N,N-Diethyl-β-alanine Hydrochloride (Vb).—To Ib (5.0 mmoles), hydrogen chloride dissolved in dry ether was added gradually with swirling. A violently exothermic reaction occurred and the white precipitates of Vb appeared. The solvent and trimethylchlorosilane formed were removed and dried at reduced pressure. This reaction proceeded quantitatively. The recrystallization was performed with dry ethanol. N,N-Dialkyl-β-alanine hydrochlorides from Ia,c–f were obtained in the same manner as Ib. Melting points and analytical data were shown in Table I.

Hydrolysis of the Trimethylsilyl Ester of N,N-Diethyl-β-alanine (Ib).—Four millimoles of water was added to Ib (4.0 mmoles). The reaction was slightly exothermic and a white precipitate was formed. The product, the zwitterion of N,N-diethyl-β-alanine (IV), was washed with dry ether and dried under reduced pressure. Yield was 82%, mp 75.5–76.0° (lit.[19] mp 74–75°), $\nu_{C=O}$ 1601 and 1395 cm^{-1}. *Anal.* Calcd for $C_7H_{15}NO_2$: H, 10.58; N, 9.73. Found: H, 10.96; N, 9.52.

The Reaction of Ib and β-Propiolactone.—β-Propiolactone (2.7 mmoles) was added dropwise to Ib (3.3 mmoles) at 70°. The reaction was completely finished in a few minutes. The infrared spectrum of this reaction mixture showed strong and broad absorptions at 1740, 1610, and 1395 cm^{-1}.

Trimethylsilyl Ester of Mono(N,N-diethylamido)succinic Acid (VII).—Succinic anhydride (10 mmoles) was added to the same amounts of trimethylsilyldiethylamine. An exothermic reaction was occurred, characteristic infrared absorptions ascribed to succinic anhydride vanished, and two strong absorptions of carbonyl stretching frequencies at 1720 and 1645 cm^{-1} appeared. The former was ascribed to the trimethylsilyl ester and the latter to the N,N-diethylamide. Distillation of VII was performed [bp 130.0–130.6° (4 mm)] and the viscous, oily liquid product was obtained in 62% yield. The methanolysis of VII was done by adding the excess amounts of dry methanol, distilling off methanol and trimethylmethoxysilane, obtaining a white crystal of succinic acid mono-N,N-diethylamide, and reprecipitating from acetone and petroleum ether (bp 30–70°) mp 85.0–86.0°. *Anal.* Calcd for $C_8H_{15}NO_3$: C, 55.47; H, 8.75; N, 8.09. Found: C, 55.54; H, 8.83; N, 8.10.

Polymerization of β-Propiolactone.—Polymerization studies were carried out in glass ampoules filled with dry nitrogen. After β-propiolactone (4.32 g) was added, 0.1 mole of trimethylsilyldialkylamine was introduced and sealed. The ampoules were set in a water bath controlled at 30.0 ± 0.1° for 110 hr. The white powder of poly-β-propiolactone precipitated gradually. Reaction mixtures were dissolved in small amounts of chloroform and precipitated by adding the solution to 60 ml of dry ether. Solvents and unreacted β-propiolactone were separated and polymers were washed with dry ether. Polymers were dried at 50° (1 mm). Intrinsic viscosity of polymers was determined in chloroform at 35.0°. The molecular weights were estimated with eq 9 proposed by Kagiya, *et al.*[11]

$$[\eta] = 2.74 \times 10^{-4} M^{0.74} \qquad (9)$$

The results were summarized in Table II.

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[19] K. Morsch, *Monatsh. Chem.*, **63**, 220 (1933).

