Anal. Calcd for $C_{16}H_{23}NO_3$: C, 69.28; H, 8.36; N, 5.05. Found: C, 69.60; H, 8.46; N, 4.94.

Acknowledgment. We wish to extend our appreciation to Dr. J. P. Li for his active interest and helpful discussions.

Registry No.—**1,** 52455-66-0; **2,** 52455-67-1; **2** HCl, 52455-68-2; **3,** 52455-69-3; **4,** 52455-70-6; **4** HCl, 52539-61-4; **5,** 52455-71-7; **6,** 52455-72-8; **6** HCl, 52455-73-9; **7,** 52455-74-0; **11,** 52455-75-1; **11** HCl, 52455-76-2; **12,** 52455-77-3; **13,** 52539-62-5; **14,** 52455-78-4; **15,** 52539-63-6; **16,** 52455-79-5; **17,** 52455-80-8; **18,** 52455-81-9; **18** HCl, 52455-82-0; **19,** 52455-83-1; 3,4,5-trimethoxybenzaldehyde, 86-81-7; *p*-bromobenzaldehyde, 1122-91-4; benzaldehyde, 100-52-7; bicyclo[2.2.2]octanone, 2716-23-6; 3-quinuclidinone, 3731-38-2.

Supplementary Material. A listing of atomic coordinates will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-74-3511.

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(6) (a) Ultraviolet spectral data was also found to be of little use in configurational assignments of the 2-benzal derivatives of 1-tetralone and 1-indanone; see ref 5. (b) In ref 3 the configurational assignments of the isomers of 6′-methoxy-7-oxo-8-rubrene (the condensation product of 6-methoxyquinoline-4-carboxaldehyde and 3-quinuclidinone) were based on the presence of a 362-nm absorption band (one of several maxima) in one isomer and the absence of any absorption maxima above 337 nm in the other isomer. The latter was assigned the configuration where the quinoline moiety was cis to the carbonyl and the uv results were attributed to steric inhibition of resonance due to steric interaction when the two groups are coplanar. The configuration of the isomer where the quinoline moiety and the quinuclidine nitrogen are cis was substantiated by the use of this isomer as a ligand in the preparation of transition metal dichloride complexes of cobalt: D. L. Coffen and T. E. McEntree, *J. Org. Chem.*, **35,** 503 (1970). The results of our work invalidate the above argument of severe steric interaction when the aromatic group and the carbonyl are cis.
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(8) The magnitude of the change in the chemical shift has been observed to be highly dependent on the orientation of the substrate protons to the lanthanide–substituent complex, pseudocontact shift being the main contribution to the observed values. The dependency of the pseudocontact shifts[7] upon R^{-3} (R is the Eu–hydrogen distance in the complex) and 3 $\cos^2\phi - 1$ (ϕ is the hydrogen–Eu–substituent angel) has been used in assigning configuration where pseudocontact shift = $K(3\cos^2\phi - 1)R^{-3}$. See J. R. Campbell, *Aldrichim. Acta*, **4,** 55 (1971), and R. von Ammon and R. D. Fischer, *Angew. Chem., Int. Ed. Engl.*, **11,** 675 (1972).
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Reaction of Carbodiimide with Aldehyde

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Reactions of carbodiimide with aromatic aldehyde gave rise to the formation of isocyanate and Schiff base *via* 1,2 cycloaddition. In the reaction of diphenylcarbodiimide with aliphatic aldehyde, no isocyanate and Schiff base were obtained but 4-anilino-3-alkylquinoline (**7a–c**), 2,4-dianilino-3-alkylquinoline (**8a,b**), and 1,3-diphenyl-2,4-diphenylimino-5-alkylpyrimidine (**11**) were formed. The formation mechanisms of these products were discussed.

