over-all reaction can be represented by the following scheme, using benzene as the chain transfer agent.

$$C_6H_5Li + C_2H_4 \longrightarrow C_6H_5CH_2CH_2Li \qquad (11)$$

$$C_6H_5CH_2CH_2Li + (n - 1)C_2H_4 \longrightarrow C_6H_5(CH_2CH_2)nLi \qquad (12)$$

$$C_6H_5(CH_2CH_2)_nLi + C_6H_6 \longrightarrow C_6H_5(CH_2CH_2)_nH + C_6H_5Li \qquad (13)$$

It should be emphasized that the amine component must be strongly coordinated with the organolithium compound throughout the reaction since neither the transmetalation steps nor the addition to ethylene occurs in hydrocarbon solvents in its absence. Coordination with the lithium has the effect of diffusing the polarizing power of the metal atom and thus weakening the carbon–lithium bond. In this manner, the carbanion is rendered more independent of the lithium and consequently more reactive. The existence of the carbanion as a discrete species is highly unlikely, however, and ion pairs or partially covalently bonded species are suggested.

In the reaction sequence suggested above, the initial transmetalation (eq. 10) is fast and irreversible as demonstrated by independent studies of the transmetalation of butyllithium to aromatic hydrocarbons in the presence of the amines. The chain-transfer step (eq. 13) is analogous to eq. 10 and would be expected to proceed at a similar rate. Likewise, the propagation step (eq. 12) must be rapid since the over-all chain life is dependent upon the rate of the competitive chain-transfer reaction. Thus, the initial addition of ethylene to the aromatic carbanion (eq. 11) must be the rate-controlling step. This is to be expected on the basis of energy considerations alone, since the aromatic carbon–lithium bond is transformed to an energetically less favorable aliphatic carbon–lithium bond.

Unlike the rate of chain transfer (eq. 13), the propagation rate (eq. 12) is dependent upon the ethylene pressure. The average number of ethylene units ($\bar{n}$) incorporated into the telomer product is therefore a function of the ethylene partial pressure for a given system. In particular, it depends on the ratio (β) of rate of chain transfer to rate of propagation where

$$\bar{n} = \frac{1 + \beta}{\beta}$$

The value of β may be readily determined experimentally by comparing the relative mole fractions of the telomer product at any successive values of n and

$$\beta = \frac{N_n}{N_{(n+1)}} - 1$$

the value of β determined in this manner may be used to calculate mole fraction of product at all values of n.

$$N_n = \frac{\beta}{(1 + \beta)^n}$$

The observed product distributions were in excellent agreement with the calculated values. The values of β for various aromatic reactants under equivalent conditions (Table III) reflect the transmetalation rates particular to the aromatic hydrocarbon involved.

Acknowledgment.—The authors wish to thank Mr. W. R. Davis for his technical assistance in carrying out the experimental work. The investigations of the Analytical Department of Sun Oil Company, particularly of Dr. D. Barmby and Mr. R. Warren, are gratefully acknowledged. We also wish to thank the Sun Oil Company for permission to publish this research.

The Reactions of 1,1-Di(1-piperidinyl)ethylene with Isocyanates and Isothiocyanates

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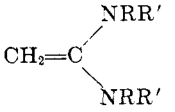
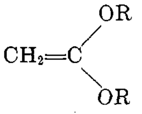
1,1-Di(1-piperidinyl)ethylene reacts with 1 or 2 moles of alkyl or aryl isocyanates and isothiocyanates to produce monoamide-, diamide-, and thioamide-substituted diaminoethylenes. The latter derivatives, as well as dipiperidinylethylene itself, react with acids and alkyl halides to give the corresponding substituted amidinium salts. Some implications of the nuclear magnetic resonance spectra with regard to the electronic structure of the various substituted diaminoethylenes and amidinium salts are discussed.

The structural relationship of the 1,1-diaminoethylenes (I) (vinylidenediamines, enediamines) to the ketene acetals[1] (II) and the enamines[2] (III) prompted a study of the reactions of these compounds with various electrophilic reagents. It had been suggested some time ago[1] that compounds of type I would show enhanced nucleophilic reactivity compared to the ketene acetals, but preparative difficulties precluded an early demonstration of this proposal. Thus, McElvain and Tate[3] did not recognize the ready availability of 1,1-di(1-piperidinyl)ethylene from the reaction of piperidine with ketene diethylacetal.[4] Similarly, Arens and Rix[5] reported that the reaction of diethylamine with ethoxyacetylene gave only a low yield of impure 1,1-bis(diethylamino)ethylene. More recent work[6] has shown that high yields of dipiperidinylethylene can be obtained from ethyl orthoacetate and piperidine under carefully controlled conditions.



