Reactions of 2-Acyl-3(2*H*)-benzofuranones with Hydrazines and Diamines

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2-Acetyl-3(2*H*)-benzofuranone (**1a**) reacts with hydrazine to yield 2-(1-hydrazino-1-hydroxyethyl)-3(2*H*)-benzofuranone (**2**), the α-azine of 2-acetyl-3(2*H*)-benzofuranone (**4**) or 3(2*H*)-benzofuranone hydrazone depending upon the conditions, whereas 2-benzoyl- and 2-(2,4-dimethylbenzoyl)-3(2*H*)-benzofuranones (**1b** and **1c**) give 3-phenyl- and 3-(2,4-xylyl)-1*H*-benzofuro[3,2-*c*]pyrazoles (**5a** and **5b**), respectively. Phenylhydrazine reacts with acylbenzofuranones **1** to give the corresponding α-phenylhydrazones (**6a–c**) or the corresponding 3-substituted 1-phenyl-1*H*-benzofuro[3,2-*c*]pyrazoles (**7a–c**). Treatment of compounds **1a** and **1b** with ethylenediamine affords the corresponding substituted 2,2′-[ethylenebis(nitriloalkylidene)]bis-3(2*H*)-benzofuranones (**8a** and **8b**), instead of the expected 5-substituted 2,3-dihydrobenzofuro[3,2-*e*][1,4]diazepines. 1,8-Naphthalenediamine reacts with compounds **1** in the presence of *p*-toluenesulfonic acid to give 2-substituted perimidine *p*-toluenesulfonates (**9a–c**).

Our interest in the reactions of 2-acyl-1,3-indandiones with hydrazine[1] and other diamines[2,3] prompted us to investigate the reactions of the structurally related 2-acyl-3(2H)-benzofuranones (**1a–c**) with various diamines.

As previously reported, 2-acyl-1,3-indandiones react with hydrazine to form monohydrazones.[1] In the present study of the reaction of acylbenzofuranones with hydrazine, we were unable to isolate the corresponding hydrazones. Instead various products were obtained depending upon the reaction conditions and the structure of the acyl group.

Ethanolic solution of equimolar amounts of 2-acetyl-3(2*H*)-benzofuranone (**1a**) and hydrazine stirred at room temperature gave a 1:1 addition product, 2-(1-hydrazino-1-hydroxyethyl)-3(2*H*)-benzofuranone (**2**). Under the same conditions the aroyl derivatives **1b** and **1c** were recovered unchanged. Structure **2** is based on the elemental analyses, the ir spectrum, and the method of preparation, which is analogous to that used by Braun[4] to prepare the 1:1 addition product from 2-phenylacetyl-1,3-indandione and hydrazine. All attempts to form the corresponding monohydrazone **3** from the addition product **2** were unsuccessful. Treatment of **2** with ethanolic solutions of hydrochloric acid at room temperature or at refluxing temperature without acid reversed the reaction and compound **1a** was recovered.

Slow addition of hydrazine to a refluxing ethanolic solution of an equimolar amount of **1a**, so that the reaction took place essentially in the presence of an excess of **1a**, gave the α-azine of 2-acetyl-3(2*H*)-benzofuranone (**4**) in 55% yield. The aroylbenzofuranones **1b** and **1c** failed to give the corresponding azines.

Reversed addition of the reactants, compound **1a** to a refluxing ethanolic solution of excess hydrazine, yielded 3(2*H*)-benzofuranone hydrazone. The structure of this hydrazone is supported by elemental analyses and spectral data. Under the same conditions compounds **1b** and **1c** did not give this hydrazone. However, when acetic acid was added to the reaction mixture, 3(2*H*)-benzofuranone hydrazone was formed. Examples of deacylation of 2-acyl-3(2*H*)-benzofuranones are reported in the literature.[5] In this reaction, addition of **1** to excess hydrazine, the azine **4** was never obtained. This can be attributed to the fact that azine **4** reacts with excess hydrazine to give the hydrazone of 3(2*H*)-benzofuranone.

