suspended solid dissolved. Dilution with 150 ml of water, followed by evaporation under reduced pressure to a small volume, cooling, and filtering gave 0.7 g (97%) of yellow needles, mp 201°. The analytical sample, mp 213°, was prepared by recrystallization from water: nmr (DMSO-d_6) δ 2.94 (s, 3, N_3-CH_3), 4.32 (s, 2, C_4-CH_2).

Anal. Calcd for $C_{12}H_{17}N_5O_3$: C, 48.47; H, 6.44; N, 23.56. Found: C, 48.57; H, 6.13; N, 23.88.

3,8-Dimethylisoxanthopterincarboxylic Acid Ethyl Ester (78).—A solution of 0.108 g of 2-amino-3,8-dimethyl-6-carbethoxy-7-oxo-7,8-dihydropteridinium tosylate (**71**) and 0.165 g of potassium ferricyanide in 27 ml of pH 7 buffer was stirred at room temperature for 4 days and the light yellow precipitate was collected by filtration, washed with ether, and dried, yield 0.033 g (49%), mp 305° (lit.[28] mp 308°). The product was identical (tlc) with an authentic sample of 3,8-dimethylisoxanthopterincarboxylic acid ethyl ester, and its uv spectrum was also in agreement with published data: λ_{max}^{pH6} 266 nm (log ϵ 3.92), 290 (3.87), 375 (4.38) [lit.[28] 265 (3.94), 289 (3.81), 374 (4.38)].

Dimroth Rearrangement of 2-Amino-3,8-dimethyl-6-carbethoxy-7-oxo-7,8-dihydropteridinium Tosylate (71).—A solution of 75 mg of **71** in 10 ml of saturated sodium bicarbonate solution was stirred at room temperature for 3 hr, and the bright yellow solid which had separated was collected by filtration, washed well with water, and dried, yield 19 mg (42%), mp 197–198°. The product was identical with an authentic sample of ethyl 2-methylamino-8-methyl-7(8*H*)-pteridinone-6-carboxylate (**29**).

Heating 100 mg of **71** in 10 ml of pH 9 buffer under reflux for 20 min, followed by acidification, gave 25 mg (46%) of 2-methylamino-8-methyl-7(8*H*)-pteridinone-6-carboxylic acid (**31**), identical in every respect with an authentic sample.

Registry No.—**4**, 31937-01-6; **5**, 31937-02-7; **6**, 31937-03-8; **11**, 31937-04-9; **12**, 31937-05-0; **13**, 31937-06-1; **15**, 31937-07-2; **17**, 31937-08-3; **18**, 5177-26-4; **20**, 31937-10-7; **21**, 31937-11-8; **22**, 31937-12-9; **23**, 31937-13-0; **24**, 31937-14-1; **25**, 31937-15-2; **26**, 31937-16-3; **27**, 31937-17-4; **28**, 31937-18-5; **29**, 31937-19-6; **30**, 31937-20-9; **31**, 31937-21-0; **32**, 2046-74-4; **33**, 2046-73-3; **34**, 2046-72-2; **35**, 2539-49-3; **36**, 31937-26-5; **37**, 2046-69-7; **38**, 2046-68-6; **39**, 2235-77-0; **40**, 2046-67-5; **41**, 2235-76-9; **42**, 2047-23-6; **43**, 31934-03-9; **44**, 31934-04-0; **45**, 31934-05-1; **46**, 31934-06-2; **47**, 31981-27-8; **48**, 31934-07-3; **49**, 31934-08-4; **50**, 31934-09-5; **51**, 31934-10-8; **52**, 2144-73-2; **53**, 31934-12-0; **57**, 31934-13-1; **59**, 1471-66-5; **60**, 1471-87-0; **61**, 1639-38-9; **62**, 1471-67-6; **63**, 1471-81-4; **67**, 31934-17-5; **69**, 31934-18-6; **70**, 31934-19-7; **71**, 31981-30-3; **72**, 31981-31-4; **73**, 31934-20-0; **74**, 31934-21-1; **75**, 31934-22-2; **76**, 31934-23-3; **77**, 31934-24-4.