Studies on the reaction of aldehydes with heterocumulenes such as isocyanates,[1] *N*-sulfinylamines,[2] sulfurdiimides,[3] and ketenes[4] have been reported. These reactions can be generalized as [2 + 2] cycloadditions to the carbonyl group of aldehydes, followed by decomposition into olefins.

$$RN{=}X{=}Y + R'CHO \longrightarrow RN{=}CHR' + Y{=}X{=}O$$

a, X = C; Y = O b, X = S; Y = O c, X = S; Y = NR

$$R_2C{=}C{=}O + R'CHO \longrightarrow R_2C{=}CHR' + CO_2$$

These reactions are mainly limited to aromatic aldehydes except for the reaction with ketene[4] and sulfonylisocyanate.[5] We now report some reactions of carbodiimides with various aldehydes and the dependence of the reaction products on substituents in the aldehydes.

Results and Discussion

Aromatic Aldehydes. The reaction of dipenylcarbodiimide (**1a**) with benzaldehyde (**2a**) at 200° gave phenyl isocyanate (**3a**) and benzylideneaniline (**4a**) in 16 and 33% yields. The reaction using dicyclohexyl- (**1b**) and dibutylcarbodiimide (**1c**) in place of **1a** similarly afforded corresponding isocyanates, **3b,c,** and imines, **4c,d,** respectively (Table I). The formation of these compounds may be explained by analogy with the reaction of other heterocumulenes with aldehydes.

Table I
The Reaction of Carbodiimide with Aromatic Aldehyde[a]

$$RN{=}C{=}NR + ArCHO \longrightarrow RN{=}C{=}O + RN{=}CHAr$$
1 2 3 4

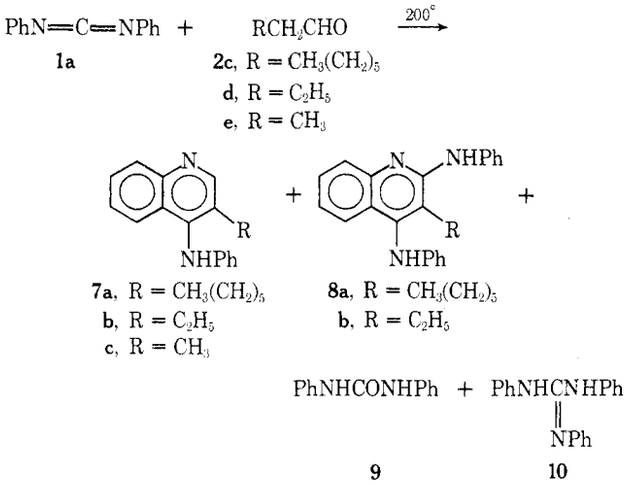
R	Ar	Time	Yields, %[b] 3	4
C_6H_5 (**1a**)	C_6H_5 (**2a**)	6	16	33
C_6H_5	4-Cl-C_6H_4 (**2b**)	5	19	40
cyclo-C_6H_{11} (**1b**)	C_6H_5	7	18	42
n-C_4H_9 (**1c**)	C_6H_5	7	9	20

[a] Reaction temperature 200°. [b] Based on aldehyde.

The significant difference in yields between isocyanates **3** and imines **4** suggests that **3** formed initially reacts further with aldehydes to give **4.** This is also supported by the

fact that the intensity of the absorption at 2275 cm^{-1} due to the N=C=O group increased over a period of several hours and then decreased gradually in the course of the reaction.

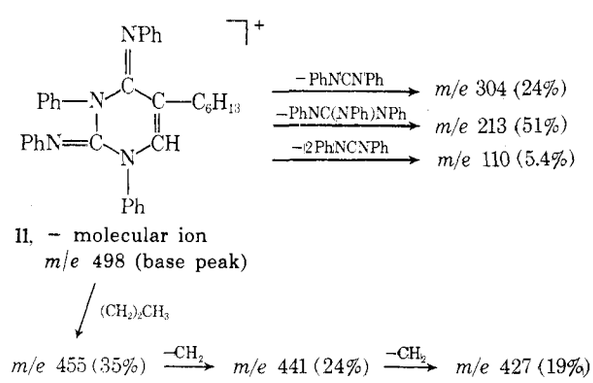
Aliphatic Aldehyde. The reaction of diphenylcarbodiimide (**1a**) with aliphatic aldehyde did not lead to isocyanates and imines. Quinoline and pyrimidine derivatives were isolated as main products. The reaction of **1a** with *n*-butyraldehyde (**2d**) at 200° for 5 hr gave 4-anilino-3-ethylquinoline (**7b**), 2,4-dianilino-3-ethylquinoline (**8b**), and *N,N'*-diphenylurea (**9**) in 30, 10, and 14% yields, respectively.



