Experimental Section

The amines were dried over potassium hydroxide pellets and the thiophosphonates **1** were redistilled before use. Acetonitrile was distilled from P_2O_5. The nmr spectra were determined on a Varian A-60 spectrometer using deuteriochloroform as solvent and tetramethylsilane as an internal standard. Chemical analyses were performed by Geller Microanalytical Laboratories, Saddle River, N. J.

Preparation of Enamines Thiophosphonates 2a–h. General Procedure.—The diethyl alkynyl-1-thiophosphonates **1** were refluxed with a 10–12 molar excess of the amines. The reflux was continued for 2–4 days until the ir spectra of a test portion of the reaction mixture showed almost complete disappearance of the absorption band in the region of 4.52–54.6 μ ($C{\equiv}C$). In the case of cyclohexylamine, the reaction solution was diluted by the addition of a volume of acetonitrile equal too ne-fourth the original reaction volume. This addition was necessary to keep the reflux temperature low. The solvent and the excess amines were evaporated *in vacuo* at aspirator pressure. The resulting adducts were short path distilled at reduced pressure from anhydrous potassium carbonate.

Diethyl 2-*n*-Butylaminohexenyl-1-thiophosphonate (2a).—The ir spectrum ($CHCl_3$) displayed short absorption bands at 2.92 and 3.08 μ and strong bands at 3.41, 6.25, 9.75, and 10.54 μ: nmr 4.09 (m, 5 H, $-CH_2OP$, $PCH{=}$), 3.08 (m, 2 H, NCH_2), 2.51 (m, 2 H, $=CCH_2$), 1.21 (m, containing t, $J = 6.8$ Hz, 20 H, the remaining methyl and methylene protons; the amino proton was observed as low multiplets at 7.35 and 4.45 ppm.

Diethyl 2-*n*-Butylaminooctenyl-1-thiophosphonate (2b).—The ir spectrum ($CHCl_3$) showed short bands at 2.92 and 3.08 μ and strong bands at 3.42, 6.25, 9.65, and 10.55 μ: nmr 7.40 and 4.81 (two low m, 1 H, amino), 4.08 (m, 5 H, CH_2OP and $PCH{=}$), 3.02 (m, 2 H, (NCH_2), 2.50 (m, 2 H, $=CCH_2$), 1.24 ppm (m containing t, $J = 6.9$ Hz), 24 H, the remaining methyls and methylenes.

Diethyl 2-*tert*-Butylaminoheptenyl-1-thiophosphonate (2c).—The ir spectrum ($CHCl_3$) showed short bands at 2.85 and 3.05 μ and strong bands at 3.38, 6.24, 9.74 and 10.47 μ: nmr 4.12 (m, 5 H, CH_2OP and $PCH{=}$), 2.41 (m, 2 H, $=CCH_2$), 1.32 (m, 24 H, the remaining methyl and methylene), 7.40 and 4.35 (two low m, 1 H, NH).

Diethyl 2-*tert*-butylaminooctenyl-1-thiophosphonate (2d).—The ir spectrum ($CHCl_3$) displayed a short band at 2.91 μ and strong bands at 3.41, 6.26, 9.74, and 10.56 μ: nmr 4.16 (m, 5 H, CH_2OP and $PCH{=}$), 2.41 (m, 2 H, $=CCH_2$), 1.25 (m containing t, $J = 6.5$ Hz), 26 H, the remaining methyls and methylenes; the amino proton was observed as two low multiplets at 7.35 and 4.41 ppm.

Diethyl 2-Cyclohexylaminopentenyl-1-thiophosphonate (2e).—The ir spectrum ($CHCl_3$) displayed short bands at 2.95 and 3.10 μ and strong bands at 3.46, 6.30, 9.76 and 10.56 μ: nmr 4.08 (m, 5 H, CH_2OP and $PCH{=}$), 3.48 (m, 1 H, NCH), 2.48 (m, 2 H, $=CCH_2$, 1.27 (m containing t, $J = 6.7$ Hz), 21 H, the remaining methyl and methylenes; the amino proton showed two low multiplets at 7.31 and 4.65 ppm.