The Action of Bromine in Acetic Acid on 4,5-Diphenyl-2-imidazolone

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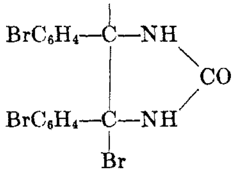
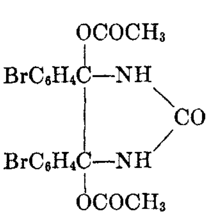
The action of bromine in acetic acid on 4,5-diphenyl-2-imidazolone leading to 4,4′-dibromobenzil and 4,5-di(*p*-bromophenyl)glycoluril has been reexamined, and the reaction has been studied in the presence of varying amounts of water, of sodium acetate as a buffer, and of urea. Under suitable conditions, 4,5-diacetoxy-4,5-diphenyl-2-imidazolidinone could be isolated and this substance, as well as the corresponding glycol, appears to be a labile intermediate during the oxidation of the imidazolone to benzil. Biltz isolated an intermediate compound in the reaction which he regarded as 4,5-dibromo-4,5-di(*p*-bromophenyl)-2-imidazolidinone, for which we propose a different structure. A reaction sequence for the oxidation leading to the various products is proposed. A number of phenyl-substituted imidazolones were also oxidized under different conditions.

Biltz[1] found that when 4,5-diphenyl-2-imidazolone was refluxed with bromine in acetic acid, 4,4′-dibromobenzil and 3a,6a-di(*p*-bromophenyl)glycoluril were formed; we have investigated this reaction in order to identify any intermediates and to apply the reaction to the synthesis of benzils.

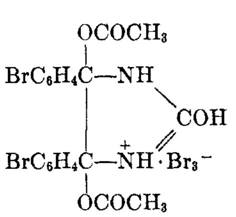
Biltz had found that the sparingly soluble 4,5-di(*p*-bromophenyl)-2-imidazolone dissolved readily when bromine was added to a suspension of the compound in acetic acid; from this solution a solid separated to which he assigned the structure I. We have reexamined this compound and found that it contains two acetate groups and two active bromine atoms, and elemental analysis indicated the formula $C_{19}H_{17}Br_5N_2O_5$; we propose structure IV for it. When the compound was heated or an aqueous suspension of it was treated with a reducing agent or it was allowed to stand with glacial acetic acid containing anhydrous sodium acetate, a diacetate was obtained. This diacetate was also formed when 4,5-di(*p*-bromophenyl)-2-imidazolone was treated with glacial acetic acid containing bromine and anhydrous sodium acetate; it was hydrolyzed by cold, aqueous acetic acid to the known 4,5-dihydroxy-4,5-di(*p*-bromophenyl)-2-imidazolidinone[2] (II). Spectral evidence and elemental analysis suggested the structure III for the diacetate.



I



III



IV

Scheme I following is proposed for the oxidation of 4,5-di(*p*-bromophenyl)-2-imidazolone (V) and for the formation of the various intermediates which are mentioned.

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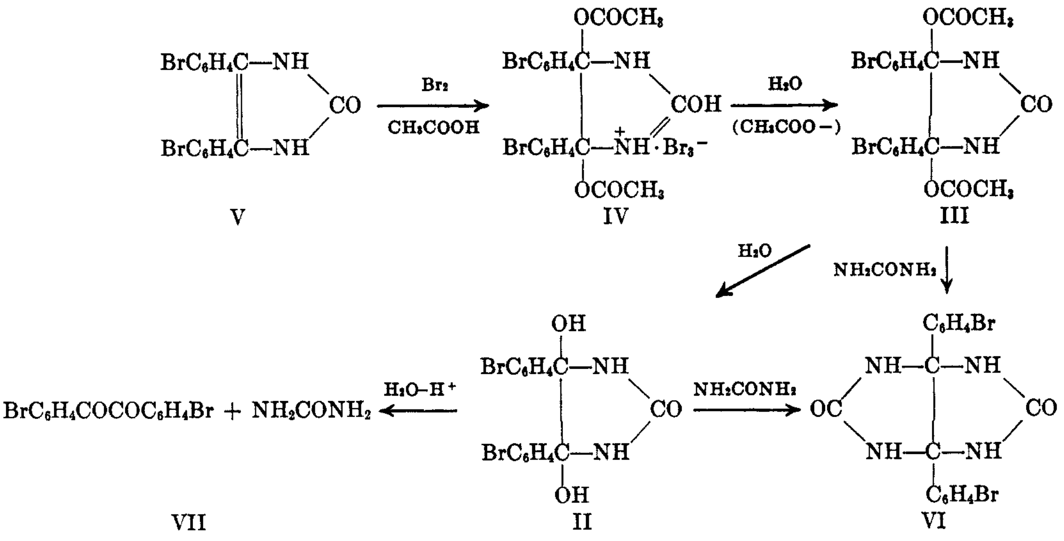
[1] H. Biltz, *Ber.*, **41**, 1754 (1908).