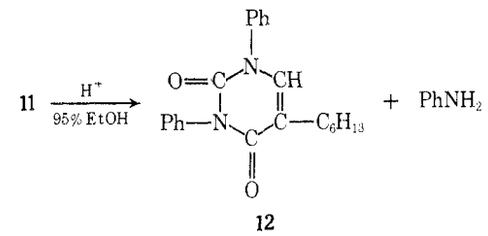
The structure of **7b** was confirmed by comparison with a sample prepared by an independent method.[6]

The structural assignment of **8b** was based on its elemental analysis and spectral data. The mass spectrum exhibits the molecular ion at *m/e* 339 and nmr the spectrum is very similar to that of **7b** except for disappearance of the C-2 proton at δ 8.75 and appearance of the six protons, which correspond to the phenyl protons (5 H) and anilino NH (D_2O exchangeable) in the aromatic region. Hence the structure of **8b** was identified as 2,4-dianilino-3-ethylquinoline.

With *n*-octanal (**2c**) the reaction only with excess **1a** was different; 1,3-diphenyl-2,4-diphenylimino-5-*n*-hexylpyrimidine (**11**) was obtained in 29% yield along with **7a** (38%), **9** (10%), and **10** (34%). The product **11** contains two strong absorption bands at 1610 and 1640 cm^{-1} due to the C=N bond in the ir spectrum and two multiplets at δ 0.70–1.40 (13 H, methyl and methylene protons) and δ 5.95–7.15 (21 H, phenyl and olefinic protons) in the nmr spectrum. The mass spectrum exhibits a molecular ion peak at *m/e* 498 (base peak), *m/e* 213 ($C_{14}H_{17}N$, 51%), and other peaks as shown below.



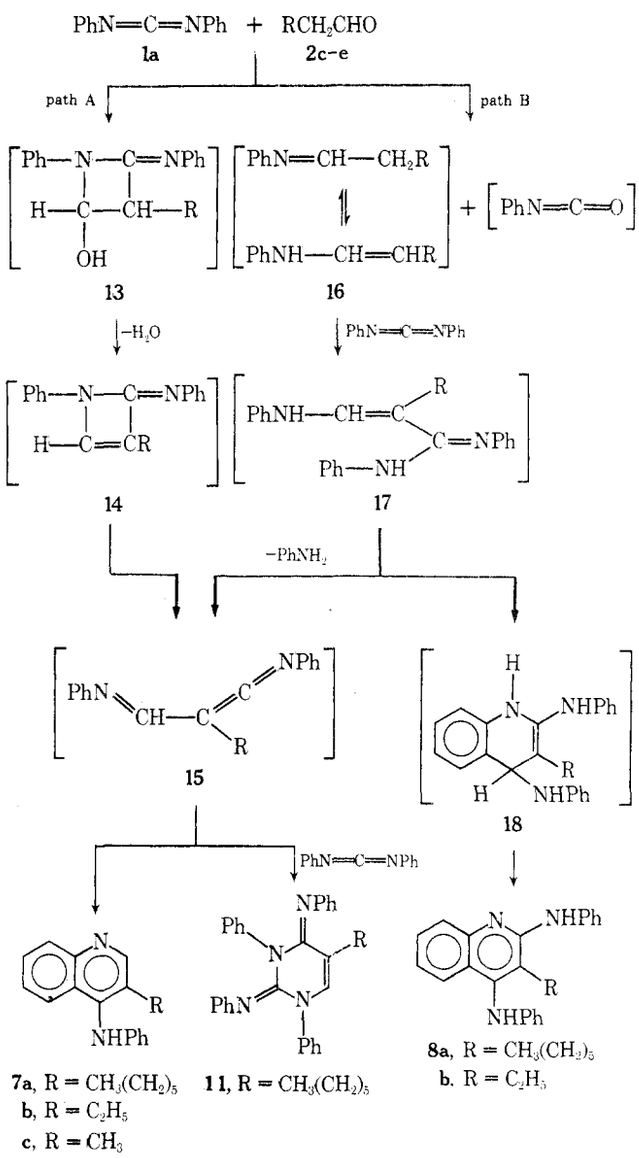
Thus, these spectral data are consistent with structure **11**. Furthermore, the structure was confirmed by the following chemical properties. Acidic hydrolysis of **11** in aqueous ethanol led to 1,3-diphenyl-5-*n*-hexyluracil (**12**): nmr ($CDCl_3$) δ 0.65–2.50 (13 H, m, methyl and methylene), 7.0 (1 H, s, vinylic[7]), 7.05–7.50 (10 H, m, aromatic); ir 1715 and 1665 cm^{-1} (C=O).



