Reaction of Tetramethylguanidinium Azide with Nitriles to Give 5-Substituted Tetrazoles.—The tetrazoles prepared are shown in Table II. One general procedure for the synthesis and isolation of the tetrazoles was employed. This procedure is illustrated by the preparation of 5-dimethylaminotetrazole. A mixture of 3.5 g (0.05 mole) of dimethylcyanamide and 7.9 g (0.05 mole) of tetramethylguanidinium azide was stirred and heated at 100° for 7 hr. The reaction mixture was cooled to room temperature, dissolved in 30 ml of water, and acidified with glacial acetic acid (concentrated hydrochloric acid was used with all the other tetrazoles listed in Table II). (*Caution:* Some hydrazoic acid could be evolved on acidification.) The precipitated product was collected, washed with cold water, and dried: yield 4.7 g (83%) mp 238° dec. Recrystallization from ethanol gave 4.0 g (71%), mp 240° dec.

Acknowledgment.—The author gratefully acknowledges Drs. W. C. Smith and R. A. Braun of this laboratory for helpful discussions and Dr. H. Foster of the Analytical Laboratory for aid in interpreting the nmr spectra.

Oxidation of Active Hydrogen Compounds with 2-Chlorotetramethylguanidine

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Oxidative condensation of certain active hydrogen compounds was accomplished by reaction with 2-chlorotetramethylguanidine in nonaqueous systems. In general, methylene compounds afforded ethylenes while methine and sterically hindered methylene derivatives gave ethanes. Triethyl 1,2,3-tricyanocyclopropane-1,2,3-tricarboxylate and tetramethylguanidinium pentacyanopropenide were obtained when ethyl cyanoacetate and malononitrile, respectively, were employed in the reaction. In contrast, α-bromo-*p*-nitrotoluene alkylated 2-chlorotetramethylguanidine to give 1,1-di(*p*-nitrotolyl)tetramethylguanidinium perbromide.

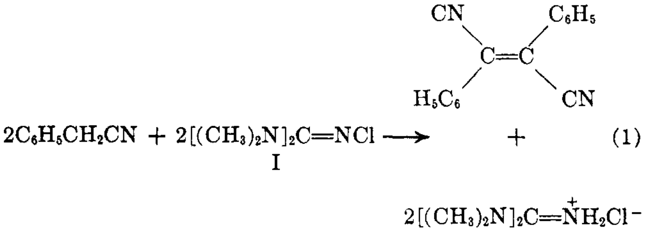
A number of N-halo compounds are known to undergo a variety of interesting reactions.[1] A few examples of oxidation of organic compounds by N-haloamides and imides have been previously reported. The compounds studied included primary and secondary alcohols,[2-8] α-amino acids,[9] and cyclic systems.[10-13]

This paper describes a study of the oxidation of compounds containing active hydrogen atoms by 2-chlorotetramethylguanidine (I) and reports on the reaction of I with α-bromo-*p*-nitrotoluene.

Certain active hydrogen compounds have been found to undergo oxidative condensation on treatment with I to produce ethylenes, ethanes, and a cyclopropane. The reactions proceed smoothly at room temperature in a nonaqueous solvent or neat with the precipitation of tetramethylguanidine hydrochloride by-product during the reaction.

The results of the reactions studied are summarized in Table I. Yields are based on purified compounds and products were identified by elemental analysis, physical constants, and infrared spectrum.

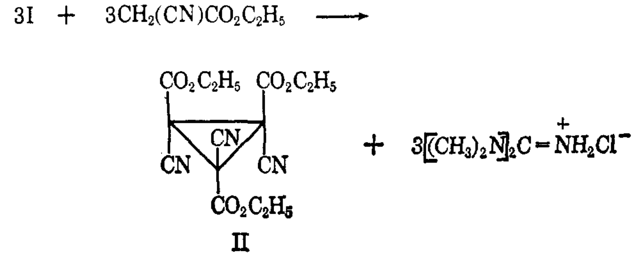
Diethyl malonate, phenylacetonitrile, *p*-chlorophenylacetonitrile, and *p*-nitrophenylacetonitrile each gave the corresponding ethylene upon treatment with an equimolar amount of I. On the other hand, both bis(*p*-nitrophenyl)methane and diphenylacetonitrile reacted with I in a 2:1 molar ratio, respectively, to give the ethanes. The general reactions giving ethylene and ethane are shown by eq 1 and 2, respectively.