[2] H. Greenberg and T. van Es, *J. Org. Chem.*, **30**, 3937 (1965).

SCHEME I



3a,6a-Di(*p*-bromophenyl)glycoluril (VI) is formed by reaction of urea with either the glycol (II) or the diacetate (III) since both of these react quantitatively with urea whereas 4,4′-dibromobenzil does not react with it at all. It is possible that the dibromo compound (I) is formed during the oxidation, but its lack of stability may preclude its isolation. An attempt was made to prepare it by treating the glycol (II) with phosphorus tribromide or thionyl bromide but in each case the product was 4,5-di(*p*-bromophenyl)-2-imidazolone.

When 4,5-diphenyl-2-imidazolone is treated with bromine in acetic acid, bromination of the phenyl groups apparently occurs first, giving the imidazolone (V); it was not found possible to prepare a compound corresponding to I but without nuclear substitution. 4,5-Diacetoxy-4,5-diphenyl-2-imidazolidinone (similar to III) was prepared by treating 4,5-diphenyl-2-imidazolone with acetic acid containing bromine and anhydrous sodium acetate or iodine and silver acetate. This diacetate was hydrolyzed by cold, aqueous acetic acid to the known 4,5-dihydroxy-4,5-diphenyl-2-imidazolidinone.[2]

Chabrier, *et al.*,[3] treated 4,5-diphenyl-2-imidazolone in ethanol with iodine and morpholine or piperidine; the reaction conditions were similar to those used by us for the oxidation of imidazolones. However, they claimed to have isolated morpholine (or piperidine) substitution products with the enolic form of the imidazolone. We reexamined these products and have found that they are the known 4,5-diethoxy-4,5-diphenyl-2-imidazolidinone.[4]

The oxidation of 4,5-diphenyl-2-imidazolone with bromine in acetic acid was studied under different conditions. When it was refluxed with an excess of bromine in acetic acid containing different amounts of water, it was found that some bromination occurred at water concentrations below 20 moles; if this quantity of water, or more, was present no bromination occurred, only benzil and 3a,6a-diphenylglycoluril being obtained. When the reaction was repeated, but in the presence of sodium acetate, no bromination at all occurred and the yield of benzil reached a maximum (approximately 70%) when 20 moles of water was present.

When 4,5-diphenyl-2-imidazolone was treated with bromine in acetic acid containing an excess of anhydrous sodium acetate and urea, 3a,6a-diphenylglycoluril was obtained as the only product. It is presumably formed from reaction between the intermediate 4,5-diacetoxy-4,5-diphenyl-2-imidazolidinone and urea. If water was present in the reaction mixture, part of the diacetate was hydrolyzed to the glycol which in turn gave benzil as the final product. A number of new substituted glycolurils were prepared by the above procedure.

The influence of N substituents on the oxidation of 4,5-diphenyl-2-imidazolones was studied by using 1,3-dimethyl- and 1,3-diacetyl-4,5-diphenyl-2-imidazolone. The dimethyl compound gave benzil and 1,3-dimethyl-4,5-dihydroxy-4,5-diphenyl-2-imidazolidinone. The formation of this glycol may be due to its greater resistance (compared with the unsubstituted glycols mentioned above) to acid-catalyzed cleavage. The oxidation of the N-diacetyl compound gave benzil in high yield (95%) at a low water concentration (5 moles). In both these cases it was found that unless sodium acetate or water (20 moles or more) was present during the oxidation, brominated products were formed.