Synthesis of the 1,4-Dihydropyrazine Ring System. A Stable 8-π-Electron Heterocycle

SHUE-JEN CHEN AND FRANK W. FOWLER*

Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11790

Received May 11, 1971

A previous report on the synthesis of the 1,4-dihydropyrazine ring system by the reaction of carboxylic anhydrides with dihydropyrazine **4** has been shown to be incorrect. The tetrahydropyrazine **6** is the product of this reaction. A stable dihydropyrazine **5a** has been prepared from **4** using acetyl chloride. Chemical reactions and physical properties of this 8-π-electron heterocycle are reported.

It has been known since the last century that certain conjugated cyclic molecules, such as benzene, possess unusual properties not consistent with those of simple open-chain conjugated olefins. However, it remained until the 1930's with the advent of quantum mechanics, for a theoretical understanding of these molecules to be developed. Now, due initially to the investigations of Hückel,[1] conjugated cyclic molecules can be divided into two groups. The first group contains molecules possessing $(4n + 2)$ π electrons (where $n = 0, 1, 2, \ldots$). Those molecules are predicted to have additional stability due to the cyclic delocalization of π electrons and should display aromatic properties analogous to benzene. Considerable research effort in recent years has verified this original prediction.[2]

The second group consists of molecules containing $4n$ π electrons (where $n = 1, 2, 3 \ldots$) which were originally predicted not to be stabilized by the cyclic delocalization of π electrons. Therefore, molecules in this group were designated simply as nonaromatic. The best and most classical representative of this group is cyclooctatetraene which behaves as a cyclic polyene.

Molecules containing $4n$ π electrons where the cyclic delocalization of π electrons can occur have recently attracted attention. Simple HMO theory predicts that monocyclic molecules containing $4n$ π electrons should possess zero delocalization. Since some delocalization is predicted for the open-chain analogs containing $4n$ π electrons, the cyclic compared to the noncyclic structures are actually destabilized. For this reason cyclic molecules containing $4n$ π electrons have been designated as antiaromatic.[3]

Most work on the concept of antiaromaticity has been concerned with electronic systems containing 4 π electrons. However, antiaromaticity should also be observed in molecules containing 8 π electrons *if* electron delocalization can occur.

Cyclooctatetraene, 1*H*-azepine, and 1,4-dihydropyrazine potentially all contain 8 π electrons. Since the π overlap of two p orbitals is proportional to cos θ (where θ = angle between the axis bisecting each p orbital),[4] molecular models indicate that little delocalization should occur in cyclooctatetraene. The smaller seven-membered 1*H*-azepine ring is more planar and more delocalization should be possible compared to cyclooctatetraene. However, molecular models indi-

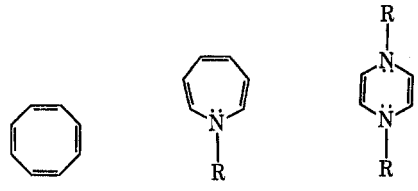
(1) (a) E. Hückel, *Z. Phys.*, **70**, 204 (1931); (b) *Z. Electrochem.*, **43**, 752 (1937).

(2) J. P. Snyder, "Nonbenzenoid Aromatics," Academic Press, New York, N. Y., and London, 1969.

(3) (a) R. Breslow, J. Brown, and J. Grajewski, *J. Amer. Chem. Soc.*, **89**, 4383 (1967); (b) R. Breslow, *Angew. Chem., Int. Ed. Engl.*, **7**, 565 (1968).

(4) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., and London, 1961, p 16.

