chlorohydrin there was prepared 31.5 g (0.17 mol) of Meerwein salt[2] following the published procedure. The salt was dissolved in 100 ml of dry methylene chloride. A solution of 33.9 g (0.15 mol) of **1b** in 50 ml of methylene chloride was added and the mixture was kept at room temperature overnight. This was poured on a solution prepared from 3.8 g (0.17 mol) of sodium in 200 ml of absolute ethanol. The mixture was stirred at room temperature for 4 h. The solvent was evaporated and the residue was extracted with ether, washed with water, and dried over K_2CO_3. After evaporation of the solvent 28.2 g (62%) of a liquid was obtained which was distilled (bp 110–130 °C, 0.13 mm) to yield 27.8 g (61%) of **2**: *m/e* 294 (M^+); ^1H NMR ($CDCl_3$) δ 0.9–1.5 (m, 9, 3 CH_3), 1.6–2.2 (m, 2, CH_2), 3.1–3.8 (m, 8, 4 CH_2), 4.10 (q, 2, J = 7 Hz, OCH_2CH_3), 6.5–7.4 (m, 5, C_6H_5); ^1H NMR ($CDCl_3$ + CCl_4 + shift reagent at 60 °C) δ 0.90 (t, 3, J = 7 Hz, NCH_2CH_3), 1.45 and 1.57 (t, 3, J = 7 Hz, 2 OCH_2CH_3), 2.0–3.0 (broad, 2, $NCH_2CH_2CH_2$), 3.20 (q, 2, J = 7 Hz, NCH_2CH_3), 3.40 (t, 2, J = 6 Hz, CH_2CH_2OEt), 4.07 (q, 2, J = 7 Hz, $CH_2OCH_2CH_3$), 5.3–6.0 (broad, 2, $COOCH_2CH_3$), 6.4–6.9 (m, 2, NCH_2CH_2); ^{13}C NMR (see Table I); ir (film) 1710 (COOEt), 1608 cm^{-1} (aromatic). Anal. Calcd for $C_{16}H_{26}N_2O_3$ (294.38): C, 65.3; H, 8.9; N, 9.5. Found: C, 65.3; H, 9.2; N, 9.7.

1-(3-Ethoxypropyl)-2-ethyl-1-methyl-2-phenylhydrazine (3). To the suspension of 1.5 g (0.04 mol) of lithium aluminum hydride in 100 ml of dry ether, a solution of 7.0 g (0.024 mol) of **2** was added dropwise. The mixture was heated to reflux for 3 h and then worked up following the usual procedures to give 4.6 g (82%) of **3**: GLC one component, a sample was distilled in a Kugelrohr; *m/e* 236 (M^+); ^1H NMR ($CDCl_3$) δ 1.17 (t, 3, J = 7 Hz, CH_2CH_3), 1.22 (t, 3, J = 7 Hz, CH_2CH_3), 1.72 (quintet, 2, J = 6.5 Hz, $CH_2CH_2CH_2$), 2.45 (s, 3, NCH_3), 2.77 (t, 2, J = 6.5 Hz, NCH_2CH_2), 3.30 (q, 2, J = 7 Hz, NCH_2CH_3), 3.46 (q, 2, J = 7 Hz, OCH_2CH_3), 3.48 (t, 2, J = 6.5 Hz, OCH_2CH_2), 6.5–7.4 (m, 5, C_6H_5); ^{13}C NMR (see Table I); ir (film) 1598 cm^{-1} (aromatic). Anal. Calcd for $C_{14}H_{24}N_2O$ (236.35): C, 71.1; H, 10.2; N, 11.9. Found: C, 71.4; H, 10.5; N, 11.8.

1-Ethyl-2-(3-ethoxypropionyl)-1-phenylhydrazide. This compound was prepared from 7.2 g (0.042 mol) of 1-ethylphenylhydrazine[3] hydrochloride and 6.8 g (0.05 mol) of 3-ethoxypropionyl chloride in the presence of 150 ml of 2 N NaOH solution following the usual procedures to give 7.1 g (72%) of product: ^1H NMR ($CDCl_3$) δ 1.0–1.4 (m, 6, 2 CH_3), 2.4–2.8 (m, 2, $OCH_2CH_2C{=}O$), 3.3–3.9 (m, 6, 3 CH_2), 6.7–7.5 (m, 5, C_6H_5), 7.9 (broad, 1, NH); ir (film) 3250 (NH), 1675 cm^{-1} (NC=O).