The oxidation was also applied to a number of phenyl-substituted imidazolones and it was found that the nature of the resultant benzil depended upon the reaction conditions. Using excess bromine and adding water after 1 hr, it was found that bromination occurred in unsubstituted phenyl groups while electron-donating groups such as methoxy or acetamino groups in the *para* position, led to bromination *ortho* to these groups. Hydrolysis of the acetamino group occurred, resulting in the formation of *o*-dibromoamino compounds. The presence of sodium acetate prevented the bromination of unsubstituted phenyl groups as well as the hydrolysis of the acetamino group. When the oxidation was conducted in aqueous acetic acid containing excess sodium acetate and 1 mole of bromine, no bromination took place. The presence of electron-withdrawing groups such as bromo or sulphonamido groups, prevented bromination under the above conditions.

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[3] P. Chabrier, K. Smarzewska, and G. Thuillier, *Compt. Rend.*, **236**, 929 (1953).

[4] H. Biltz, *Ann.*, **368**, 181 (1909).

Experimental Section

Melting points were determined in an electrically heated copper block. Known compounds were identified by mixture melting points. Infrared spectra were determined in potassium bromide disks.

Biltz's Intermediate Compound.—The compound was prepared as described by Biltz.[1] It separated more readily from the acetic acid solution containing excess bromine if a small quantity of water was present. Infrared absorption appeared at 3390 (OH), 3226 (NH), 1802 (ester), and 1700 (shoulder, ring CO) cm^{-1}.

Anal. Calcd for $C_{19}H_{17}Br_5N_2O_5$: C, 30.3; H, 2.26; active Br, 21.2. Found: C, 29.1; H, 1.90; active Br, 22.7.

The product analyzed had crystallized from the reaction mixture and could not be further purified. When this compound was (i) heated at 100° overnight, (ii) allowed to stand overnight at room temperature with acetic acid containing sodium acetate, and (iii) stirred with an aqueous solution of sodium sulfite, the diacetate (described next) was formed.

4,5-Diacetoxy-4,5-di(*p*-bromophenyl)-2-imidazolidinone (III).—4,5-Di(*p*-bromophenyl)-2-imidazolone[1] (3.94 g, 0.01 mole) was added to a solution of 35 ml of acetic acid containing 3 g of anhydrous sodium acetate and 1.60 g (0.01 mole) of bromine; the solution was allowed to stand at room temperature for 2 days and then poured into water. The product was rapidly filtered off and air dried, yielding 4.2 g (82%), mp 240–245°. This diacetate could not be crystallized; on heating it in any solvent it gave 4,4'-dibromobenzil. Infrared absorption appeared at 1730 (ester) and 1660 (shoulder, ring CO) cm^{-1}.

4,5-Diacetoxy-4,5-diphenyl-2-imidazolidinone. i.—This compound was prepared as described above. The dried product crystallized from ethyl acetate giving 1.80 g (51%), mp 185–187°. Infrared absorption appeared at 1725 (ester) and 1650 (shoulder, ring CO) cm^{-1}.

Anal. Calcd for $C_{19}H_{18}N_2O_5$: N, 7.91. Found: N, 7.96.

ii.—4,5-Diphenyl-2-imidazolone[5] (2.36 g, 0.01 mole) was stirred at room temperature with 50 ml of acetic acid and 3.4 g (0.02 mole + 5% excess) of dry silver acetate; 2.54 g (0.01 mole) of iodine was gradually added to the solution and the reaction was completed by refluxing for 0.5 hr. The silver iodide was filtered off and the filtrate was evaporated to dryness under reduced pressure. The residue crystallized from ethyl acetate, mp 186–187°.