$$2C_6H_5CH_2CN + 2[(CH_3)_2N]_2C{=}NCl \longrightarrow (CN)(C_6H_5)C{=}C(CN)(C_6H_5) + 2[(CH_3)_2N]_2C{=}\overset{+}{N}H_2Cl^- \qquad (1)$$

$$2(p\text{-}O_2NC_6H_5)_2CH_2 + I \longrightarrow (p\text{-}O_2NC_6H_5)_2CHCH(C_6H_5NO_2\text{-}p)_2 + [(CH_3)_2N]_2C{=}\overset{+}{N}H_2Cl^- \qquad (2)$$

The reaction with both ethyl cyanoacetate and malononitrile proceeded rapidly and exothermally in benzene and tetrahydrofuran solution, respectively. Unexpectedly, the former gave triethyl 1,2,3-tricyanocyclopropane-1,2,3-tricarboxylate (II). The product



II

from the reaction with malononitrile was tetramethylguanidinium pentacyanopropenide (III).

$$[(CN)_2C{=}C(CN)C(CN)_2]^-[((CH_3)_2N)_2C{=}NH_2]^+$$

III

Evidence in support of III was obtained from elemental analysis and comparison of infrared and ultraviolet spectra with an authentic sample prepared by the reaction of malononitrile with tetracyanoethylene

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[1] S. S. Navikov, V. V. Sevost'yanova, and A. A. Fainzil'berg, *Russian Chem. Rev.*, **31**, 671 (1962).

[2] R. D. Chattaway and K. J. P. Orton, *Ber.*, **32**, 3573 (1899).

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[7] L. F. Fieser and S. Raiagopalan, *J. Am. Chem. Soc.*, **71**, 3935 (1949).

[8] L. F. Fieser, W. P. Schneider, and W.-Y. Huang, *ibid.*, **75**, 124 (1953).

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[11] R. A. Barnes and G. R. Buckwalter, *ibid.*, **73**, 3858 (1951).

[12] T. A. Geissman and E. Hinreiner, *ibid.*, **73**, 782 (1951).

[13] T. A. Geissman and T. G. Halsall, *ibid.*, **73**, 1280 (1951).

TABLE I

PRODUCTS FROM THE REACTION OF 2-CHLOROTETRAMETHYLGUANIDINE WITH ACTIVE HYDROGEN COMPOUNDS

Active hydrogen compd	Reaction Solvent	Reaction Temp, °C	Product (% yield)	Recrystn solvent	Mp, °C Found	Mp, °C Lit.
Diethyl malonate	C_6H_6	35	Ethyl ethylenetetracarboxylate (43)	Ethanol	52–53	52.5–53.5[a]
Phenylacetonitrile	C_6H_6	25	*trans*-α,α′-Dicyanostilbene (23)	[b]	159	161[c]
p-Chlorophenylacetonitrile	Neat	25	4,4′-Dichloro-α,α′-dicyanostilbene (42)	[d]	188–189	189–190[e]
p-Nitrophenylacetonitrile	C_6H_6	30	4,4′-Dinitro-α,α′-dicyanostilbene (59)	Acetone	278–280	275[f]
Bis(*p*-nitrophenyl)methane	Neat	25	Tetrakis(*p*-nitrophenyl)ethane (50)	DMF	341–343 dec[g]	. . .
Diphenylacetonitrile	C_6H_6	45	Tetraphenylsuccinonitrile (22)	Dichloromethane–methanol	207.5–211	205–207[h]
Ethyl cyanoacetate	C_6H_6	15–20	Triethyl 1,2,3-tricyanocyclopropane-1,2,3-tricarboxylate (45)	Ethanol	117–119	122–123[i]
Malonitrile	THF	−10	Tetramethylguanidinium[j] Pentacyanopropenide (45)	Methanol	156.5–158	. . .