Diethyl 2-Cyclohexylamino-2-phenylethenylthiophosphonate (2f).—The ir spectrum ($CHCl_3$) showed short bands at 2.92 and 3.08 μ and strong absorption bands at 3.41, 6.31, 9.75, 10.55, and 11.81 μ: nmr 7.41 (br s, 5 H, phenyl), 4.11 (m, 5 H, (CH_2OP and $PCH{=}$), 2.88 (m, 1 H, NCH), 1.32 (m containing t, $J = 6.8$ Hz), 16 H, the remaining methyls and methylenes; 7.30 and 4.65 ppm, two low multiplets, 1 H, amino.

Diethyl 2-Diethylaminononenyl-1-thiophosphonate (2g).—The ir spectrum ($CHCl_3$) displayed strong absorption bands at 3.44, 6.50, 9.75, and 10.58 μ: nmr 4.12 (m, 5 H, CH_2OP and $PCH{=}$), 3.26 (q, $J = 7.2$ Hz, 4 H, NCH_2), 2.63 (m, 2 H, $=CCH_2$), 1.24 ppm (m containing a t, ($J = 6.6$ Hz), 25 H, the remaining methyls and methylenes.

Diethyl 2-Diethylamino-2-phenylethenylthiophosphonate (2h).—The ir spectrum ($CHCl_3$) displayed strong absorptions at 3.42, 6.55, 9.76, 10.54, and 12.15 μ: nmr 7.36 (s, 5 H, phenyl), 4.52 (d, $J = 16$ Hz, 1 H, $PCH{=}$), 3.79 (two crude q, 4 H, CH_2OP), 3.17 (q, $J = 7$ Hz, 4 H, NCH_2), 1.13 ppm (t, $J = 7.2$ Hz, 12 H, methyls).

Preparation of α,β-Ethylenic Ketones. General Procedure.—Diethyl alkynyl-1-thiophosphonate (0.01 mol) was dissolved in a 10 molar excess of *n*-butylamine and refluxed for 2 days. The excess amine was evaporated on an aspirator and its last traces were removed on a vacuum pump. The resultant adduct was dissolved in 100 ml of tetrahydrofuran and was cooled to 0°. To this THF solution 0.01 mol of NaH was added and stirred for 0.5 hr, 0.01 mol of the aldehyde was added, and the reaction mixture was stirred at 0° for 1 hr and then at room temperature for 6 hr. The solvent was evaporated, and the residue was stirred well with 100 ml of ether and filtered. The ether solution was stirred for 6–7 hr with 100 ml of 1% aqueous solution of oxalic acid. The two phases were separated, and the ether layer was washed with water, dried ($MgSO_4$), filtered, and evaporated. The resulting oil was distilled at reduced pressure to obtain the α,β-ethylenic ketones.

1-(4-Methoxyphenyl)-3-one-1-hexene gave the following data: bp 124–127° (0.05 mm); mp 38–40° (lit.[9] mp 40–41°); yield 34%; the ir spectrum ($CHCl_3$) showed strong absorption bands at 6.07 ($C{=}O$) and 6.25 μ ($C{=}C$); nmr 7.54 (d, $J = 15.5$ Hz, 1 H, $ArCH{=}$), 7.56–6.78 (m, 4 H, aromatic), 6.62 (d, $J = 15.5$ Hz, 1 H, $=CHCO$), 3.76 (s, 3 H, CH_3O), 2.62 (t, $J = 7.5$ Hz, 2 H, $OCCH_2$), 1.68 (m, 2 H, $OCCCH_2$), 0.96 ppm (t, ($J = 7.5$ Hz, the terminal methyl).

1-Phenyl-3-one-1-nonene gave the following data: bp 118–120° (0.05 mm); mp 42–43° (lit.[10] mp 44°); yield 37%; the ir spectrum displayed strong absorptions at 6.05 ($C{=}O$) and 6.22 μ ($C{=}C$); nmr 7.59 (d, $J = 15$ Hz), 1 H, $ArCH{=}$), 7.38 (m, 5 H, phenyl), 6.73 (d, $J = 15$ Hz, 1 H, $=CH{-}CO$), 2.61 (t, $J = 7.5$ Hz, 2 H, $-COCH_2$), 1.62–0.64 ppm (multiplet, the remaining protons).