In refluxing acetic acid acetylbenzofuranone **1a** reacted with hydrazine, giving azine **4** in almost quantitative yield, whereas the aroylbenzofuranones **1b** and **1c** yielded the corresponding 3-substituted 1*H*-benzofuro[3,2-*c*]pyrazoles **5a** and **5b**.

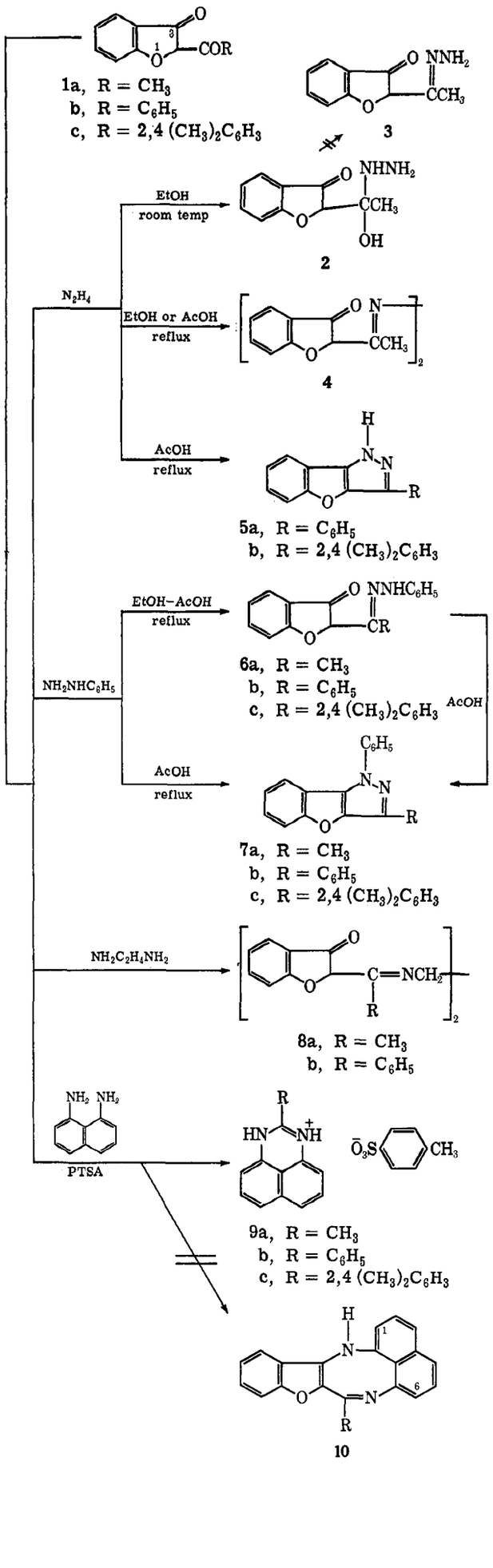
Treatment of phenylhydrazine with 2-acyl-3(2*H*)-benzofuranones (**1a–c**) in refluxing ethanol–acetic acid mixtures gave the corresponding monophenylhydrazones (**6a–c**). The assignment of the hydrazono group on the side chain is based on the mass spectra of these compounds and on the similarities of their chemical properties with those of the known α-hydrazones of 2-acyl-1,3-indandiones.[1]

Phenylhydrazones **6a–c** when heated at reflux in acetic acid cyclized to give 3-substituted 1-phenyl-1*H*-phenylbenzofuro[3,2-*c*]pyrazoles (**7a–c**). The structures of these compounds are based on elemental analyses and spectral data. The benzofuropyrazoles **7a–c** were also obtained directly from the acylbenzofuranones **1a–c** and phenylhydrazine by refluxing in acetic acid.