The yields of the reaction products from carbodiimide and aliphatic aldehydes are summarized in Table II.

Two pathways (path A and B) for the formation of these products are conceivable. As shown in Scheme I, path A

Scheme I



can be accounted for by addition of **1a** to RCH_2CHO, dehydration, ring opening to the iminoketenimine derivative **15**, followed by intramolecular cycloaddition to give **7** and/or 1,4-cycloaddition of **15** across the C=N double bond of a second molecule of **1a** to afford **11**. A similar mechanism

Table II
Reaction of Diphenylcarbodiimide with Aliphatic Aldehyde

No.	R	Molar ratio of carbodiimide to aldehyde	Yields, % 7[a]	8[b]	9[a]	10[a]	11[b]
1	n-C_6H_{13}	1:1	25	28	2	52	
2	n-C_6H_{13}	2:1	38		10	34	29
3[c]	C_2H_5	1:1	30	10	14		
4[c]	C_2H_5	2:1	24	12	96		
5[c,d]	CH_3	1:1	34		6		

[a] Based on aldehyde. [b] Based on carbodiimide. [c] Reacted in a sealed tube. [d] Aniline was isolated in 18% yield.

for formation of a quinoline derivative has been reported in the reaction of phenyl isocyanate with ynamines.[8]

In path B, [2 + 2] cycloaddition of **1a** to carbonyl group and subsequent ring scission of the cycloadduct would similarly take place to give isocyanates and imines **16**. The resulting imines **16**, which are in equilibrium with enamines, would further react with **1a** to yield **17**, followed by the formation of iminoketenimine with elimination of aniline, which reacts with **1a** and generated phenyl isocyanate to yield triphenylguanidine (**10**) and diphenylurea (**9**), leading to **7** and/or **11** and intramolecular cyclization to **18** and subsequent oxidation to the 2,4-dianilinoquinoline derivative **8**. Since the formation of aniline and **8** is difficult to explain by path A, path B seems preferable. Furthermore, the above observation is in agreement with the fact that the 4-anilinoquinoline derivative and aniline were obtained from **1a** and acetophenone anil under similar condition.[9]

Experimental Section

General. All melting points were determined on a Yanagimoto micro melting apparatus and are uncorrected. The ir spectra were recorded on a Jasco IR-E spectrometer. The nmr spectra were obtained on a JEOL JNM-3H-60 and JEOL JNM-PFT-100 spectrometers with TMS as an internal standard. The mass spectra were taken with a Hitachi RMU-6E spectrometer.

