TABLE I
NMR ASSIGNMENTS FOR CYCLOPROPYL 2-PYRROLYL KETONE PROTONS

	τ (CDCl3)	τ (C6D6)	Coupling, Hz
H-3	3.0 (m)	3.12 (m)	$J_{3,4}$ = 3.9, $J_{3,5}$ = 1.4, $J_{3,NH}$[a] = 2.4
H-4	3.75 (m)	3.85 (m)	$J_{4,5}$ = 2.5; $J_{4,NH}$[a] = 2.5
H-5	3.0 (m)	3.28 (m)	$J_{3,NH}$ not observed[b]
AA′	9.07 (m)	9.45 (m)	$J_{A,C}$ = $J_{A'C}$ = 7.8 (cis)
BB′	8.82 (m)	8.80 (m)	$J_{B,C}$ = $J_{B'C}$ = 4.5 (trans)
C	7.56 (m)	7.91 (tt)	

[a] All couplings to NH disappear upon shaking with D_2O. [b] Due to overlapping signals.

were made from the values of the aromatic coupling constants by comparison with known values.[6]

Bromination of **6** with bromine in ethanol afforded di- and tribromopyrrolyl derivatives, **7** and **8**, respectively. The two bromine atoms of the dibromo derivative **7** are assigned tentatively to the 4 and 5 positions, there being existing evidence that a 2-substituted pyrrole dihalogenates preferentially in these positions.[7] Additionally, the nmr spectra show the disappearance of the highest field aromatic proton (H-4) of the parent ketone. In contrast to the bromination of 3-acetyl-5-bromo-4-ethyl-2-methylpyrrole (**9**) where the acetyl group is displaced[8] to form 2,4-dibromo-3-ethyl-4-methylpyrrole (**10**), bromination of **6** does not yield any tetrabromopyrrole *via* displacement of the cyclopropylcarbonyl group.

Experimental Section

Melting points are uncorrected. The ir spectra were recorded on a Perkin–Elmer Infracord 137 as KBr disks. Nmr spectra were obtained with a JEOL JNM-4H-100 spectrometer at 100 MHz, field position values being recorded relative to tetramethylsilane as an internal standard. Peak multiplicities are abbreviated as d (doublet), t (triplet), q (quintet), tt (triplet of triplets), and m (multiplet). Uv spectra were recorded upon a Perkin–Elmer 402 uv-visible spectrometer in ethanol.

4-Chloro-*N*,*N*-dimethylbutyramide was obtained from butyrolactone by the following sequence: butyrolactone → 4-chlorbutyric acid[9] → 4-chlorobutyroyl chloride[10] → 4-chloro-*N*,*N*-dimethylbutyramide. The last step was accomplished by adding (dropwise) a solution of 4-chlorobutyroyl chloride (7.5 g) in cold, dry ether (15 ml) to a stirred solution of dimethylamine (5.0 g, 2:1 molar ratio) in dry ether (100 ml) at −20° over a period of 0.75 hr. The mixture was allowed to stand in a refrigerator overnight (0°) and the dimethylamine hydrochloride was filtered off. The ether was removed and the crude product was distilled to afford 4-chloro-*N*,*N*-dimethylbutyramide as a colorless liquid (5.3 g, 67%): bp 74–76° (0.1 mm); ν_{max} 6.08 μ (CO); nmr τ (CDCl3) 6.38 (2, t, *J* = 6 Hz, $ClCH_2$), 7.04 [6, d, $N(CH_3)_2$], 7.52 (2, t, CH_2CO), and 7.90 (4, q, $CH_2CH_2CH_2$). *Anal.* Calcd for $C_6H_{12}NOCl$: C, 48.16; H, 8.08; N, 9.36. Found: C, 48.12; H, 8.07; N, 9.16.