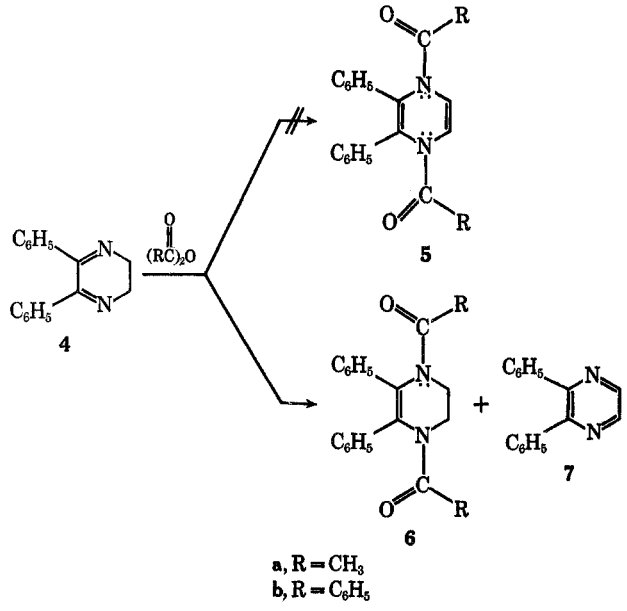
cate that the magnitude of this delocalization still must be small and it is unlikely that there is a large degree of antiaromatic character associated with 1*H*-azepine.[5] In contrast to cyclooctatetraene and 1*H*-azepine, molecular models indicate that the 1,4-dihydropyrazine ring system is nearly planar and that substantial delocalization of π electrons can occur. Clearly, the 1,4-dihydropyrazine ring system would be a suitable model for a study of antiaromaticity in 8-π-electron molecules.



1 2 3

The 1,4-dihydropyrazine ring system is reported in the older literature to be a known structure. Because of our interest in this ring system as a potential synthetic intermediate for the preparation of large heterocyclic molecules, we have repeated what would appear to be the most plausible syntheses. We have been unable to reconfirm any of these earlier claims.[6]

One logical approach to the 1,4-dihydropyrazine ring system has been reported by Mason and Dryfoos.[7] They state that when 2,3-diphenyl-5,6-dihydropyrazine is heated with either acetic or benzoic anhydride a derivative of the 1,4-dihydropyrazine ring system is produced. The melting points of the products from these reactions that we obtain, in addition to an equivalent amount of 2,3-diphenylpyrazine, are consistent with those originally reported. However, the nmr spectrum and elemental analysis are not in agreement with the proposed structures. The elemental analysis of the



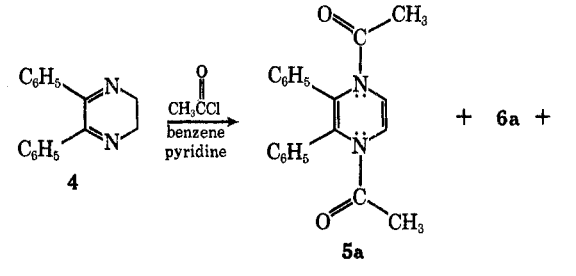
4 5 6 7

a, R = CH_3
b, R = C_6H_5

product from the reaction of **4** with acetic anhydride suggests a formula $C_{20}H_{20}N_2O_2$ which contains two additional hydrogens compared to **5a**. This is confirmed by the nmr spectrum, which shows a four-hydrogen singlet at τ 5.90. We conclude from this data that the product must possess the 1,4,5,6-tetrahydropyrazine structure **6a**. Although the mechanism for the formation of **6** is unknown, it is likely that an intermediate leading to **5** is reduced by the 5,6-dihydropyrazine **4** to **6**. This would also explain the formation of 1 equiv of 2,3-diphenylpyrazine.