1-Ethyl-2-(3-ethoxypropyl)-1-phenylhydrazine. To the suspension of 1.5 g (0.04 mol) of $LiAlH_4$ in 100 ml of dry THF the solution of 5.0 g (0.02 mol) of the above hydrazide was added slowly. The mixture was heated to reflux overnight. The mixture was worked up the usual way to give 3.8 g (85%) of the product as a liquid: *m/e* 222 (M^+); ir (film) 3250 cm^{-1} (NH). This sample was contaminated with approximately 10% starting material (GLC).

1-Carbethoxy-1-(3-ethoxypropyl)-2-ethyl-2-phenylhydrazine (2). A sample (1.0 g, 0.004 mol) of the above product in 30 ml of ether was treated with 0.7 g (0.006 mol) of ethyl chloroformate in the presence of 4 ml of 2 N NaOH solution. The mixture was stirred at room temperature overnight and then worked up the usual way. The liquid was distilled two times to give 0.8 g (60%) of **2**: bp 80–90 °C (0.07 mm); GLC one component, identical with a sample of **2** prepared via **1b** (coinjection); ir (film) identical in every respect with that of **2**.

Registry No.—**1a**, 35267-14-2; **1b**, 58074-51-4; **2**, 58074-52-5; **3**, 58074-53-6; ethyl chloroformate, 54-41-3; Meerwein salt, 368-39-8; 1-ethyl-2-(3-ethoxypropionyl)-1-phenylhydrazide, 58074-54-7; 1-ethyl-1-phenylhydrazine hydrochloride, 58074-55-8; 3-ethoxypropionyl chloride, 49775-37-3; 1-ethyl-2-(3-ethoxypropyl)-1-phenylhydrazine, 58074-56-9.

Supplementary Material Available. A discussion of the NMR spectral data (2 pages). Ordering information is given on any current masthead page.

References and Notes

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Novel Pyridazine Formation in the Base-Catalyzed Reaction of *trans*-1,2-Dibenzoyl-3,3-diphenylcyclopropane with Hydrazine[1a,b]

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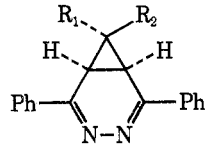
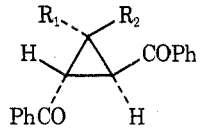
The synthesis of *exo*-2,5,7-triphenyl-3,4-diazabicyclo[4.1.0]hepta-2,4-diene (**1**) from *trans*-1,2-dibenzoyl-3-phenylcyclopropane (**2a**) has been accomplished in good yield by adding sodium hydroxide to a mixture of **2a** and hydrazine in ethanol. An attempt at producing 2,5,7,7-tetraphenyl-3,4-diazabicyclo[4.1.0]hepta-2,4-diene (**4**) from *trans*-1,2-dibenzoyl-3,3-diphenylcyclopropane (**3a**) by an analogous reaction produced only 3,6-diphenyl-4-benzhydrylpyridazine (**5**). It was the purpose of this study to investigate the mechanistic pathway followed in the formation of **5** and to elucidate the reasons for preferred production of **5** from **3a**. The desired heterocyclic **4** was synthesized by addition of either phenylmagnesium bromide or diphenylcadmium to 6,6-diphenyl-3-oxabicyclo-[3.1.0]hexane-2,4-dione (**6**) to form 4,6,6-triphenyl-3-oxabicyclo[3.1.0]hexan-2-on-4-ol (**7**), which, on treatment with hydrazine, gave 5,7,7-triphenyl-3,4-diazabicyclo[4.1.0]hept-4-en-2-one (**8**), which, on treatment with phenyllithium, gave **4**. The heterocyclic **4** gave **5** on heating under acidic, but not basic, conditions, thus ruling out the presence of **4** during the production of **5** from **3a**. A mechanistic scheme involving 1,4,4-triphenyl-3-benzoylbut-2-en-1-one (**12**) and/or 1,4,4-triphenyl-3-benzoylbut-3-en-1-one (**13**) is presented. It is concluded that diazanorcaradiene formation from *trans*-1,2-diacylcyclopropanes under base catalysis is synthetically feasible only in cases where the *cis*-diacylcyclopropanes are sterically accessible and/or the anionic ring opening process is energetically unfavorable.