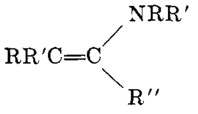
$CH_2{=}C(NRR')(NRR')$

I



$CH_2{=}C(OR)(OR)$

II



$RR'C{=}C(NRR')(R'')$

III

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(1) S. M. McElvain, *Chem. Rev.*, **45**, 453 (1949).

(2) J. Szmuszkowicz in "Advances in Organic Chemistry, Methods and Results," Vol. 4, Interscience Publishers, Inc., New York, N. Y., 1963.

(3) S. M. McElvain and B. E. Tate, *J. Am. Chem. Soc.*, **67**, 202 (1945).

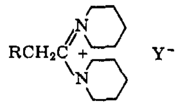
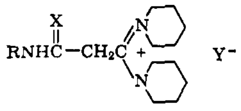
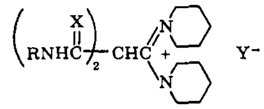
(4) H. Böhme and F. Soldan, *Chem. Ber.*, **94**, 3109 (1961).

(5) J. F. Arens and Th. R. Rix, *Koninkl. Ned. Akad. Wetenschap. Proc.*, **57B**, 270 (1954).

(6) H. Baganz and L. Domaschke, *Chem. Ber.*, **95**, 2095 (1962).

Table I

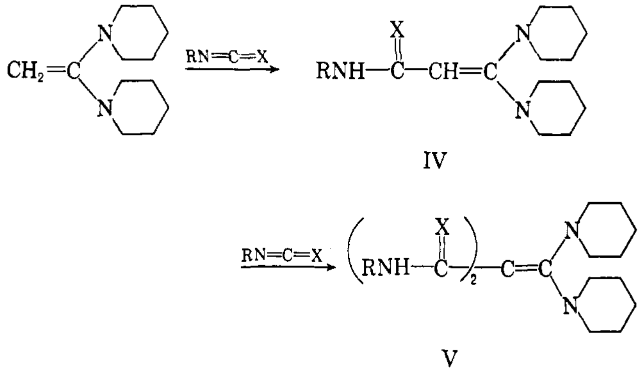
N.m.r. Spectra Associated with Amidinium Salt α-Protons

Compd. type	No.	R	Y	X	Position
	1	CH_3	I	. . .	7.23 (quadruplet)
	2	C_2H_5	I	. . .	7.18 (triplet)
	3	H	$OC_6H_2N_3O_6$	. . .	7.46
	4	C_6H_5	$OC_6H_2N_3O_6$	S	5.33
	5	C_2H_5	$OC_6H_2N_3O_6$	S	5.58
	6	C_2H_5	ClO_4	S	5.81
	7	C_6H_5	Cl	S	5.00
	8	2,5-$Cl_2C_6H_3$	Cl	O	5.20
	9	C_2H_5	$OC_6H_2N_3O_6$	S	3.45
	10	C_2H_5	ClO_4	S	4.44

Recently, both Brannock[7] and Hasek[8] have illustrated the expected similarity in the reactivity of I, II, and III with certain electrophilic olefins in some interesting cycloaddition reactions. The work of Berchtold,[9a] Clemens,[9b] and Hünig[9c] has established the role of isocyanates and isothiocyanates as electrophilic reagents in reactions with enamines (III).

In the present work we have extended the synthesis of Arens and Rix from ethoxyacetylene and shown that it can be used to prepare dipiperidinylethylene in excellent yield. With this starting material readily available, we have examined its reaction with isocyanates and isothiocyanates, as well as with acids and alkyl halides, to produce a series of substituted diaminoethylenes and amidinium salts which are not readily accessible by other means.

Reactions with Isocyanates and Isothiocyanates.—Dipiperidinylethylene reacts smoothly with both alkyl and aryl isocyanates and isothiocyanates to form the mono- (IV) and diadducts (V). The synthesis of the mixed diadduct from phenyl isocyanate and phenyl isothiocyanate was carried out by both of the two possible routes. The fact that the identical product was obtained by both routes lends support to the structure V and eliminates possible structures resulting from attack of the second mole of reagent at the hetero atom, X. In this respect, the course of the reaction parallels that of simple enamines with 2 moles of isocyanate,[9a] except that in the present case both moles of reagent attack the same carbon atom.