In a previous paper we reported that treatment of 2-benzoyl-1,3-indandione with ethylenediamine in the presence of formic acid gave 5-phenyl-2,3-dihydro-6*H*-indeno[1,2-*e*][1,4]diazepin-6-one.[2] Attempts to form the 5-substituted 2,3-dihydrobenzofuro[3,2-*e*][1,4]diazepines by treating the acylbenzofuranones **1a** and **1b** with ethylenediamine in the presence of formic acid failed. The products isolated were 2,2′-[ethylenebis(nitriloethylidyne)]- and 2,2′-[ethylenebis(nitrilobenzylidyne)]bis-3(2*H*)-benzofuranones (**8a** and **8b**, respectively). Under the same conditions compound **1c** did not react, the starting material being recovered. The structures of these compounds are based on elemental analyses and spectral data. In addition, attempts to prepare 6-substituted 11*H*-benzo[*b*]benzofuro[3,2-*e*][1,4]diazepines from acylbenzofuranones **1** and *o*-phenylenediamine under the conditions used by Mosher and Piesch to prepare benzoindenodiazepinones[6] failed.

The reaction of the acylbenzofuranones **1a–c** with 1,8-naphthalenediamine in the presence of *p*-toluenesulfonic acid was investigated as a possible route to eight-membered heterocyclic compounds. It was

(1) R. A. Braun and W. A. Mosher, *J. Amer. Chem. Soc.*, **80**, 2749 (1958).
(2) W. A. Mosher and S. Piesch, *J. Org. Chem.*, **35**, 1026 (1970).
(3) W. A. Mosher and T. E. Banks, *ibid.*, **36**, 1477 (1971).
(4) R. A. Braun, University Microfilms, Ann Arbor, Mich., L. C. Card No. Mic 58-5283, 104 pp; *Diss. Abstr.*, **19**, 953 (1958).
(5) R. Bryant and D. L. Haslam, *J. Chem. Soc.*, 1345 (1967).
(6) W. A. Mosher and S. Piesch, *J. Org. Chem.*, **35**, 2109 (1970).



found that this reaction proceeds similarly to that already reported by this laboratory between 2-acyl-1,3-indandiones and 1,8-naphthalenediamine[3] giving 2-substituted perimidine *p*-toluenesulfonates (**9a–c**) instead of 8-substituted 14*H*-benzofuro[3,2-*f*]naphtho[1,8-*bc*][1,5]diazocines (**10**). It is believed that the mechanism of this reaction is the same as that proposed by Mosher and Banks[3] for the formation of 2-substituted perimidines from 2-acyl-1,3-indandiones. However, we failed to isolate the expected by-product, 3(2*H*)-benzofuranone.

Experimental Section[7]

2-Acyl-3(2*H*)-benzofuranones (**1a–c**) were prepared according to known methods.[8,9] 2-(2,4-Dimethylbenzoyl)-3(2*H*)-benzofuranone (**1c**) is not reported in the literature. It was obtained in 38% yield from methyl salicylate and 2-chloro-2′,4′-dimethylacetophenone as light yellow crystals: mp 88–90°; nmr δ 6.8–7.6 (m, 7 H), 2.0–2.1 (m, 6 H); mass spectrum *m/e* 266, 249, 234, 205, 133.

Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.69; H, 5.26; N, 18.05. Found: C, 76.73; H, 5.04; N, 18.09.

2-(1-Hydrazino-1-hydroxyethyl)-3(2*H*)-benzofuranone (**2**).—A mixture of hydrazine (0.16 g, 5 mmol) and 2-acetyl-3(2*H*)-benzofuranone (**1a**) (0.9 g, 5 mmol) in ethanol (50 ml) was stirred at room temperature for 1 hr. The precipitate was collected by filtration to give 0.66 g (62%) of **2** as a white powder: mp >300°; ir 3300–3280, 3200–3180, and 1630–1620 cm^{-1}.

Anal. Calcd for $C_{10}H_{12}N_2O_3$: C, 57.68; H, 5.81; N, 13.46. Found: C, 57.67; H, 5.71; N, 13.27.

A solution of **2** in ethanol stirred at reflux for 1 hr gave **1a**, mp 90–91° alone and in mixture with **1a** prepared as in ref 8. Compound **1a** was obtained also when a solution of **2** in ethanol containing a few drops of hydrochloric acid was stirred at room temperature for 1 hr.