[a] B. B. Carson and W. L. Benson, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1955, p 273. [b] Purified by sublimination at 100–105° (0.01 mm). [c] M. V. Sargent and C. J. Timmons, *J. Chem. Soc.*, 2222 (1964). [d] Sublimed at 160° (0.05 mm). [e] O. Vogl and C. S. Rondestvedt, Jr., *J. Am. Chem. Soc.*, **78**, 3799 (1956). [f] J. W. Baker and C. K. Ingold, *J. Chem. Soc.*, 446 (1929). [g] Product contains two molecules of DMF of solvation. *Anal.* Calcd for $C_{32}H_{32}N_6O_{10}$: C, 58.18; H, 4.88; N, 12.72. Found: C, 58.10; H, 4.99; N, 12.64. J. H. Garvin [*J. Chem. Soc.*, 678 (1959)] reported a melting point of 330–335° dec for nonsolvated material. [h] W. D. Emmons and J. P. Freeman, *J. Am. Chem. Soc.*, **77**, 4416 (1955). [i] D. G. J. Felton, *J. Chem. Soc.*, 515 (1955). Mixture melting point with an authentic sample prepared by the procedure of Felton showed no depression, 117–119°. [j] Calcd for $C_{13}H_{14}N_8$: C, 55.31; H, 5.00; N, 39.69. Found: C, 55.57; H, 5.27; N, 39.70. The ultraviolet spectrum showed $\lambda_{max}^{C_2H_5OH}$ 412 mμ (ε 21,455) and 394 mμ (ε 22,019).

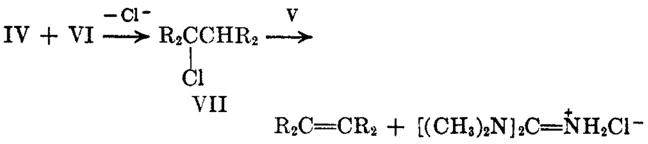
in the presence of tetramethylguanidine according to a known type of reaction.[14]

Less reactive active hydrogen compounds, such as acetonitrile, chloroacetonitrile, ethyl phenylacetate, benzophenone, and acetonylacetone failed to react with I in the absence of a solvent over a 6-day period.

It appears that electron-attracting groups, in particular the cyano group, raise the yield of the condensation products formed. Additionally, the sensitivity of the reaction to steric factors is indicated by the formation of the ethane, tetrakis(*p*-nitrophenyl)ethane. These effects and the relatively low temperature required for reaction suggest that the reactions proceed *via* an ionic mechanism. On this basis, the reactions might be rationalized by a simple halogenation–dehydrohalogenation sequence in the following way.

$$\mathrm{I} + R_2CH_2 \longrightarrow \underset{\mathrm{IV}}{R_2CHCl} + \underset{\mathrm{V}}{[(CH_3)_2N]_2C{=}NH}$$

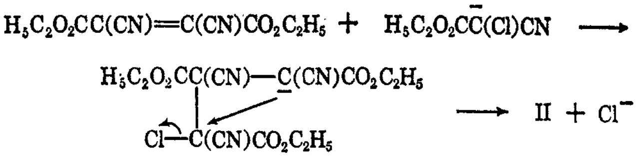
$$\mathrm{IV} + \mathrm{V} \longrightarrow \underset{\mathrm{VI}}{R_2\bar{C}Cl} + [(CH_3)_2N]_2C{=}\overset{+}{N}H_2$$



$$\mathrm{IV} + \mathrm{VI} \xrightarrow{-\mathrm{Cl}^-} \underset{\mathrm{VII}}{R_2\underset{\displaystyle Cl}{\underset{|}{C}}CHR_2} \xrightarrow{\mathrm{V}} R_2C{=}CR_2 + [(CH_3)_2N]_2C{=}\overset{+}{N}H_2Cl^-$$

Formation of the chlorinated species IV is consistent with well-known chemical behavior of N-halo compounds in halogenation reactions.[1] The chlorocarbanion VI, formed from IV and the strongly basic tetramethylguanidine V,[15] could react with IV in an anionic displacement reaction to give the intermediate chloroethane VII. Dehydrohalogenation of VII by V would lead to the formation of ethylene derivatives. Ethanes might be expected to arise by attack of a carbanion formed from the active methylene or methine derivative on the corresponding chlorinated species of type IV.