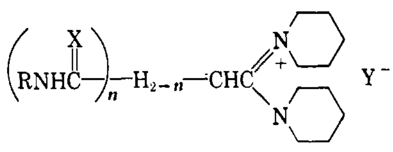
IV

V

Hydrolysis of the phenyl isocyanate monoadduct (IV, R = C_6H_5; X = O) readily gave a product whose elemental analysis agreed with that for N-pentamethylene-N′-phenylmalonamide. This product was identical with the compound obtained by stepwise aminolysis of diethyl malonate with aniline and piperidine, according to a procedure suggested by the work of Chattaway and Olmstead.[10]

On the other hand, the phenyl isocyanate diadduct (V, R = C_6H_5; X = O) was quite stable towards hydrolysis, being unaffected by refluxing overnight with aqueous sodium hydroxide.

Reactions with Acids and Alkyl Halides.—Dipiperidinylethylene and its mono- (IV) and diadducts (V) react readily with acids to form a series of substituted amidinium salts (VI). The perchlorate salts are particularly easy to prepare since they crystallize in analytically pure form on titration of the parent compound with 0.1 *N* perchloric acid in acetic acid.



VI

The behavior of these salts with aqueous base is interesting. The hydrochlorides of the monoadducts undergo the expected reaction, namely hydrolysis of the amidinium portion of the molecule to give a substituted malonamide, but the salts of the diadducts react by removal of a proton from the α-position to regenerate the parent compounds, which are quite insensitive to hydrolysis.

Dipiperidinylethylene reacts readily with alkyl halides to form the corresponding alkyl substituted amidinium salts. The phenyl isocyanate monoadduct (IV, R = C_6H_5; X = O) also reacts with methyl iodide in hot acetonitrile to yield the substituted amidinium salt. Under the latter conditions, the diadduct (V, R = C_6H_5; X = O) failed to react.

Nuclear Magnetic Resonance Spectra.—The n.m.r. spectra of the amide-substituted diaminoethylenes and

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[7] K. C. Brannock, R. D. Burpitt, and J. G. Thweatt, *J. Org. Chem.*, **28**, 1697 (1963).

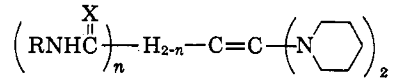
[8] R. H. Hasek, P. G. Gott, R. H. Meen, and J. C. Martin, *ibid.*, **28**, 2496 (1963).

[9] (a) G. A. Berchtold, *ibid.*, **26**, 3043 (1961); (b) D. H. Clemens and W. D. Emmons, *ibid.*, **26**, 767 (1961); (c) S. Hünig, K. Huebner, and E. Benzing, *Chem. Ber.*, **95**, 926 (1962).

[10] F. Chattaway and J. Olmstead, *J. Chem. Soc.*, 938 (1910).

TABLE II

CARBAMYL-SUBSTITUTED DIAMINOETHYLENES OF THE GENERAL FORMULA[a]



R	X	n	Yield, %	M.p., °C.	Formula	Prep. solvent	Recryst. solvent
C_6H_5-	S	1	86	(See text)	$C_{19}H_{27}N_3S$	(See text)	(See text)
C_2H_5-	S	1	28	113.5–115	$C_{15}H_{27}N_3S$	Toluene	Ethanol–water
C_6H_5-	O	1	90	163–165 dec.	$C_{19}H_{27}N_3O$	Ether	Toluene
3,4-$Cl_2C_6H_3$	O	1	94	134–136 dec.	$C_{19}H_{25}Cl_2N_3O$	Ether	Acetone
2,5-$Cl_2C_6H_3$	O	1	...	132–133	$C_{19}H_{25}Cl_2N_3O$	Ether	Isopropyl alcohol
C_6H_5	S	2	90	151–152 dec.	$C_{26}H_{32}N_4S_2$	Tetrahydrofuran	Acetonitrile
C_2H_5	S	2	60	187–189 dec.	$C_{18}H_{32}N_4S_2$	Toluene (reflux)	Toluene
C_6H_5	O	2	87	220–222 dec.	$C_{26}H_{32}N_4O_2$	Ether	Dimethylformamide
C_2H_5	O	2	58	188–190	$C_{18}H_{32}N_4O_2$	Ether	Toluene
3,4-$Cl_2C_6H_3$	O	2	89	201–236 dec.	$C_{26}H_{28}Cl_2N_4O_2$	Ether	Toluene
2,5-$Cl_2C_6H_3$	O	2	83	237–238	$C_{26}H_{28}Cl_2N_4O_2$	Ether	Tetrahydrofuran–toluene

