CH_2CH_2O), 3.40 [t, J = 7.0 Hz, $CH(CO_2)_2$], 2.41–1.98 (m, OCH_2CH_2CH), and 1.25 ppm (t, J = 7.2 Hz, OCH_2CH_3). A satisfactory analysis of **6** was not obtained.

A larger scale reaction was carried out for 8 hr. From 28.9 g (0.12 mol) of **1a**, NaOEt prepared from 3.0 g (0.13 g-atom) of sodium, and 130 ml of EtOH was obtained 4.86 g (24%) of **3**, bp 105–106° (19 mm), $n^{24}D$ 1.4562, 3.55 g (18%) of **4**, bp 108–110° (11 mm), $n^{24}D$ 1.4742, 3.91 g of intermediate fractions containing varying amounts of **3** and **4**, and 6.10 g of residue, which contained 1.95 g of **4**, 0.85 g of **6**, and 2.68 g of **1a**. The conversion of **1a** to **3** and **4** was 78%.

B. With Potassium *tert*-Butoxide in Dimethyl Sulfoxide.—A mixture prepared from 11 ml of dry DMSO, 2.35 g (21 mmol) of KO-*t*-Bu, and 5.1 g (21 mmol) of **1a** was heated at 100° for 4 hr and then worked up as described for the reaction with NaOEt in EtOH. Vpc analysis of the ether solution indicated the presence of diethyl carbonate, **3**, **6**, compounds subsequently identified as the *tert*-butyl homolog of **3** and 4-carboethoxy-5,6-dihydro-3-ethoxycarbonylmethyl-1,2-oxin (**5**), and at least three other products which had retention times similar to those of the cyclic products and which were not identified. Distillation gave a 1.2-g fraction, bp 50–65° (0.4 mm), which was estimated by vpc to contain 0.36 g (10%) of **3**, 0.06 g (1.5%) of the *tert*-butyl homolog of **3**, 0.14 g (2.8%) of **5**, and 0.18 g (3.5%) of **6**. These products were isolated by preparative vpc, and **3** and **6** were identified by comparison with previously identified material.

4-Carbo-*tert*-butoxy-5,6-dihydro-3-methyl-1,4-oxin had nmr δ 6.16 (q, J = 1 Hz, OCH=C), 1.61 (d, J = 1 Hz, $OCH=CCH_3$), and 1.43 ppm [s, $C(CH_3)_3$].

5 had $n^{23}D$ 1.4705; uv λ_{max} 223 mμ (ε 7380); ir 1735 (vs, unconjugated C=O), 1710 (conjugated C=O), 1655 cm^{-1} (conjugated C=C); nmr δ 4.12 (q, J = 7.0 Hz, $C=CCO_2CH_2CH_3$), 4.08 (q, J = 7.0 Hz, $CH_2CO_2CH_2CH_3$), 4.05–4.00 (m, $OCH_2C=$), 3.69 (t, J = 5.5 Hz, OCH_2CH_2CH), 3.29 (s, $=CCH_2CO_2$), 2.54–2.20 (m, $OCH_2CH_2C=$), 1.26 (t, J = 7.0 Hz, $=CCO_2CH_2CH_3$), 1.23 (t, J = 7.0 Hz, $CH_2CO_2CH_2CH_3$); mass spectrum m/e (rel intensity) 197 (29), 196 (78), 169 (34), 168 (45), 140 (62), 111 (25), 29 (100).

Anal. Calcd for $C_{12}H_{18}O_5$: C, 59.52; H, 7.43. Found: C, 59.36; H, 7.57.

The reaction was repeated using 2.17 g (19.4 mmol) of KO-*t*-Bu and 4.80 g (19.8 mmol) of **1a** except that heating at 100° was maintained for 1 rather than 4 hr. Work-up gave a 2.1-g fraction with bp 45–124° (0.2 mm), which was estimated by vpc to contain 0.20 g (6%) of **3**, 0.08 g (2.1%) of the *tert*-butyl homolog of **3**, 0.47 g (10%) of **5**, and 0.87 g (18%) of **6**.