In their investigation of *exo*-2,5,7-triphenyl-3,4-diazabicyclo[4.1.0]hepta-2,4-diene (diazanorcaradiene, **1**), Amiet and Johns[2] reported that **1** could be synthesized in only low yields (7%) from *trans*-1,2-dibenzoyl-3-phenylcyclopropane (**2a**) by heating **2a** with hydrazine in ethanol for extended periods of time, whereas the cis isomer **2b** reacted rapidly and quantitatively at room temperature. In our laboratory, **1** was produced in satisfactory yield (55%) from **2a** and hydrazine in ethanol at room temperature, if sodium hydroxide was added to the mixture.[3] In view of the ready availability of *trans*-1,2-dibenzoylcyclopropane derivatives, the alkaline base–hydrazine treatment appeared to offer a

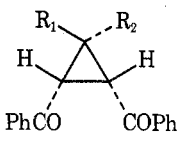
convenient and direct synthetic route to 2,5-diphenyldiazanorcaradienes.



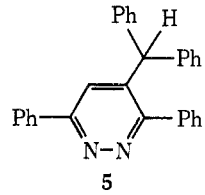
1, R_1 = Ph; R_2 = H
4, R_1 = R_2 = Ph



2a, R_1 = Ph; R_2 = H
3a, R_1 = R_2 = Ph



2b, R_1 = Ph; R_2 = H
3b, R_1 = R_2 = Ph



5

The present report describes an interesting aberrant to the pathway expected when the above hydrazine–base method is applied to the preparation of 2,5,7,7-tetraphenyl-3,4-diazabicyclo[4.1.0]hepta-2,4-diene (4) from the known *trans* - 1,2 - dibenzoyl - 3,3 - diphenylcyclopropane (**3a**).[4] As **4** was required for other mechanistic studies,[5] its synthesis was subsequently accomplished by a more laborious, but unambiguous four-step sequence reported herein.

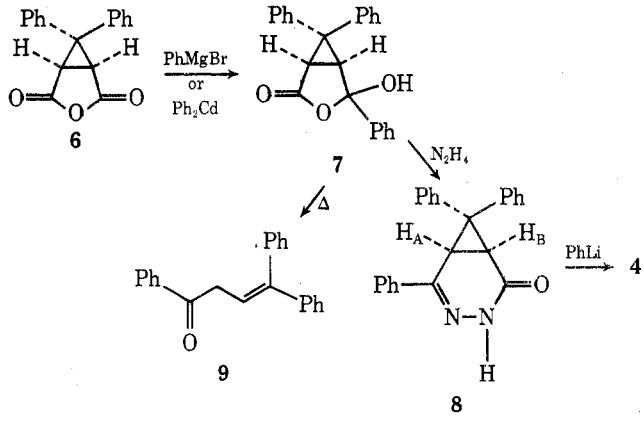
At room temperature, a stirred solution of **3**, hydrazine, and sodium hydroxide in ethanol gave no indication of the formation of the desired compound **4** as revealed by the absence of the yellow color characteristic of the 2,5-diphenyldiazanorcaradiene system. On refluxing, the reaction mixture developed an encouraging yellow color that disappeared completely after a total of 72 h. That the colorless crystals isolated from the reaction mixture were not the desired **4**, but rather an isomer **5**, was clearly discernible from NMR, mass spectral, and elemental analysis. The colorless isomer was readily identified as 3,6-diphenyl-4-benzhydrylpyridazine by its NMR spectrum (see Experimental Section), which is discussed below, and by authentic synthesis (vide infra).