α-Azine of 2-Acetyl-3(2*H*)-benzofuranone (**4**).—A solution of hydrazine (0.08 g, 2.5 mmol) in ethanol (25 ml) was added dropwise to a refluxing solution of **1a** (0.45 g, 2.5 mmol) in ethanol (25 ml). The mixture was refluxed for an additional 2 hr and cooled, and the precipitate was collected by filtration to give 0.25 g (55%) of **4** as bright red needles;[10] mp 250–251°; ir 1640, 1600–1590, and 1520–1500 cm^{-1}. No bands at 3500–3100 cm^{-1} were observed.

Anal. Calcd for $C_{20}H_{16}N_2O_4$: C, 68.96; H, 4.63; N, 8.04. Found: C, 68.98; H, 4.51; N, 7.92.

A 90% yield of azine **4** (mp 250–251° alone and in mixture with the azine prepared as described above) was obtained when a solution of acetylbenzofuranone **1a** (3.6 g, 20 mmol) and hydrazine (1.3 g, 40 mmol) in acetic acid (25 ml) was heated at reflux for 3 hr.

3(2*H*)-Benzofuranone Hydrazone from 1a.—A solution of **1a** (0.45 g, 2.5 mmol) in ethanol (25 ml) was added dropwise to a refluxing solution of hydrazine (0.32 g, 10 mmol) in ethanol (25 ml). The mixture was refluxed for an additional 1.5 hr, cooled, and chromatographed on neutral alumina (chloroform as the eluent) to give 94 mg (25%) of 3(2*H*)-benzofuranone hydrazone as a yellow solid. A sample was crystallized from chloroform–hexane mixtures to yield pale yellow platelets: mp 105–106°;

(7) Melting points were determined with a Fisher-Johns melting point apparatus and are uncorrected. The infrared spectra were recorded on a Perkin-Elmer spectrophotometer, Models 137 and 421. Unless otherwise specified, they were taken as Nujol mulls between sodium chloride plates. The nuclear magnetic resonance spectra were obtained on a Varian Associates spectrometer, Model A-60A, using DMSO-d_6 as the solvent, unless otherwise noted. Chemical shifts are reported as δ values (parts per million) relative to TMS as an internal standard. Mass spectra were recorded on a CEC 21/110B spectrometer. Elemental analyses were performed by M-H-W Laboratories, Garden City, Mich., by Micro Analysis, Inc., Marshallton Del., and by Dr. A. Bernhardt, Microanalytisches Laboratorium in Max Planck Institute für Kohlenforschung, Germany.

(8) T. A. Geissman and A. Armen, *J. Amer. Chem. Soc.*, **77**, 1623 (1955).

(9) R. Bryant and D. L. Haslam, *J. Chem. Soc.*, 2361 (1965).

(10) The red color can be attributed to the conjugation of the enol form as in the analogous sulfur compound, the azine of 2-acetylbenzo[*b*]thiophen-3(2*H*)-one, which is reported to be red: W. J. Barry and E. W. McClelland, *J. Chem. Soc.*, 472 (1935).

ir 3100, 3000, and 1600 cm^{-1}; nmr ($CDCl_3$) δ 6.7–7.7 (m, 4, aromatic H), 4.9 (s, broad, 2 H), and 5.0 (sharp, 2 H). The mass spectrum shows a molecular ion peak at m/e 148.

Anal. Calcd for $C_8H_8N_2O$: C, 63.91; H, 5.18; N, 17.70. Found: C, 63.83; H, 5.10; N, 17.50.

3(2*H*)-Benzofuranone Hydrazone from 1b and from 1c.—A solution of the appropriate acylbenzofuranone (10 mmol) in ethanol (50 ml) was added dropwise to a refluxing solution of hydrazine (excess) in ethanol (50 ml) and then acetic acid (2 drops) was added. The mixture was refluxed for an additional 0.5 hr and worked up as described above for the hydrazone from **1a**. A 70% yield of 3(2*H*)-benzofuranone hydrazone was obtained as pale yellow platelets from chloroform–hexane, mp (alone and in mixture with the hydrazone obtained from **1a**) 105–106°.