Registry No.—**1a**, 38858-63-8; **3**, 38858-64-9; **3** *tert*-butyl homolog, 38858-65-0; **4**, 38858-66-1; **5**, 38858-67-2; **6**, 38858-68-3; 6-bromo-4-oxa-1-hexyne, 18668-74-1; diethyl malonate, 105-53-3; sodium ethoxide, 141-52-6; potassium *tert*-butoxide, 865-47-4.

Acknowledgments.—Availability of the mass spectrometer was made possible by a grant from the National Science Foundation. We wish to thank Mr. J. Voth for determination of the mass spectra.

o-Dibenzoyl Heterocycles *via* Cycloaddition Reactions. A Convenient Route to Fused Pyridazine Systems[1]

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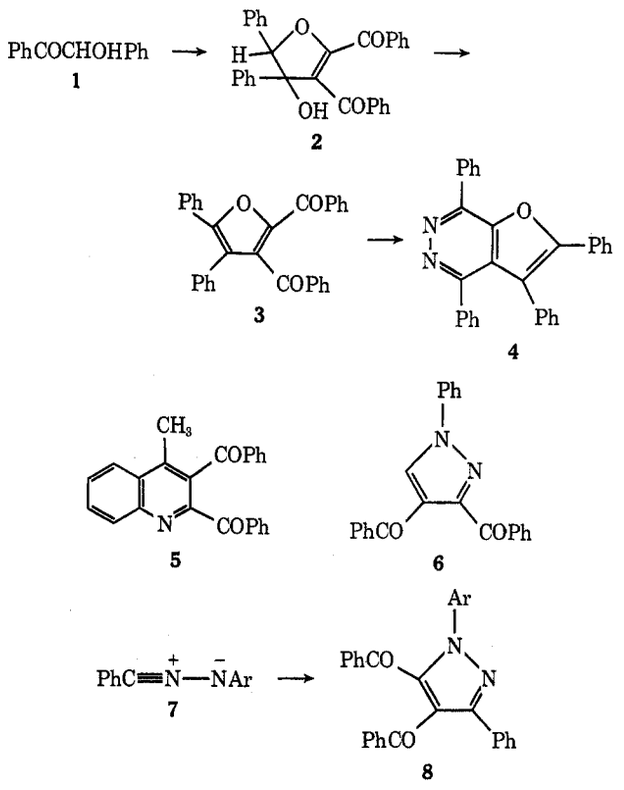
Received November 9, 1972

The synthesis of pyridazines from 1,4 diketones and hydrazine hydrate is well-established procedure,[2] its major limitation being the availability of the required 1,4-dicarbonyl precursors. These are especially difficult to obtain in heterocyclic ring systems and this study was undertaken to evaluate cycloaddition procedures as routes to heterocycles with the requisite vicinal dicarbonyl substituents, as well as the final ring closure to the fused pyridazine derivatives themselves.

Utilizing Michael additions[3] as well as a variety of 1,3-dipolar cycloadditions[4] with the acetylenic dipolarophile dibenzoylacetylene, it has been possible to obtain several heterocyclic systems with the requisite substitution pattern. The following reactions illustrate a procedure which should be capable of extension to the synthesis of other heterocycles with analogous substitution patterns.

Condensation of benzoin (**1**) with dibenzoylacetylene in the presence of potassium carbonate gave the hydrated furan **2**, which was readily dehydrated with methanolic hydrochloric acid to 2,3-dibenzoyl-4,5-diphenylfuran (**3**). Treatment of **3** with hydrazine hydrate afforded 2,3,4,7-tetraphenylfuro[2,3-*d*]pyridazine (**4**) in 80% yield. The analytical and spectral data described in Table I and the Experimental Section for this series of products clearly establish their structures.



Similarly, condensation of *o*-aminoacetophenone with dibenzoylacetylene gave 2,3-dibenzoyl-4-methylquinoline (**5**), which was converted into 1,4-diphenyl-10-methylbenzo[*g*[pyrido[2,3-*d*]pyridazine in quantitative yield.

Two isomeric dibenzoylpyrazoles are readily synthesized by 1,3-dipolar cycloaddition techniques. We have recently shown[5] that the reaction of *N*-phenyl-

(1) Support of this work by U. S. Public Health Service Research Grant CA 08495, National Cancer Institute, is gratefully acknowledged.

