agent from 58 g. (0.33 mole) of 1-bromo-2-heptyne was prepared as previously described.[25] Gaseous formaldehyde was prepared by the thermal decomposition of 60 g. of paraformaldehyde. The reaction product of the formaldehyde with the Grignard reagent was hydrolyzed with ammonium chloride solution, the ether layer washed with sodium bisulfite and dried. Distillation yielded 69 g. of liquid boiling from 75–88° at 3 to 1 mm. pressure, n_D^{25} 1.4645–1.4630. Redistillation yielded 32 g. (76% yield) of the allenic alcohol, b.p. 57° at 0.6 mm. n_D^{25} 1.4686.

Anal. Calcd. for $C_8H_{14}O$: C, 76.1; H, 11.2. Found: C, 76.1; H, 11.8.

Its *3,5-dinitrobenzoate* (Comp. 36) was crystallized from petroleum ether (b.p. 30–60°) to a constant melting point of 36–37°.

Anal. Calcd. for $C_{15}H_{16}N_2O_6$: C, 56.2; H, 5.0. Found: C, 56.2; H, 5.4.

When a sample of it was mixed 3,5-dinitrobenzoate derived from 3-octynol-1[46] a ten degree melting point depression was noted.

2,2-Dimethyl-4-butyl-4,5-hexadiene-3-ol (Comp. 37) was prepared by the Reformatsky reaction using 18 g. (0.28 gram-atom) of freshly sanded zinc strips, 44 g. (0.25 mole) of 1-bromo-2-heptyne and 24 g. (0.3 mole) trimethylacetaldehyde, and a mixture of ether, benzene, tetrahydrofurane, and dioxane as solvents. The reaction started during the removal of ether by distillation. The reaction product was hydrolyzed by pouring it on a mixture of ice and acetic acid. The products were dissolved in ether and the ether solution washed with sodium carbonate. Distillation yielded 24.7 g. (66% yield) of product boiling from 76–84° at 2 mm., n_D^{25} 1.4551–1.4547, and 12 g. of higher boiling liquids.

Anal. Calcd. for $C_{12}H_{22}O$: C, 79.1; H, 12.2. Found C, 79.1; H, 12.5.

Infrared analysis showed the fraction, b.p. 82° at 2 mm., n_D^{25} 1.4550 to be the allenic alcohol contaminated with some of its acetylenic isomer, $C_4H_9C{\equiv}CCH_2CHOH{-}C(CH_3)_3$ (very weak C≡C band at 2200 cm.$^{-1}$).

2,2-Dimethyldeca-4,5-dien-3-one. (Comp. 44). The mixture of Comp. 37 and its acetylenic isomer (7 g., 0.038 mole) was dissolved in 20 ml. of acetone, cooled to −4°, and oxidized by the addition of 3.3 g. (0.033 mole) of chromium trioxide in a solution of 2.8 ml. of sulfuric acid and 20 ml. of water.[47] The temperature was kept under 5° by external cooling. The reaction product was continuously extracted with ether for 12 hr. The ether extract was washed with a small portion of water and dried. Evaporation of the ether left 7.6 g. of a residue which upon distillation yielded 3.1 g. of product, b.p. 88–91° at 0.7 mm., n_D^{25} 1.4504–1.4495.

Anal. Calcd. for $C_{12}H_{20}O$: C, 79.9; H, 11.2. Found: C, 77.9; H, 12.5.

Spectroscopic analysis showed that the allenic alcohol was destroyed by the oxidation and that the distillate was a mixture of the starting acetylenic alcohol and its oxidation product, $C_4H_9C{\equiv}C{-}CH_2{-}CO{-}C(CH_3)_3$. To 1 g. of this mixture in 10 ml. of ethanol was added 20 ml. of 5% aqueous sodium carbonate.[48] The mixture was agitated at 50° under nitrogen for 24 hr., and then extracted with ether. Distillation yielded Comp. 44, b.p. 65° at 0.8 mm., n_D^{25} 1.4523.