Since the C-6 phenyl in pyridazine **5** is relatively free to assume coplanarity with the pyridazine ring, the ortho protons of this phenyl ring should be strongly deshielded thus accounting for the low-field two-proton multiplet at τ 1.8–2.2. However, the C-3 phenyl is sterically crowded by the bulky benzhydryl group in the 4 position and is unable to achieve coplanarity with the pyridazine ring. The C-3 ortho protons therefore occur at approximately the same chemical shift, τ 2.4–3.2, as the other remaining three protons on the C-6 phenyl and the benzhydryl group phenyl protons. The lone pyridazine ring proton is masked by the higher field aromatic multiplet. By comparison, the NMR spectrum of 3,6-diphenylpyridazine exhibits a multiplet at τ 1.72–2.02 (4 H), a singlet at 2.10 (2 H), and a multiplet at 2.32–2.67 (6 H) accounting for, respectively, the four ortho protons on the two phenyl rings, the two pyridazine ring protons, and the remaining phenyl ring protons.[3] The slightly lower chemical shift of the benzhydrylpyridazyl proton (τ 4.31) in **5** as compared to the methine proton of triphenylmethane (τ 4.538 ± 0.028)[6] is not unexpected when one considers the greater electron-withdrawing power of pyridazyl as compared to phenyl.

The intensely yellow diazanorcaradiene **4** was prepared by the method outlined in Scheme I, which is essentially a modification of the sequence of reactions developed by Maier.[7,8]

The known anhydride **6**[4,9] was prepared in good yield (61%) from diphenyldiazomethane[10] and commercial maleic anhydride. Reaction of **6** with aluminum chloride in benzene failed to produce the desired pseudoacid **7**; however, this pseudoacid was obtained in very low yield by treatment of **6** with phenylmagnesium bromide or diphenylcadmium. Pseudoacid **7** was characterized by spectral means and by its conversion to the known 1,4,4-triphenylbut-3-en-1-one (**9**)[11] on pyrolytic decarboxylation.

Scheme I



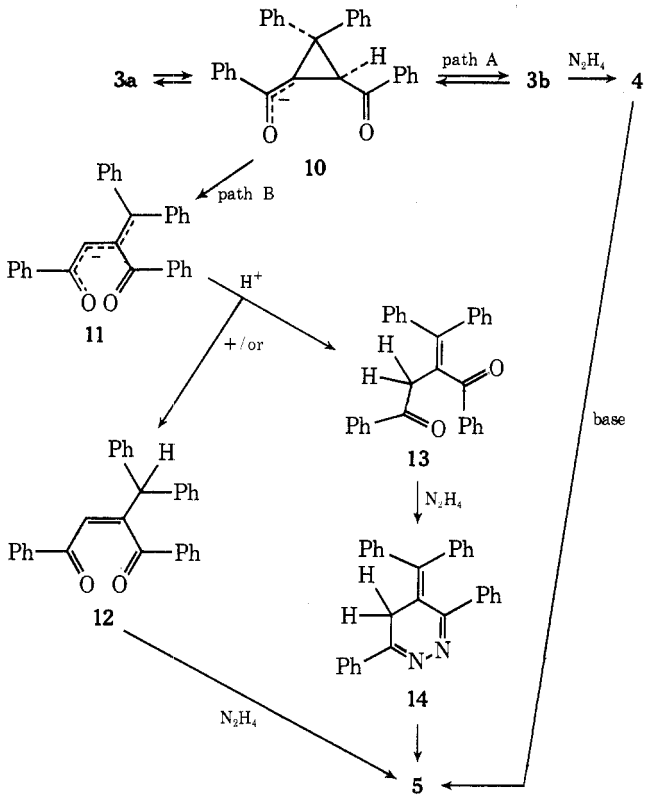
The fairly insoluble hydrazide **8** was remarkable only so far as its combustion analysis and NMR spectrum. Combustion data appeared to be consistent with the inclusion of one-half molecule of water per molecule of **8** in the crystal lattice while the NMR spectrum of **8** revealed that proton H_B (see Scheme I) was coupled not only to H_A, but also to the NH proton to the extent of 1.5 Hz. This is presumably a consequence of the "W" pattern arrangement[12] of these protons.

Treatment of **8** with phenyllithium and subsequent mild acid work-up afforded the bright yellow diazanorcaradiene **4** in moderate yield. The NMR spectrum (see Experimental Section) of **4** was consistent with two unhindered phenyls on an azine linkage (vide supra) showing multiplets at τ 1.60–2.0 (4 H, ortho protons) and 2.34–2.7 (6 H, meta and para protons). The C-7 phenyl protons appear as singlets at τ 2.71 (5 H, exo phenyl) and 3.03 (5 H, endo phenyl). The singlet at τ 6.58 (2 H) is, of course, assignable to the now magnetically indistinguishable cyclopropyl bridgehead protons. All other data for **4** were unremarkable and consistent with the assigned structure.