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TABLE I
SOME RING-FUSED PYRIDAZINES

Fused pyridazine derived from	Yield, %	Mp, °C	Formula[f]	M·+ (rel intensity)	Uv data, λ_{max}, nm (log ϵ)
2,3-Dibenzoyl-4,5-diphenylfuran	80	203–204[a]	$C_{30}H_{20}N_2O$	424 (100)	222[b] (4.35), 274 (4.25), 310 (4.27)
3,4-Dibenzoyl-1-phenylpyrazole	100	251–252[c,d]	$C_{23}H_{16}N_4$	348 (52)	237 (4.35), 304 (4.38)
4,5-Dibenzoyl-1-(2,4-dibromophenyl)-3-phenylpyrazole	100	224–225[a]	$C_{29}H_{18}Br_2N_4$	580 (66)	224[b] (4.69), 305 (4.14)
2,3-Dibenzoyl-4-methylquinoline	100	240[c,e]	$C_{24}H_{17}N_3$	347 (100)	212 (4.45), 255 (4.64), 360 (3.73)

[a] Colorless needles. [b] Shoulder. [c] Yellow needles from benzene. [d] Nmr ($CDCl_3$) τ 1.27 (s, 1, H_3), 1.1–2.7 (m, aromatic). [e] Nmr ($CDCl_3$) τ 7.30 (s, 3, 10-CH_3), 1.5–2.8 (m, 14, aromatic). [f] Satisfactory analytical values (±0.3 for C, H, and N) were reported for all compounds. Ed.

sydnone with dibenzoylacetylene is a convenient route to 3,4-dibenzoyl-1-1-phenylpyrazole (**6**), and the isomeric system, 4,5-dibenzoyl-1-(2,4-dibromophenyl)-3-phenylpyrazole (**8**), was obtained from the reaction of the nitrilimine[6] **7** with dibenzoylacetylene. Both these pyrazoles underwent ready ring closure with hydrazine hydrate to give the anticipated 2,4,7-triphenylpyrazolo[3,4-*d*]pyridazine and 1-(2,4-dibromophenyl)-3,4,7-triphenylpyrazolo[3,4-*d*]pyridazine, respectively, in quantitative yields (Table I). This ring system has been synthesized previously[7] by ring closure of pyrazine-3,4-dicarboxaldehyde with hydrazine hydrate.

The possibility that these ring-fused pyridazine derivatives would undergo cycloadditions was also of interest. Despite its inherent *o*-quinoidal structure, 3,4,7-triphenylpyrazolo[3,4-*d*]pyridazine did not undergo cycloaddition with *N*-phenylmaleimide and the stability of such systems may be attributed to the introduction of two nitrogen atoms.[8] Thus 2-methyl-2*H*-pyrrolo[3,4-*b*]quinoxaline is a stable entity,[9] whereas 2*H*-naphtho[2,3-*c*]pyrrole can only be trapped as its *N*-phenylmaleimide product.[10] The incorporation of two or more heteroatoms into the five-membered ring may also inhibit the cycloaddition reactions, as *naphtho[2,3-c][2,1,3]thiadiazole* is unreactive toward dienophiles.[11]

Experimental Section[12]

4,5-Dibenzoyl-1-(2,4-dibromophenyl)-3-phenylpyrazole (8, Ar = 2,4-$Br_2C_6H_3$).—*N*-α-Bromobenzylidene-*N'*-(2,4-dibromophenyl)hydrazine[13] (4.33 g, 0.01 mol), dibenzoylacetylene (2.34 g, 0.01 mol), and anhydrous acetonitrile (100 ml) were stirred together at room temperature, and triethylamine (5 ml) was added. After the solution had stirred overnight, the solvent was removed and the residue was washed well with water. Two crystallizations from ethanol gave colorless needles: 60%; mp 174–175°; ir (KBr) 3080, 3045 (CH), 1670, 1650 cm^{-1} (CO); $\lambda_{max}^{CH_3OH}$ 242 nm (sh, log ϵ 4.41), 302 (4.08); nmr ($CDCl_3$) τ 2.9–2.1 (m, aromatic); mass spectrum *m/e* (rel intensity) M·+ 584 (95).