2-Methyl-2-chloro-3-pentyne. Into a solution of 151 g. (1.5 moles) of 2-methyl-3-pentynol[49] (prepared in 39% yield by the condensation of propynylmagnesium bromide and acetone, b.p. 55° at 25 mm., n_D^{18} 1.4438) in 400 ml. of dry petroleum ether (b.p. 30–60°) containing 2 g. of hydroquinone and 60 g. of powdered calcium chloride, was passed anhydrous hydrogen chloride.[50]

The temperature was kept at 0°. The solution was treated with solid anhydrous potassium carbonate, filtered and distilled, yielding 120 g. (67% yield), b.p. 55° at 70 mm., n_D^{25} 1.4475. Its infrared spectrum contained the C≡C stretching frequency at 2210 cm.$^{-1}$ and was void of absorption bands in the double bond absorption region. Attempted preparation of the chloride as described by Zakharova[49] or by using thionyl chloride gave impure products.

2-Methyl-2,3-pentadiene (Comp. 51) was prepared by the dehalogenation[6,22] of 38 g. (0.33 mole) of 2-methyl-2-chloro-3-pentyne using 14 g. (0.37 mole) of lithium aluminum hydride in 1000 ml. of dry dioxane. Upon distillation, 4.7 g. (18% yield), b.p. 70–72°, n_D^{25} 1.4285, of the allene was isolated. Its infrared and Raman effect analyses revealed the presence of less than 20% of its acetylenic isomer, $(CH_3)_2CH{-}C{\equiv}C{-}CH_3$.[51]

Tetraphenylallene (Comp. 54) was prepared by the dehydrohalogenation of 213 g. (0.5 mole) of 2-bromo-1,1,3,3-tetraphenylpropene[52] (prepared by Wen-Yang Wen) using 100 g. of potassium hydroxide in 500 ml. of refluxing alcohol. From 190 g. of the crude product, 90 g. (53% yield) of the pure allene, m.p. 164–165°, was obtained by crystallization from acetone. Its infrared spectrum contains a band at 1920 cm.$^{-1}$, which is due, however, to the phenyl ring. Its Raman effect[2] analysis revealed a weak line at 1938 cm.$^{-1}$ due to the allene. Because of the large amount of light scattering which caused a heavy background on the Raman plate, it was impossible to establish the exact intensity of the bands.

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[CONTRIBUTION FROM DEPAUW UNIVERSITY AND THE INDIANA STATE BOARD OF HEALTH]

A Study of the Infrared Spectra of Some Alkyl-Substituted Carbostyrils

D. J. COOK, R. S. YUNGHANS, T. R. MOORE, AND B. E. HOOGENBOOM

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The infrared spectra of several substituted carbostyrils are presented and discussed.

Characteristic absorption bands originating in the out-of-plane deformation vibrations of the hydrogen atoms on an aromatic ring have been found to appear in the infrared spectrum between 1225 and 650 cm.$^{-1}$ Well established correlations between the positions of these bands and various types of aromatic substitution compounds have made possible the identification of isomeric compounds in many cases.

Although phenyl ring generalizations can be applied to heterocyclic aromatics such as quinoline and pyridine,[1] all interpretations of infrared spectra of this type substance must be made with some caution until spectra of known compounds are established. For the past several years a number of studies in this laboratory have been concerned with the properties of alkyl substituted carbostyrils. Except for a few reports[2,3] the infrared spectra of carbostyrils or 2-quinolones have not been studied nor interpreted. It is the purpose of this article to record the infrared spectra of a number of these compounds and to correlate the observed bands in the 1000 to 650 cm.$^{-1}$ region with the structures of the molecules. The preparation of the substituted carbostyrils has already been described.[4,5] In this study two new compounds have been prepared, 1,4,6-trimethylcarbostyril and a compound which, from an interpretation of its infrared spectrum, has been assigned the structure of 1,4,7-trimethylcarbostyril. These two compounds were prepared by the action of diketene on *p*-N-methyltoluidine and *m*-N-methyltoluidine. In the reaction of diketene on the latter and subsequent ring closure in concentrated sulfuric acid, two compounds, 1,4,5- and 1,4,7-trimethylcarbostyril, are possible. Previous studies on quinoline compounds have shown that generally steric influences have favored the formation of a 4,7-substituted compound over its 4,5-isomer. A study of the spectra plus confirming chemical data has indicated that 1,4,7-trimethylcarbostyril is the isomer formed in this case.

