(B) 3,5-dibromo-4-acetaminobenzil (71), and 4-acetaminobenzil (15), (C) 4-acetaminobenzil (83).

4,5-Di(*p*-methoxyphenyl)-2-imidazolone gave the following per cent yields: (A) 3,3′-dibromo-4,4′-dimethoxybenzil (73), (B) 3,3′-dibromo-4,4′-dimethoxybenzil (61), and 4,4′-dimethoxybenzil (22), (C) 4,4′-dimethoxybenzil (93).

4-*p*-Methoxyphenyl-5-phenyl-2-imidazolone gave the following per cent yields: (A) 3,4′-dibromo-4-methoxybenzil (70), (B) 3-bromo-4-methoxybenzil (97), mp 112–113° (*Anal.* Calcd for $C_{15}H_{11}BrO_3$: C, 56.5; H, 3.45. Found: C, 56.3; H, 3.31), (C) 4-methoxybenzil (92).

4-*p*-Sulphonamido-5-phenyl-2-imidazolone gave the following per cent yields: (A) 4-bromo-4′-sulphonamidobenzil (60), (B) 4-sulphonamidobenzil (76), (C) 4-sulphonanidobenzil (78).

4-*p*-Bromophenyl-5-phenyl-2-imidazolone gave the following per cent yields: (A) 4,4′-dibromobenzil (71), (B) 4-bromobenzil (97), (C) 4-bromobenzil (76).

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The Synthesis of *o*-Di-*t*-butyl Heteroaromatic Compounds

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Thiodipivalic acid diethyl ester (II) is converted into 3,3,6,6-tetramethyl-1-thiacycloheptan-4-on-5-ol (III) by means of an acyloin condensation. Oxidation yielded 3,3,6,6-tetramethyl-1-thiacycloheptane-4,5-dione (IV). Condensation of hydroxy ketone III and diketone IV with suitable reagents yielded an oxazole (V), an imidazole (VI), and a quinoxaline (VII). Desulfurization of these compounds gave, respectively, 4,5-di-*t*-butyloxazole (VIII), 4,5-di-*t*-butylimidazole (IX), 2,3-di-*t*-butyl-5,6,7,8-tetrahydroquinoxaline (X), and 2,3-di-*t*-butylquinoxaline (XI). The ultraviolet spectrum of the latter is compared with other 2,3-disubstituted quinoxalines.

The interest in strained *o*-di-*t*-butyl aromatics has led to several methods for the synthesis of *o*-di-*t*-butylbenzenes. Hübel[1] and co-workers have successfully cyclized *t*-butylacetylene compounds with cobalt carbonyl catalysts to *o*-di-*t*-butylbenzenes. Arnett[2] and co-workers synthesized *o*-di-*t*-butylbenzenes in a similar fashion. A purely organic route to *o*-di-*t*-butylbenzenes was reported by Barclay[3] and co-workers and by Burgstahler[4] and co-workers. Both groups used a cyclic alkylation of benzene with 2,2,5,5-tetramethyltetrahydro-3-furanone as starting point in their synthesis.

The interesting chemistry of *o*-di-*t*-butylbenzenes[5] has had few extensions in the field of heteroaromatics thus far. In our laboratory Wynberg and Wiersum[6] synthesized the first heteroaromatic *o*-di-*t*-butyl compound by direct alkylation of 2,5-di-*t*-butylfuran with *t*-butyl chloride to 2,3,5-tri-*t*-butylfuran. Later Ramasseul and Rassat[7] used the same method for the synthesis of 2,3,5-tri-*t*-butylpyrrole. Since these syntheses are of limited scope we have developed a new method (Chart I) which appears to be general for the preparation of *o*-di-*t*-butyl aromatics.[8]

Discussion of Results

Chloropivalic acid[9] was readily transformed to thiodipivalic acid[10] (I) by treatment with sodium sulfide. The ease of nucleophilic displacement of this hindered chloro acid is probably due to anchimeric assistance by the carboxylate ion. Esterification of the acid I, followed by an acyloin condensation of the ester using sodium in xylene gave the hydroxy ketone (III), mp 82–83°, in 75% yield from the ester.[11]

Oxidation of the hydroxy ketone to diketone IV must be carried out with a reagent which does not oxidize the sulfur atom and rupture of the ring must be avoided. Lead tetraacetate in pyridine[12] as solvent appeared to be the most suitable oxidizing agent for this purpose. The diketone IV is formed in 80% yield as a slightly yellow liquid, bp 68°, (0.35 mm), $n^{20}D$ 1.4658. The nmr spectrum shows singlets at τ 8.75 and 7.43 assigned to methyl and methylene protons.

The cyclic diketone IV is the principal starting material in this synthetic scheme though the hydroxy ketone III and the monoketone XIV are also very suitable starting materials for a variety of ring-closure reactions. The normal chemical behavior of these compounds is in marked contrast to that of bipivaloyl or pivaloin which fail to undergo any of the condensation reactions to form cyclic systems.[13,14]

Chart II shows the preparation of a variety of monosubstituted products of diketone IV, some of which are suitable for further ring-closure reactions. It is noteworthy that no disubstituted derivatives of the ketone IV were ever isolated even though cyclic compounds are formed with ease and in good yield.