The Oxidation of 4,5-Diphenyl-2-imidazolone. i.—The imidazolone (2.36 g, 0.01 mole) was refluxed for 1 hr with 25 ml of acetic acid and 10 ml of 3 *M* bromine in acetic acid and varying amounts of water. The reaction mixture was poured into water and the solid which separated, was filtered off and stirred with 100 ml of methanol to give the insoluble 3a,6a-diphenylglycoluril. The filtrate, on evaporation, gave benzil. In those cases where the water concentration was less than 20 moles, the reaction mixture was cooled after refluxing and the solid which separated was fractionally crystallized from ethanol; 4,4'-dibromobenzil was removed by extraction with hot benzene. The remainder of the work-up was as described above. The yields of the products, *viz.* benzil, 3a,6a-diphenyl-glycoluril, 4,4'-dibromobenzil, 3a,6a-di(*p*-bromophenyl)glycoluril, and 4,5-di(*p*-bromophenyl)-2-imidazolone, respectively, are indicated as percentages for the presence of 0, 0.05, 0.2, and 0.4 mole of water in the reaction mixture: 0, 0, 0, 0, 84; 24, 0, 11, 9, 38; 73, 27, 0, 0, 0; 57, 41, 0, 0, 0.

ii.—The procedure described in i was used, except that 3.0 g of anhydrous sodium acetate were added. When water (0.2 mole) was present, benzil (88%) and 3a,6a-diphenylglycoluril (1%) were obtained.

iii.—The imidazolone (2.36 g, 0.01 mole) was allowed to stand overnight with 25 ml of acetic acid, 3.0 g of anhydrous sodium acetate, 12 g (20 moles) of urea, 10 ml of 1 *M* bromine in acetic acid, and varying amounts of water; the isolation procedure described in i was used. The yields of the products, 3a,6a-diphenylglycoluril and benzil, respectively, are given as percentages for the presence of 0, 0.05, 0.2, and 0.4 moles of water in the reaction mixture: 92, 0; 69, 29; 43, 49; 34, 58.

Improved Method for the Preparation of Phenyl-Substituted Glycolurils.—The appropriate imidazolone (0.01 mole), 6 g of urea (0.1 mole), 6 g of anhydrous sodium acetate, and 25 ml of acetic acid, were heated to boiling when 10 ml of 1 *M* bromine in acetic acid was added and the solution was allowed to stand at room temperature overnight. The solution was poured into water and the glycoluril, which separated, crystallized from dilute acetic acid.

3a,6a-Di(*p*-acetaminophenyl)glycoluril (86%) had mp 338–339°.

Anal. Calcd for $C_{20}H_{20}N_4O_6$: N, 20.6. Found: N, 20.3.

3a,6a-Di(*p*-bromophenyl)glycoluril (89%) had mp 360–362° (lit.[1] mp 360°).

3a,6a-Di(*p*-methoxyphenyl)glycoluril (95%) had mp 338–340°.

Anal. Calcd for $C_{18}H_{18}N_4O_4$: N, 15.8. Found: N, 15.9.

3a,6a-Di(*p*-sulphonamidophenyl)glycoluril (89%) had mp 360–362°.

Anal. Calcd for $C_{16}H_{16}N_6O_6S_2$: N, 18.6. Found: N, 18.4.

Oxidation of 1,3-Dimethyl-4,5-diphenyl-2-imidazolone.[6]—The imidazolone (2.64 g, 0.01 mole) was refluxed for 1 hr with 25 ml of acetic acid, 10 ml of 3 *M* bromine in acetic acid, and varying amounts of water. The reaction mixture was poured into water and the material which separated was treated with ether to remove benzil. The ether-insoluble material crystallized from ethanol and proved to be 1,3-dimethyl-4,5-dihydroxy-4,5-diphenyl-2-imidazolidinone, mp 196–198° (lit.[7] mp 205°). When water (0.2 mole) was present, benzil (43%) and the glycol (54%) were obtained, whereas water (0.6 mole) gave benzil (62%) and the glycol (30%). In the presence of sodium acetate, the oxidation gave similar results.