Anal. Calcd for $C_{29}H_{18}Br_2N_2O_2$: C, 59.41; H, 3.10; N, 4.78. Found: C, 59.18; H, 2.94; N, 4.67.

2,3-Dibenzoyl-4,5-dihydro-4,5-diphenyl-4-hydroxyfuran (2).—Benzoin (0.6 g), dibenzoylacetylene (0.7 g), anhydrous sodium carbonate (0.4 g), and dry acetone (20 ml) were boiled together under reflux for 24 hr. The mixture was cooled, poured into water (250 ml), and extracted with ether. The extract was dried ($MgSO_4$), the ether was removed, and the residue was crystallized from methanol (charcoal), forming colorless needles: 39%; mp 171°; ir (KBr) 3500 (OH), 3080, 3045 (CH), 1680 cm^{-1} (CO); $\lambda_{max}^{CH_3OH}$ 255 nm (log ϵ 4.19), 305 (sh, 3.80); nmr ($CDCl_3$) τ 5.77 (s, 1, OH), 4.17 (s, 1, H_5), 2.8–2.0 (m, 20, aromatic); mass spectrum *m/e* (rel intensity) M·+ 446 (27).

Anal. Calcd for $C_{30}H_{22}O_4$: C, 80.70; H, 4.97. Found: C, 80.87; H, 4.96.

2,3-Dibenzoyl-4,5-diphenylfuran (3) was prepared from **2** by the action of boiling methanolic hydrochloric acid during 5 min. Upon concentration the product separated as colorless, matted needles: 100%; mp 157°; ir (KBr) 3080 (CH), 1680 cm^{-1} (CO); $\lambda_{max}^{CH_3OH}$ 256 nm (log ϵ 4.19), 342 (3.68); nmr ($CDCl_3$) τ 2.9–1.8 (m, aromatic); mass spectrum *m/e* (rel intensity) M·+ 428 (100).

Anal. Calcd for $C_{30}H_{20}O_3$: C, 84.09; H, 4.71. Found: C, 84.08; H, 4.64.

2,3-Dibenzoyl-4-methylquinoline (5).—Equivalent amounts of *o*-aminoacetophenone and dibenzoylacetylene were refluxed in methanol for 10 min. On cooling, yellow needles of an adduct were deposited. Without further characterization the product was dissolved in methanolic hydrochloric acid and refluxed for 30 min. Partial removal of the methanol gave a colorless solid which crystallized from benzene as colorless needles: 40%; mp 204–205°; ir (KBr) 3090 (CH), 1680, 1660 cm^{-1} (CO); $\lambda_{max}^{CH_3OH}$ 207 nm (log ϵ 4.62), 255 (4.54); nmr ($CDCl_3$) τ 7.42 (s, 3, CH_3), 2.8–1.6 (m, 14, aromatic); mass spectrum *m/e* (rel intensity) M·+ 351 (58).

Anal. Calcd for $C_{24}H_{17}NO_2$: C, 82.03; H, 4.88; N, 3.99. Found: C, 82.37; H, 4.66; N, 3.85.

Ring-Fused Pyridazines.—The following method illustrates the general procedure used. The dibenzoyl compound was dissolved in the minimum quantity of boiling ethanol, hydrazine hydrate (85%, twofold excess) was added, and the solution, after refluxing for 15 min, was filtered and allowed to cool, whence the products described in Table I separated.

Registry No.—**1**, 119-53-9; **2**, 38974-10-6; **3**, 38899-31-9; **4**, 38899-32-0; **5**, 38899-33-1; **6**, 37687-10-8; **8** (Ar = 2,4-$Br_2C_6H_3$), 38899-35-3; 1,4-diphenyl-10-methylbenzo[*g*]pyrido[2,3-*d*]pyridazine, 38899-36-4; 2,-4,7-triphenylpyrazolo[3,4-*d*]pyridazine, 38974-11-7; 1-(2,4-dibromophenyl)-3,4,7-triphenylpyrazolo[3,4-*d*]-pyridazine, 38899-37-5; *N*-α-bromobenzylidine-*N'*-(2,-4-dibromophenyl)hydrazine, 2516-46-3; dibenzoylacetylene, 1087-09-8; *O*-aminoacetophenone, 551-93-9.

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