The condensation reactions carried out with the diketone IV and with the hydroxy ketone III are all well-known reactions. The quinoxaline VII, mp 97–98°, is formed in 70% yield by condensation of diketone IV with *o*-phenylenediamine in boiling acetic acid. Its nmr and infrared spectra are in accord with

(1) U. Krüerke, C. Hoogzand, and W. Hübel, *Chem. Ber.*, **94**, 2817 (1961); C. Hoogzand and W. Hübel, *Tetrahedron Letters*, 637 (1961).

(2) E. M. Arnett, M. E. Strem, and R. A. Friedel, *ibid.*, 658 (1961); E. M. Arnett and J. M. Bollinger, *ibid.*, 3803 (1964).

(3) L. R. C. Barclay, C. E. Milligan, and N. D. Hall, *Can. J. Chem.*, **40**, 1664 (1962).

(4) A. W. Burgstahler and M. O. Abdel-Rahman, *J. Am. Chem. Soc.*, **85**, 173 (1963).

(5) See for interesting reviews E. E. van Tamelen, *Angew. Chem.*, **77**, 759 (1965); H. G. Viehe, *ibid.*, **77**, 768 (1965).

(6) H. Wynberg and U. E. Wiersum, *Chem. Commun.*, **1** (1965).

(7) R. Ramasseul and H. Rassat, *ibid.*, 453 (1965).

(8) H. Wynberg and Ae. de Groot, *ibid.*, 171 (1965).

(9) M. S. Kharash and H. C. Brown, *J. Am. Chem. Soc.*, **62**, 925 (1940).

(10) We wish to express our gratitude to Tennessee-Eastman Co. for supplying us with a generous sample of the acid.

(11) The acyloin condensation of thiodipivalic acid diethyl ester appears to be the first one reported for a sulfide diester. No detectable desulfurization occurred during the reaction though the reaction conditions are rather severe. The steric hindrance to desulfurization is advantageous at this stage.

(12) R. E. Partch, *Tetrahedron Letters*, 3071 (1964).

(13) H. Bredereck and G. Theilig, *Chem. Ber.*, **86**, 88 (1953); M. S. Newman and G. R. Kahle, *J. Org. Chem.*, **23**, 666 (1958); unpublished work in this laboratory.

(14) N. J. Leonard and P. M. Mader, *J. Am. Chem. Soc.*, **72**, 5388 (1950).

CHART I

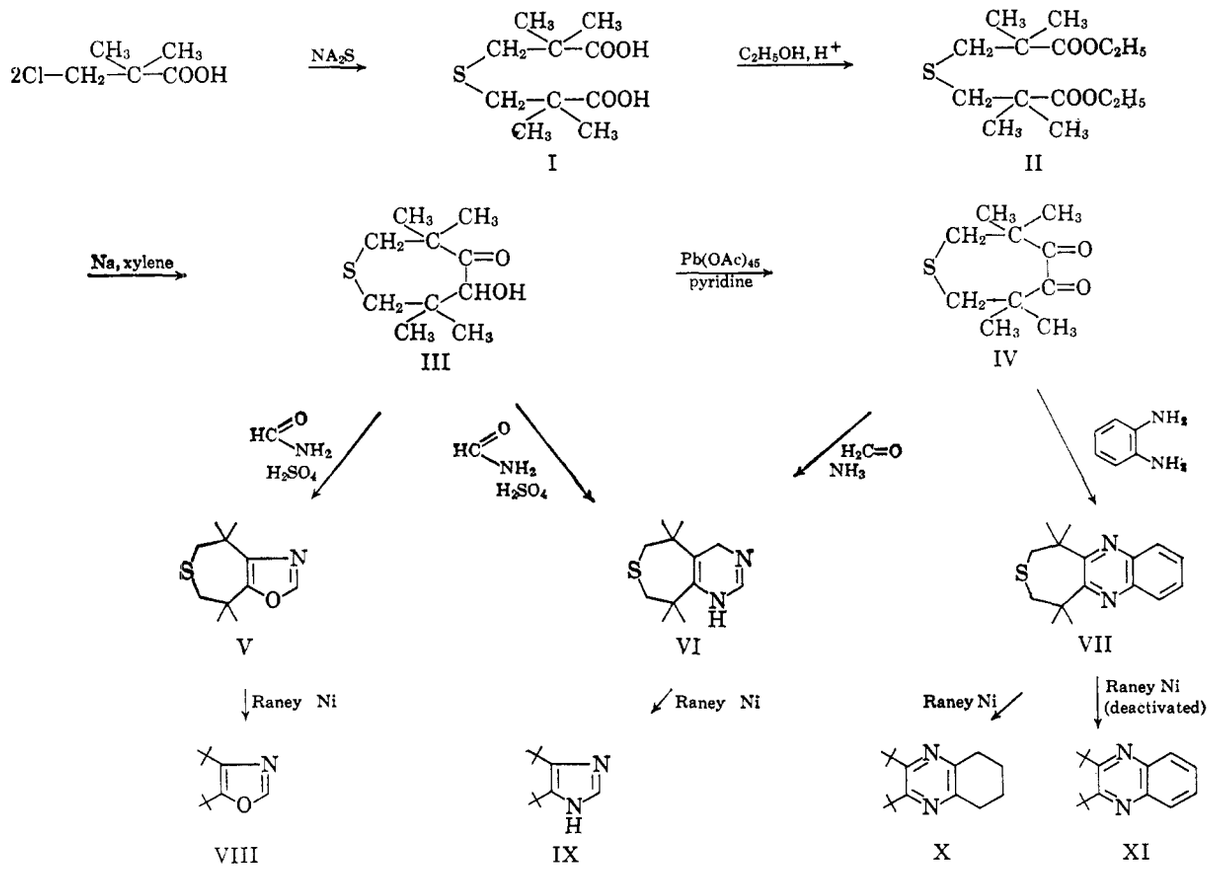
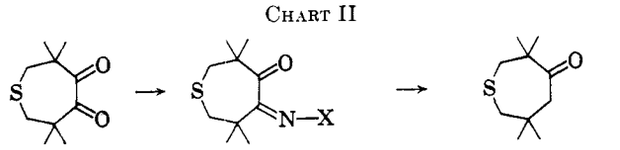