Discussion of the spectra. The spectra were obtained on carbon disulfide solutions in a 0.098-mm. cell, except for one (A) which is a composite of a carbon tetrachloride solution up to 1300 cm.$^{-1}$ and a carbon disulfide solution the remainder of the spectrum. A rock salt plate was in the reference beam. The instrument, a Baird Associates, was run on slow scan through the entire region of interest. Solute concentrations were approximately 50 mg./ml. except 1,4-dimethyl, and 1,4,6- and 1,4,7-trimethylcarbostyrils which were saturated solutions. The spectra are recorded in Fig. 1 along with the spectrum of carbon disulfide for comparison purposes. Significant bands were accurately measured and the relative intensities were given to bands based on the strong band appearing at 13.4 μ in the spectra A through F and the strong band at 12.4 μ in G and H. In Table I the following designations are made for intensities. The letters v s

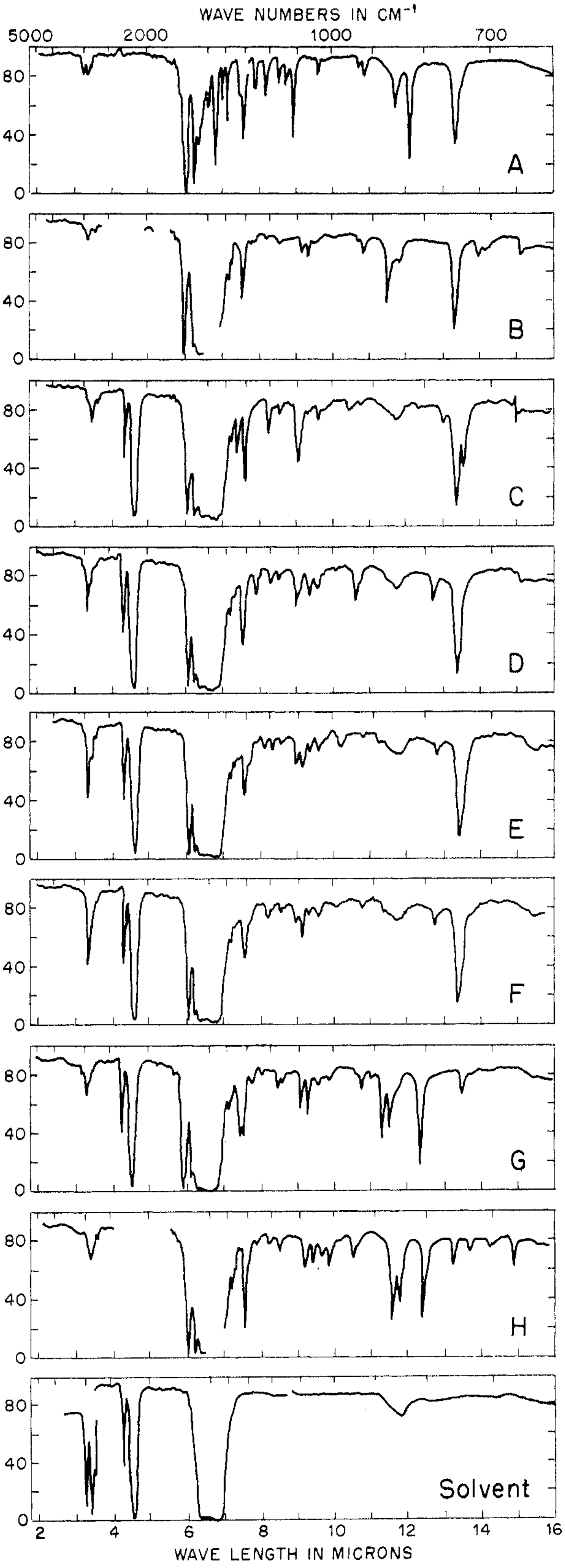

FIG. 1

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are given those bands whose intensity is greater than that of the 13.4 μ or 12.4 μ bands, s when intensity is equal to 13.4 μ or 12.4 μ bands, m when two thirds to one third the intensity of the strong band, w when the intensity is one third to one fourth that of the strong band and v w when less than one fourth the intensity of the strong band. A study of the spectrum of carbon disulfide in Fig. 1 will show that the sharp bands at 4.2 μ and 4.6 μ and the broad bands at approximately 6.3 μ to 7.2 μ and near 11.7 μ are solvent bands.