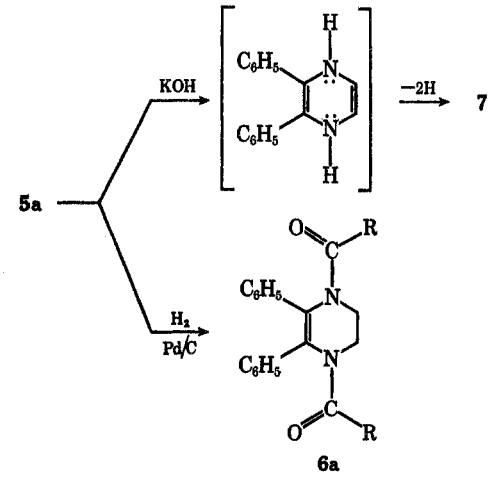
We have prepared what we believe to be the first characterized derivative of the 1,4-dihydropyrazine ring system[8] by the slow addition of acetyl chloride to 5,6-dihydropyrazine **4** in benzene containing 2 equiv of pyridine. In addition to a 30% yield of **5a**, **6a** and **7** are also produced. The nmr spectrum shows olefinic hydrogens occurring as a two-hydrogen singlet at τ 3.15. Hydrolysis of **5a** with potassium hydroxide in diethylene glycol gave 2,3-diphenylpyrazine. This reaction probably involves the intermediate dihydropyrazine, which is rapidly oxidized in air. An attempt to carry out the hydrolysis at $-20°$ using methyllithium and working up the reaction in an inert atmosphere gave only a small quantity of pyrazine **7** and a red polymer.

Confirmation of the proposed structure was obtained by catalytic hydrogenation (Pd/C). This resulted in



4 5a

the rapid uptake of 1 mol of hydrogen with the formation of 1,4,5,6-tetrahydropyrazine **6a** previously prepared from **4** and acetic anhydride.

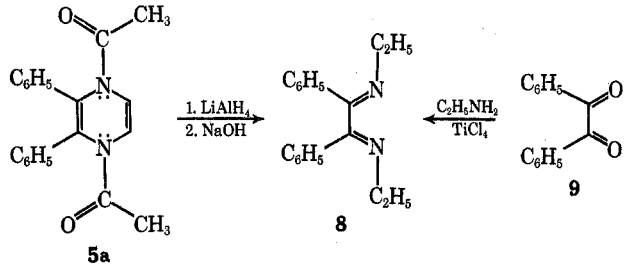


5a 6a 7

Reduction of **5a** with lithium aluminum hydride did not give the expected *N*,*N*′-diethyl derivative. The major product was *N*,*N*′-diethylbenzilimine **8**, in addition to a small amount of pyrazine **7** and benzil which was probably formed by hydrolysis of **8** in the work-up procedure. The structure of **8** was indicated by the

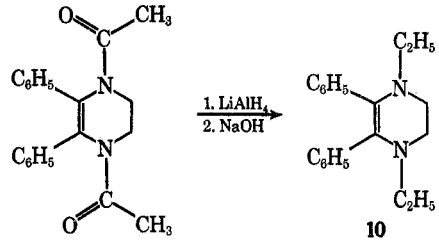
(5) L. A. Paquette in "Nonbenzenoid Aromatics," J. P. Snyder, Ed., Academic Press, New York, N. Y., 1969, p 250.
(6) S.-J. Chen and F. W. Fowler, *J. Org. Chem.*, **35**, 3987 (1970).
(7) A. T. Mason and L. Dryfoos, *J. Chem. Soc.*, **63**, 1293 (1893).
(8) After this work was written up for publication, another report of a 1,4-dihydropyrazine derivative appeared: R. A. Sulzbach and A. F. M. Agbal, *Angew. Chem., Int. Ed. Engl.*, **10**, 127 (1971).

spectral data and chemical analysis. The structure was confirmed by independent synthesis.[9]



5a 8 9

The unusual course of this reduction is probably due to the presence of the completely conjugated π system, since the reduction of partially hydrogenated ring systems (**6a**) occurs normally.