Registry No.—**2a**, 30669-38-6; **2b**, 30669-39-7; **2c**, 30669-40-0; **2d**, 30669-39-7; **2e**, 30669-42-2; **2f**, 30669-43-3; **2g**, 30669-44-4; **2h**, 30669-45-5; 1-(4-methoxyphenyl)-3-one-1-hexene, 30669-46-6; 1-phenyl-3-one-1-nonene, 30669-47-7.

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Electric Discharge Reactions of C_1 to C_3 Hydrocarbons[1a]

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The effects of various electric discharges on simple hydrocarbons have been subjected to extensive investigations.[2] Most of these investigations have been concerned with the formation of the low molecular weight products; methane, ethane, ethylene, and actylene have been formed in almost every reported electric discharge reaction on any hydrocarbon. However, a detailed analysis of the higher molecular weight products have not been reported, although a few individual compounds have been identified.[3]

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[1] (a) Supported by NSF Grant GB-8056. (b) University of California, San Diego.

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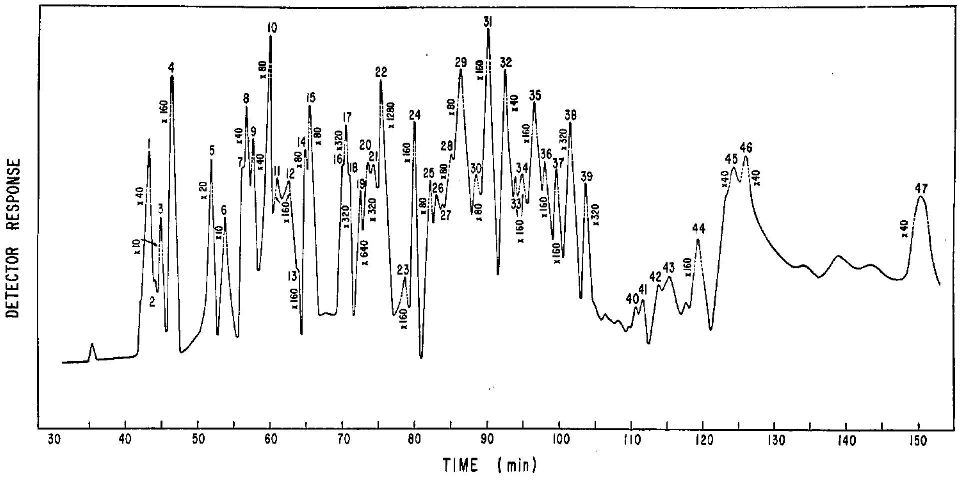

Figure 1.—Gas chromatographic analysis of products not volatile at −78° from ethylene. Varian Model 1200 was used with 10-ft, $^1/_8$-in.-o.d. stainless steel Porapak Q. The column temperature was programmed as follows: isothermal at 40° for 10 min and then 2°/min to a temperature of 250° where it remained isothermal to the end of the run. (a) denotes identification by known gc retention time and mass spectral cracking pattern; (b) by mass spectral cracking pattern; (c) guess based on mass spectral molecular weight. When a formula (*e.g.*, C_5H_6) is given, the mass spectral data indicated a nonaromatic hydrocarbon. When the molecular weight only is given, the mass spectral data were insufficient to determine whether an aromatic ring was present. (1) Vinylacetylene (a); (2) isobutane (a); (3) butadiene (b); (4) butadiyne (a); (5) 2-butyne (b); (6) butatriene (c); (7) 3-methyl-1-butyne (b); (8) cyclopentadiene (a); (9) 1-pentene (b); (10) 3-penten-1-yne (b); (11) 1-pentyne (b); (12) 2-pentyne (b); (13) 2-methyl-1-buten-3-yne (b); (14) 1,2-pentadiyne (b); (15) C_5H_6; (16) C_5H_4; (17) 1-methyl-1-ethylcyclopropane (b); (18) 1,3,5-hexatriene (b); (19) 1-hexene (b); (20) 3-hexene (b); (21) C_6H_8; (22) benzene (a) + 2,3-dimethyl-1,3-butadiene (b); (23) C_6H_{10}; (24) 3-hexene-1,5-diyne (b); (25) 1,3-hexadien-5-yne (b); (26) 1,6-heptadiene (b); (27) 3-ethyl-2-pentene (b); (28) 1-heptyne (b); (29) 3-ethylcyclopentene (b); (30) C_7H_{10}; (31) toluene (a); (32) 1,3,5-cycloheptatriene (b); (33) 2-ocytne (b); (34) 4-octene (b); (35) 1-ocytne (b); (36) xylene (b); (37) mol wt 110; (38) phenylacetylene (a); (39) styrene (a); (40) C_3-benzene (mol wt 120) (c); (41) 2,3-dihydroindene (b); (42) mol wt 118; (43) mol wt 136; (44) indene (a); (45) C_4-benzene (mol wt 132) (c); (46) diethylbenzene (c); (47) naphthalene (a).

