The large distribution of end products makes it difficult to discuss a mechanism on the basis of a specific reactive intermediate. In the case of methane the formation of a larger number of end products can be explained on the basis of the formation of a C_1 radical or ion (*e.g.*, CH_3 or CH_3^+). The number of possible ways for a C_1 to recombine to form higher molecular weight compounds is larger than in the case of C_2 or C_3 radicals or ions. This is consistent with the smaller number of products obtained by sparking C_2 and C_3 hydrocarbons. Clearly, in the latter case, C_1 radicals are also present since odd-numbered carbon molecules are also formed. The formation of liquid hydrocarbons with the C_2 and C_3 parent compounds is much faster than in the case of methane. This was observable visually by the rapid appearance of yellow liquid in the reaction vessel, while with methane the time required for the liquid formation was about twice as long. In the case of acetylene, a dark brown polymer coated the reaction vessel after 0.5-hr sparking. The volatile products were largely dimers, trimers, and tetramers of acetylene. Longer periods of sparking of acetylene resulted in less distillable material.

A less detailed analysis[3] of the products of semicorona and arc discharges show that benzene and toluene are minor products of the semicorona but a major product of the arc. Among other differences, these discharges can be classified by their "temperatures." The order of increasing "temperature" is semicorona, spark, and arc. The higher "temperature" discharges yield fewer compounds and compounds of greater unsaturation and aromaticity. The arc discharge approaches pyrolysis reactions in this regard.

The formation of hydrocarbons by electric discharges is particularly important in prebiological chemistry since electric discharges in the atmosphere were a significant source of energy for prebiological synthesis.[9] Hydrocarbons formed by such reactions may be useful as starting materials in prebiotic synthetic reactions, for example, phenylalanine from phenylacetylene.[4] Furthermore, the products formed by such reactions are likely to have been present in the primitive reducing atmosphere.[10]

A number of organic compounds such as HCN, H_2CO, and cyanoacetylene have been found in interstellar space recently.[11] These molecules are major products of electric discharge reactions. It is possible that some of the hydrocarbons identified in this investigation may also be present in interstellar space.

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Cyclopropyl 2-Pyrrolyl Ketone

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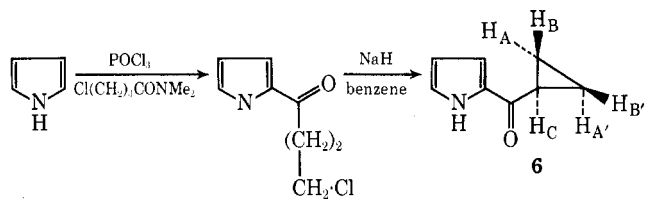
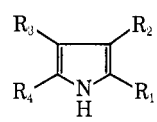
Cyclopropyl ketones in which the cyclopropylcarbonyl group is bonded directly to a heterocyclic ring (either unsaturated or fully reduced) are few. From among the common six-membered heterocycles the 2-[1] and 3-pyridyl[2] compounds (**1** and **2**, respectively) appear to provide the only examples. Of the three common five-membered heterocycles, the 2-furyl[3] and 2-thienyl[4] cyclopropyl ketones (**3** and **4**, respectively) have been recorded in the literature but to date no preparation of the corresponding 2-pyrrolyl ketone (**6**) has been described. This note reports a synthesis of the title compound from easily accessible materials.

1, Ar = 2-pyridyl
2, Ar = 3-pyridyl
3, Ar = 2-furyl
4, Ar = 2-thienyl



5



7, R_1 = —CO—; R_2 = H; R_3 = R_4 = Br
8, R_1 = —CO—; R_2 = R_3 = R_4 = Br
9, R_1 = Me; R_2 = Ac; R_3 = Et; R_4 = Br
10, R_1 = Me; R_2 = Br; R_3 = Et; R_4 = Br

The Vilsmeier–Haack acylation of pyrrole rings is well established.[5] In the present synthesis, using the procedure of Silverstein, *et al.*,[5] the reaction between pyrrole and 4-chloro-*N*,*N*-dimethylbutyramide was smoothly accomplished and afforded 3-chloropropyl 2-pyrrolyl ketone (**5**) in good yield. Subsequent treatment of **5** with sodium hydride in benzene gave the desired cyclopropyl 2-pyrrolyl ketone (**6**). (This cyclization may also be performed using potassium sand or sodium hydride in xylene, but yields are generally lower.) The nmr spectrum of the 2-thienyl ketone (**4**) has been recently presented[4b] and the cyclopropyl ring protons discussed in terms of an AA'BB'X system assuming that $J_{BC} = J_{B'C}$, $J_{AC} = J_{A'C}$, and $J_{AB} = J_{A'B'}$. In the present case, the 100-MHz nmr spectrum of the 2-pyrrolyl ketone (**6**) in $CDCl_3$ exhibits chemical shifts and splitting patterns for the cyclopropyl ring protons very similar to those for the 2-thienyl case (Table I). In C_6D_6 proton C resolves into a triplet of triplets, enabling computation of J_{AC} and J_{BC} from the spectrum. The assignments for the protons H-3 and H-5

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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