[a] Complete elemental analyses were run on all compounds in this table and all were in good agreement with theory.

their salts were determined in $CDCl_3$ or $CHCl_3$ whenever solubility permitted and are in agreement with the proposed structures. All of the monosubstituted diaminoethylenes have single resonances which may be associated with the single vinyl proton. In three examples, this resonance appeared at τ 5.18, 5.43, and 6.05. In the disubstituted diaminoethylenes, which possess no vinyl hydrogens, this resonance disappears.

The resonances associated with the α-protons of the various substituted amidinium salts are interesting in that they vary in a systematic fashion, depending on the type of substitution. The values are given in Table I. The unsubstituted acetamidinium salt **3** resonates at τ 7.46. As would be expected, the alkyl-substituted salts **1** and **2** absorb energy at slightly lower field and the carbonyl and thiocarbonyl analogs **4–10** because of their strong electronegative substitution, absorb at considerably lower field, *i.e.*, τ 5.0–5.8 for the monoamide-substituted materials and 3.4–4.5 for diamide-substituted materials.

The piperidine ring protons of the various diaminoethylenes and amidinium salts occur as two symmetrical peaks with an area ratio 8:12. The lower field peak is assigned to the protons on carbons next to nitrogen and the higher field peak to the protons on the remaining carbons of the piperidine ring. The lower field peak is of particular interest since its position seems to be influenced by the degree of positive charge which might logically be assigned to the piperidine nitrogen atoms. For example, this peak occurs at τ 7.33 in piperidine itself, at 7.15 in dipiperidinylethylene, at 6.92 in the monoamide-substituted diaminoethylenes, and at 6.58 in the diamide-substituted diaminoethylenes. These shifts to progressively lower field may be attributed to the increasingly positive character of the piperidine nitrogen.

When a full positive charge is placed on the piperidine nitrogen atoms, as is the case in all the amidinium salts, this resonance occurs at even lower field (τ 6.37) and is not sensitive to substitution on the α-carbon atom. The position of the peak assigned to protons on carbons once and twice removed from nitrogen follows the same pattern but with much smaller shifts, reflecting a considerable insulation of these protons from the influence of the piperidine ring nitrogens.

Experimental

1,1-Di(1-piperidinyl)ethylene.—In a 500-ml. three-necked flask equipped for stirring, reflux, and addition through a pressure-equalized dropping funnel, there was placed 300 g. (3.6 moles) of dry piperidine. A small positive pressure of nitrogen was placed over the piperidine and it was cooled to 2°. Ethoxyacetylene, 70 g. (1 mole), was added dropwise while the temperature was maintained at 2–10°. Four hours after the addition was complete, the ice bath was removed and the mixture was allowed to warm to 50°. After stirring overnight, the excess piperidine and ethanol were distilled off under aspirator vacuum. The residual oil was distilled through a short Vigreux column to yield 148 g. (77%) of 1,1-di(1-piperidinyl)ethylene, b.p. 69–75° (0.4 mm.), $n^{25}D$ 1.5064.

Anal. Calcd. for $C_{12}H_{22}N_2$: C, 74.17; H, 11.41; N, 14.42. Found: C, 73.54; H, 11.34; N, 14.36.

1,1-Di(1-piperidinyl)ethylene prepared as described contains about 10% of 1-acetylpiperidine as determined by v.p.c. analysis. This impurity will not interfere in most of its reactions. A careful fractionation easily gave a very pure product with the following analysis.

Anal. Found: C, 73.79; H, 11.26; N, 14.04.

General Procedure for the Preparation of Carbamyl-Substituted Diaminoethylenes (Table II).—To a stirred solution of 0.05 mole of 1,1-di(1-piperidinyl)ethylene in 250 ml. of the appropriate solvent was added a solution of the isocyanate or isothiocyanate (0.05 mole for preparation of a monocarbamyl derivative or 0.10 mole for preparation of a dicarbamyl derivative) in 50 ml. of the same solvent. In most cases, the product began to precipitate within a few minutes. After stirring overnight, the solid was isolated by filtration and recrystallized from the indicated solvent. If the product did not precipitate the solvent was evaporated on a rotating evaporator and the residue crystallized from the indicated solvent.