We have previously reported the formation of numerous hydrocarbons by high-temperature pyrolysis of simple hydrocarbons[4,5] and have shown that at least some of them were also synthesized during an electric discharge reaction.[4] Since a large number of hydrocarbons are formed by electric discharge reactions of which only a few have been identified, we have attempted to identify most of the compounds from the sparking of C_1 to C_3 hydrocarbons and to show the differences among the various hydrocarbons studied.

Experimental Section

Material.—Methane pure grade was obtained from Phillips Petroluem Co. Lecture bottles of ethane, ethylene, propane, allene, and cyclopropane were obtained from Matheson Co. and were used without further purification. Acetylene was synthesized from calcium carbide and purified on a vacuum line directly before use.

Apparatus.—The electric discharge apparatus consisted of a 3-l. flask in which a pair of movable tungsten electrodes were inserted.[6] The hydrocarbons were introduced into the flask through a vacuum line. The pressure in all runs was approximately 400 mm. The spark source was a spark discharge from Tesla Coil (Cenco no. 80721). During the 6 hr of sparking the vessel was immersed in an ethanol bath maintained between −35 and −20° by adding Dry Ice. The cooling of the walls allowed hydrocarbons having low vapor pressures at these temperatures to accumulate on the walls and not to be subjected to further reactions in the electric discharge. When the reactions was completed the flask was cooled to −78°, and the products volatile at this temperature were saved for analysis. The vessel was then brought to room temperature and the visible liquid at the bottom was distilled overnight into a tube cooled with Dry Ice. The distillation was completed by heating the reaction vessel to 100°. This distilled material was weighed and then sealed in a tube until used for analysis.

The hydrocarbons were identified by combined gas chromatography and mass spectrometry. The gas chromatograph was a Varian Aerograph Model 1200 and a flame ionization detector. The mass spectrometer was a Hitachi Perkin-Elmer Model RMU-6D single focusing instrument. A 10-ft, $^1/_8$-in. stainless steel Porapak Q column was used for the separation. A 4 to 1 splitter divided the column effluent so that 80% of the sample went to the flame ionization detector and 20% went to the mass spectrometer inlet system. A Watson-Biemann helium separator served to enrich the sample and reduce the pressure at the mass spectrometer inlet.[7] The identifications of some hydrocarbons are based on the comparison of the known and unknown on the gc–ms instrument. Others are based on the literature mass spectrometer patterns.[8] Some identifications are based on only the mass numbers and guesses of the cracking pattern. The method of identification is indicated in the figure legends. The identifications of benzene, toluene, styrene, phenylacetylene, indene, and naphthalene were confirmed by their uv spectra.

Results and Discussion

The action of electric discharges on ethane, ethylene, propane, allene, and cyclopropane produces about the same end products with similar distribution. As an example, Figure 1 gives the gas chromatogram obtained after ethylene was subjected to an electric discharge generated by a spark type discharge from a Tesla coil. Acetylene and methane give a significantly different distribution of products. In the case of acetylene, the gas chromatogram obtained contained fewer peaks which were mainly benzene, toluene, phenylacetylene, and styrene. In addition, there was a large quantity of tar, indicating that acetylene polymerizes rapidly in the discharge rather than forming ions or radicals which reform to small molecules. In the case of methane, the situation is reversed, with more products