Materials. Diphenylcarbodiimide[10] and di-n-butylcarbodiimide[11] were prepared according to the established procedures.

Reaction of Carbodiimide 1 with Aromatic Aldehyde 2. All reactions of carbodiimides **1a–c** with aromatic aldehydes **2a,b** listed in Table I were carried out by the same procedure. Hence, the reaction of diphenylcarbodiimide (**1a**) with benzaldehyde (**2a**) will be described in detail as only one example of them.

A mixture of **1a** (4.90 g, 0.025 mol) and **2a** (2.70 g, 0.025 mol) was heated at 200° for 6 hr without solvent under nitrogen atmosphere and then distilled. The first fraction, bp 82–90° (29 Torr), containing phenyl isocyanate (**3a**) and unreacted **2a** was refluxed for 5 hr in absolute methanol (30 ml). After removal of excess methanol, the residue was distilled to give **2a** (1.6 g, 59%, bp 84–86° (32 Torr)) and O-methyl-N-phenylurethane (0.60 g, 16%, obtained from the residue after distillation). The second fraction, bp 120–153° (1.0 Torr), containing **4a** and unreacted **1a**, was heated with 99% ethanol (50 ml) in the presence of CH_3ONa (0.1 g) for 8 hr. After ethanol was evaporated, the residue was washed with benzene. After the benzene insoluble product, N,N'-diphenylurea, was filtered off, the filtrate gave benzylidineaniline (**4a**, 1.50 g, 38%), which was recrystallized from ethanol to afford pure **4a**, mp 51–51.5° (lit.[12] 52°).

Reaction of Diphenylcarbodiimide (1a) with n-Butyraldehyde (2d). A mixture of **1a** (6.40 g, 0.033 mol) and **2d** (2.16 g, 0.03 mol) was heated at 200° for 5 hr in a sealed tube without solvent. After cooling, the reaction mixture was dissolved in benzene (20 ml) and chromatographed on neutral alumina using benzene and benzene–ethanol (98:2) as eluent. The first fraction afforded 2,4-dianilino-3-ethylquinoline (**8b**, 0.50 g, 10%) which was recrystallized from benzene–hexane to give a pure sample: mp 177.5–178°; ir (Nujol) 3365, 1593, 1570, 1535 cm^{-1}; nmr ($CDCl_3$) δ 1.15 (t, 3, J = 7.2 Hz, CH_3), 2.68 (q, 2, J = 7.2 Hz, CH_2), 5.55 (s, 1, NH, D_2O exchangeable), 6.5–7.9 (m, 15, aromatic protons and anilino NH on C-2, one D_2O exchangeable); mass spectrum (70 eV) 339 (M^+), 324, 310, 219, 156, 128.

Anal. Calcd for $C_{23}H_{21}N_3$: C, 81.38; H, 6.24; N, 12.38. Found: C, 81.82; H, 6.21; N, 12.18.

The second fraction afforded 4-anilino-3-ethylquinoline (**7b**, 2.20 g, 30%), which was recrystallized from benzene: mp 177–178°; ir (Nujol) 3140, 1610, 1595, 1560, 1515 cm^{-1}; uv_{max} (95% ethanol) 249 (ϵ 39,500), 290 nm (ϵ 8100); nmr ($CDCl_3$) δ 1.23 (t, 3, J = 7.25 Hz, CH_3), 2.73 (q, 2, J = 7.2 Hz, CH_2), 6.02 (s, 1, NH, D_2O exchangeable), 6.6–8.15 (m, 9, aromatic protons), 8.75 (s, 1, proton on C-2;[13] mass spectrum (70 eV) m/e 248 (M^+), 233, 219, 271, 156, 128.

Anal. Calcd for $C_{17}H_{16}N_2$: C, 82.22; H, 6.50; N, 11.28. Found: C, 82.48; H, 6.44; N, 11.43.

The third fraction afforded **9** (0.90 g, 14%); mp 234.5–235° (lit.[15] 234–235°).