The cyclopropane II could have resulted from cyclization of the intermediate formed by a Michael addition of the corresponding chlorocarbanion to the ethylene, diethyl 1,2-dicyanoethylene-1,2-dicarboxylate.



$$H_5C_2O_2CC(CN){=}C(CN)CO_2C_2H_5 + H_5C_2O_2C\bar{C}(Cl)CN \longrightarrow \begin{array}{l} H_5C_2O_2CC(CN){-}\bar{C}(CN)CO_2C_2H_5 \\ \quad | \\ Cl{-}C(CN)CO_2C_2H_5 \end{array} \longrightarrow \mathrm{II} + Cl^-$$

The formation of III is not completely clear. The reaction of tetracyanoethylene and halomalonitrile in the presence of a base to give pentacyanopropenide anion has been reported.[14,16] Ferris and Orgel[16] favor the reaction of tetracyanoethylene with itself over condensation of halomalononitrile and tetracyanoethylene.

Mechanisms involving carbene intermediates are unlikely since carbenes could not be trapped in reactions with added cyclohexene. Additionally, the electrophilic cyano- and carboxylcarbenes would not be expected to dimerize.[17]

α-Bromo-*p*-nitrotoluene, under the same conditions as described for active hydrogen compounds in Table I, did not give any of the simple condensation compounds with I. Oxidation of the methylene group of an α-halo ketone by selenium dioxide to the corresponding acid halide has been demonstrated.[18]

Heating α-bromo-*p*-nitrotoluene with I at 40° for 2 hr resulted in the isolation of a yellow, crystalline solid.

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[14] W. J. Middleton, E. T. Little, D. D. Coffman, and V. A. Engelhardt, *J. Am. Chem. Soc.*, **80**, 2795 (1958).

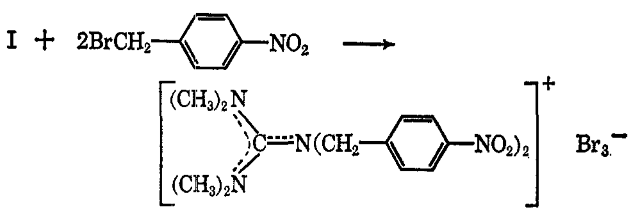
[15] Technical Bulletin 8342-1000, American Cyanamid Co., 30 Rockefeller Plaza, New York, N.Y., Nov 1958.

[16] J. P. Ferris and L. E. Orgel, *J. Org. Chem.*, **30**, 2365 (1965).

[17] W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, p 79.

[18] J. P. Schaefer and E. J. Corey, *J. Org. Chem.*, **24**, 1825 (1959).

Elemental analysis and spectral data indicate alkylation of I had occurred to give the stable 1,1-di(*p*-nitrotolyl)-tetramethylguanidinium perbromide (VIII) in 18% yield.



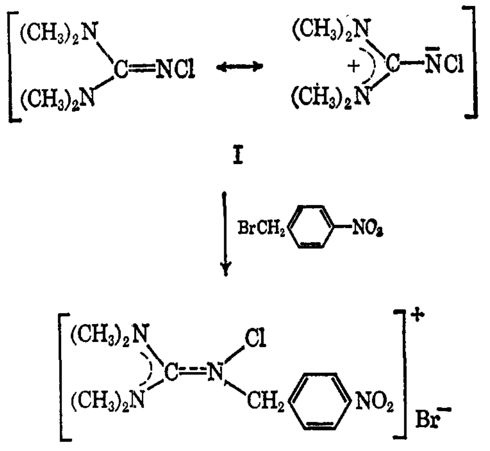
VIII

Mild heating of a suspension of VIII in acetone caused the discharge of the yellow color with the formation of colorless 1,1-di(*p*-nitrotolyl)tetramethylguanidinium bromide (IX) and brominated acetone as by-product.

The structure of the salt IX has been established by elemental analysis, molecular weight, and infrared and nmr spectroscopy. The nmr spectra of VIII and IX are identical in every detail.

Final confirmation of the proposed structure of VIII was provided by the demonstrated reversibility of the bromination reaction. Thus, when IX was treated with excess bromine in dichloromethane solution, the perbromide VIII was obtained in quantitative yield.

Although mechanistic details of the perbromide formation have not been investigated, it appears reasonable to postulate an alkylation pathway which proceeds with the initial formation of X.