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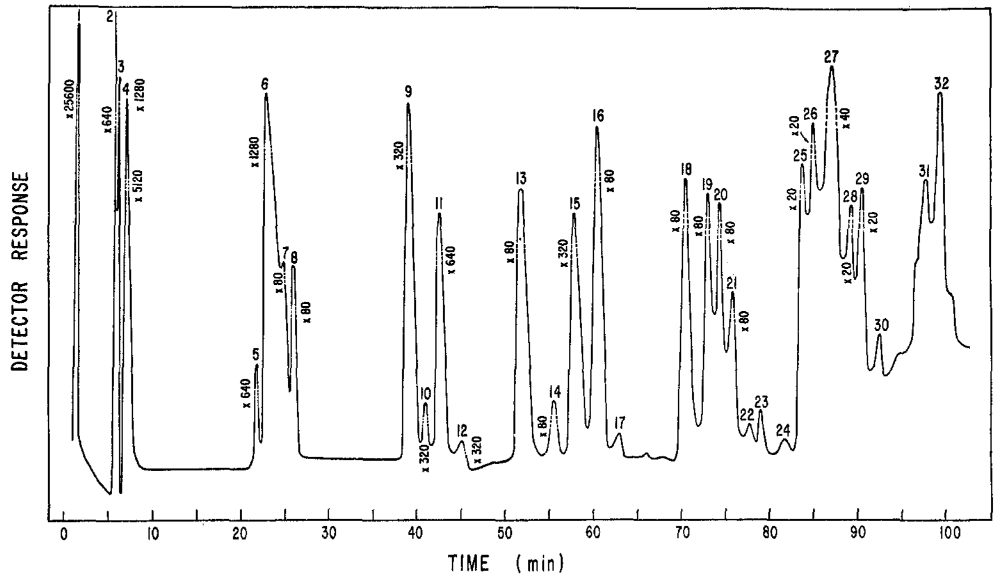

Figure 2.—Gas chromatographic analysis of products volatile at room temperature from sparking methane. Varian Model 1200 was used with 10-ft, $^1/_8$-in.-o.d. stainless steel Porapak Q. The column temperature was programmed as follows: isothermal at 40° for 10 min and then 2°/min to the end of the run. (1) Methane (a); (2) ethylene (a); (3) acetylene (a); (4) ethane (a); (5) propene (b); (6) propane (a); (7) propyne (b); (8) allene (a); (9) isobutane (a); (10) 2-butene (b); (11) butane (a); (12) butadiyne (a); (13) neopentane (b); (14) C_5H_{10}; (15) isopentane (a); (16) methylcyclobutane (b); (17) C_5H_{10}; (18) 2,2-dimethylbutane (a); (19) isohexane (a); (20) 3-methylpentane (a); (21) mol wt 84; (22) benzene (a); (23) cyclohexane (a); (24) C_7H_{16}; (25) C_7H_{16}; (26) C_7H_{16}; (27) C_7H_{16}; (28) C_7H_{16}; (29) C_7H_{16}; (30) toluene (a); (31) mol wt 112; (32) mol wt 114.