CHART II



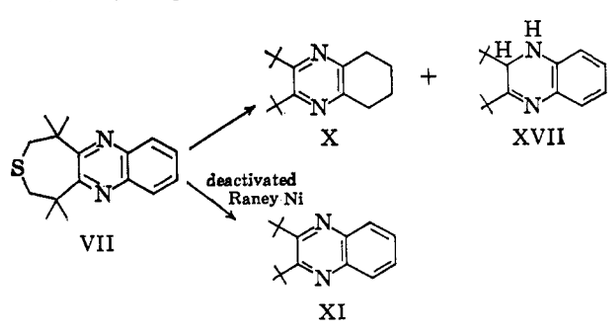
IV XII, X = OH
XIII, X = NH_2
XV, X = $NHSO_2C_6H_4CH_3$ (p)
XVI, X = $NHCONH_2$

XIV (from XIII)

the structure assigned and the ultraviolet spectrum (Figure 1) shows the same characteristics as those published by Leonard and Mader[14] who condensed carbocyclic analogs of diketone IV with o-phenylenediamine.

The condensation of diketone IV with ammonia and formaldehyde proceeded in 76% yield to give the imidazole VI, mp 207–208°. The condensation of hydroxy ketone III with formamide and sulfuric acid is carried out as described by Bredereck and Gompper.[15] When the reaction temperature is 150°, the oxazole V, mp 64.5–66°, is the principal reaction product and only a trace of imidazole is formed. At higher temperatures the imidazole VI is formed as the principal product.

The desulfurization reaction was first tried with the imidazole VI because imidazoles are very stable toward reduction. Raney nickel W7 in boiling dioxane appeared to give the best results and 4,5-di-t-butylimidazole (IX) was isolated in 35% yield as a stable microcrystalline solid, mp 149–151°. The nmr spectrum showed three singlets at τ 0.42, 2.90, and 8.55 assigned to the N–H, aromatic and t-butyl protons, respectively (area ratio aromatic:t-butyl protons 1:18). Desulfurization of the oxazole V gave the 4,5-di-t-butyloxazole (VIII) which could be isolated as its picrate, mp 150–151°. The nmr spectrum of this picrate showed singlets at τ 8.58, 8.55, 1.78, 0.88, and 0.30 assigned to the t-butyl and aromatic protons of the oxazole ring and to the aromatic and hydroxy protons of the picric acid, respectively. The ultraviolet spectrum showed a maximum at λ 214 mμ (ϵ 2.3 × 10^4). The desulfurization of the quinoxaline VII caused some difficulty. The nmr spectrum of the product showed that several reduction products were present and after some experiments two of these products were isolated, each in 35% yield, namely the 5,6,7,8-tetrahydroquinoxaline X and the 1,2-dihydroquinoxaline XVII.



The nmr spectrum of 2,3-di-t-butyl-5,6,7,8-tetrahydroquinoxaline (X), mp 79–80°, showed a singlet at τ 8.55 and two multiplets at 7.22 and 8.12, assigned to the t-butyl and α- and β-methylene protons, respectively (area ratio 18:4:4). The ultraviolet spectrum had maxima at λ 219 mμ (ϵ 9150) and 283 mμ (ϵ 9570) and a shoulder at λ 300 mμ (ϵ 2500).

(15) H. Bredereck and R. Gompper, *Chem. Ber.*, **87**, 726 (1954).