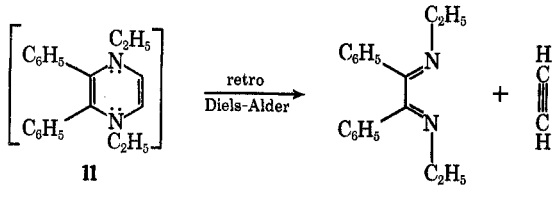


6a 10

It is possible that the *N*,*N*′-diethyl-1,4-dihydropyrazine ring system **11** is being formed in the reaction but is extremely reactive, decomposing to give imine **8**. Instability of **11** would be expected compared to the diacetyl derivative **5**, since the ethyl groups would allow the nonbonding electrons on nitrogen to interact with the π system. Even with azepine the *N*-methyl derivative is extremely reactive and it can only be isolated at low temperatures.

Attempts to carry out the reduction at lower temperature changed the course of the reaction completely. Only 2,3-diphenylpyrazine could be isolated. Also, carrying out the reaction in the more polar tetrahydrofuran gave only 2,3-diphenylpyrazine.

Although imine **8** could be explained as being the product from a retro Diels–Alder reaction of **11**, all attempts to detect acetylene in this reaction have been unsuccessful.



11

Dihydropyrazine **5a** does not undergo thermal cycloadditions with either dimethyl acetylenedicarboxylate or tetracyanoethylene. An attempted photochemical cycloaddition between **5a** and dimethyl acetylene dicarboxylate gave 2,3-diphenylpyrazine as the only isolable product.

In summary, dihydropyrazine **5a**, which has strong electron-withdrawing substituents on the nitrogen, does not appear to possess any significant antiaromatic character.

(9) H. Weingarten, J. P. Chupp, and W. A. White, *J. Org. Chem.*, **32**, 3246 (1967).

Experimental Section[10]

2,3-Diphenyl-1,4-dibenzoyl-1,4,5,6-tetrahydropyrazine (6b).—A mixture of 2.34 g (0.01 mol) of 2,3-diphenyl-5,6-dihydropyrazine (**4**) with 4.52 g (0.02 mol) of benzoic anhydride, in the proportion of 1 mol to 2 was heated over a naked flame under diminished pressure (20–30 mm). The mixture was slowly brought to boiling, and, after being allowed to cool, it was dissolved in hot alcohol and left overnight. A yellow solid was removed by filtration. The solvent was stripped from the filtrate, the residue was dissolved in ether, and the crystals formed were recrystallized from ethanol: mp 192–195°; yield 0.846 g; nmr ($CDCl_3$) τ 2.55–2.75 (m, 20 H), 5.7 (s, 4 H); ir (KBr) 2929, 1660 (C=O), 1470, 1380, 725, and 700 cm^{-1}.

Anal. Calcd for $C_{30}H_{24}N_2O_2$: C, 81.06; H, 5.44; N, 6.30. Found: C, 80.99; H, 5.42.

2,3-Diphenyl-1,4-diacetyl-1,4,5,6-tetrahydropyrazine (6a).—2,3-Diphenyl-5,6-dihydropyrazine (10 g) was heating to boiling under reduced pressure (20–30 mm), and allowed to cool to about 100°; 10 g (0.98 mol) of acetic anhydride was then added, and the mixture was boiled in a reflux apparatus for 15 min. The product was digested on a water bath with 10% sodium hydroxide solution until the excess of anhydride was decomposed. The residue was dissolved in ethanol and the yellow solid was removed by filtration. The solvent was stripped from the filtrate, and the residue was chromatographed on tlc plate (1.5 mm silica gel, eluted with ether). The first band eluted was recrystallized from ethanol, giving 2,3-diphenylpyrazine: nmr ($CDCl_3$) τ 1.41 (s, 2 H), 2.4–2.8 (m, 10 H); mp 113–115° (lit.[11] 112–116°). The second band eluted was recrystallized from ethyl acetate: mp 131–132°; nmr ($CDCl_3$) τ 2.52–2.92 (m, 10 H), 5.9 (s, 4 H), and 8.2 (s, 6 H); ir (KBr) 1660 (C=O), 1385, 1300, 1225 cm^{-1}.