On refluxing in acidic dioxane, diazanorcaradiene **4** was isomerized to pyridazine **5**, thus providing an acceptable synthetic[7] verification of the structure for this pyridazine. However, **4** was unaffected (78% recovery) by the basic reaction conditions (sodium hydroxide–ethanol) utilized in the formation of **5** from **3a** and hydrazine. Thus, the mechanistic sequence depicted in Scheme II (path A) involving **4** as an intermediate (and thereby possibly accounting for the transient yellow color noted previously) in the formation of **5** is ruled out.

The most straightforward mechanistic rationalization for the formation of **5** from **3a** is that outlined in path B of Scheme II. Electrocyclic ring opening of the enolate ion **10** to give the oxapentadienyl anion **11** is expected to be an energetically favorable process. Protonation of **11** should afford either or both enediones **12** and **13**, although **13** would be favored on kinetic and thermodynamic grounds. In this regard Schecter and co-workers[13] have recently isolated an enedione analogous to **13** from mild acid work-up of the "blood-red filtrate" obtained from the treatment of *trans*-2,3-dibenzoylspiro[cyclopropane-1,9′-fluorene] (**3a**, R_1, R_2 = *o*,*o*′-biphenylene) with methanolic potassium hydroxide. These workers provide convincing evidence that this fluo-

Scheme II



renyl enedione is the same diketone isolated earlier by Horner and Lingnau[14] and shown to react with hydrazine hydrate to yield an "inner azine", $C_{29}H_{20}N_2$.[14] The latter workers[14] did not assign structures for either the diketone or the cyclic azine.

While in our system no separate attempt was made to isolate the diketones **12** or **13** from treatment of **3a** with base, the presence of one or the other or both may be inferred by analogy to the fluorenyl system[13,14] and by subsequent trapping with hydrazine to afford **5** either directly, in the case of **12**, or indirectly, via the cyclic azine **14**, in the case of **13**. The transient yellow color observed during the progress of the reaction is consistent with the intermediacy of the enediones and/or cyclic azine **14**.

In accord with the preceding mechanistic scheme the contrasting reactivity of the *trans*-1,2-dibenzoylcyclopropanes **2a** and **3a** toward hydrazine in basic media can now be explained on the basis of different steric and electronic requirements for base-catalyzed isomerization vs. ring opening. Thus, the additional phenyl substituent at C-3 would be expected to greatly enhance the rate of ring opening of **3a** relative to **2a** through the extra conjugation provided in the transition state. On the other hand, isomerization of **3a** to the cis diketone **3b** should be severely hampered by the increased steric crowding between cis benzoyl groups and phenyl ring. This steric problem is avoided in the monophenyl derivative **2a** by preferential isomerization to diketone **2b** in which the benzcyl groups and phenyl ring have the cis,anti configuration shown. Hence, it may be reasonably concluded that diazanorcaradiene formation from *trans*-1,2-diacylcyclopropanes under base catalysis is synthetically feasible only in cases where the *cis*-diacylcyclopropanes are sterically accessible and/or the anionic ring opening process is energetically unfavorable.

Experimental Section[15]

2,5,7-Triphenyl-3,4-diazabicyclo[4.1.0]hepta-2,4-diene (1). The stirring of 1.27 g (3.90 mmol) of *trans*-1,2-dibenzoyl-3-phenylcyclopropane (**2a**), 90 mg of sodium hydroxide, and 0.50 ml (10 mmol) of hydrazine hydrate in 500 ml of absolute ethanol for 72 h at room temperature resulted in the formation of a yellow suspended solid. Filtration followed by recrystallization from 95% ethanol yielded 687 mg (2.15 mmol, 55%) of bright yellow needles, mp 232–233 °C dec (lit.[2] 235 °C). The spectral data were in agreement with those reported.[2]

3,6-Diphenyl-4-benzhydrylpyridazine (5). A. A solution of 7.51 g (18.7 mmol) of *trans*-1,2-dibenzoyl-3,3-diphenylcyclopropane (**3a**), 1.84 ml (56.1 mmol) of anhydrous 97% hydrazine, and 0.36 g of sodium hydroxide in 700 ml of absolute ethanol was refluxed for 72 h. During reflux, the reaction mixture initially turned yellow, but at the end was totally colorless. The solid that resulted on evaporation of solvent was recrystallized first from chloroform–hexane and then from 95% ethanol to yield two crops of colorless rhombs weighing a total of 4.85 g (12.2 mmol, 65%), mp 185.7–186.0 °C.