I

X

Nucleophilic attack by I upon the alkyl halide to give the intermediate pentasubstituted guanidinium salt is consistent with observations which have been made in related reactions of I with carboxylic acid halides. For example, the reaction of I with benzoyl chloride in ether at 0° afforded the 1:1 adduct, 1-chloro-1-benzoyltetramethylguanidinium chloride, in 98% yield. Hydrolysis gave 2-benzoyltetramethylguanidine hydrochloride which was characterized by analysis and comparison with an authentic sample synthesized by the reaction of tetramethylguanidine and benzoyl chloride. Conversion of X to product VIII may be rationalized in terms of further alkylation to a hexasubstituted guanidine salt with subsequent halide exchange.

Experimental Section[19]

Reaction of 2-Chlorotetramethylguanidine (I) with Active Hydrogen Compounds.—These products are given in Table I. The general procedure employed is illustrated by the reaction of 2-chlorotetramethylguanidine with phenylacetonitrile. 2-Chlorotetramethylguanidine (15 g, 0.1 mole) was added at one time to a solution of 11.7 g (0.1 mole) of phenylacetonitrile in 10 ml of benzene. In some cases, an exothemic reaction occurred on mixing which necessitated slower addition of 2-chlorotetramethylguanidine. The temperature was controlled as indicated in Table I. All reactions were run in flasks wrapped with aluminum foil to retard photochemical decomposition of I. After stirring for 2 days, the precipitated solid was collected and washed thoroughly with benzene and dried: yield 12.0 g (79%) of crude tetramethylguanidine hydrochloride, mp 197.5–200°. Recrystallization from ethanol raised the melting point to 207–210°. The mixture melting point with an authentic sample of tetramethylguanidine hydrochloride showed no depression.

The combined filtrate from the original reaction mixture and benzene washings was concentrated under reduced pressure and the brown residue was washed with methanol and dried: yield 3.2 g (28%), mp 150–153°. Recrystallization from ethanol afforded 2.8 g (24%) of pure white product. Sublimination at 100–105° (0.01 mm) gave 2.6 g (23%) of *trans*-α,α′-dicyanostilbene, mp 159°.

1,1-Di(*p*-nitrotolyl)tetramethylguanidinium Perbromide (VIII).—α-Bromo-*p*-nitrotoluene (10.8 g, 0.05 mole) was added portionwise to 7.5 g (0.05 mole) of 2-chlorotetramethylguanidine with stirring over a period of 30 min. The reaction was run in the dark, and there was no exotherm during the addition. The reaction mixture was heated at 40° for 2 hr and allowed to stand overnight, with stirring, at room temperature. Chloroform was added to the greenish brown reaction mixture until precipitation of crude product was complete. The yellow solid was collected by filtration and washed successively with ethanol, benzene, and ether and dried: yield 2.8 g (18%) of perbromide, mp 174–180°. Crystallization from DMF–ether at 20° raised the melting point to 195–197°. A satisfactory elemental analysis could not be obtained due to the facile elimination of bromine.

Anal. Calcd for $C_{19}H_{24}Br_3N_5O_4$: Br, 38.91; N, 11.37. Found: Br, 38.22; Cl, 0.00; N, 11.00.

An infrared spectrum of III exhibited strong absorption bands at 6.28 (C=N), 6.50 (NO_2), and 7.48 μ (C—N<). The ultraviolet spectrum had $\lambda_{max}^{CH_3CN}$ 268 mμ (ε 63,246). The nmr spectrum showed two doublets (J = 8.5 cps), the low-field doublet centered at 8.05 and the high-field doublet centered at 7.85 due to *ortho* hydrogens, a singlet at 4.53 due to $-CH_2-$, and two singlets at 3.05 and 2.95 ppm due to $(CH_3)_2N$ with a peak area ratio of 8:4:12, respectively.

1,1-Di(*p*-nitrotolyl)tetramethylguanidinium Bromide (IX).—A suspension of 10.6 g (0.017 mole) of 1,1-di(*p*-nitrotolyl)tetramethylguanidinium perbromide in 50 ml of acetone was heated under gentle reflux for 30 min and cooled. Filtration afforded 6.8 g (87%) of crude white salt (IX). Crystallization from DMF–ether gave 6.0 g (77%) of product, mp 264–265° dec. This bromide is soluble in water and gives an instantaneous precipitate with aqueous silver nitrate.

Anal. Calcd for $C_{19}H_{24}BrN_5O_4$: Br, 17.51; N, 15.37; mol wt, 456. Found: Br, 17.29; N, 15.14; mol wt (ebullioscopic method in H_2O), 480.

