 min. On diluting the solution with water, **methyl *N*-phenylcarbamate (9)** is separated as a colorless oil, which is extracted with dichloromethane. Evaporation of solvent leaves 3.72 g (88%) of **9,** mp 47 °C, identical in IR comparison with authentic material.

On neutralizing the aqueous phase with concentrated hydrochloric acid, the indazole **3** precipitates from the solution, which is isolated by filtration and washing with water: 4.35 g (74%), identical in IR comparison with authentic material.

B. Treatment of 0.55 g (1.7 mmol) with 3 mL of 10% methanolic potassium hydroxide as described under A gives 0.18 g (72%) of **9** and 0.35 g (100%) of **3**.

1,1,5,5-Tetraphenyl-2-benzoylcarbohydrazide (11). Benzoyl chloride (2.80 g, 0.02 mol) is added dropwise to a stirred cold suspension of 7.90 g (0.02 mol) of 1,1,5,5-tetraphenylcarbohydrazide (**10**) in pyridine. A tan solution is formed on storing the suspension for 64 h at ambient temperature. Evaporation of most of the solvent under vacuum and treatment of the remaining oil with water leads to separation of a solid which is filtered off and washed with water. TLC (in benzene) indicates the solid (9.6 g) to be a mixture of **10** and **11**. On briefly boiling it with 100 mL of benzene, the product **11** dissolves, leaving 2.60 g (33%) of **10** behind. Evaporating the benzene gives 6.70 g (67%) of **11,** mp 168–170 °C (from DMF/methanol/water): off-white crystals; IR ($CHCl_3$) 1670 and 1740 cm^{-1} (C=O). Anal. Calcd for $C_{32}H_{26}N_4O_2$: C, 77.09; H, 5.20; N, 11.24. Found: C, 77.23; H, 5.28; N, 11.14.

Thermal decomposition of 11 (2.0 g) in 5 mL of chlorobenzene at 150–155 °C for 5 h was followed by TLC (benzene). Initially **4** and **5** were formed along with *N,N*-diphenyl-*N'*-benzoylhydrazine (**12**). Continued heating beyond the complete disappearance of starting material **11** led to conversion of **4** and **5** into **3**. Evaporating the solvent under vacuum left a solid residue which was separated into **3** and **12** by fractional recrystallization from methanol (not quantitatively). The isolated **3** was identical in IR comparison with authentic material; **12,** mp 194 °C (lit.[14] 191–193 °C), was found to be identical with a sample independently prepared from *N,N*-diphenylhydrazine and benzoyl chloride.[15]

Registry No.—**1,** 17223-83-5; **3,** 28561-80-0; **4,** 66358-00-7; **5,** 66358-01-8; **6,** 66358-02-9; **7,** 66358-03-0; **8,** 38633-54-4; **9,** 2603-10-3; **10,** 51616-56-9; **11,** 66402-62-8; **12,** 970-31-0; phenyl isocyanate, 103-71-9.

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(11) Heating of **1** in refluxing tetraline leads to 88% and in xylene to 90% of **3** (see ref 1 and 8).
(12) TLC indicates that **4** and **5** are formed initially during the decomposition but are, as in the cases described above, converted to **3** on extended heating.

(13) Elemental analyses and molecular weight determinations were by Galbraith Laboratories, Knoxville, Tenn.; IR spectra were determined using a Beckman Acculab 4 and Perkin-Elmer 625 spectrophotometer; H NMR spectra were determined with a Varian T-60 (in $CDCl_3$ or Me_2SO-d_6 with Me_4Si as internal standard). All melting points are uncorrected. TLC comparisons of products and reaction mixtures were carried out on silica gel plates (Quantum Industries) with benzene–hexane–methanol (4:6:1) or benzene as solvent.
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α-Hetero-Substituted Phosphonate Carbanions. 7.[1] Synthesis of Deoxybenzoins and Benzo[*b*]furans

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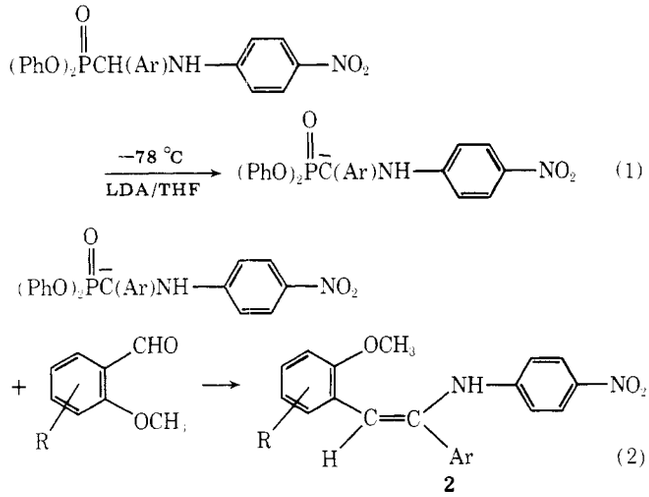
In a series of papers, we have described the utility of α-hetero-substituted phosphonate carbanions for the preparation of a wide variety of different classes of compounds.[3a–e] We now report the synthesis of new deoxybenzoins, which are readily converted to the corresponding benzofurans through the use of diphenyl 1-(4-nitroanilino)-1-arylmethanephosphonate as the carbanion precursor.