The 1:1 adduct of phenyl isothiocyanate and 1,1-di(1-piperidinyl)ethylene was obtained in two different forms with quite different solid infrared spectra, which were identified for convenience as form A and form B. Form A is yellow in color and melts at 160–161°, whereas form B is colorless or white and melts at 150–152°. A mixture of the two melts at 154–158°. Form A has been generally obtained when the preparation is made in toluene whereas form B resulted when the reaction was run in ether. The yellow form A is converted to the white form B by heating in toluene. The white form B is converted to the yellow by recrystallization from aqueous ethanol. The white form yields a yellow solution in all the solvents in which it is soluble and the solution infrared spectra of the two forms are identical. Both forms have the same analysis and react with perchloric acid in acetic acid to give the same perchlorate. These facts can be accommodated by a simple difference in crystalline forms, by a facile equilibrium between a monomeric and a dimeric or trimeric form, or by tautomerism involving the thiocarbamyl group. (The latter was suggested by a referee.)

1,1-Di(1-piperidinyl)-2-(N-phenylcarbamyl)-2-(N-phenylthiocarbamyl)ethylene. A. From 1,1-Di(1-piperidinyl)-2-(N-phenyl-

carbamyl)ethylene and Phenyl Isothiocyanate.—A mixture of 5.1 g. of 1,1-di(1-piperidinyl)-2-(N-phenylcarbamyl)ethylene, 2.1 g. of phenyl isothiocyanate and 100 ml. of chloroform was stirred for 24 hr. at room temperature. The chloroform was evaporated on a rotating evaporator and the crude product was recrystallized from a chloroform–ether mixture. The yield of 1,1-di(1-piperidinyl)-2-(N-phenylcarbamyl)-2-(N-phenylthiocarbamyl)ethylene, m.p. 183–184° dec., was 5.2 g. (72%).

Anal. Calcd. for $C_{26}H_{32}N_4OS$: C, 69.61; H, 7.19; N, 12.49. Found: C, 69.61; H, 7.07; N, 12.37.

B. From 1,1-Di(1-piperidinyl)-2-(N-phenylthiocarbamyl)ethylene and Phenyl Isocyanate.—A mixture of 2.3 g. of 1,1-di(1-piperidinyl)-2-(N-phenylthiocarbamyl)ethylene, 0.95 g. of phenyl isocyanate, and 45 ml. of chloroform was stirred at room temperature for 22 hr. The chloroform was evaporated on a rotating evaporator and the crude product was recrystallized from a chloroform–ether mixture. The yield of 1,1-di(1-piperidinyl)-2-(N-phenylcarbamyl)-2-(N-phenylthiocarbamyl)ethylene, m.p. 183–184° dec., was 2.2 g. The infrared spectrum of this compound was identical with that of the same compound prepared in A and mixing of the two products did not depress the melting point.

Hydrolysis of 1,1-Di(1-piperidinyl)-2-(N-phenylcarbamyl)ethylene.—A mixture of 1.4 g. of 1,1-di(1-piperidinyl)-2-(N-phenylcarbamyl)ethylene and 100 ml. of a 7:3 by volume mixture of ethanol and water was heated under reflux for 3 hr. Volatile materials were evaporated under reduced pressure, leaving an oily residue which was dissolved in 5 ml. of methanol and transferred to a crystallizing dish where it was allowed to stand overnight. There remained 1.0 g. (90%) of N-pentamethylene-N′-phenylmalonamide, m.p. 114–117°. After recrystallization from benzene it melted at 118–119°.

Anal. Calcd. for $C_{14}H_{18}N_2O_2$: C, 68.26; H, 7.37; N, 11.38; O, 12.99. Found: C, 68.02; H, 7.39; N, 11.21; O, 12.81.

Independent Synthesis of N-pentamethylene-N′-phenylmalonamide.—A mixture of 40 g. of aniline and 100 g. of diethyl malonate were charged to a 500-ml. flask equipped for distillation through a steam condenser. The mixture was heated under reflux until 26 ml. of ethanol had been collected, cooled, and diluted with 230 ml. of 95% ethanol. After standing a short time the reaction mixture was filtered to remove N,N′-diphenylmalonamide and the filtrate was added to 500 ml. of water. An oil separated which partly crystallized after standing 15–20 min. This oily layer was taken up in 150 ml. of chloroform and the chloroform solution was dried over magnesium sulfate and stripped of solvent on a rotating evaporator. There remained 50 g. of dark, oily liquid.