3(2*H*)-Benzofuranone Hydrazone from Azine 4.—A mixture of azine **4** (0.5 g, 0.29 mmol) and hydrazine (20 ml), stirred at room temperature for 1 hr, gave a red solution, which gradually became pale yellow. After removal of the excess hydrazine under reduced pressure, the residue was chromatographed on neutral alumina (chloroform as the eluent) to give 160 mg (38%) of 3(2*H*)-benzofuranone hydrazone, mp 105–106° alone and in mixture with the hydrazone obtained as described above. The yield increased to 56% when the above mixture of azine **4** and hydrazine was heated at reflux for 15 min.

3-Phenyl-1*H* benzofuro[3,2-*c*]pyrazole (5a).—Hydrazine (0.65 g, 20 mmol) was added to a solution of **1b** (2.38 g, 10 mmol) in acetic acid (50 ml) and the mixture was refluxed for 24 hr. The acid was removed *in vacuo* and the residue was chromatographed on alumina (ethanol as the eluent) to give 1.52 g (65%) of **5a** as buff crystals: mp 217–219°; ir (KBr) 3230, 1600–1610 cm^{-1}; nmr δ 7.1–7.8 (m, 9 H); mass spectrum m/e 234, 176, 151, 132, 117, 103, 77.

Anal. Calcd for $C_{15}H_{10}N_2O$: C, 76.92; H, 4.27; N, 11.96. Found: C, 76.80; H, 4.47; N, 11.70.

3-(2,4-Xylyl)-1H-benzofuro[3,2-*c*]pyrazole (5b) was obtained as a light yellow powder, mp 162–163°, in 9% yield from **1c** and hydrazine following the procedure above described for compound **5a**. The ir spectrum is similar to that of **5a**; nmr δ 6.7–7.8 (m, 7 H), 2.0–2.1 (s, 6 H); mol wt, 262 (mass spectrum).

Anal. Calcd for $C_{17}H_{14}N_2O$: C, 77.86; H, 5.34; N, 10.69. Found: C, 77.60; H, 5.62; N, 10.53.

2-Acetyl-3(2*H*)-benzofuranone α-Phenylhydrazone (6a).—Phenylhydrazine (1.1 g, 10 mmol) was added to a solution of **1a** (1.8 g, 10 mmol) in ethanol (50 ml) and acetic acid (0.5 ml) and the mixture was heated at reflux for 12 hr. The solvent was removed *in vacuo* and the residue was chromatographed on alumina (chloroform as the eluent) to give 1.2 g (45%) of **6a** as a yellow solid, mp 135–140°. A sample was recrystallized from petroleum ether (bp 30–60°)–ether to yield pale yellow crystals: mp 147–148°; ir (KBr) 3400–3350, 1600–1595 cm^{-1}; nmr δ 7.0–7.4 (m, 9 H), 3.3 (s, 1 H), and 1.7 (s, 3 H). The mass spectrum shows a molecular ion at m/e 266 and major fragments at m/e 235, 196, 159, 133, 120, 105, 93, and 77. This compound gave a positive Tollens test.[1,11]

Anal. Calcd for $C_{16}H_{14}N_2O_2$: C, 72.16; H, 5.30; N, 10.52. Found: C, 72.07; H, 5.31; N, 10.33.

2-Benzoyl-3(2*H*)-benzofuranone α-Phenylhydrazone (6b).—A mixture of **1b** (2.38 g, 10 mmol), phenylhydrazine (1.1 g, 10 mmol), and acetic acid (2 ml) in ethanol (50 ml) was heated at reflux for 12 hr. The solvent was removed *in vacuo* and the residue was worked up as described under **6a** and gave 1.7 g (54%) of **6b**. Recrystallization from petroleum ether–ether gave yellow crystals: mp 220–221°; ir (KBr) 3350–3390, 1600–1610 cm^{-1}; the mass spectrum shows a molecular ion peak at m/e 328 and a prominent peak at m/e 195, which probably is the fragment $C_6H_5C{=}NNHC_6H_5^+$. This compound gave a positive Tollens test.[1,11]

Anal. Calcd for $C_{21}H_{16}N_2O_2$: C, 76.83; H, 4.88; N, 8.54. Found: C, 77.12; H, 4.61; N, 8.47.