TABLE I

SIGNIFICANT ABSORPTION BANDS FOR ALKYL CARBOSTYRILS

		Lactam Vibrations		H-Deformation Vibrations		N-Alkyl Vibration (?)	
Carbostyril		Microns	Wave Nos.	Microns	Wave Nos.	Microns	Wave Nos.
N-Methyl	(A)	6.04	1656 v s	11.74	852 m	7.65	1307 m
				12.12	825 v s		
				13.35	749 s		
1,4-Dimethyl	(B)	6.05	1653 v s	11.53	867 m	7.62	1312 m
				13.35	749 s		
1,3,4-Trimethyl	(C)	6.12	1634 v s	13.03	767 v w	7.62	1312 m
				13.39	747 s		
				13.60	735 w		
1,4-Dimethyl-3-ethyl	(D)	6.12	1634 v s	12.75	784 v w	7.62	1312 m
				13.39	747 s		
1,4-Dimethyl-3-propyl	(E)	6.12	1634 v s	12.79	781 v w	7.62	1312 m
				13.40	746 s		
1,4-Dimethyl-3-butyl	(F)	6.12	1634 v s	12.77	782 v w	7.62	1312 m
				13.40	746 s		
1,4,6-Trimethyl	(G)	6.03	1658 v s	11.39	879 m	7.62	1312 m
				11.59	862 m		
				12.41	806 s		
1,4,7-Trimethyl	(H)	6.03	1658 v s	11.56	865 s	7.58	1319 v s
				11.75	853 m		
				12.40	806 s		

In all spectra the lactam band falls between 1658 and 1634 cm.$^{-1}$ as previously reported.[2] Substitution in the hetero ring appears to decrease the frequency of the vibration, while substitution in the homocyclic ring appears to increase the frequency. There is a medium band common to all spectra between 1307 and 1319 cm.$^{-1}$ which is possibly due to the N-alkyl group in each molecule. The spectra of carbostyrils made in this laboratory which have no substituent on the nitrogen do not show this absorption peak. In all the compounds where methyl substitution is only in the hetero ring, it is to be noted that a strong band appears between 746 and 749 cm.$^{-1}$ and in the compounds with a methyl substituent in the 6 or 7 positions no strong band appears in this region. The position and intensity of this band can be identified as due to the four adjacent hydrogens in the homocyclic ring. In the spectrum for N-methylcarbostyril (A) another strong band appears at 825 cm.$^{-1}$ which, based on literature information[1] as to position and intensity, can be recognized as due to the vibration of the two adjacent hydrogens in the heterocyclic ring. The medium intense 852 cm.$^{-1}$ band for the compound is anomalous. In the spectrum for 1,4-dimethylcarbostyril (B) a medium intense band appears at 867 cm.$^{-1}$ and can be assigned to the vibration arising from the one hydrogen of the heterocyclic ring. The spectra, C, D, E and F, are those of compounds with substituents on the 1, 3, and 4 positions and which show only one strong absorption peak at 746–747 cm.$^{-1}$. These spectra establish this peak as due to the vibration of the four adjacent hydrogens in the homocyclic ring.

An inspection of the spectrum for the known compound 1,4,6-trimethylcarbostyril (G) shows a strong band at 806 cm.$^{-1}$ which can be assigned to the vibration of the two hydrogens in the homocyclic ring while medium intense bands appearing at 862 and 879 cm.$^{-1}$ can be due to the single hydrogen atoms in the homocyclic and heterocyclic rings. Since both of these bands fall in the region indicative of one unsubstituted hydrogen, no attempt has been made to decide which one is more significant. The similar spectrum of the compound assigned the 1,4,7-trimethylcarbostyril structure (H) plus the lack of any medium intense band in the 725–680 cm.$^{-1}$ region, which would be indicative of the presence of three adjacent hydrogens, appears sufficient evidence to assign this compound a structure containing two and one unsubstituted hydrogens and not three adjacent hydrogens as would be found in the isomer 1,4,5-trimethylcarbostyril.

That the evidence given by the infrared data is correct was supported by the following chemical study. When the compound believed to be 1,4,7-trimethylcarbostyril was oxidized with selenium dioxide, the 4-formyl derivative was formed which was further oxidized with dichromate and acid to 1,7-dimethyl-4-carboxycarbostyril. Decarboxylation of this product led to a substance which melted at 105–107°. This agrees with the reported melting point for 1,7-dimethylcarbostyril.[6]

EXPERIMENTAL[7]

The 1,4-dimethyl and 1,3,4-trimethylcarbostyrils have been previously reported.[4,6] 1,4,6- and 1,4,7-Trimethylcarbostyrils are new compounds and were prepared by the action of diketene on *p*-N-methyltoluidine and *m*-N-methyltoluidine. The description of the preparation of one of these compounds follows.