Anal. Calcd for $C_{20}H_{20}N_2O_2$: C, 74.97; H, 6.29; N, 8.74. Found: C, 74.95; H, 6.53; N, 8.72.

2,3-Diphenyl-1,4-diacetyl-1,4-dihydropyrazine (5a).—To a mixture of 3.16 g (0.04 mol) of pyridine and 3.95 g (0.05 mol) of acetyl chloride in refluxing benzene stirred with magnetic stirrer was slowly added over 3 hr 4.68 g (0.02 mol) of 2,3-diphenyl-5,6-dihydropyrazine in 30 ml of chloroform, and the mixture refluxed for 12 hr. The reaction mixture was cooled and washed thoroughly with water. The organic layer was dried with magnesium sulfate, the solvent was stripped off, and the residue was chromatographed on tlc (1.5 mm silica gel, eluted with ether). The first band gave a compound possessing an nmr spectrum identical with that of 2,3-diphenylpyrazine (**7**) from previous work. The second band was crystallized from ethanol and from ethyl acetate and gave **5a**: mp 194–195°; nmr ($CDCl_3$) τ 2.54–2.92 (m, 10 H), 3.12 (s, 2 H), and 8.20 (s, 6 H); ir (KBr) 1680 (C=O), 1624, 1380, 780, and 700 cm^{-1}.

Anal. Calcd for $C_{20}H_{18}N_2O_2$: C, 75.45; H, 5.70; N, 8.80. Found: C, 75.12; H, 5.99; N, 8.56.

The third band gave 2,3-diphenyl-1,4-diacetyl-1,4,5,6-tetrahydropyrazine (**6a**). The relative yield of each compound **4**, **5a**, and **6a** was determined to be 34:32:34 from the nmr spectrum of the crude product. Pure **5a** can more conveniently be prepared by recrystallizing the crude product several times from ethyl acetate–ethanol (7:5).

Hydrogenation of 2,3-Diphenyl-1,4-diacetyl-1,4-dihydropyrazine (5a).—2,3-Diphenyl-1,4-diacetylpyrazine (0.136 mg) was added to a solution with 0.02 g of 10% Pd/C in 20 ml of ethyl acetate. The mixture was subjected to microhydrogenation at room temperature for up to 2 hr. The nmr spectrum showed 90% conversion to 2,3-diphenyl-1,4-diacetyl-1,4,5,6-tetrahydropyrazine (**6a**).

Alkali Hydrolysis of 5a.—2,3-Diphenyl-1,4-diacetylpyrazine (0.318 g) and 0.5 g of potassium hydroxide was added to 11 ml of diethylene glycol and refluxed for 1.5 hr. The reaction mixture was cooled to room temperature, extracted with ether, and washed thoroughly with water. The ethereal solution was evaporated and the residue was crystallized from *n*-pentane, mp 112–116°; nmr ($CDCl_3$) shows this to be pyrazine **7**.

Reduction of 5a.—To 0.3 g of lithium aluminum hydride in 21 ml of anhydrous ether was slowly added 0.478 g (0.0015 mol) of 2,3-diphenyl-1,4-diacetylpyrazine (**5a**) and the mixture was

(10) Melting points are uncorrected. The microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were determined with a Perkin-Elmer Model 137 Infracord. The nmr spectra were determined with a Varian A-60 spectrophotometer.