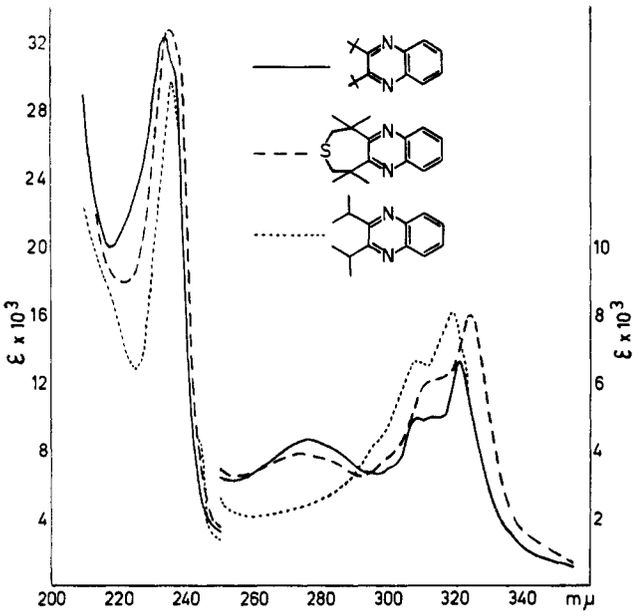


Figure 1.

The nmr spectrum of 2,3-di-*t*-butyl-1,2-dihydroquinoxaline (XVII), mp 110–114°, showed two singlets at τ 9.17 and 8.68 of two nonequivalent *t*-butyl groups, two doublets at 6.06 and 4.35 of the protons at the 2 and 1 positions, and a multiplet at 3.3 of the aromatic protons at the 5, 6, 7, and 8 position, (area ratio 9:9:1:1:4, respectively). The infrared spectrum showed a strong N–H absorption at 3400 cm^{-1} and the ultraviolet spectrum had maxima at λ 213 mμ (ϵ 16,000), 234 (23,400), 270 (4000), and 355, (3500).

It is reasonable to assume that the steric hindrance exhibited by the *t*-butyl groups is the reason for the formation of these unusual reduction products. Quinoxaline itself can be selectively reduced to 1,2,3,4-tetrahydroquinoxaline by treatment with Raney nickel under a hydrogen pressure of 80 psi[16] at 30°. A 1,2-dihydroquinoxaline is very easily reduced further to a 1,2,3,4-tetrahydroquinoxaline.

We have not isolated any 1,2,3,4-tetrahydro-, hexahydro-, or octahydroquinoxalines. Nmr spectra of the crude reaction products show no signals which could be assigned to one of these higher reduction products.

Aromatization of the 5,6,7,8-tetrahydroquinoxaline X to 2,3-di-*t*-butylquinoxaline XI using sulfur or Pd on carbon was unsuccessful because the high reaction temperatures caused loss of one of the *t*-butyl groups. The formation of 2-*t*-butylquinoxaline was confirmed by synthesis of this compound by means of a condensation between *t*-butylglyoxal and *o*-phenylenediamine.

Using *deactivated* Raney nickel, 2,3-di-*t*-butylquinoxaline (VI), mp 53–54°, was prepared in 50% yield by desulfurization of VII. The nmr spectrum showed a singlet at τ 8.40 and a multiplet at 2.40 of the *t*-butyl and aromatic protons, respectively (area ratio 18:4). The ultraviolet spectrum is shown in Figure 1 along with the spectra of 2,3-diisopropylquinoxaline and the sulfur-containing quinoxaline VII. These ultraviolet spectra show the normal characteristics of this class of compounds. Three bands can be distinguished and, in accordance with current assignment, indicated as ^1L_b (±315 mμ), ^1L_a (275 mμ), and ^1B_b (235 mμ) bands.[17]

An interesting feature of the spectra of 2,3-di-*t*-butylquinoxaline and quinoxaline VII is the high intensity of the 275-mμ band. Although this band can be noticed as a shoulder in the spectra of the other quinoxalines, it is clear that the intensity is much lower in the latter cases. Presumably the bulky substituents introduce strain which in turn causes a decrease in the symmetry of the pyrazine ring, sufficient to make the transition more intense. Remarkably the presence of the *o*-*t*-butyl groups seems to cause an increase in the fine structure of the ^1L_b band rather than a decrease as was noted with *o*-di-*t*-butyl benzene.[18]

A characteristic feature of the nmr spectra of this crowded compound should be mentioned too.

In the nmr spectra of crowded benzenes all *ortho* groups experience downfield shifts amounting to about 0.18 ppm for *o*-*t*-butyl groups when compared with the monosubstituted compounds and somewhat less for *o*-methyl groups. In our case the proton signal of the *t*-butyl groups is located at τ 8.40 for 2,3-di-*t*-butylquinoxaline and at 8.50 for 2-*t*-butylquinoxaline; so a slight downfield shift of 0.10 ppm could be noticed. Gibbons and Gil[19] attribute this downfield shift to the effect of intramolecular van der Waals forces and not to puckering of the ring. Ring puckering should produce shifts to higher fields of the protons attached to the ring. This is opposite to what is observed for *o*-di-*t*-butylbenzene. According to these authors the strain is relieved predominantly by changes in the angle between the ring and the substituent.

Experimental Section

Melting points were take in open capillaries in an electrically heated silicon oil bath. Melting points and boiling points are uncorrected. Infrared spectra were determined in carbon tetrachloride, in potassium bromide plates or neat on a Perkin-Elmer Infracord Model 137 or on a Unicam SP 200 instrument. Ultraviolet spectra were recorded in 95% ethanol on a Zeiss PMQ II spectrophotometer. Nuclear magnetic resonance spectra were taken on a Varian A-60 spectrometer with tetramethylsilane as internal standard and are reported in τ values. The solvents used are indicated. Microanalyses were performed by the analytical department of our laboratory under the supervision of Mr. W. M. Hazenberg.