B. A sample of 100 mg of 2,5,7,7-tetraphenyl-3,4-diazabicyclo[4.1.0]hepta-2,4-diene (**4**) was refluxed for 3 h in 50 ml of dioxane containing 0.5 ml of 37% hydrochloric acid to yield a bright yellow solution which, after neutralization, removal of solvent, and chromatography over basic alumina with chloroform, gave 46 mg (46%) of **5**. Recrystallization from ethanol gave material melting at 177.5–179 °C: NMR ($CDCl_3$) τ 1.86–2.16 (m, 2 H, aromatic), 2.4–3.23 (m, 19 H, aromatic), and 4.31 (s, 1 H, benzhydryl proton); mass spectrum (70 eV) *m/e* (rel intensity) 398 (100), 67 (13), and 65 (13); ir (KBr) 2950, 1575, 1490, 1450, 1390, 1190, 1080, 1030, 1000, 790, 765, 740, 705, and 700 cm^{-1}.

Anal. Calcd for $C_{29}H_{22}N_2$: C, 87.40; H, 5.57; N, 7.03. Found: C, 87.39; H, 5.61; N, 6.98.

6,6-Diphenyl-2,4-diketo-3-oxabicyclo[3.1.0]hexane (6). To a solution of 5.45 g (55.6 mmol) of commercial maleic anhydride in 400 ml of warm benzeneas added with magnetic stirring 11.99 g (61.75 mmol) of diphenyldiazomethane in a small amount of benzene. On mixing, immediate gas evolution and decolorization began. After stirring for 12 h, the mixture was flash evaporated and the resulting slightly pink mass was broken up, washed with low-boiling petroleum ether, and recrystallized from cyclohexane to yield 9.0 g (34 mmol, 61%, lit.[10] 25.3%) of snow-white, fine needles, mp 161.0–161.3 °C (lit.[10] 162 °C). The NMR spectrum of **6** agreed with that previously cited.[10]

4,6,6-Triphenyl-3-oxabicyclo[3.1.0]hexan-2-on-4-ol (7). A. Phenylmagnesium bromide (39.5 mmol), prepared by the standard technique in 75 ml of diethyl ether, was added over 45 min to a vigorously stirred solution of 10.4 g (39.4 mmol) of **6** in 1200 ml of dry toluene precooled to −68 to −75 °C. The reaction mixture was allowed to warm to room temperature and added to an ice–water slush containing 8.6 g (87 mmol) of 37% hydrochloric acid. Upon flash evaporation the dried toluene layer yielded a gummy mass which was crystallized by the addition of a small amount of cold benzene. The crude, brown crystals were dissolved in an aqueous solution of 8.4 g (100 mmol) of sodium bicarbonate and the resulting solution was filtered. The pseudoacid **7** was precipitated from the bicarbonate solution by acidification with 37% hydrochloric acid. The resulting solid was recrystallized from benzene to give two crops of pseudoacid weighing a total of 1.49 g (4.37 mmol of 11.1%) and melting at 197–198 and 188.5–189.5 °C (effervescence).

B. Using the standard technique, diphenylcadmium was synthesized from 9.72 g (400 mmol) of magnesium, 47.1 g (300 mmol) of bromobenzene, and 31.2 g (171 mmol) of anhydrous cadmium chloride.

The diphenylcadmium reagent was leached from its reaction mixture with two 100-ml portions of benzene, filtered, and mixed with 8.98 g (34.0 mmol) of **6** in 300 ml of benzene to yield, after standing for 36 h, a gummy precipitate to which was added 9.0 g (91 mmol) of 37% hydrochloric acid in an ice–water slush. Upon evaporation the benzene layer yielded yellow crystals which were stirred overnight with a solution of 8.4 g (100 mmol) of sodium bicarbonate. Acidification of the aqueous solution produced very little of the desired pseudoacid as the residue remaining from the bicarbonate treatment contained most of the product. The total yield after a recrystallization from benzene was 2.45 g (7.17 mmol, 21%) of the colorless, crystalline **7**: mp ca. 190 °C (effervescence); NMR ($CDCl_3$) τ 1.76–2.0 (m, 2 H, benzoyl ortho protons), 2.20–2.97 (m, 13 H, aromatic), 6.48 (AB quartet, J_{AB} = 8.0 Hz, 2 H, cyclopropyl protons), −1.4 (v br s, 1 H, COOH); mass spectrum (70 eV) *m/e* (rel intensity) 342 (1), 298 (16), 220 (23), 193 (23), 192 (13), 191 (13), 165 (10), 105 (21), 103 (100), 77 (29); ir (KBr) 2940, 2510, 1730, 1630, 1590, 1570, 1460, 1250, 1240, 955, 750, 720, 710, 695, and 690 cm^{-1}.

