TABLE I

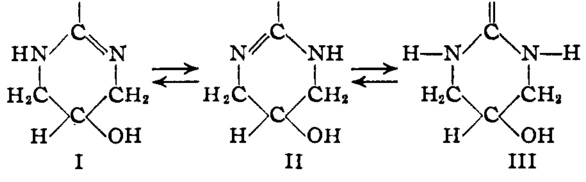
2-NITRAMINO-Δ²-1,3-DIAZACYCLOALKENES

Compound	Yield, %	M. p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
2-Nitramino-Δ²-1,3-diazacyclopentene	65.4	220–221 dec.	27.9	27.8	4.61	4.52	43.1	43.0
4(or 5)-Methyl-2-nitramino-Δ²-1,3-diazacyclopentene	64.0	170.5	33.3	33.5	5.54	5.60	38.9	39.2
2-Nitramino-Δ²-1,3-diazacyclohexene	55.0	251–252 dec.	33.3	33.3	5.54	5.55	38.9	38.7
4(or 6)-Methyl-2-nitramino-Δ²-1,3-diazacyclohexene	40.0	147–148.5	38.0	37.9	6.33	6.70	35.4	35.8
2-Nitramino-Δ²-1,3-diazacycloheptene	64.3	219–220 dec.	38.0	38.4	6.33	6.68	35.4	35.5
5-Hydroxy-2-nitramino-Δ²-1,3-diazacyclohexene	59.0	233–233.5 dec.	30.0	29.6	5.00	5.05	35.0	34.6

aminoalkylnitroguanidine to give a cyclic nitramine after a second molecule of ammonia is liberated. Five, six and larger membered rings can thus be synthesized.

It has been found[4] that the yields of alkylnitroguanidines can be improved over those previously reported, by treating nitroguanidine dissolved in aqueous alkali with the alkylamine hydrochloride. The mixture is heated to 60–70° for twenty to thirty minutes, cooled and the product recovered by filtration. This revised method is also found considerably to increase (by 15–55%) the yields of 2-nitramino-Δ²-1,3-diazacycloalkenes (1, $n = 2$ to 4) obtained from the reaction of alkyldiamines with nitroguanidine. The synthesis is found to be successful with diamines containing branched as well as straight chains. The compounds which have been prepared thus far are listed in Table I. No tautomeric forms have yet been detected. Although the products isolated from the reaction of the unsymmetrical diamines with nitroguanidine are chemical individuals, we cannot at present assign definite positions to the methyl groups.

It is interesting to note that in the substituted 2-nitramino-Δ²-1,3-diazacycloalkenes described in Table I an asymmetric carbon atom occurs. Thus the 4(or 5)-methyl-2-nitramino-Δ²-1,3-diazacyclopentene and 4(or 6)-methyl-2-nitramino-Δ²-1,3-diazacyclohexene are racemates. Especially interesting is the 5-hydroxy-2-nitramino-Δ²-1,3-diazacyclohexene. If a labile tautomerism exists between I and II, or if the acid salts of I are resonance hybrids, then resolution would be impossible. If, on the other hand, the tautomeric nitrimino form III were stable then resolution of the allene-like structure should be possible.



I II III

Work on structure and synthesis of these 2-nitramino-Δ²-1,3-diazacycloalkenes is in progress. The authors are grateful to Messrs. Scott and Farmer of London, England, from whom the original idea of cyclization was obtained. The National Research Council of Canada has supported this work by a grant-in-aid.

Experimental

Preparation of 2-Nitramino-Δ²-1,3-diazacycloalkenes.—One mole of nitroguanidine is dissolved in 250–300 cc. of water containing two moles of potassium hydroxide and then one mole of the diamine dihydrochloride is added with stirring. A thick sludge forms which is heated at 65–70° with stirring over a period of twenty to thirty minutes. During this time the sludge becomes less viscous and it may dissolve completely. At the end of the reaction time, the reaction mixture is cooled to 1° in an ice–salt-bath and the white solid is recovered by filtration. The occluded potassium chloride may be removed by trituration with water. The final yields vary from 40–65% of theoretical, depending on the specific compound.