A 10-g. sample of this liquid was mixed with 26 g. of piperidine and heated under reflux for 4 hr. After cooling, this mixture was diluted with an equal volume of water and acidified with concentrated hydrochloric acid. Filtration yielded 7 g. of N-pentamethylene-N′-phenylmalonamide, which after recrystallization from benzene melted at 117–118° and had an infrared spectrum identical with that of the hydrolysis product of 1,1-di(1-piperidinyl)-2-(N-phenylcarbamyl)ethylene. The melting point of a mixture was not depressed.

N,N′-Bispentamethyleneacetamidinium Picrate.—In a 500-ml. three-necked flask equipped with a stirrer and a water separator were placed 100 ml. of benzene and 2.52 g. of moist picric acid (containing *ca.* 10% water). The benzene was heated under reflux for 10 min. at which time no more water was collected in the water separator. The solution of picric acid in benzene thus prepared was cooled in ice and 1.94 g. of 1,1-di(1-piperidinyl)-ethylene was added slowly. After standing a few minutes an oil separated. The benzene layer was decanted and the oil was washed by decantation with an additional 100 ml. of benzene. On removal of the last traces of benzene under vacuum the oil crystallized to give 3.5 g. (80%) of N,N′-bispentamethyleneacetamidinium picrate, melting at 86–88°. After recrystallization from ethyl acetate the melting point was essentially unchanged, 86.5–88°, λ_{max} 250 mμ (log ϵ 4.32).

Anal. Calcd. for $C_{18}H_{25}N_5O_7$; C, 51.06; H, 5.95; N, 16.54; O, 26.45. Found: C, 50.70; H, 5.96; N, 16.33; O, 26.17.

N,N′-Bispentamethylenepropionamidinium Iodide.[11]—To a mixture of 1.9 g. of 1,1-di(1-piperidinyl)ethylene and 10 ml. of acetonitrile was added 2.5 g. of methyl iodide. A considerable exotherm was noted and the reaction was cooled in ice. After the exotherm had subsided it was allowed to stand overnight. When volatile materials were removed on the rotating evaporator there remained 3.2 g. (95%) of crude N,N′-bispentamethylenepropionamidinium iodide. After three crystallizations from acetone it melted at 158–159°, λ_{max} 257 mμ (log ϵ 4.14).

Anal. Calcd. for $C_{13}H_{25}IN_2$: C, 46.43; H, 7.49; I, 37.74; N, 8.44. Found: C, 46.54; H, 7.38; I, 37.94; N, 8.07.

N,N′-Bispentamethylenebutyramidinium Iodide.—A mixture of 18 g. of ethyl iodide and 2.0 g. of 1,1-di(1-piperidinyl)ethylene was stirred under nitrogen for 24 hr. There was isolated by filtration 3.6 g. (92%) of N,N′-bispentamethylenebutyramidinium iodide. After recrystallization from a 7:3 by volume mixture of acetone and ethyl acetate it melted at 212–212.5°, λ_{max} 255 mμ (log ϵ 4.10).

Anal. Calcd. for $C_{14}H_{27}IN_2$: C, 48.00; H, 7.77; I, 36.22; N, 7.99. Found: C, 48.04; H, 7.76; I, 36.01; N, 7.45.

N,N′-Bispentamethylene-β-phenylpropionamidinium Bromide.—To a mixture of 8.5 g. of benzyl bromide and 50 ml. of acetonitrile was added 10.0 g. of 1,1-di(1-piperidinyl)ethylene. An exotherm was noted and the reaction was allowed to stir overnight. Volatile materials were stripped off on the rotating evaporator leaving 14 g. (75%) of N,N′-bispentamethylene-β-phenylpropionamidinium bromide. After recrystallization from a 6:3 by weight mixture of ethyl acetate and chloroform it melted at 185–186°, λ_{max} 259 mμ (log ϵ 4.05).

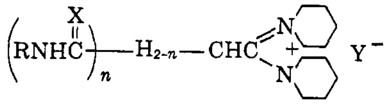
Anal. Calcd. for $C_{19}H_{29}BrN_2$: C, 62.45; H, 8.00; Br, 21.87; N, 7.66. Found: C, 62.65; H, 8.20; Br, 22.10; N, 7.64.

Preparation of the Amidinium Salts Described in Table III.—The perchlorate salts were prepared by titration of an acetic acid solution of the appropriate diaminoethylene with 0.1 *N* perchloric acid in acetic acid. They precipitated from acetic acid in analytically pure form.