Thiodipivalic Acid (I).—Chloropivalic acid (136 g, 1 mole), bp 110–116° (5 mm), prepared by the method of Kharash and Brown,[9] was neutralized with 53 g (0.5 mole) of sodium carbonate in 100 ml of water. This solution was added to a solution of 240 g (1 mole) of sodium sulfide hydrate ($Na_2S \cdot 9H_2O$) in 100 ml of water over 30 min and stirred for 24 hr at room temperature. After filtration, the solution was acidified with 50% sulfuric acid. The precipitated acid was stirred for 15 min with cooling and filtered. The moist acid was recrystallized from acetic acid to give 57 g acid (50% yield), mp 163–164°.

Thiodipivalic Acid Diethyl Ester (II).—The ester was prepared as described by Greene and Hagemeyer,[20] yield 90%, bp 122–124° (0.7 mm), $n^{20}D$ 1.4600.

3,3,6,6-Tetramethyl-1-thiacycloheptan-4-on-5-ol (III).—Sodium (46 g, 2 g-atoms) was dispersed in 1 l. of boiling xylene with a vibrator. A solution of 145 g (0.5 mole) of thiodipivalic acid diethyl ester (II) in 100 ml of xylene was added over about 2 hr. The solution was refluxed for 3 hr and after cooling was acidified with 50% sulfuric acid. The organic layer was separated,

(16) W. Christie, W. Rohde, and H. P. Schultz, *J. Org. Chem.*, **21**, 243 (1956).

(17) H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p 305.

(18) Y. Dale, *Chem. Ber.*, **94**, 2021 (1961).

(19) W. A. Gibbons and V. M. S. Gil, *Mol. Phys.*, **9**, 163 (1965).

(20) J. L. Greene and H. J. Hagemeyer, *J. Am. Chem. Soc.*, **77**, 3016 (1955).

washed with water and sodium bicarbonate solution, and dried over potassium carbonate, and the solvent was evaporated. The residue was poured into 100 ml of acetic acid and the hydroxy ketone crystallized on cooling to give 76 g (yield 75%), mp 80–82°. An analytical pure sample was obtained by recrystallization from acetic acid, mp 82–83°.

Anal. Calcd for $C_{10}H_{18}O_2S$: C, 59.41; H, 8.91; S, 15.84. Found: C, 59.16; H, 8.87; S, 15.75.

The nmr spectrum (in carbon tetrachloride) showed singlets at τ 9.22, 8.88, and 8.73 (methyl protons), a singlet and a quartet at 7.37 and centered on 7.43 (methylene protons), and singlets at 6.65 and 5.93 (hydroxyl and hydroxymethylene protons); area ratios 3:6:3:2:2:1:1, respectively. The infrared spectrum showed carbonyl and hydroxyl absorptions at 1700 and 3450 cm^{-1}.

Acetate of III.—A mixture of 20 g (0.1 mole) of hydroxy ketone III, 11 ml of acetic acid, 11 ml of acetic anhydride, and 1 ml of concentrated sulfuric acid was heated for 15 min at 75°. The mixture was poured on 200 g of crushed ice and the precipitated acetate was recrystallized from ethanol to give 18 g (yield 75%), mp 127–128°.

Anal. Calcd for $C_{12}H_{20}O_3S$: C, 59.02; H, 8.20; S, 13.11. Found: C, 58.91; H, 8.25; S, 12.73.

The nmr spectrum (in carbon tetrachloride) showed singlets at τ 9.08, 8.92, 8.83, and 8.80 (methyl protons), a singlet at 7.93 (acetate methyl protons), a singlet and a quartet at 7.33 and centered on 7.43 (methylene protons), and a singlet at 5.00 (hydroxy methylene proton). The infrared spectrum indicated carbonyl absorptions at 1710 and 1740 cm^{-1}.

3,3,6,6-Tetramethyl-1-thiacycloheptane-4,5-dione (IV).—Hydroxy ketone III (50 g, 0.25 mole) was dissolved in 1 l. of pyridine. To this solution 133 g (0.3 mole) of lead tetraacetate[21] was added and the dark brown mixture was stirred for 36 hr. Then water (200 ml) was added and the solution was acidified with concentrated hydrochloric acid. The pyridine–hydrochloric acid salt was removed by filtration and washed with ether. The solution was thoroughly extracted with ether. The combined ether extracts were washed with a little water and with sodium bicarbonate solution and dried over anhydrous potassium carbonate, and the solvent was evaporated. The residue, distilled *in vacuo*, yielded 40 g of diketone (yield 80%), bp 68° (0.35 mm), $n^{20}D$ 1.4954. Upon standing the diketone solidified.

Anal. Calcd for $C_{10}H_{16}O_2S$: C, 60.00; H, 8.00; S, 16.00. Found: C, 60.11; H, 8.00; S, 15.88.

The ultraviolet spectrum showed λ_{max} 219 mμ (ϵ 665), 300 (53), and λ 333 (42).