2-(2,4-Dimethylbenzoyl)-3(2*H*)-benzofuranone α-phenylhydrazone (6c) was obtained as yellow crystals, mp 227–229°, in 16% yield from **1c** and phenylhydrazine following the procedure above described for **6b**. The ir spectrum is similar to that of **6b**; nmr δ 6.7–7.8 (m, 12 H), 3.4 (s, 1 H), and 2.0–2.1 (s, 6 H); the mass spectrum shows a prominent peak at m/e 223 probably due to the fragment $C_6H_5(CH_3)_2C{=}NNHC_6H_5^+$. Fragment $C_6H_3(CH_3)_2CO$ (m/e 133) was absent.

Anal. Calcd for $C_{23}H_{20}N_2O_2$: C, 77.65; H, 5.59; N, 7.82. Found: C, 77.43; H, 5.68; N, 7.59.

3-Methyl-1-phenyl-1*H*-benzofuro[3,2-*c*]pyrazole (7a).—Phenylhydrazine (0.54 g, 5 mmol) was added to a refluxing solution of **1a** (0.9 g, 5 mmol) in acetic acid (25 ml). The dark red mixture was refluxed for an additional 0.5 hr, the acetic acid was removed *in vacuo*, and the residue was chromatographed on alumina (chloroform as the eluent) to give 0.16 g (13%) of **7a** as pale yellow crystals: mp 71–72° (petroleum ether); ir 1600 1595 cm^{-1}; nmr δ 7.3–8.0 (m, 9 H), 2.5 (s, 3 H); the mass spectrum shows the required molecular ion and major peaks at m/e 233, 222, 206, 195, 179, 152, 146, 124, 105, 77, and 51.

Anal. Calcd for $C_{16}H_{12}N_2O$: C, 77.40; H, 4.87; N, 11.28. Found: C, 77.21; H, 5.07; N, 11.15.

1,3-Diphenyl-1*H*-benzofuro[3,2-*c*]pyrazole (7b) was obtained as pale yellow crystals, mp 155–157° (ether–hexane), in 76% yield from **1b** and phenylhydrazine following the procedure above described for **7a** (refluxing time 48 hr and chloroform–methanol as eluent).

Anal. Calcd for $C_{21}H_{14}N_2O$: C, 81.29; H, 4.52; N, 9.03. Found: C, 81.15; H, 4.53; N, 8.76.

1-Phenyl-3-(2,4-xylyl)-1*H*-benzofuro[3,2-*c*]pyrazole (7c) was obtained as pale yellow crystals, mp 173–175° (glyme), in 14% yield from **1c** and phenylhydrazine following the procedure above described for **7b** (refluxing time 72 hr).

Anal. Calcd for $C_{23}H_{18}N_2O$: C, 82.74; H, 4.17; N, 8.34. Found: C, 82.41; H, 4.29; N, 8.30.

The above three compounds **7a**, **7b**, and **7c** were also obtained by refluxing the corresponding α-phenylhydrazones **6a**, **6b**, and **6c** in acetic acid for 12, 48, and 72 hr, respectively. The yields were 32% for **7a**, 83% for **7b**, and 17% for **7c**.

2,2′-[Ethylenebis(nitriloethylidyne)]bis-3(2*H*)-benzofuranone (8a).—Ethylenediamine (0.3 g, 5 mmol) was added dropwise to a solution of **1a** (0.9 g, 5 mmol) in ethanol (50 ml). Formic acid (0.5 ml) was added and the mixture was heated at reflux for 1 hr. The solvent was removed *in vacuo* and the residue was chromatographed on alumina (chloroform as eluent) to give 70 mg (7.5%) of **8a**: mp 217–219°; ir 1640–1645 and 1550–1560 cm^{-1}; nmr δ 7.1–7.9 (m, 8 H), 3.5–3.8 (broad peak, 4H), 2.6 (s, 2 H), and 2.4 (s, 6 H).

Anal. Calcd for $C_{22}H_{20}N_2O_4$: C, 69.82; H, 5.86; N, 7.40. Found: C, 69.69; H, 5.81; N, 7.31.