1,4,6-Trimethylcarbostyril. A mixture of 33.9 g. (0.28 mole) of *p*-N-methyltoluidine and 50 ml. of benzene was heated to reflux. Diketene (34.5 g., 0.41 mole) was added dropwise over a period of 3 hr. The benzene was removed under reduced pressure and the residue poured into 100 ml. of concentrated sulfuric acid in 5-ml. portions so as to keep the temperature below 70°. The sulfuric acid mixture was then heated on the steam bath for 15 min. This mixture was then poured into 1 l. of ice water and neutralized with solid sodium hydroxide. After standing overnight the solid was collected and crystallized from ethanol. A recrystallization of the product from ethanol-water gave a white product melting at 106–107°. The yield was 90%.

Anal. Calcd. for $C_{12}H_{13}NO$: N, 7.48. Found N, 7.17.

1,4,7-Trimethylcarbostyril. This compound was prepared in an exactly analogous manner starting with *m*-N-methyltoluidine. The yield was 93.5% and the compound melted at 103–104°. No other compound was isolated. This compound and 1,4,6-trimethylcarbostyril are both prone to retain large quantities of alcohol from the solvent, and constant melting points can be obtained only after lengthy drying in vacuum over anhydrous calcium chloride.

Anal. Calcd. for $C_{12}H_{13}NO$: N, 7.48. Found: N, 7.15.

1,6-Dimethyl-4-formylcarbostyril. This compound was obtained (38% yield) as lemon-yellow needles, m.p. 181–183°, by a method previously described.[8]

Anal. Calcd. for $C_{12}H_{11}NO_2$: N, 6.96. Found: N, 7.21.

1,7-Dimethyl-4-formylcarbostyril. This compound was obtained (69% yield) as orange-yellow needles, m.p. 185–187°, by a method described earlier.[8]

Anal. Calcd. for $C_{12}H_{11}NO_2$: N, 6.96. Found: N, 6.91.

1,6-Dimethyl-4-carboxycarbostyril. A mixture of 8 g. (0.039 mole) of 1,6-dimethyl-4-formylcarbostyril and 3.51 g. of sodium dichromate (0.0134 mole) was suspended in 100 ml. water and mixed with a mechanical stirrer. Thirteen and one-tenth g. of concentrated sulfuric acid was added dropwise. After addition was complete the mixture was heated on the steam bath for 30 min. After cooling in ice the solid was collected and dissolved in 22 ml. of a 5% sodium hydroxide solution and filtered. Upon acidification of the filtrate with hydrochloric acid, 19.8 g. (61%) of the product was obtained. Recrystallization of a sample from ethanol and water gave pale yellow crystals which charred at 270° and decomposed at 290–295°.

Anal. Calcd. for $C_{12}H_{11}NO_3$: N, 6.45; Neut. equiv., 217. Found: N, 6.70; Neut. equiv., 220.

1,7-Dimethyl-4-carboxycarbostyril. This compound was prepared in a manner analogous to that described above. The substance decomposed at 238–240°.

Anal. Calcd. for $C_{12}H_{11}NO_3$: N, 6.45. Found: N, 6.78.

1,7-Dimethylcarbostyril. A 2.4-g. sample (0.011 mole) of 1,7-dimethyl-4-carboxycarbostyril was ground with 1.5 g. of soft glass and placed in a small distilling flask. The flask was left open to the air and heated in a Wood's metal bath at a temperature of 300–350° for 24 hr. At the end of this time the liquid was distilled under a pressure of 2 mm. The red-orange distillate solidified on cooling and was recrystallized from 15 ml. petroleum ether (35–60°) containing a few drops of benzene to bring the product into solution. A m.p. was 87–97°. A vacuum sublimation of this substance gave pale yellow needles, m.p. 105–107°. The reported m.p. is 107–108°.[6]

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OHIO UNIVERSITY]

Fulvenes. III. Heat of Combustion and Resonance Energy[1]

JESSE H. DAY AND CHARLES OESTREICH[2]

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The heats of combustion and the calculated resonance energies are reported for dimethylfulvene and diphenylfulvene. The reported values are consistent with the known properties of the fulvenes.

Although the fulvenes have been known for more than half a century[3] and many theoretical calculations made of the resonance energy of fulvene,[4] no experimental data for the estimation of resonance energies have appeared. This paper reports the heats

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[2] Present address, Department of Chemistry, Virginia Military Institute.

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