The reaction using **1a** in double the molar quantity of **2d** gave **8b**, **7b**, and **9** in 12, 24, and 96% yields, respectively.

Reaction of Diphenylcarbodiimide (1a) with n-Octylaldehyde (2c). The reaction was carried out as described above using **1a** (7.80 g, 0.04 mol) and **2c** 95.10 g, 0.04 mol). After similar treatment, 2,4-dianilino-3-n-hexylquinoline (**8a**), 4-anilino-3-n-hexylquinoline (**7a**), **9**, and **10** were obtained in 2.20 g (28%), 3.00 g (25%), 0.09 g (2%) and 3.00 g (52%) yields, respectively.

8a had mp 128–129°; ir (KBr) 3365, 2940, 1593, 1570, 1500 cm^{-1}; nmr (CCl_4) δ 0.5–2.7 (m, 13, n-C_6H_{13}), 5.49 (s, 1, NH), 6.4–7.8 (m, 15, aromatic protons and one NH).

Anal. Calcd for $C_{27}H_{29}N_3$: C, 81.98; H, 7.39; N, 10.62. Found: C, 82.17; H, 7.50; N, 10.42.

7a had mp 140.5–141°; ir (KBr) 3160, 2940, 1598, 1563, 1520 cm^{-1}; nmr ($CDCl_3$) δ 0.6–2.7 (m, 13, n-C_6H_{13}), 6.13 (s, 1, NH), 6.6–7.75 (m, 9, aromatic protons), 8.78 (s, 1, proton on C-2).

Anal. Calcd for $C_{21}H_{24}N_2$: C, 82.82; H, 7.95; N, 9.20. Found: C, 83.02; H, 7.68; N, 9.20.

The reaction using **1a** in double the molar quantity of **2c** gave 1,3-diphenyl-2,4-diphenylimino-5-n-hexylpyrimidine (**11**) in 29% yield along with **7a** (38%), **9** (10%), and **10** (34%).

11 had mp 105–106°; ir (KBr) 2940, 1640 (C=N), 1610 (C=N) cm^{-1}; nmr (CCl_4) δ 0.8–1.6 (m, 13, n-C_6H_{13}), 5.95–7.1 (m, 21, aromatic protons and a proton on C-6); mass spectrum (70 eV) m/e 498 (M^+), 455, 441, 427, 413, 304, 213, 110.

Anal. Calcd for $C_{34}H_{34}N_4$: C, 81.89; H, 6.87; N, 11.24. Found: C, 82.02; H, 6.86; N, 11.19.

Acid Catalyzed Hydrolysis of 11. A solution of **11** (1.0 g, 0.002 mol) in ethanol was refluxed for 10 hr in the presence of concentrated hydrochloric acid (0.5 ml). After removal of solvent, the residue was extracted with benzene, washing with water, and dried over sodium sulfate. The benzene layer gave 1,3-diphenyl-5-n-hexyluracil (**12**) in 0.75 g (100%) yield: mp 116–117°; ir (Nujol) 1713 (C=O), 1665 (C=O) cm^{-1}; nmr (CCl_4) δ 0.75–2.5 (m, 13, n-C_6H_{13}), 7.00 (s, 1, vinylic proton), 7.05–7.65 (m, 11, aromatic protons); mass spectrum (70 eV) m/e 348 (M^+), 229, 202, 146, 119.

Anal. Calcd for $C_{22}H_{24}O_2N_2$: C, 75.83; H, 6.94; N, 8.04. Found: C, 75.57; H, 6.96; N, 7.64.

Reaction of Diphenylcarbodiimide (1a) with Propionaldehyde (2e). The reaction was carried out as described above using **1a** (5.80 g, 0.03 mol) and **2e** (1.80 g, 0.03 mol). After similar treatment, **9**, aniline, and 4-anilino-3-methylquinoline (**7c**) were obtained in 0.35 g (6%), 0.65 g (18%), and 2.40 g (34%) yields.