2,2′-[Ethylenebis(nitrilobenzylidyne)]bis-3(2*H*)-benzofuranone (8b) was obtained as yellow crystals, mp >300° (methanol), in 16% yield from **1b** and ethylenediamine following the procedure above described for **8c** (refluxing time 72 hr and elution with methanol instead of chloroform). The ir spectrum is similar to that of **8a**; nmr δ 7.1–7.9 (m, 18 H), 3.5–3.7 (broad, 4H), 2.7 (s, 2 H); mol wt, 500 (mass spectrum).

Anal. Calcd for $C_{32}H_{24}N_2O_4$: C, 76.80; H, 4.79; N, 5.60. Found: C, 76.64; H, 4.71; N, 5.76.

Under the same conditions compound **1c** did not react with ethylenediamine. The starting material was recovered.

Reaction of 2-Acyl-3(2*H*)-benzofuranones with 1,8-Naphthalenediamine.—A solution of the appropriate 2-acyl-3(2*H*)-benzofuranone (20 mmol) in ethanol (100 ml) was added dropwise over 0.5 hr to a refluxing solution of 1,8-naphthalenediamine (4.5 g, 28 mmol) and *p*-toluenesulfonic acid (4.0 g, 20 mmol) in ethanol (200 ml). The mixture was refluxed for an additional 24 hr and concentrated to half volume *in vacuo*, and the precipitate was collected by filtration. Compound **1a** gave 5.5 g (77%) of 2-methylperimidine *p*-toluenesulfonate, identical (mixture melting point and ir spectrum) with an authentic sample,[3] and compound **1b** gave 3.3 g (29%) of 2-phenylperimidine *p*-toluenesulfonate, also identical with an authentic sample.[3] Compound **1c** gave 1.4 g (11%) of 2-(2,4-xylyl)perimidine *p*-toluenesulfonate, mp 250–252°, as brown crystals.

Anal. Calcd for $C_{26}H_{24}N_2SO_3$: C, 70.27; H, 5.41; N, 10.81. Found: C, 70.02; H, 5.35; N, 10.64.

Several attempts to isolate the expected by-product, the 3(2*H*)-benzofuranone, from the reaction mixture failed.

Registry No.—**1c**, 34823-84-2; **2**, 34839-58-2; **4**, 34823-85-3; **5a**, 34823-86-4; **5b**, 34823-87-5; **6a**, 34823-88-6; **6b**, 34823-89-7; **6c**, 34823-90-0; **7a**,

(11) S. P. Mulliken, "Identification of Pure Organic Compounds," Vol. 2, Wiley, New York, N. Y., 1916, p. 29.

34823-91-1; **7b**, 34823-92-2; **7c**, 34823-93-3; **8a**, 34823-94-4; **8b**, 34823-95-5; **9c**, 34823-96-6; 3(2*H*)-benzofuranone hydrazone, 34823-97-7.

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Synthesis and Reactions of 3-Diazo-1,4-diphenyl-4-hydroxy-2-butanone

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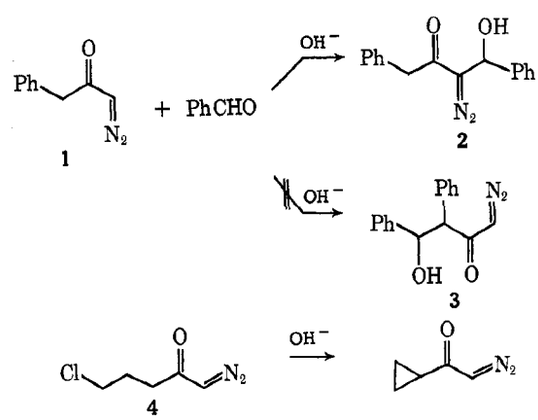
1-Diazo-3-phenyl-2-propanone (**1**) underwent aldol condensation with benzaldehyde at the diazo carbon to give 3-diazo-1,4-diphenyl-4-hydroxy-2-butanone (**2**) in 63% yield. Irradiation of **2** in benzene or methanol below 50° gave 1,4-diphenyl-1,3-butanedione (**5**) in 50% yield. Pyrolysis of **2** in refluxing chlorobenzene gave 40% of **5**. Treatment of **2** with hydrogen chloride in ether gave 20% of the dione **5** and 31% of 3-chloro-1,4-diphenyl-4-hydroxy-2-butanone (**6**). Similarly, when treated with hydrogen bromide in ether, **2** gave 10% of the dione **5** and 45% of 3-bromo-1,4-diphenyl-4-hydroxy-2-butanone (**10**). The structures of **5** and **10** rest on the physical data and their reduction to 2-chloro-1,4-diphenyl-1,3-butanediol (**8**) and 2-bromo-1,4-diphenyl-1,3-butanediol (**11**), respectively.