CHEMICAL LABORATORIES OF THE
UNIVERSITY OF TORONTO AND
QUEEN'S UNIVERSITY
TORONTO AND KINGSTON, ONTARIO

RECEIVED AUGUST 14, 1947

The Addition of Methyl Alcohol to Fluoroethylenes[1]

BY WILLIAM T. MILLER, JR.,[2] EDWARD W. FAGER[3] AND PAUL H. GRISWOLD[4]

The addition of alcohols to tetrafluoroethylene and to chlorotrifluoroethylene[5] has been reported in the patent literature. In the present work, which was carried out independently, the base catalyzed addition of methyl alcohol to these substances and to *unsym*-dichlorodifluoroethylene was shown to occur. Reaction occurred rapidly and exothermically at from zero to room temperature with a reagent prepared by dissolving two moles of sodium in 500 cc. of absolute methanol. The tetrafluoroethylene was added in portions as a gas at 20 atm. pressure to the methylate solution in a steel bomb of the rocker type with the temperature maintained below 40°. The other olefins were added at atmospheric pressure to the stirred methylate solution cooled in an ice-bath.

---

(4) A. F. McKay and G. F. Wright, THIS JOURNAL, 69, 3028 (1947).

(1) This paper was largely based on work done for the Manhattan Project under Contract No. W-7405-Eng-50 at S. A. M. Laboratories, Columbia University and under contract No. W-7405-Eng-26, Supplement No. 4 at S. A. M. Laboratories Carbide and Carbon Chemicals Corporation, New York City. Part of the information contained in this document will appear in Volume I of Division VII of the Manhattan Project Technical Series.

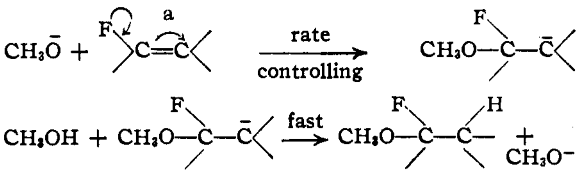
Present addresses: (2) Department of Chemistry, Cornell University, Ithaca, N. Y.; (3) Department of Chemistry, University of Chicago, Chicago, Illinois; (4) Department of Chemistry, Yale University, New Haven, Connecticut.

(5) Hanford and Rigby, U. S. Patent 2,409,274, Oct. 15, 1946.

Trichlorofluoroethylene was also observed to react readily but with some loss of halogen acid, while tetrachloroethylene did not react at 0°.

The physical properties and analytical data for the three ethers obtained pure are summarized in Table I. All three ethers were saturated to permanganate solution. They yielded fluoride ion in large amount when heated with alcoholic potash along with trace amounts of chloride ion from the chlorine containing compounds. The structures assigned are consistent with the above observation, and the presence of $-CF_2-$groupings alpha to oxygen explained the observed stability toward the sodium methylate reagent.

The mechanism of addition is postulated as follows



The role of fluorine relative to chlorine in promoting addition of nucleophilic type reagents and effecting the orientation of addition is considered to be due to its greater tendency to enter into resonance with the double bond so as to predispose the system to polar activation of the type indicated above (arrow *a*). There is also considerable reason to believe that fluorine is capable of electron release relative to chlorine as an activation mechanism.[7] The general electron withdrawal (inductive effect) by the halogens on the double bond favors the development of acceptor activity by activation in marked contrast to the exclusively nucleophilic reactivity shown by simple ethylenic hydrocarbons.