3,3,6,6-Tetramethyl-1-thiacycloheptane-4,5-dione, Monooxime XII.—Diketone IV (5 g, 0.025 mole) and 9 g of hydroxylamine hydrochloride were dissolved in a mixture of 75 ml of water and 125 ml of ethanol. A solution of 11.5 g of potassium hydroxide in 50 ml of water was added; the mixture was refluxed for 2 hr. After cooling, the mixture was acidified and cooled further with Dry Ice. The precipitated oxime was filtered and recrystallized from carbon tetrachloride to give 3.8 g (70% yield), mp 124–125°.

Anal. Calcd for $C_{10}H_{17}NO_2S$: C, 55.81; H, 7.92; N, 6.52; S, 14.88. Found: C, 55.54; H, 7.99; N, 6.55; S, 14.94.

The nmr spectrum (in deuteriochloroform) showed two singlets at τ 8.75 and 8.70 (methyl protons) and two singlets at 7.47 and 7.42 (methylene protons).

3,3,6,6-Tetramethyl-1-thiacycloheptane-4,5-dione. Monohydrazone XIII.—Diketone IV (8 g, 0.04 mole), 14 g of hydrazine (98%), and a few drops of acetic acid were dissolved in a mixture of 25 ml of ethanol and 50 ml of benzene. The mixture was refluxed through a 5-in. Vigreux column topped by a Dean–Stark water trap until no more aqueous layer collected. Water was added and the benzene layer was separated and evaporated. The residue was recrystallized from methanol, yield 80%, mp 45.5–48°.

Anal. Calcd for $C_{13}H_{18}N_2OS$: C, 56.12; H, 8.48; S, 14.98. Found: C, 55.88; H, 8.41; S, 14.87.

3,3,6,6-Tetramethyl-1-thiacycloheptanone-4 (XIV).—Hydrazone XIII (5 g) was dissolved in 125 ml of dry xylene and 1.4 g of potassium *t*-butylate was added. The mixture was refluxed for 4 hr and poured on 100 g of crushed ice. The organic layer was separated and dried over anhydrous magnesium sulfate, and the solvent was removed. The residue was crystallized from petroleum ether (bp 40–60°) to give 2.2 g (yield 50%), mp 47.5–49°.

Anal. Calcd for $C_{10}H_{18}OS$: C, 64.6; H, 9.68; S, 17.20. Found: C, 64.6; H, 9.82; S, 17.00.

The nmr spectrum (in carbon tetrachloride) indicated singlets at τ 8.97 and 8.90 (methyl protons) and singlets at 7.63, 7.53, and 7.38 (methylene protons).

A Wolff–Kishner reduction of the hydrazone XIII with potassium hydroxide in triethylene glycol at 200° also gave the monoketone XIV in 75% yield.

Mono-*p*-toluenesulfonylhydrazone XV.—Diketone IV (4 g, 0.02 mole) and 3.8 g (0.02 mole) of *p*-tosylhydrazine were dissolved in a mixture of 25 ml of ethanol and 50 ml of benzene. The mixture was refluxed through a 5-in. Vigreux column topped by a Dean–Stark water trap until no more aqueous layer collected. Water was added to the reaction mixture and the benzene layer were separated and distilled until the volume was about 10 ml. Petroleum ether (bp 40–60°) was added to precipitate the hydrazone to give 5.5 g (yield 74%). An analytically pure sample was obtained by recrystallization from carbon tetrachloride, mp 150–151°.

Anal. Calcd for $C_{17}H_{24}N_2O_3S_2$: C, 55.45; H, 6.53; N, 7.62; S, 17.38. Found: C, 55.30; H, 6.55; N, 7.86; S, 17.31.

The nmr spectrum (in deuterioacetone) showed singlets at τ 8.87 and 8.70 (methyl protons), at 7.55 (aromatic methyl protons), singlets at 7.43 and 7.37 (methylene protons), a quartet centered on 2.35 (aromatic protons), and a singlet at 1.13 (N–H proton).

Monosemicarbazone XVI.—Diketone IV (4 g, 0.02 mole) and 2.4 g of semicarbazide hydrochloride were dissolved in 40 ml of acetic acid. The mixture was refluxed for 1.5 hr and poured on crushed ice. The precipitate was filtered and washed with water, yield 80%. An analytically pure sample was obtained by crystallization from acetic acid, mp 234–235°.

Anal. Calcd for $C_{11}H_{19}N_3O_2S$: C, 51.3; H, 7.44; S, 11.99. Found: C, 51.3; H, 7.5; S, 11.93.

4,4,8,8-Tetramethyl-4,5,7,8-tetrahydro-6-thiacycloheptoxazole (V).—A mixture of 10 g (0.05 mole) of hydroxy ketone III, 40 g of formamide, and 12 g of concentrated sulfuric acid was heated for 6 hr on an oil bath (bath temperature 160–180°).