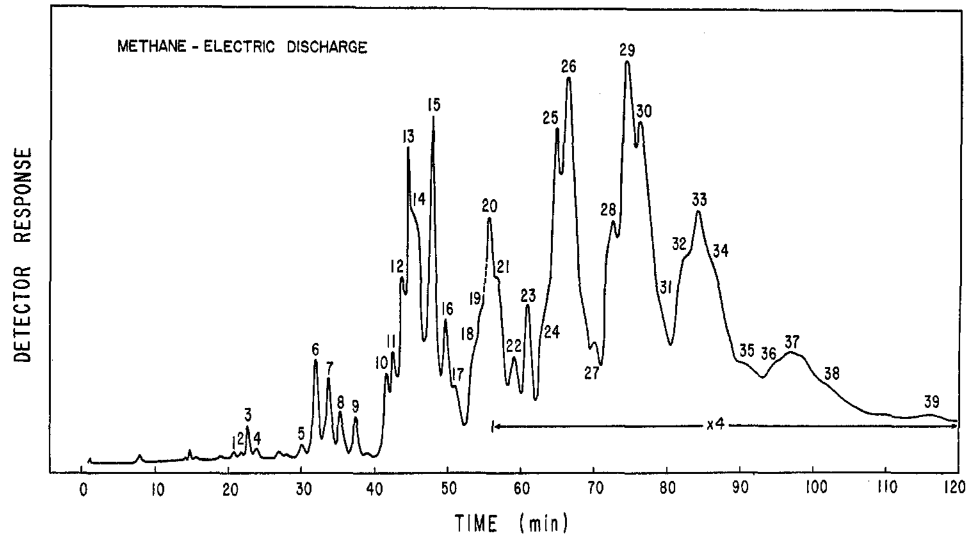

Figure 3.—Gas chromatographic analysis of products nonvolatile at −78° from sparking methane. Varian Model 1200 was used with 10-ft, $^1/_8$-in.-o.d. stainless Porapak Q. The column temperature was programmed as follows: isothermal for 5 min and then 8°/min for 10 min, followed by 2°/min to a temperature of 250° where it remained isothermal to the end of the run. (1) Isobutane (a); (2) 1-butene (b); (3) butane (a); (4) butadiyne (a); (5) 3-methyl-1-butene (b); (6) isopentane (a); (7) 1-pentene (b); (8) 3-penten-1-yne (b); (9) cyclopentadiene (a); (10) 2,2-dimethylbutane (a); (11) 2-ethyl-1-butene (b); (12) isohexane (a) + 1-methylcyclopentene (b); (13) 2-methyl-1-pentene (b) + 3-methylpentane (a); (14) 3-methyl-2-pentene (b); (15) benzene (a) + 2-methyl-1,3-pentadiene (b); (16) 2-hexyne (b); (17) mol wt 98; (18) mol wt 100, 98, 96; (19) mol wt 98; (20) 5-methyl-1-hexyne (b) + mol wt 100, 98; (21) mol wt 98; (22) mol wt 96; (23) toluene (a); (24) mol wt 112, 110, 108, 106; (25) mol wt 114, 112, 110, 108, 106; (26) mol wt 114, 112, 110, 108, 106; (27) mol wt 114; (28) phenylacetylene (a) + ethylbenzene (b); (29) styrene (a) + mol wt 126, 124; (30) mol wt 128; (31) mol wt 128; (32) C_3-benzene (mol wt 120) (c) + mol wt 140, 138, 136, 134, 132; (33) mol wt 142; (34) mol wt 142; (35) indene (a); (36) mol wt 156; (37) mol wt 156; (38) mol wt 156; (39) naphthalene (a).

being obtained than with the C_2 and C_3 hydrocarbons. In fact, a substantial fraction of the possible hydrocarbons of 5 and 6 carbons without strained rings were identified. This is clearly demonstrated by listing of compounds at the bottom of Figures 2 and 3.

The distillable compounds not volatile at −78° accounted for 13, 4, 6, 6, 16, 8, and 24% of the initial methane, ethane, ethylene, acetylene, propane, cyclopropane, and allene, respectively. The compounds found in the gc–ms analysis accounted for 10–50% of the distillable material. The remainder of the distilled material consists of compounds of longer retention time and material that polymerized in the collection tube. Considerable amounts of a brown polymer were observed in the collection tube, especially with the acetylene. Some oxidation may have occurred in the collection tube during the short periods that it was exposed to air.

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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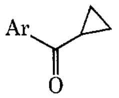
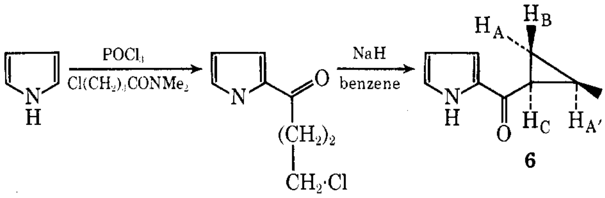
Cyclopropyl ketones in which the cyclopropylcarbonyl group is bonded directly to a heterocyclic ring (either unsaturated or fully reduced) are few. From among the common six-membered heterocycles the 2-[1] and 3-pyridyl[2] compounds (**1** and **2**, respectively) appear to provide the only examples. 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



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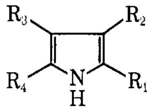
6



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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