3-Chloropropyl 2-Pyrrolyl Ketone (**5**).—Freshly distilled phosphorus oxychloride (48.2 g, 0.2 *M* excess) was added, over 5 min, to ice-cold 4-chloro-*N*,*N*-dimethylbutyramide (50 g, 0.33 mol) with stirring. The mixture was allowed to reach room temperature and, with continued stirring (*ca.* 30 min), cooled as necessary to keep the temperature below 30°. Ethylene dichloride (92 ml) was added and the mixture (bright yellow) cooled to 5°. Freshly distilled pyrrole (20.4 g, 0.304 mol) in ethylene dichloride (92 ml) was added to the stirred, cooled mixture over 1 hr. The solution was brought to room temperature, refluxed for 20 min, and cooled. A solution of sodium acetate ($3H_2O$, 228 g) in water (300 ml) was added and the mixture was refluxed for a further 15 min. The cooled mixture was extracted with three 300-ml portions of ether and the combined ether solutions were washed with concentrated sodium carbonate solution and dried over anhydrous sodium carbonate. Removal of ether afforded a brown crystalline solid which was chromatographed upon silica (Merck), elution with 50% ether in benzene yielding **5** as a white solid (32 g, 62%): mp 70–71°; ν_{max} 3.04 (NH) and 6.09 μ (CO); λ_{max} 291 nm (ε 21,300); nmr τ ($CDCl_3$) 6.42 (2, t, $ClCH_2$), 7.05 (2, t, $COCH_2$, *J* = 7.0 Hz), and 7.76 (4, q, $CH_2CH_2CH_2$), and aromatic protons H-3, H-4 and H-5 as multiplets at τ 3.05, 3.76, and 2.97, rspectively, with $J_{3,4}$ = 3.9, $J_{4,5}$ = 2.5, $J_{3,5}$ = 1.4, $J_{4,NH}$ = 2.5, and $J_{3,NH}$ = 2.4 Hz. *Anal.* Calcd for $C_8H_{10}NOCl$: C, 55.98; H, 5.87; N, 8.16. Found: C, 56.06;H, 5.85; N, 8.04.

Cyclopropyl 2-Pyrrolyl Ketone (**6**).—A solution of **5** (6.0 g, 0.035 mol) in dry benzene (50 ml) was added over 1.25 hr to a stirred suspension of sodium hydride (2.0 g, 0.116 mol) in benzene (200 ml) at room temperature. The stirred mixture was gradually (over 1 hr) warmed to reflux temperature, the gray solids dissolving to afford a brown solution. After refluxing for 5 min, sodium chloride started to precipitate. Reflux was continued for a further 2 hr, the mixture was then cooled, and excess sodium hydride was destroyed with methanol. The solution was washed with water (three 50-ml portions) and the organic solvents were removed by distillation *in vacuo* to yield a pale yellow solid. Purification was best achieved by column chromatography on silica, elution with 2% ether in benzene affording **6** as a white solid (3.71 g, 79%): mp 71.5°; ν_{max} 3.05 (NH) and 6.18 μ (CO); λ_{max} 290 nm (ε 18,700), *Anal.* Calcd for C_8H_9NO: C, 71.09; H, 6.71; N, 10.36. Found: C, 70.61; H, 6.86; N, 9.98.

The 2,4-dinitrophenylhydrazone had mp 271°; λ_{max} 312 nm (ε 10,000) and 418 (25,100). *Anal.* Calcd for $C_{14}H_{13}N_5O_4$: C, 53.33; H, 4.16; N, 22.21. Found: C, 53.39; H, 4.34; N, 22.07.

Bromination of 6.—A solution of bromine (2.93 g, 0.037 mol) in ethanol (20 ml) was added dropwise to a stirred solution of **6** (0.5 g, 0.0037 mol) in ethanol (5 ml). After *ca.* 10 ml was added, crystals separated (0.3 g) which were filtered off and crystallized from ethanol to afford **cyclopropyl 4,5-dibromo-2-pyrrolyl ketone** (**7**): mp 174–175°; ν_{max} 3.18 (NH) and 6.10 μ (CO); nmr τ (DMSO-d_6) 2.63 (1, d, H-3, $J_{3,NH}$ = 2.7 Hz), 7.40 (1, m, COCH), and 9.04 (4, broad asymmetric d, CH_2CH_2). *Anal.* Calcd for $C_8H_7NOBr_2$: C, 32.80; H, 2.41; N, 4.78. Found: C, 32.88; H, 2.38; N, 4.76.

The remainder of the bromine solution was added to the filtrate from above. When addition was complete the mixture was diluted with water to precipitate a pale yellow solid (1.0 g) which was crystallized from ethanol to afford **cyclopropyl 3,4,5-tribromopyrrolyl ketone** (**8**) as prisms: mp 208–210°; ν_{max} 3.15 (NH) and 6.13 μ (CO); nmr τ (DMSO-d_6) 7.11 (1, q, COCH) and 8.91 (4, asymmetric d, CH_2CH_2). *Anal.* Calcd for $C_8H_6NOBr_3$: C, 25.84; H, 1.63; N, 3.77. Found: C, 25.94; H, 1.62; N, 3.78.