The chloride salts were prepared by treatment of a chloroform solution of the appropriate diaminoethylene with an excess of anhydrous hydrogen chloride dissolved in chloroform.

TABLE III

CARBAMYL-SUBSTITUTED ACETAMIDINIUM SALTS OF THE GENERAL FORMULA[a]



$$\left(\mathrm{RNH}\overset{\overset{\displaystyle X}{\|}}{C}\right)_n\!\!-H_{2-n}-CHC\overset{+}{\begin{matrix}=N(CH_2)_5\\ -N(CH_2)_5\end{matrix}}\ Y^-$$

R	X	Y	*n*	M.p., °C.	Formula
C_6H_5–	S	ClO_4	1	209–211	$C_{19}H_{28}ClN_3O_4S$
C_2H_5–	S	ClO_4	1	151–154	$C_{15}H_{28}ClN_3O_4S$
C_6H_5	O	ClO_4	1	223–226	$C_{19}H_{28}ClN_3O_5$
3,4-$Cl_2C_6H_3$	O	ClO_4	1	196–197	$C_{19}H_{26}Cl_3N_3O_5$
2,5-$Cl_2C_6H_3$	O	ClO_4	1	241–243	$C_{19}H_{26}Cl_3N_3O_5$
C_6H_5	S	ClO_4	2	209–210	$C_{26}H_{33}ClN_4O_4S_2$
C_2H_5	S	ClO_4	2	148–149	$C_{18}H_{33}ClN_4O_4S_2$
3,4-$Cl_2C_6H_3$–	O	ClO_4	2	196–197	$C_{26}H_{28}Cl_5N_4O_6$
C_6H_5	O	Cl	1	195–195	$C_{19}H_{28}ClN_3O$
C_6H_5	S	Cl	1	72–74	$C_{19}H_{28}ClN_3S$
2,5-$Cl_2C_6H_3$	O	Cl	1	177–180 dec.	$C_{19}H_{26}Cl_3N_3O$
C_6H_5	O	Cl	2	200–202 dec.	$C_{26}H_{33}ClN_4O_2$
3,4-$Cl_2C_6H_3$	O	Cl	2	185–187 dec.	$C_{26}H_{29}Cl_5N_4O_2$
2,5-$Cl_2C_6H_3$	O	Cl	2	175–177 dec.	$C_{26}H_{29}Cl_5N_4O_2$
C_6H_5	S	Picrate	1	160–162	$C_{25}H_{30}N_6O_7S$
C_2H_5	S	Picrate	1	154–155	$C_{21}H_{30}N_6O_7S$
C_2H_5	S	Picrate	2	138–140 dec.	$C_{24}H_{35}N_7O_7S_2$

[a] All of the compounds in this table had elemental analyses in agreement with theory.

The picrate salts were prepared by treatment of the appropriate diaminoethylene with a saturated ethanol solution of picric acid.

N,N′-Bispentamethylene-1-(N-phenylcarbamyl)propionamidinium Iodide.—A mixture of 10.0 g. of methyl iodide, 3.0 g. of 1,1-di(1-piperidinyl)-2-(N-phenylcarbamyl)ethylene and 125 ml. of dry acetonitrile were heated under reflux (reaction temperature 45°) for 16 hr. After evaporation of volatile materials on the rotating evaporator there remained 4.0 g. (89%) of N,N′-bispentamethylene-1-(N-phenylcarbamyl)propionamidinium iodide.

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[11] This compound is very probably identical with the "double salt of the mono- and dimethiodides of 1,1,1-tripiperidinoethylene," m.p. 157-162° previously reported by McElvain and Tate.[8]

After two reprecipitations from ethanol by addition of ether it melted at 197–199°.

Anal. Calcd. for $C_{20}H_{30}IN_3O$: C, 52.74; H, 6.64; I, 27.87; N, 9.23; O, 3.51. Found: C, 52.31; H, 6.63; I, 27.71; N, 9.33; O, 3.51.

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The Polymerization of Acetylenes by Nickel Halide–Tertiary Phosphine Complexes

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The polymerization of several acetylenic compounds by nickel complexes of the type $NiX_2 \cdot 2R_3P$ is described. Acetylene and phenylacetylene are polymerized chiefly to the linear *trans* polyenes. Propynol gives equal amounts of linear polymer and aromatic trimers. The catalytic efficiency increases in the series: $NiCl_2 \cdot 2R_3P$, $NiBr_2 \cdot 2R_3P$, and $NiI_2 \cdot 2R_3P$.