Oxidation of 1,3-Diacetyl-4,5-diphenyl-2-imidazolone.[8]—The imidazolone (3.20 g, 0.01 mole) was refluxed for 1 hr with 25 ml of acetic acid, 3.0 g of anhydrous sodium acetate, 10 ml of 1 *M* bromine in acetic acid, and varying amounts of water. When the reaction mixture was poured into water, benzil separated, the yields being 67, 95, and 95% when 0.01, 0.05, and 0.1 mole of water, respectively, had been added.

Preparation of Phenyl-Substituted Imidazolones.—The appropriate benzoin (5.0 g), 3 g of urea, and 20 ml of acetic acid were refluxed for 6 hr and the reaction mixture was poured into water; the solid which separated was crystallized from a suitable solvent. 4,5-Di(*p*-acetaminophenyl)-2-imidazolone (75%) had mp 331–334° (lit.[9] mp 313–314°). 4,5-Di(*p*-chlorophenyl)-2-imidazolone (82%) had mp 282–287° (lit.[9] mp 269–271°). 4,5-Di(*p*-methoxyphenyl)-2-imidazolone (92%) had mp 280–283° (lit.[10] mp 278–280°). 4-*p*-Acetaminophenyl-5-phenyl-2-imidazolone (98%) had mp 292–296°.

Anal. Calcd for $C_{17}H_{15}N_3O_2$: N, 14.3. Found: N, 14.3.

4-*p*-Bromophenyl-5-phenyl-2-imidazolone (92%) had mp 157°.

Anal. Calcd for $C_{15}H_{11}BrN_2O$: N, 8.9. Found: N, 8.9.

4-*p*-Methoxyphenyl-5-phenyl-2-imidazolone (91%) had mp 251–253°.

Anal. Calcd for $C_{16}H_{14}N_2O_2$: N, 10.5. Found: N, 10.6.

4-*p*-Sulphonamidophenyl-5-phenyl-2-imidazolone (65%) had mp 323°.

Anal. Calcd for $C_{15}H_{13}N_3O_3S$: N, 13.3. Found: N, 13.1.

Oxidation of Phenyl-Substituted Imidazolones.—The imidazolones (0.01 mole) were oxidized as described below. The yields of benzils formed are given (per cent) and except where indicated, the physical constants agree with those recorded.[11]

(A) The compounds were refluxed for 1 hr in 50 ml of acetic acid, 10 ml of 6 *M* bromine in acetic acid, and 3.6 g (0.2 mole) of water.

(B) The procedure was the same as for A except that 6.0 g of sodium acetate was added.

(C) The compounds were allowed to stand overnight at room temperature with 50 ml of acetic acid, 10 ml of 1 *M* bromine in acetic acid, 6.0 g of sodium acetate, and 9.0 g (0.5 mole) of water.

4,5-Di(*p*-acetaminophenyl)-2-imidazolone gave the following per cent yields: (A) di(3,5-dibromo-4-amino)benzil (58), (B) 3,3',5-tribromo-4,4'-diacetaminobenzil (57), (C) 4,4'-diacetaminobenzil (80).

4-*p*-Acetaminophenyl-5-phenyl-2-imidazolone gave the following per cent yields: (A) 3,5,4'-tribromo-4-aminobenzil (69),

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[5] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 231.

[6] H. Biltz, *Ann.*, **368**, 206 (1909).

[7] H. Biltz, *Ber.*, **41**, 167 (1908).

[8] H. Biltz, T. Arnd, and C. Stellbaum, *Ann.*, **339**, 262 (1905).

[9] Kalle and Co., German Patent, 1,060,713 (July 2, 1959); *Chem. Abstr.*, **55**, P20735c (1961).

[10] A. Novelli, *Anales Assoc. Quim. Arg.*, **40**, 112 (1952); *Chem. Abstr.*, **47**, 9321*d* (1953).

[11] T. van Es and O. G. Backeberg, *J. Chem. Soc.*, 1371 (1963).

(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).

Acknowledgment.—H. G. thanks the South African Council for Scientific and Industrial Research for a bursary.

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

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[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).

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[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.

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