Registry No.—**5**, 21187-88-2; **6**, 30625-80-0; **6** 2,4-DNP, 30625-81-1; **7**, 30625-82-2; **8**, 30625-83-3; 4-chloro-*N*,*N*-dimethylbutyramide, 22813-58-7.

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Halogenation with Copper(II) Halides. Synthesis of Dehydroadiponitrile

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The synthesis of chloroiodoalkanes from olefins, iodine, and copper(II) chloride in hydrocarbon media

has recently been described.[1] When this reaction was extended to butadiene, no chloroiodide was recovered, but a high yield of isomeric dichlorobutenes was produced. Consideration of the reaction mechanism indicated that the butenyl dichlorides arose from a halogen exchange reaction between initially formed chloroiodide and by-product copper(I) chloride. This observation prompted an investigation of the synthesis of other 1,4-difunctional compounds derived from butadiene through reactions with halogen donors and copper salts. This note describes the synthesis of dehydroadiponitrile (1,4-dicyanobutene-2) based on this concept.

Butadiene reacted with iodine and copper(I) cyanide in inert alkane diluents to produce 85–97% yields of dehydroadiponitrile di[copper(I) iodide] (eq 1). The

$$CH_2{=}CHCH{=}CH_2 + I_2 + 2CuCN \xrightarrow[80\text{–}150^\circ]{RH} ICu\cdot NCCH_2CH{=}CHCH_2CN\cdot CuI \quad (1)$$

complex was degraded by hot water, sublimation, or reaction with aqueous hydrogen cyanide solution (eq 2)

$$ICu\cdot NCCH_2CH{=}CHCH_2CN\cdot CuI + 2HCN \xrightarrow{H_2O} NCCH_2CH{=}CHCH_2CN + 2CuCN + I_2 + H_2 \quad (2)$$

to release the isomerically pure 1,4-dinitrile in yields ranging from 85 to 96%.

The reaction is considered to proceed through the intermediate formation of 1,4-diiodobutene-2,[2] which subsequently experienced anion exchange with copper(I) cyanide. In this sense the reaction was analogous to that of simple allylic halides with copper(I) cyanide.[3] The driving force is partially provided by the relative stabilities of the copper(I) salts involved.[4]

Aromatic hydrocarbons as a class were unsatisfactory as solvents for this preparation of dehydroadiponitrile. In benzene ~50% yields of the dinitrile were produced in addition to large amounts of intractable iodine containing by-product. Alkyl benzenes gave no nitrile product, but experienced extensive alkylation by iodonium ion intermediates. Chlorocarbons were equally unsuited as reaction diluents due to extensive formation of tarry organic iodides. Optimum results were achieved in carbon tetrachloride, where a 61% yield of dinitrile was recovered. The nitrile-forming reaction is believed to be inhibited by complexation of copper(I) cyanide by the chlorocarbon.[5]

If the reaction was carried out in acetonitrile, 60–80% yields of dehydroadiponitrile resulted. In this case the product was recovered from the reaction free of its copper(I) iodide complex, the salt being preferentially coordinated with the more potent ligand, acetonitrile.[6] This reaction was complicated by the loss of both inorganic reagents through the formation of copper(I) iodide and cyanogen.[3]

A second synthesis of dehydroadiponitrile was realized by the reaction of butadiene with copper(II) bromide and copper(I) cyanide. The diolefin reacted with copper(II) bromide to produce a mixture of isomeric dibromobutenes (eq 3). The reaction occurred

$$CH_2{=}CHCH{=}CH_2 + 2CuBr_2 \xrightarrow[75^\circ]{RH} \begin{cases} BrCH_2CH{=}CHCH_2Br\ (87\%) \\ BrCH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH{=}CH_2\ (13\%) \end{cases} + 2CuBr \quad (3)$$

89% yield

at room temperature if a catalytic quantity of acetonitrile was present. Increasing the reaction temperature to ~75° obviated the need for this catalyst, and comparable yields were obtained in pure alkane media. In this case the reaction is driven by the thermal dissociation of copper(II) bromide.[7] Control experiments demonstrated the feasibility of the dibromobutene–copper(I) cyanide reaction, and combination of the individual reactions gave a single-step conversion of butadiene to dehydroadiponitrile di[copper(I) bromide] in 80% yield (eq 4). The dinitrile was shown to be isomerically

$$CH_2{=}CHCH{=}CH_2 + 2CuBr_2 + 2\ CuCN \xrightarrow[100^\circ]{RH} BrCu\cdot NCCH_2CH{=}CHCH_2CN\cdot CuBr + 2CuBr \quad (4)$$

pure 1,4-dicyanobutene-2. The production of a single dinitrile from the mixture of dibromobutenes (eq 3) was due to the fact that only the 1,4-dibromide reacted with copper(I) cyanide.[8] Since the isomeric dihalides are equilibrated by copper(I) halides in nonaqueous systems,[9] the reaction proceeded with the exclusive formation of the 1,4-dinitrile.