The mixture was poured on ice and the acidic water layer was extracted with ether. The ether layer was dried over magnesium sulfate and concentrated to a volume of 30 ml. Gaseous hydrochloric acid was led into the solution and a precipitate of the oxazole hydrochloric acid salt soon formed (2.4 g). This salt was filtered and dried and mixed thoroughly with 4 g of anhydrous potassium carbonate. Sublimation of this mixture *in vacuo* gave the free oxazole V, yield 1.7 g, mp 64.5–66° (the yield is 40% based on converted hydroxy ketone). Further evaporation of the ether layer yielded 6 g of unchanged hydroxy ketone.

When the water layer was made basic and again extracted with ether, 0.6 g of imidazole VI was obtained after drying and evaporation of the ether.

An analytically pure sample of the oxazole V was obtained by sublimation.

Anal. Calcd for $C_{11}H_{17}NOS$: C, 62.6; H, 8.06; N, 6.64; S, 15.17. Found: C, 62.4; H, 8.07; N, 6.68; S, 15.13.

The nmr spectrum (in deuteriochloroform) showed singlets at τ 8.63 (methyl protons), 7.30 (methylene protons), and 2.13 (aromatic proton). The ultraviolet spectrum indicated λ_{max} 220 mμ (ϵ 5100).

4,4,8,8-Tetramethyl-4,5,7,8-tetrahydro-6-thiacycloheptimidazole (VI).—A mixture of 5 g (0.025 mole) of diketone IV, 0.65 g of hexamethylenetetramine, 15 g of ammonium acetate, and 100 ml of acetic acid was refluxed for 1 hr and poured into 300 ml of water. The water solution was saturated with ammonia and extracted thoroughly with ether. The ether layer was dried over potassium hydroxide pellets and the solvent was evaporated. The residue could be crystallized from carbon tetrachloride, chloroform, or pyridine to give 4 g (yield 76%), mp 207–208°.

Anal. Calcd for $C_{11}H_{18}N_2S$: C, 62.86; H, 8.57; N, 13.33; S, 15.24. Found: C, 62.94; H, 8.74; N, 13.27; S, 15.79.

The nmr spectrum (in deuteriochloroform) indicated singlets at τ 8.59 (methyl protons), 7.28 (methylene protons), and at 2.70 (aromatic proton). The infrared spectrum showed absorptions at 3200, 1560, and 1500 cm^{-1}.

6,6,10,10-Tetramethyl-6,7,9,10-tetrahydro-8-thiacyclohepta[*b*]quinoxaline (VII).—A mixture of 10 g (0.05 mole) of diketone IV and 9 g of *o*-phenylenediamine in 25 ml of acetic acid was refluxed for 3 hr. The mixture was poured on ice and the precipitated quinoxaline was recrystallized from 96% ethanol to give 10.2 g (yield 75%), mp 97–98°.

(21) J. C. Bailar, *Inorg. Syn.*, **1**, 47 (1939).

Anal. Calcd for $C_{16}H_{20}N_2S$: C, 70.59; H, 7.35; N, 10.29; S, 11.77. Found: C, 70.47; H, 7.44; N, 10.06; S, 11.69.

The nmr spectrum (in carbon tetrachloride) showed singlets at τ 8.40 (methyl protons), 7.13 (methylene protons), and a multiplet centered on 2.28 (aromatic protons). The infrared spectrum showed absorptions at 3100, 1550, and 1570 cm^{-1}.

4,5-Di-*t*-butylimidazole (IX).—The Raney nickel necessary for the desulfurization reaction was prepared by dissolving 50% nickel–aluminium alloy in concentrated sodium hydroxide solution at 50°.[22] After all the alloy had been added, stirring was continued for 45 min and the Raney nickel was washed four times with distilled water and three times with dioxane. To this still basic Raney nickel (60 g) in 200 ml of dioxane was added 4 g of the sulfur-containing imidazole VI. The mixture was stirred by a vibrator and refluxed for 7 hr. The warm solution was filtered and the Raney nickel was refluxed twice with 200 ml of dioxane to remove all the absorbed imidazole. The combined dioxane filtrates were concentrated in a rotatory evaporator and the residue recrystallized from carbon tetrachloride to give 1.2 g (yield 35%), mp 150–151°.

Anal. Calcd for $C_{11}H_{20}N_2$: C, 73.33; H, 11.11; N, 15.56. Found: C, 72.99; H, 11.28; N, 15.54.

The nmr spectrum (in carbon tetrachloride at 70°) gave singlets at τ 8.55 (*t*-butyl protons), 2.90 (aromatic proton), and 0.42 (N–H proton).

4,5-Di-*t*-butyloxazole (VIII, Picrate).—The desulfurization reaction was carried out as described for the imidiazole VI. The residue from the dioxane filtrates was dissolved in 50% ethanol and picric acid in 50% ethanol was added. Crystals of the picrate were collected, mp 150–151°.

Anal. Calcd for $C_{17}H_{22}N_4O_8$: C, 49.80; H, 5.41; N, 13.67. Found: C, 49.80; H, 5.47; N, 13.65.

For spectral data see the Discussion of Results.

2,3-Di-*t*-butyl-5,6,7,8-tetrahydroquinoxaline (X) and 2,3-Di-*t*-butyl-1,2-dihydroquinoxaline (XVII).—The desulfurization reaction of quinoxaline VII was carried out as described for the imidazole VI. The residue obtained by concentration of the dioxane filtrates was dissolved in hot methanol. Upon cooling bright, white needles began to crystallize and after filtration and recrystallization from methanol analytically pure 2,3-di-*t*-butyl-5,6,7,8-tetrahydroquinoxaline (X) was obtained, yield 25%, mp 79–80°.