Anal. Calcd for $C_{23}H_{18}O_3$: C, 80.68; H, 5.30. Found: C, 80.48; H, 5.43.

1,4,4-Triphenylbut-3-en-1-one (9). A sample of 100 mg (0.292 mmol) of **7** was heated neat at about 200 °C until gas evolution ceased. The brown melt was recrystallized twice from diethyl ether–light petroleum ether to yield 14 mg (0.047 mmol, 16%) of slightly yellow needles, mp 125.0–125.7 °C (lit.[11] 126–126.5 °C). A separate sample of **7** was pyrolyzed neat in an NMR tube to give the spectrum described below.

NMR ($CDCl_3$) showed τ 2.05–2.31 (m, 2 H, benzoyl ortho protons), 2.42–3.0 (m, 13 H, aromatic), 3.59 (t, J = 7.0 Hz, 1 H, H_3), 6.21 (d, J = 7.0 Hz, 2 H, H_2); ir (KBr) 2900, 1670 (lit.[11] 1690), 1435, 1330, 1210, 995, 770, 765, 745, 700, 695, 685 cm^{-1}.

5,7,7-Triphenyl-3,4-diazabicyclo[4.1.0]hept-4-en-2-one (8). To 4.3 ml (4.3 g, 86 mmol) of hydrazine hydrate in 400 ml of absolute ethanol was added 2.47 g (7.22 mmol) of **7**. After stirring for 12 h, a precipitate appeared and was filtered off after another 24 h of stirring to yield 1.77 g (5.22 mmol, 72.3%) of colorless crystals of **8**, mp 244.0–245.0 °C. An analytical sample was obtained on recrystallization from ethanol: mp 244.7–245.2 °C; NMR ($CDCl_3$) τ 1.9 (v br s, 1 H, NH), 1.95–2.13 (m, 2 H, C-5 phenyl ortho protons), 2.40–3.16 (m, 13 H, aromatic), and 6.88 (AB quartet, J_{AB} = 8.0 Hz, 2 H, H_A and H_B) (the upfield half of the AB quartet appears as a doublet of doublets owing to further coupling with the NH proton, J_{BN} = 1.5 and J_{AN} = 0.0 Hz as determined from an HA-100 spectrum); mass spectrum (70 eV) *m/e* (rel intensity) 338 (24), 337 (16), 235 (39), 193 (22), 192 (100), 191 (28), 166 (13), 165 (47), 115 (12), and 77 (13); ir (KBr) 3100, 3000, 2850, 1670, 1495, 1445, 1365, 1320, 1070, 775, 760, 705, and 692 cm^{-1}.

Anal. Calcd for $C_{23}H_{18}N_2O$: C, 81.63; H, 5.36; N, 8.28. Found: C, 79.50, 79.63; H, 5.71, 5.63; N, 8.04. Calcd for $C_{23}H_{18}N_2O \cdot \frac{1}{2}H_2O$: C, 79.51; H, 5.51; 8.07.

2,5,7,7-Tetraphenyl-3,4-diazabicyclo[4.1.0]hepta-2,4-diene (4). Phenyllithium (9.94 mmol) prepared from 197 mg (28.4 mmol) of lithium and 2.23 g (14.2 mmol) of bromobenzene in 60 ml of dry diethyl ether was added dropwise to a magnetically stirred solution of 674 mg (1.99 mmol) of **8** in about 100 ml of freshly distilled tetrahydrofuran (THF). The initial transient red color that appeared as each drop of phenyllithium made contact with the THF solution remained firm after about one-fifth of the addition had been completed.