A comparable reaction utilizing copper(II) chloride and copper(I) cyanide was not realized owing to the inability of copper(II) chloride to effect the chlorination of butadiene in hydrocarbon media. If this reaction was performed in acetonitrile containing a catalytic quantity of iodine, 60–80% yields of 1,4-dicyanobutene-2 were recovered.

Experimental Section

Infrared spectra were recorded on a Beckman IR-5A spectrophotometer. Nmr spectra were measured on a Varian Associates A-60 spectrometer using deuteriochloroform as a solvent and tetramethylsilane as an internal standard. Vapor phase chromatography (vpc) was performed on a Perkin–Elmer 154D fractometer. Melting points and boiling points are not corrected. All reagents were CP grade and were used as received.

Reaction of Butadiene with Copper(I) Cyanide and Iodine.—In a typical experiment a Parr low-pressure reactor[10] was charged with 100 ml of *n*-heptane, 25.4 g (0.1 mol) of iodine, and 18.0 g (0.2 mol) of copper(I) cyanide. The reactor was evacuated to ~50 mm, and butadiene (~0.3 mol) was pressurized into the system. The reaction was rocked at 85° for 4–5 hr. The reaction mixture was filtered; the filter cake was rinsed with *n*-pentane and methylene chloride and air-dried to give 46.4 g (95%) of dehydroadiponitrile di[copper(I) iodide].[11] The complex was suspended in 500 ml of water, and the suspension was stirred at reflux for 3 hr. The mixture was filtered hot, and the filter cake was air-dried to yield 36.7 g (95%) of copper(I) iodide. The aqueous filtrate was concentrated on a

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rotary evaporator to crystallize the dinitrile; the crude product was dried over calcium chloride to give 10.2 g (96%) of dehydroadiponitrile, mp 72–74° (lit.[12] 76°). Recrystallization from ethanol or sublimation gave white needles, mp 75–76°. *Anal.* Calcd for $C_6H_8N_2$: C, 67.90; H, 5.70; N, 26.40. Found: C, 68.36; H, 5.92; N, 25.86. The dinitrile was shown to be identical with an authentic sample by comparative analytical techniques. The isomeric purity was established by vpc (2 ft × 0.25 in. 10% silanized polypropylene glycol column, 160°, 250-ml/min helium flow; t_R[13] 2.8 min from air) and by nmr: δ 5.83 (m, 2, J = 11.5 Hz, HC=CH) and 3.18 (m, 4, CH_2CN).

The dinitrile–copper(I) iodide complex was also degraded by vacuum sublimation [100° (50 mm)] or by treatment with aqueous hydrocyanic acid. In the latter case 20–40 g of complex was suspended in 100–300 ml of chloroform and 400–500 ml of 2% hydrocyanic acid. The mixture was stirred at room temperature for 1 hr and the two phases were separated. The chloroform layer contained 30% of the free dinitrile. From the aqueous layer the undecomposed complex and copper(I) cyanide were recovered. Air oxidation of the aqueous phase liberated iodine, which was assayed by thiosulfate titration and shown to be equivalent to the amount of nitrile liberated and copper(I) cyanide produced. The total material balance on the reaction was generally ~95%.

Acetonitrile was substituted for *n*-heptane as the reaction diluent. The reaction was agitated at 60° for 1 hr, and the mixture was poured into 10% sodium thiosulfate solution and extracted with methylene chloride (three 100-ml portions). The extract was dried over magnesium sulfate; the solvent was removed on a rotary evaporator to give 8.8 g (84%) of 1,4-dicyanobutene-2. From the aqueous phase was recovered 34.5 g of copper(I) salts.