Under appropriate conditions diazomethyl ketones undergo normal base-catalyzed reactions without the destruction of the $-COCN_2-$ moiety.[1,2] For example, base-catalyzed intramolecular aldol and Dieckman-type condensation reactions have been shown to take place at the diazo carbon of some diazomethyl ketones.[1] Normal base-catalyzed intramolecular alkylation can also apparently occur at the α-methylene carbon of a suitable diazomethyl ketone.[2] Similar intermolecular condensation reactions of diazomethyl ketones, however, have not been investigated.

We wish to report here the first example of a normal base-catalyzed intermolecular condensation reaction of a diazomethyl ketone of the type RCH_2COCHN_2, which has two potential condensation sites. Successful condensation of 1-diazo-3-phenyl-2-propanone (**1**) with benzaldehyde resulted in exclusive reaction at the diazo carbon to give 3-diazo-1,4-diphenyl-4-hydroxy-2-butanone (**2**). The photochemical, thermal, and acid-catalyzed decompositions of this novel α-diazo-β-hydroxy ketone **2** were also investigated.

Synthesis of 2.—Treatment of a dilute, ethanolic solution of the diazo ketone **1** and an excess of benzaldehyde with 2% sodium hydroxide solution at room temperature resulted in an immediate development of a red color characteristic of diazo ketone decomposition.[3] When the solution was held at -5 to 0° and then treated with base, no such color developed but the aldol reaction product was formed. Extraction of the reaction solution with carbon tetrachloride and chromatography of the concentrated extract on alumina gave, besides unreacted starting materials, a deep yellow oil which crystallized to give 3-diazo-1,4-diphenyl-4-hydroxy-2-butanone (**2**) in 63% yield. The infrared spectrum of **2** showed bands at 4.78 and 6.08 μ, confirming retention of the diazo ketone moiety, and a band at 2.94 μ supported the presence of a hydroxyl group. The nmr spectrum of a pure and dry sample of **2** in carbon tetrachloride revealed a doublet at δ 7.21 and a singlet at δ 3.68 due to ten phenyl and two methylene protons, respectively. The one-proton doublets at δ 5.91 (J = 4 Hz), and 4.3 (J = 4 Hz) were attributed to the methine and the hydroxyl protons, respectively. Exchange of the hydroxyl proton with deuterium oxide, as judged by the disappearance of the δ 4.3 peak and the collapse of the δ 5.91 peak to a singlet, confirmed this assignment. No evidence for the formation of the aldol product **3** which would have resulted from condensation at the α-methylene carbon was obtained by nmr spectroscopic examination of various chromatographic fractions. The remainder of the unrecovered starting material apparently decomposed during the reaction or the work-up. We cannot, however, eliminate the possible formation of a small amount of **3**.



The fact that **1** condenses with benzaldehyde largely at the diazo carbon contrasts with the intramolecular cyclization of 5-chloro-1-diazo-2-pentanone (**4**) to give cyclopropyldiazomethyl ketone.[2] The azomethine protons of both **1** and **4** were shown to be more acidic than the respective methylene protons by the addition of a drop of deuterium oxide containing a catalytic amount of sodium carbonate to a carbon tetrachloride solution of **1** or **4**. In both cases the azomethine peak was rapidly and completely removed from the nmr spectra. The methylene peaks in both cases remained unaffected. The cyclization of **4** to give cyclopropyldiazomethyl ketone demonstrates the ease of formation of a three-membered ring over a five-membered ring, probably due to a more favorable entropy of activation for the former process.[4] The intramolecular alkylation in

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(4) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, p 198.