(11) L. H. Amundsen, *J. Chem. Educ.*, **16**, 567 (1939).

stirred for 1 hr. The reaction mixture was cooled in an ice bath and 3 ml of 20% sodium hydroxide solution was carefully added. Stirring was continued for another hour at room temperature and the white precipitate was removed by filtration. The filtrate was dried with magnesium sulfate and the ether was removed. Chromatography of the residue on a thin layer plate (1.5 mm silica gel eluted with 10% ether in benzene) gave 0.119 g of benzil (yield 37%), nmr ($CDCl_3$) τ 1.9–2.8 (only aromatic hydrogens), mp 94–95° (lit.[12] 94°), and 0.177 g of 2,3-diphenyl-1,4-diethyl-1,4-diaza-1,3-butadiene (**8**): yield 44%; mp 37–39°; nmr ($CDCl_3$) τ 2.1–2.35 and 2.55–2.85 (m, 10 H), 3.61 (q, 4 H), and 8.75 (t, 6 H); ir (KBr) 1630, 1580, 1450, 775, and 700 cm^{-1}. A small amount of 2,3-diphenylpyrazine (0.022 g) is also produced.

1,4-Diethyl-2,3-diphenyl-1,4-diaza-1,3-butadiene (8).—The method of imine synthesis by Weingarten[9] was modified as described below.

Benzil (4.2 g, 0.02 mol) was placed in a 250-ml flask and mixed with a solution of 100 ml of ether containing 15 ml of anhydrous ethylamine at −10°. A solution of 20 ml of pentane containing 3.6 ml of $TiCl_4$ (6.2 g, 0.0326 mol) was then added over 45 min. After all of the $TiCl_4$ was added, the material was allowed to warm up to room temperature over 1 hr, then heated to reflux for 0.5 hr. The solvent was removed and 4.0 g of **8** was obtained (76% yield). The analytical sample was purified by recrystallization from ether: mp 37–39°; nmr ($CDCl_3$) τ 2.1–2.35 and 2.55–2.85 (m, 10 H), 3.61 (q, 4 H), and 8.75 (t, 6 H); ir (KBr) 1630, 1580, 1450, 775, and 700 cm^{-1}.

Anal. Calcd for $C_{18}H_{20}N_2$: C, 81.77; H, 7.63; N, 10.60. Found: C, 81.61; H, 7.77; N, 10.62.

Reduction of 6a.—To 0.3 g of lithium aluminum hydride in 21 ml of anhydrous ether was slowly added 0.48 g (0.0015 mol) of 2,3-diphenyl-1,4-diacetyl-1,4,5,6-tetrahydropyrazine (**6a**) and the mixture was stirred for 1 hr. The reaction mixture was cooled in an ice bath and 3 ml of 20% sodium hydroxide was carefully added. Stirring was continued for another hour at room temperature and the white precipitate was removed by filtration. The filtrate was dried with magnesium sulfate and the ether was removed. The residue was crystallized on standing and recrystallized from ethyl acetate: mp 100–102°; 0.43 g (98% yield); nmr ($CDCl_3$) τ 2.65–3.06 (m, 10 H), 7.03 (s, 4 H), 7.33 (q, 4 H), and 9.0 (t, 6 H); ir (KBr) 2970, 2850, 1590, 1445, 1380, 1128, 755, and 700 cm^{-1}.

Anal. Calcd for $C_{20}H_{24}N_2$: C, 82.14; H, 8.27; N, 9.58. Found: C, 82.28; H, 8.43.

Registry No.—**5a**, 32174-84-8; **6a**, 32174-85-9; **6b**, 32174-86-0; **7**, 1588-89-2; **8**, 32174-88-2; **10**, 32174-89-3.

Acknowledgment.—We are indebted to the Research Foundation of the State University of New York, The Research Corporation, and the National Science Foundation (GP-20099) for financial support of this work.

(12) "Handbook of Chemistry and Physics," 40th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1958–1959, p 844.