Reaction of Butadiene with Copper(II) Bromide and Copper(I) Cyanide.—Into a Parr low-pressure reactor were charged 100 ml of *n*-heptane, 44.6 g (0.2 mol) of copper(II) bromide, and 0.3 mol of butadiene. The reactor was rocked at 75° for 90 min. The reaction mixture was filtered, and the filter cake was rinsed with pentane to give 29.3 g of copper(I) bromide (theory, 28.6 g). The pentane washings were combined with the filtrate, and the hydrocarbon solvents were removed on a rotary evaporator. The yield of crystalline dibromobutenes was 19.0 g (89%); the product was identified by comparative analytical techniques. Vpc analysis (1 m × 0.25 in. 20% silicone DC-200, 100°, 145 ml/min) gave the following isomer distribution: 3,4-dibromobutene-1, t_R 4.4 min (13%); *cis*-1,4-dibromobutene-2, t_R 9.0 min (5%); *trans*-1,4-dibromobutene-2, t_R 9.8 min (82%).

The bromination reaction was repeated in *n*-nonane at 75° for 45 min. The reaction was filtered, and the filtrate was added to 18 g (0.2 mol) of copper(I) cyanide. This reaction mixture was stirred at 130° for 5 hr. Filtration gave 34.7 g of a mixture of unreacted copper(I) cyanide and dehydroadiponitrile di[copper(I) bromide], which corresponded to an 80% yield of dinitrile. Degradation of the complex released the isomerically pure 1,4-dicyanide, which was identical with an authentic sample.

Registry No.—Dehydroadiponitrile, 1119-85-3.

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(13) t_R = retention time.

Reaction of *sym*- and *unsym*-Phthaloyl Chloride with *tert*-Butyl Hydroperoxide[1a]

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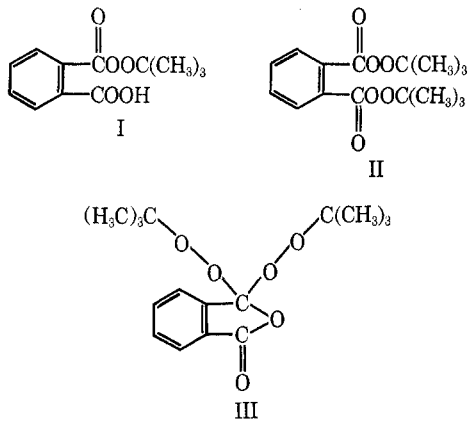
The reaction of *tert*-alkyl, *tert*-aralkyl, and acyl chlorides with *tert*-alkyl hydroperoxides to form the corresponding peroxides and peroxy esters is usually carried out in the presence of an organic or inorganic base[3] in order to avoid decomposition of the hydroperoxide by the hydrogen chloride liberated. In previous papers[4,5] we have shown that the addition of a base can be omitted by carrying out the solvolysis reaction under reduced pressure in a rotary evaporator at 50–70° and thereby removing the hydrogen chloride as soon as it is formed. Using this technique, substantial yields of di-*tert*-alkyl and mixed *tert*-alkyl aralkyl peroxides and peroxy esters have been prepared from the corresponding *tert*-alkyl chlorides, *tert*-aralkyl chlorides, and acid chlorides with *tert*-butyl hydroperoxide. We report here the solvolysis of phthaloyl chlorides with *tert*-butyl hydroperoxide.

The solvolysis of symmetrical phthaloyl chloride with *tert*-butyl hydroperoxide proceeds exothermically and produces a mixture of mono-*tert*-butyl peroxy hydrogen phthalate (I), di-*tert*-butyl diperoxyphthalate (II), and 3,3-di-*tert*-butyl diperoxyphthalide (III). Peroxy esters I and II have been reported in the literature;[6,7] 3,3-di-*tert*-butyl diperoxyphthalide (III), isomeric with



II, appears to be a new peroxide. The structure of III is based on elemental analysis, ir and nmr spectra, and hydrolysis experiments. The ir spectrum (10% in carbon tetrachloride) exhibits aromatic, *tert*-butyl peroxy, and carbonyl absorption. Compound III shows strong carbonyl absorption at 1803 cm^{-1}; compound II shows carbonyl absorption at 1772 cm^{-1}, expected for a peroxy ester. The observed carbonyl frequency for III at 1803 cm^{-1} is attributed to the γ-lactone structure in which the CO absorption of the γ-lactone has been shifted to higher frequencies by the electron-attracting peroxy groups. Compound III fails to give a positive test for a peroxy ester with an acidified sodium iodide solution in the presence of catalytic amounts of ferrous ions.[8] Alkaline hydrolysis affords *tert*-butyl hydroperoxide and phthalic acid.

The nmr spectrum of III (25% in carbon tetrachloride, TMS) shows a single peak for the (equivalent) aliphatic protons at 1.26 ppm. The aromatic proton

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