Scheme I



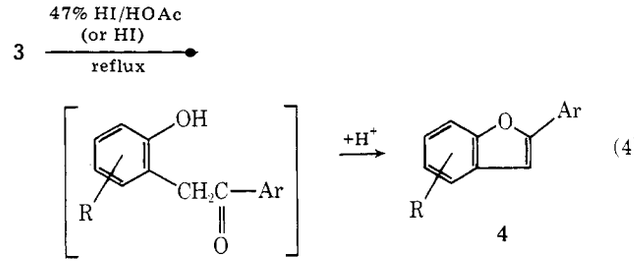
3a, Ar, 4-chlorophenyl; R = H
b, Ar, 3,4-dichlorophenyl; R = H
c, Ar, 4-chlorophenyl; R = 3,5-dibromo
d, Ar, 4-chlorophenyl; R = 3-methoxy

The reaction sequence used to obtain the desired deoxybenzoins proceeded according to the equations in Scheme I.

Reactions of various α-hetero-substituted phosphonate carbanions, generated with lithium diisopropylamine (LDA) in tetrahydrofuran at −78 °C, with substituted o-anisaldehydes afford the corresponding enamines. These enamines proved to be difficult to purify and isolate from the reaction mixture. In two cases, efforts were extended to isolate the enamines. These enamines are easily identified by the N–H stretching frequency at ~3380 cm^{-1} in the infrared and the N–H signal at δ ~6.5 ($CDCl_3$) or ~9.0 (Me_2SOd_6) in the NMR. These assignments were confirmed by D_2O exchange, thus both NMR as well as IR data support the enamine rather than the isomeric imine structure for these compounds. The NMR data for the crude (nonisolated) enamines were consistent with the data for the isolated enamines.

These enamines underwent smooth acid hydrolysis to afford the corresponding benzyl phenyl ketones (deoxybenzoins) which would be difficult to prepare via known literature methods.[4a–c] These deoxybenzoins were yellow oils and purification by column chromatography using silica gel was the most expedient method. These ketones are readily identified by NMR and IR methods. The carbonyl stretching frequency at ~1700 cm^{-1} in the infrared proved especially valuable for this purpose.

These ketones, when treated with 47% HI in HOAc (or 47% HI alone), underwent an ether cleavage and then cyclized presumably via the corresponding phenol to the desired benzofuran.[5a–e] This is illustrated in reaction 4.



4a, Ar, 4-chlorophenyl; R = H
b, Ar, 3,4-dichlorophenyl; R = H
c, Ar, 4-chlorophenyl; R = 5,7-dibromo
d, Ar, 4-chlorophenyl; R = 7-methoxy
e, Ar, 4-chlorophenyl; R = 7-hydroxy
f, Ar, 2-phenylethenyl; R = H
g, Ar, 4-chlorophenyl; R = 4,5-$(CH)_4$

In the case of 2-phenylethenyl (2-methoxyphenyl) ketone, only fusion with pyridine hydrochloride at 210–220 °C for 2 h afforded the corresponding benzofuran (**4f**). The reported yields for the benzofurans are overall yields (reaction 1–4). They vary considerably and do not reflect optimized conditions. The benzofurans thus obtained are colorless crystalline compounds. They are easily characterized by their elemental analyses and spectral data.

Compound **4e** was oxidized by Fremy's radical to the expected quinone. Thus, now readily available deoxybenzoins provide via the corresponding benzo[*b*]furans an easy entry into the hitherto little known class of benzo[*b*]furan-4,7-diones.[6]

This preparation of deoxybenzoins and benzofurans illustrates a number of features: (1) a variety of substituents can easily be introduced into the benzyl phenyl ketone (deoxybenzoin) system just by varying the substitution of the starting phosphonate and the o-anisaldehyde; (2) formation of benzofurans via this reaction route offers a more facile entry into the substituted benzofuran ring system than hitherto known methods,[7a–e] and (3) the formation of benzofurans proceeds by use of readily available starting materials.

Experimental Section

General. Melting points were determined with a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra were recorded using a Beckman IR-18A infrared spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian T-60 spectrometer with tetramethylsilane as internal standard. Mass spectra were obtained on a Perkin-Elmer RMU-7 Instrument. Mi-

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