TABLE I

	CH_3OCF_2-CHF_2	CH_3OF_2-$CHClF$	$CH_3OCF_2CHCl_2$
F. p., °C.	−107	−92[a]	− 35
B. p., °C.	+ 36.5	+70.6	+105
n^{20}_D	<1.3	1.3340	1.3861
d^{20}_4	1.2939	1.3636	1.4262
MR_D		22.46	27.18
ARE[b]		1.01	0.97
% C calcd.	27.3	24.3	21.8
% C found	27.4	24.4	21.9
% H calcd.	3.03		2.42
% H found	3.11		2.51
Mol. wt. calcd.	132	148.5	164.9
Mol. wt. found	135	149	167

[a] A second crystalline form m. p. −109° was also indicated. [b] Calculated using atomic refractivities listed by Gilman.[6]

ITHACA, N. Y. RECEIVED APRIL 30, 1947

---

[6] Gilman, "Organic Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1938, p. 1739.

[7] See for example Watson, "Modern Theories of Organic Chemistry," 2nd ed., Oxford University Press, London, 1941, p. 101.

Occurrence of Pectic Materials in Wood

BY W. W. PIGMAN, E. ANDERSON AND R. L. LEAF, JR.

Hardwoods contain small amounts (usually less than 0.5%) of materials that yield furfural and carbon dioxide when distilled with 12% hydrochloric acid.[1,2] After hydrolysis of a hemicellulose fraction of beechwood O'Dwyer[1] isolated a cinchonine salt similar to that reported for D-galacturonic acid. Anderson has isolated fractions from hardwoods and softwoods that have specific rotations and solubility characteristics similar to fruit pectins.[2] By hydrolysis of the material in the presence of bromine he produced mucic acid. This evidence proves qualitatively the presence of galacturonic acid in the original wood, which on the basis of O'Dwyer's identification is apparently the D-isomer.

In order to demonstrate more conclusively the presence of pectic materials[3] in a typical wood, it was decided to isolate galacturonic acid n ithe form of the difficultly soluble sodium calcium D-galacturonate[4] after enzymic hydrolysis[5] of wood pectic material. To give some quantitative aspects to the procedure the results were compared with those obtained with citrus pectic acid under the same conditions. Unfortunately for the quantitative aspects, the yields are greatly affected by the purity of the pectic material.[6]

Pectic material isolated from the inner bark of black spruce, in which it occurs in fairly large amounts (10%),[7] was treated with a commercial enzyme preparation. Crystalline sodium calcium galacturonate was isolated in a yield of 28% of the theoretical. Citrus pectic acid under the same conditions gave a yield of 53%. The product had the same calcium analysis and specific rotation as described by Isbell and Frush.[4] On oxidation with bromine under slightly acid conditions it gave mucic acid in a yield of 64% of the theoretical.

On the basis of this work there is no doubt that D-galacturonic acid occurs in the inner bark of the black spruce in a polymerized form. Since enzymic reactions are generally very specific, it is likely that the polymerized form is structurally similar to citrus pectic acid and that wood pectins are closely related to citrus pectins.

Experimental

The pectic acid was made by direct extraction with 5%

---

[1] M. H. O'Dwyer, *Biochem. J.*, **20**, 656 (1926); I. A. Preece, *Biochem. J.*, **25**, 1304 (1931).

[2] E. Anderson, *J. Biol. Chem.*, **165**, 233 (1946), and earlier papers.

[3] In the present sense a pectic material is one which, on hydrolysis, yields a substantial amount of D-galacturonic acid.

[4] H. S. Isbell and H. L. Frush, *J. Research Natl. Bur. Standards*, **32**, 77 (1944); R. Pasternack and P. P. Regna, U. S. patent 2,338,534 (1944).

[5] H. H. Mottern and H. L. Cole, THIS JOURNAL, **61**, 2701 (1939); W. W. Pigman, *J. Research Natl. Bur. Standards*, **25**, 301 (1940).

[6] H. S. Isbell and H. L. Frush, *J. Research Natl. Bur. Standards*, **32**, 90 (1944).

[7] E. Anderson and W. W. Pigman, *Science*, **105**, 601 (1947).