Reactions of Phosphorus Compounds. 28. Mechanism of the Formation of 2-Methyl-2*H*-1-benzopyran by the Reaction of 3-(*o*-Formylphenoxy)propylphosphonium Salts in Alcoholic Alkoxide

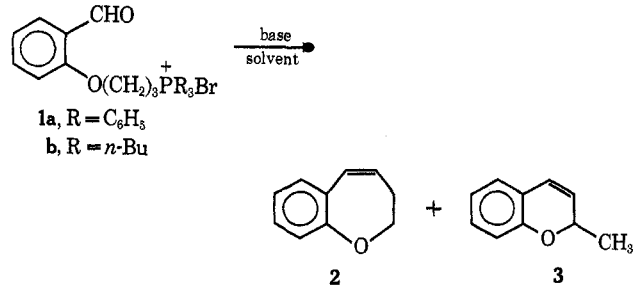
EDWARD E. SCHWEIZER,* TORU MINAMI, AND DALE M. CROUSE

Department of Chemistry, University of Delaware, Newark, Delaware 19711

Received May 4, 1971

A mechanism is proposed for the formation of 2-methyl-2*H*-1-benzopyran (**3**) by the reaction of 3-(*o*-formylphenoxy)propylphosphonium salts (**1**) in alcoholic alkoxide. 2,3-Dihydro-1-benzoxepin-4-tri-*n*-butylphosphonium bromide (**17b**) and 2-methyl-2*H*,1-benzopyran-3-triphenylphosphonium bromide (**15a**) were prepared using catalytic amounts of base in alcoholic solvent and their reactions were observed. The reaction of *o*-vinyloxybenzaldehyde (**10**) with methylene triphenylphosphorane (**11**) yielded 1-phenyl-2-(*o*-vinyloxyphenyl)ethyldiphenylphosphine oxide (**13**).

In a previous paper[1] we have discussed and discarded a number of possible mechanisms for the unexpected formation of 2-methyl-2*H*-1-benzopyran (**3**) from 3-(*o*-formylphenoxy)propyltriphenylphosphonium bromide (**1a**) under normal Wittig[2] reaction conditions. An alternate mechanism (Scheme I) has recently been proposed.[3] It is supported by (a) the data[1] which indicate that the rearrangement of **1** to **3** is favored in more highly protonic solvents, *i.e.*, inhibiting decomposition of betaine **5** to the expected benzdihydrooxepin (**2**) by protonation of **5** to **6**; (b) the β elimination (**6** → **7**) which would also be favored by a more electrophilic phosphonium species, *i.e.*, **1a** *vs.* **1b** (see Table I).



(1) E. E. Schweizer, C. J. Berninger, D. M. Crouse, R. A. Davis, and R. S. Logothetis, *J. Org. Chem.*, **34**, 207 (1969); E. E. Schweizer and R. Schepers, *Tetrahedron Lett.*, 979 (1963).

(2) A. Maercker, *Org. Reactions*, **14**, 272 (1965).

(3) Proposed by Professor H. T. Bestmann at the Chemical Societies International Symposium on Ylides, Leicester, England, July 14, 1970. Although Professor Bestmann did not really believe that this would be the right mechanism, we felt compelled to find supporting evidence or disprove it.

TABLE I

SOLVENT AND PHOSPHORUS SUBSTITUENT EFFECTS ON RATIOS OF 2 AND 3 FROM SALTS 1[a]

R in salt 1	Solvent	Overall yield of 2 + 3, %	Ratio of 2:3
Ph	DMF	70	100:0
n-Bu	DMF	43	48:52
Ph	MeOH	65	0:100
Ph	MeOH[b]	88	0:100
n-Bu	MeOH[c]	0	
n-Bu	MeOH[b,c]	0	
n-Bu	MeOH–DMF 20:80	10	1:99
n-Bu	MeOH–DMF 10:90	31	4:96
n-Bu	DMF[d]	50	78:22

[a] At 64° for 24 hr under N_2 with 1.0 equiv of NaOMe except as noted. [b] As in *a* except 4.44 equiv of NaOMe. [c] Only starting salt 1 and **17b** recovered on work-up after HBr neutralization. [d] Base used is NaH.