An infrared spectrum had strong absorption bands at 6.28 (C=N), 6.42 (NO_2), and 7.48 μ (C—N<). The spectrum was identical with that of the perbromide VIII, with the exception of the shift in the band due to NO_2 absorption. The ultraviolet spectrum showed $\lambda_{max}^{CH_3CN}$ 267 mμ (ε 22,620). The nmr spectrum was identical with that of the perbromide VIII in every detail. The filtrate from the original reaction mixture was strongly lachrymatory. Distillation afforded a mixture of brominated acetone which turned to the characteristic purple color on standing.

Bromination of 1,1-Di(*p*-nitrotolyl)tetramethylguanidinium Bromide (IX).—To a suspension of 2.0 g (4.4 mmoles) of 1,1-di(*p*-nitrotolyl)tetramethylguanidinium bromide in 30 ml of dichloromethane was added a solution of 2.0 g (12.5 mmoles) of bromine in 50 ml of dichloromethane over a period of 20 min.

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[19] Boiling points and melting points are uncorrected. Nmr spectra were obtained on a Varian Associates A-60 spectrometer (60 Mc). Infrared spectra were taken on a Perkin-Elmer Model 21 spectrophotometer.

When the addition was complete, the reaction mixture was stirred for 1 hr at room temperature, and the solvent was then evaporated by passing a stream of nitrogen gas over the mixture. The remaining yellow solid weighed 2.8 g (100%), mp 197°. A mixture melting point with authentic perbromide salt VIII was not depressed.

Reaction of 2-Chlorotetramethylguanidine with Benzoyl Chloride.—To a solution of 7.5 g (0.05 mole) of 2-chlorotetramethylguanidine in 250 ml of ether was added a solution of 7.0 g (0.05 mole) of benzoyl chloride in 100 ml of ether over a period of 1 hr while maintaining the temperature at −5 to 0°. The mixture was allowed to stand overnight, with stirring, at room temperature. The precipitated hygroscopic white solid was filtered quickly under a nitrogen atmosphere, washed thoroughly with ether and dried in a vacuum desicator: yield 14.2 g (98%) of 1-chloro-1-benzoyltetramethylguanidinium chloride, mp 175–185° dec. Tests showed the salt to be a strong oxidizing reagent. The extreme hygroscopicity of the chloride salt precluded the preparation of an analytical sample.

Conversion of 1-chloro-1-benzoyltetramethylguanidinium chloride to 2-benzoyltetramethylguanidine hydrochloride was effected by crystallization of the former compound from wet acetonitrile–ether: yield 8.4 g (66%), mp 207–211° dec. An analytical sample was prepared by another crystallization from acetonitrile–ether: mp 215–218° dec.

Anal. Calcd for $C_{12}H_{18}ClN_3O$: C, 56.36; H, 7.09; Cl, 13.86. Found: C, 56.51; H, 7.22; Cl, 13.96.

An infrared spectrum showed absorption bands consistent with the assigned structure. A mixture melting point determination with an authentic sample prepared by the reaction of tetramethylguanidine and benzoyl chloride showed no depression of melting point of either sample.

Coumarins. II. The Acid-Catalyzed Reaction of Phenols with Simple α,β-Unsaturated Acids[1]

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Received October 8, 1965

The reaction of excess phenols with crotonic acid, in the presence of 2 equiv of anhydrous aluminum chloride, yielded 4-methyldihydrocoumarins. In contrast, 2-hydroxycrotonophenones were obtained in appreciable yields by aluminum chloride catalyzed reaction of equimolar amounts of phenols and crotonic acid in tetrachloroethane solution. Resorcinol reacts smoothly with acrylic acid in ethyl ester of polyphosphoric acid (PPE) at 90–95° to furnish a good yield of dihydroumbelliferone along with the corresponding melilotic acid, while the similar reaction with crotonic acid gives 3-hydroxyphenylcrotonate. The PPE-catalyzed reaction of less reactive phenols with these acids gave several kinds of products at higher temperature.