Anal. Calcd for $C_{16}H_{26}N_2$: C, 78.11; H, 10.65; N, 11.39. Found: C, 78.34; H, 10.65; N, 11.11.

The methanol filtrates were concentrated and the residue was dissolved in petroleum ether (bp 40–60°). Upon cooling 2,3-di-*t*-butyl-1,2-dihydroquinoxaline (XVII) crystallized as a microcrystalline compound, yield 25%, mp 110–116°.

Anal. Calcd for $C_{16}H_{24}N_2$: C, 78.75; H, 9.91. Found: C, 79.07; H, 9.96.

Concentration of the petroleum ether filtrates yielded a residue consisting of a mixture of the two compounds X and XVII. These compounds were separated by chromatography over basic aluminium oxide. Each compound was thus obtained in 35% yield. For spectral data see the Discussion of Results.

2,3-Di-*t*-butylquinoxaline (XI).—The Raney nickel obtained after the four washings with water was refluxed for 0.5 hr with 200 ml of acetone and the acetone was replaced by 200 ml of dioxane, the sulfur-containing quinoxaline VII was added, and the desulfurization reaction was carried out further as described for the imidazole VI. The residue obtained by concentration of the dioxane filtrates was dissolved in petroleum ether (bp 40–60°) and chromatographed over basic aluminium oxide. Elution with petroleum ether (bp 40–60°) gave the desired quinoxaline, yield 50%, mp 53–54°.

Anal. Calcd for $C_{16}H_{22}N_2$: C, 79.34; H, 9.09; N, 11.57. Found: C, 79.43; H, 9.05; N, 11.50.

For spectral data see the Discussion of Results.

The syntheses of 2,3-diisopropylquinoxaline, 2,3-dimethylquinoxaline, and 2-mono-*t*-butylquinoxaline were carried out as described for quinoxaline VII by condensing the appropriate α-diketones with *o*-phenylendiamine in acetic acid. The nmr spectrum of 2,3-diisopropylquinoxaline (in carbon tetrachloride) showed a doublet centered on τ 8.63, heptet centered on 6.53 (isopropyl protons), and a multiplet centered on 2.25 (aromatic protons).

The nmr spectrum of 2-*t*-butylquinoxaline (in carbon tetrachloride) indicated a singlet at τ 8.50 (*t*-butyl protons), a multiplet centered on 2.13 (5,6,7,8-aromatic protons) and 1.15 (3-aromatic proton). Ultraviolet spectra are shown in Figure 1.

The ultraviolet spectra of 2,3-dimethylquinoxaline [λ_{max} 237, mμ (ϵ_{max} 25.7 × 10^3), 316 mμ (ϵ_{max} 7.1 × 10^3)], and of 2-*t*-butylquinoxaline [λ_{max} 235 mμ (ϵ_{max} 30.2 × 10^3), 307 (5.8 × 10^3), 317 (6.6 × 10^3)] show the normal characteristics for these compounds.

(22) See also H. R. Billica and H. Adkins, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 176.

Reaction of the Cyclooctatetraenyl Dianion with Methyl Iodide[1]

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The reaction of the cyclooctatetraenyl dianion with methyl iodide gives, as initial products, 7,8-dimethyl-1,3,5-cyclooctatriene (**3**) and 5,8-dimethyl-1,3,6-cyclooctatriene (**2**). These products are thermally sensitive, the first dimerizing *via* its valence tautomer, 7,8-dimethylbicyclo[4.2.0]octa-2,4-diene (**4**), and the second undergoing 1,5-hydrogen shift to 3,8-dimethyl-1,3,5-cyclooctatriene (**5**) which equilibrates with its valence tautomer, 3,8-dimethylbicyclo[4.2.0]octa-2,4-diene (**6**), which decomposes to toluene at still higher temperature. The structures were initially inferred from the products of ozonolysis and pyrolysis of Diels–Alder adducts of the original product mixtures. The 7,8-dimethyl-1,3,5-cyclooctatriene (**3**) was never isolated in a pure state because of its ease of polymerization, but each of the other products was isolated and its structure confirmed by spectral analysis.

The chemistry of the cyclooctatetraenyl dianion has received considerable attention ever since the initial report that cyclooctatetraene in ether will dissolve 2 g-atoms of lithium metal.[3] In accord with Hückel's hypothesis predicting that a planar monocyclic conjugated system containing $4n + 2$ electrons (n = 2, here) will have resonance stabilization, Katz and coworkers have shown that cyclooctatetraenyl dianion is a planar, highly resonance stabilized species.[4,5] The high electron density and negative charge of the dianion suggest that it should be a highly basic, nucleophilic species and accordingly it has been shown to react with a number of substrates, including proton sources,[3,6]

(1) Presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., 1965, p 63S.

(2) From the dissertation of David A. Bak, submitted in partial fulfillment of the requirements for the Ph.D. degree, Kansas State University, 1966.

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