The deep red reaction mixture was stirred for an additional 30 min and then poured onto an ice–water slush containing 800 mg (13 mmol) of glacial acetic acid. The pale yellow compound was extracted with diethyl ether and chromatographed over basic alumina to yield 374 mg (0.939 mmol, 47.2%) of bright yellow, beautiful needles: mp 227.0–227.5 °C dec; NMR ($CDCl_3$) τ 1.60–2.0 (m, 4 H, ortho protons C-2 and C-5 phenyls), 2.34–2.7 (m, 6 H, meta and para protons C-2 and C-5 phenyls), 2.71 (s, 5 H, exo C-7 phenyl protons), 3.03 (s, 5 H, endo C-7 phenyl protons), and 6.58 (s, 2 H, cyclopropyl protons); mass spectrum (70 eV) *m/e* (rel intensity) 398 (40), 370 (39), 296 (25), 295 (100), 294 (23), 193 (22), 192 (18), and 166 (25); ir (KBr) 2940, 1540, 1495, 1450, 1395, 765, 755, 705, and 690 cm^{-1}.

Anal. Calcd for $C_{29}H_{22}N_2$: C, 87.40; H, 5.57; N, 7.03. Found: C, 87.44; H, 5.58; N, 6.93.

Attempted Base-Catalyzed Rearrangement of 4. A mixture of 93 mg of **4** and 19 mg of sodium hydroxide was refluxed for 75 h in 25 ml of absolute ethanol to give a still yellow, but cloudy mixture which, after filtration and chromatography over basic alumina, yielded 73 mg (78% recovery) of **4**, mp 231–231.5 °C dec. The NMR spectrum of the recovered material was identical with that of authentic **4**.

Registry No.—**3a**, 57694-77-6; **4**, 57694-78-7; **5**, 57694-79-8; **6**, 57694-80-1; **7**, 57694-81-2; **8**, 57694-82-3; **9**, 57694-83-4; hydrazine, 302-01-2; phenyl bromide, 108-86-1; diphenylcadmium, 2674-04-6; phenyllithium, 591-51-5.

References and Notes

(1) (a) Taken in part from the Ph.D. Dissertation presented by R.M.W., March 1972, to the Graduate School of the University of Florida. (b) Financial support of this research, in part, by the National Science Foundation is gratefully acknowledged. (c) Address all correspondence to this author at Clinical Chemistry, North Carolina Memorial Hospital, Chapel Hill, N.C. 27514.
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Pycnolide, a *seco*-Germacradienolide from *Liatris pycnostachya*, and Other Antitumor Constituents of *Liatris* Species[1,2]

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Further study of a *Liatris pycnostachya* Michx. extract yielded pycnolide (**4a**), a 2,3-*seco*-1(10),4,5-germacradienolide, whose structure determination by means of chemical transformations and ^1H and ^{13}C NMR spectrometry is detailed. A chlorine-containing guaianolide, spicatin hydrochloride (**3b**), was also found. The previously known cytotoxic guaianolide spicatin (**1a**), the antileukemic 5,10-epoxygermacranolide chapliatrin (**11**), and euparin (**9**) were isolated from *L. tenuifolia* Nutt. whereas *L. scabra* (Greene) K. Schum. yielded the cytotoxic heliangolide eleganin (**10**). *L. earlei* (Greene) K. Schum. and *L. pauciflora* Pursh gave small amounts of complex lactone mixtures.

In a previous article[3] we reported inter alia the isolation of the complex ester guaianolides spicatin (**1a**) and epoxyspicatin (**2a**) from the less polar fractions of a *Liatris pycnostachya* Michx. extract. Since then, spicatin, also found in *L. spicata*,[3] has been shown to be cytotoxic[5] as were graminiliatrin (**2c**) and deoxygraminiliatrin (**1c**) from *L. graminifolia*[3] and eleganin (**10**) from *L. elegans*.[6] Epoxyspicatin (**2a**) and chapliatrin (**11**, stereochemistry at C-3, C-4, and C-10 tentative)[1] from *L. chapmanii*[7] and *L. gracilis*[1] also exhibited significant in vivo activity against P388 lymphocytic anemia. In the present communication we report isolation and structure determination of spicatin hydrochloride (**3b**) and pycnolide (**4a**) from the more polar fractions of the *L. pycnostachya* extract. Pycnolide, a 2,3-