The polymerization of acetylene to a high molecular weight linear polyene of predominantly *trans* structure was first described by Natta.[1] More recent publications of Greene,[2] Luttinger,[3] and Luttinger and Colthup[4] have shown that reducing agents such as sodium borohydride react with group VIII metal salts or complexes such as $NiCl_2 \cdot 2Bu_3P$ to form catalytic species which polymerize acetylene to the same polymer described by Natta.

We wish to report that nickel halide–tertiary phosphine complexes themselves are catalysts for the polymerization of acetylene, phenylacetylene, 1-hexyne, and propargyl alcohol. The catalytic activity is apparently specific for nickel–phosphine complexes, cobalt and palladium complexes being completely inactive, as was a nickel–phosphine oxide complex.

Bis(triphenylphosphine)nickel chloride was not a very active catalyst, while both bis(triphenylphosphine)nickel bromide and bis(tri-*n*-butylphosphine)-nickel bromide were good catalysts, as was bis(triphenylphosphine)nickel iodide.

The polymerization of acetylene leads to a black, insoluble solid whose infrared spectrum and X-ray diffraction pattern agreed with the data of Natta[1] and Luttinger[3] for polyacetylene.

The polymerization took place in a variety of solvents such as ethanol, tetrahydrofuran (THF), benzene, and acetonitrile. Dangerous exotherms were frequently observed when THF was used, but not with ethanol. In addition, the yield (grams of polymer/gram of catalysts) was increased about twofold on changing from THF to ethanol, and a more ordered polymer, as shown by X-ray diffraction, was obtained. An optimum yield of 12.7 g. of polymer/gram of catalyst was obtained.

Phenylacetylene yielded a yellow solid as main product in small yield, the infrared spectrum of this solid was identical with that of poly(phenylacetylene).[5]

It was found that propynol yielded, in addition to isomeric trimethylolbenzenes reported by Reppe,[6] an insoluble solid whose infrared spectrum showed the main absorptions of polyacetylene and poly(phenylacetylene) in addition to bands due to $-CH_2OH$, which is very likely polypropynol, $+CH = C(CH_2OH)+_n$. Soluble and insoluble products from propynol have been reported by Polyakova, *et al.*,[7] from thermal polymerization under pressures of 1500 to 1600 atm.

Under the above conditions, 1-hexyne yielded small amounts of linear dimers, trimers, and tetramers. Ethylene, vinyl acetate, vinyl chloride, and styrene failed to polymerize either by themselves or with acetylene. This polymerization resembles the polymerization of 1,3-butadiene by salts and complexes of rhodium and other transition metals reported by Rinehart,[8] and Canale,[9] in that no apparent cocatalyst is required.

Experimental

Chemicals.—Phenylacetylene and 1-hexyne were used as received from the Farchan Research Laboratories. Matheson acetylene was used directly. Triphenylphosphine was used as received from Eastern Chemical Co. Tri-*n*-butylphosphine was used as received from Metal and Thermit Corp. Transition metal salts were reagent grade. Tetrahydrofuran, J. T. Baker reagent grade, was used as received.

Bis(triphenylphosphine)nickel dichloride, dibromide, and diiodide[10]; bis(triphenylphosphine)cobalt dichloride, dibromide, and diiodide[11]; bis(tri-*n*-butylphosphine)nickel dibromide[12] bis(tri-*n*-butylphosphine)palladium dichloride[13]; and bis(triphenylphosphine oxide)nickel dibromide[14] were prepared by known methods.

Acetylene. Procedures.—Acetylene polymerizations were carried out in a 1-l. stainless steel, stirred autoclave at prevailing temperatures. As an example, 500 ml. of solvent (10% THF–90% EtOH) containing 3.7 g. (0.005 mole) of $NiBr_2 \cdot 2Ph_3P$ was placed in the autoclave; the autoclave was closed, flushed three times with nitrogen at 100 p.s.i.g., then pressured to 70 p.s.i.g. with N_2 and a total of 200 p.s.i.g. with acetylene. The autoclave was run at these conditions for 24 hr. After venting unreacted acetylene, the contents of the autoclave were seen to be a dark reaction mixture with much black solid suspended in the solvent. After filtration, the solid was washed with fresh solvent until all color bodies were removed, dried at about 40 mm. over KOH, bottled quickly under N_2, and weighed. There was 47.0 g.

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