7c had mp 204–205°; ir (Nujol) 3136, 1610, 1560, 1545, 1513 cm^{-1}; uv_{max} (95% ethanol) 251 nm (ϵ 33,000), 291 (ϵ 8500); nmr ($CDCl_3$) δ 2.28 (s, 3, CH_3), 6.15 (s, 1, NH, D_2O exchangeable), 6.6–8.15 (m, 9, aromatic protons), 8.68 (s, 1, proton on C-2); mass spectrum (70 eV) m/e 234 (M^+), 219, 157, 128.

Anal. Calcd for $C_{16}H_{14}N_2$: C, 82.02; H, 6.02; N, 11.96. Found: C, 82.27; H, 6.24; N, 11.90.

Preparation of 2-Anilino- and 4-Anilinoquinolines. These quinoline derivatives were prepared from quinoline 1-oxide, aniline, and p-toluenesulfonyl chloride according to the method of Hamana and coworker.[6] After a solution of quinoline 1-oxide (1.40 g, 0.0097 mol), p-toluenesulfonyl chloride (1.90 g, 0.01 mol), and aniline (1.80 g, 0.019 mol) in chloroform (50 ml) was allowed stand at room temperature for 24 hr, chloroform was removed *in vacuo* and to the resulting residue was added excess aqueous sodium carbonate, followed by extracting with ether. The ether extract was washed with aqueous 10% HCl solution and the aqueous portion was neutralized with sodium carbonate, followed by extraction with ether. After removal of ether, the residue was chromatographed on alumina to give 0.88 g (40%) of 2-anilinoquinoline (mp 98° (lit.[6] 98°); nmr (DMSO-d_6) δ 6.0–8.0 (m, aromatic protons and

NH proton)) and 0.26 g (12%) of 4-anilinoquinoline (mp 196–197° (lit.[6] 196–197°); nmr (DMSO-d_6) δ 6.9–8.2 (m, 11, aromatic protons and one NH proton), 9.4 (s, 1, a proton on C-2)).

Preparation of Authentic 4-Anilino-3-ethylquinoline. The reaction was carried out as described above using 3-ethylquinoline 1-oxide (1.70 g, 0.0098 mol), *p*-toluenesulfonyl chloride (1.90 g, 0.01 mol), and aniline (1.80 g, 0.019 mol). After similar treatment, 4-anilino-3-ethyl-qinoline, which was consistent with **7b** obtained above, was isolated in 0.56 g (23%) yield.

Acknowledgment. We wish to thank Dr. K. Matsushita, JEOL Co., for C-13 FT nmr spectrum analysis.

Registry No.—**1a**, 622-16-2; **1b**, 538-75-0; **1c**, 693-64-1; **2a**, 100-52-7; **2b**, 104-88-1; **2c**, 124-13-0; **2d**, 123-72-8; **2e**, 123-38-6; **4a**, 538-51-2; **7a**, 52699-00-0; **7b**, 52699-01-1; **7c**, 52669-02-2; **8a**, 52699-03-3; **8b**, 52699-04-4; **9**, 102-07-8; **11**, 52669-05-5; **12**, 52699-06-6; 2-anilinoquinoline, 5468-85-9; 4-anilinoquinoline, 30696-07-2.

Supplementary Material Available. Table III will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche 105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N. W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-74-3516.

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(7) The nmr spectrum of 1,3-dimethyluracil shows the peaks for the proton at the C-5 position at δ 5.75 and for the proton at the C-6 position at δ 7.20: N. S. Bhacca, D. P. Hollis, L. F. Johnson, and E. A. Pier, "NMR Spectra Catalog," Copyright Varian Associates, Lithographed in the U.S., The National Press, 1963, Spectrum No. 460.
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(13) The site of the anilino group was determined as being at the 4 position since the rather low field signal of **7b** at δ 8.75 was assigned to the 2-position proton, by comparison with the nmr spectra of 4- and 2-anilinoquinolines,[6] in which the signal at δ 9.40 assignable to the proton at the 2 position was observed in the former and no signal below δ 8.00 was present in the latter. Furthermore, in the carbon-13 FT nmr spectrum (Table III[14]), Overhauser enhancement was not observed at C-4 and C-3 carbons, suggesting that **7b** contains substituents at C-4 and C-3.
(14) See paragraph at end of paper regarding supplementary material.
(15) R. A. Franz, F. Applegath, F. V. Morriss, F. Baiocchi, and C. Bolze, *J. Org. Chem.*, **26**, 3311 (1961).