An earlier paper in this series[3] described a direct method of preparing several dihydrocoumarins by the reaction of phenols with α,β-unsaturated nitriles in the presence of anhydrous aluminum chloride and dry hydrogen chloride. These studies have now been extended to simple α,β-unsaturated acids and their esters. While the acid-catalyzed reactions of phenols with more than five-membered α,β-unsaturated acids, such as cinnamic acid or β,β-dimethylacrylic acid, have been extensively studied,[4,5] little is known of similar reactions with simple α,β-unsaturated acids and their derivatives.

It has been shown that crotonoyl chloride reacts with resorcinol in the presence of aluminum chloride to give 7-hydroxy-2-methylchromanone[6] and that crotonic acid condenses with phenols in hydrofluoric acid solution to furnish 2-methylchromanones in good yields.[7] Recently Miyano and Matsui have reported that reaction of resorcinol with crotonic acid in the presence of zinc chloride gives 7-hydroxy-2-methylchromanone.[8] No method of preparing simple dihydrocoumarins by the reaction of phenols with acrylic acid and with crotonic acid has yet appeared in the literature. The ring positions in the phenols are said to be unreactive toward crotonic acid in the presence of hydrochloric acid.[4g]

We have now examined the reaction of phenols with simple α,β-unsaturated acids, such as acrylic acid, using anhydrous aluminum chloride or the ethyl ester of polyphosphoric acid (PPE). It has been found that the aluminum chloride catalyzed reaction of equimolar amount of phenols and crotonic acid gives the 2-hydroxycrotonophenones (II, $R_2 = CH_3$); the structures follow from the infrared spectra (Table I), which showed strongly hydrogen bonded OH bands at 3200–3300 cm^{-1} and carbonyl bands at 1640–1665 cm^{-1}. With excess phenol, mainly 4-methyldihydrocoumarins (I, $R_2 = CH_3$) (Table II), identical in properties with those previously reported,[3] were obtained. Phenols, except for resorcinol, react with acrylic acid and with crotonic acid in PPE solution to give ethyl esters III and phenyl esters IV as main products, with very small amounts of 2-methylchromanones (V) and Michael addition products (VI) (Table III).

Although sulfuric acid, pyrophosphoric acid, 85% syrupy phosphoric acid, and a mixture of the phosphoric acid and pyrophosphoric acid were effective, optimum results were obtained with aluminum chloride or PPE. Heating periods over 5 hr did not afford

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(1) This investigation was supported mainly by Asahi Glass Co. for which we are grateful.

(2) To whom inquiries should be directed at the Department of Applied Chemistry, Faculty of Engineering, Yokohama National University, Yokhoma, Japan.

(3) Part I: K. Sato, T. Amakasu, and S. Abe, *J. Org. Chem.*, **29**, 2971 (1964).

(4) Syntheses of dihydrocoumarins have been reported in the following references: (a) L. I. Smith and L. J. Spillane, *J. Am. Chem. Soc.*, **65**, 282 (1943): (b) H. A. Offe and W. Barkow, *Chem. Ber.*, **80**, 464 (1947): (c) J. D. M. Simpson and S. S. Israelstem, *J. S. African Chem. Inst.*, **2**, 165 165 (1949): (d) A. Lespagnol, J. Schmitt, and P. Brunand, *Bull. Soc. Chim. France*, 82 (1951): (e) W. Baker, R. F. Curtis, and J. F. W. McOmi, *J. Chem. Soc.*, 76 (1951): (f) N. G. pH. Buu-Hoi, H. Le Bihan, F. Binon, and P. Ma P. Maleyran, *J. Org. Chem.*, **17**, 1122 (1952): (g) J. D. Simpson and H. Stephen, *J. Chem. Soc.*, 1382 (1956): (h) J. Colonge, E. Le Sech, and R. Marey, *Bull. Soc. Chim. France*, 776 (1957).

(5) Syntheses of chromanones have been described in the following references: (a) W. John and P. Günther, U. S. Patent 2,274,449 (1942); (b) H. A. Offe and W. Barkow, *Chem. Ber.*, **80**, 458 (1947); (c) A. R. Alertson, *Acta Polytech. Scand. Ser.*, **13**, No. 10, 1 (1961).

(6) J. H. Richards, R. Robertson, and W. Barkow, *J. Chem. Soc.*, 1610 (1948).

(7) O. Dann, G. Volz, and O. Huber, *Ann.*, **587**, 16 (1954).

(8) M. Miyano and M. Matsui, *Bull. Chem. Soc. Japan*, **31**, 397 (1958).