Syntheses and Some Properties of 4-Acyl-1-methylthiabenzene 1-Oxides

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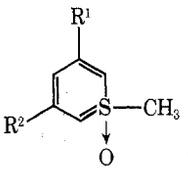
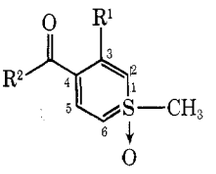
A series of 4-acyl-1-methylthiabenzene 1-oxides are prepared by the reaction of 3-ethoxymethylene-2,4-pentanedione, ethyl 2-(ethoxymethylene)acetoacetate, diethyl ethoxymethylenemalonate, and 2-acetyl-3-methoxy-2-cyclohexen-1-one with dimethyloxosulfonium methylide. Spectral (ir, uv, and nmr) and chemical (deuterium exchange, bromination, and nitration) studies suggest that the 1-oxides are represented by cyclic ylidic structures, in which a negative charge is located on the C-2, C-4, and C-6, and the carbonyl oxygen atom, but both the carbanionic and betaine-like characters are considerably lowered.

1-Methylthiabenzene 1-oxides (**1**), characterized as heterocycles with six π electrons in the ring, were first prepared in 1965 from acetylenic ketones and dimethyloxosulfonium methylide[1] and later by utilization of acetylenic esters.[2] More recently, it has been shown that some β-diketones[3] or β-ethoxyvinyl ketones[4] can also be used in place of acetylenic compounds. Hortmann and Harris[1] have suggested cyclic ylid structures for 3,5-disubstituted thiabenzene 1-oxides (**1**) on the basis of the nmr (^{1}H and ^{13}C) spectral and chemical (deuterium exchange) investigations. Essentially the same conclusion has been reached by Kishida and Ide, who have investigated 6-benzoyl-3-hydroxyl-1-methyl-5-phenylthiabenzene 1-oxide and its derivatives by nmr spectroscopy and deuterium exchange studies[2] as well as X-ray analysis.[5] These results are in fundamental contrast to those of thiabenzenes which have been believed to have aromatic character.[6]

In connection with our interest in the chemistry of the ylides stabilized by α,β-unsaturated carbonyl groups,[7] we have synthesized a series of 4-acyl-1-methylthiabenzene 1-oxides (**2**).[8] These compounds have been found to have interesting spectral and chemical properties which provide further information on the electronic nature of the thiabenzene 1-oxide nucleus.



1



2

Syntheses

4-Acyl-1-methylthiabenzene 1-oxides (**6** and **7**) were synthesized by reaction of 3-ethoxymethylene-2,4-pentanedione (**3**) and ethyl 2-(ethoxymethylene)acetoacetate (**4**) with 2 *M* equiv of dimethyloxosulfonium methylide (**5**) in dimethyl sulfoxide at room temperature in 33 and 12% yields, respectively. This method could be successfully applied to the synthesis of thiabenzene 1-oxide **12** by the use of 2 *M* equiv of dimethyloxosulfonium carbethoxymethylide (**10**) in place of **5**.

If equimolar quantities of **5** and **3** were used, the thiabenzene 1-oxide **6** was not formed, but instead, methyl 2,3-dihydro-3-ethoxy-5-methyl-4-furyl ketone (**8**) and methyl 2-methyl-3-furyl ketone (**9**) were obtained in variable yields. The longer reaction time increased the yield of