Synthetic Analogs of Busycon Mucus.—Broadly speaking a synthetic analog must be constituted of two acidic polyelectrolytes linked by a calcium ion. It should possess the viscosity properties of mucus as well as the unique characteristics[2] of "elastic recoil" and "stress-fibrilation." Two attempts were made to simulate this mucus behavior by reproducing synthetically these basic structural elements.

First, a 3% solution of polyacrylic acid ([η] 0.8) in water was mixed with calcium carbonate forming a product with 7.61 acrylic acid residues per calcium atom. The pertinent physical properties were qualitatively very similar to those of Busycon mucus. Moreover, it was found that addition of 0.5 *N* NaCl caused a decrease in these properties that was also reminiscent of Busycon mucus behavior.[2]

Finally, a somewhat closer analog was prepared from poly-2-aminoglucose bisulfate and polyacrylic acid. A solution of partially acid degraded chitosan was treated with an excess of sodium bisulfate, dialyzed and the volume subsequently adjusted to an 8% solution. This solution was stirred into an equal volume of 3% aqueous polyacrylic acid and followed by the addition of 2 ml. of 0.1 *N* $Ca(OH)_2$. The fresh mixture evidenced the typical behavior of Busycon mucus but with time further cross linking appears to have occurred with accompanying gelation.

Acknowledgment.—We wish to thank Professor R. R. Ronkin of the Department of Biological Sciences of the University of Delaware for many helpful discussions on mucus and Dr. P. Hamilton of the Alfred I. du Pont Institute for his kind help in the ion exchange chromatographic analysis.

NEWARK, DELAWARE

COMMUNICATIONS TO THE EDITOR

A NEW SYNTHESIS OF IRONES

Sir:

Since the isolation of irone from orris root by Tiemann and Krüger[1] in 1893, various syntheses have been attempted. Studies of the structure of irone by Ruzicka and co-workers[2] in 1933 were followed in 1940 by their synthesis of 6-methylionones[2] later identified with the irones. In 1947 Naves and co-workers[3] reported a practical synthesis of 3-methylcitrals and 3-methyllinalool from which irone could be made. Another approach was made in 1952 by Grütter, Helg and Schinz[4] using thujacetone for the synthesis of 3-methylcitrals and their isomers. More recently the total synthesis of 5,6-dimethyl-5-hepten-2-one from methyl isopropenyl ketone, acetylene and diketene led to a marked improvement in the synthesis of irone in about eight steps.[5]

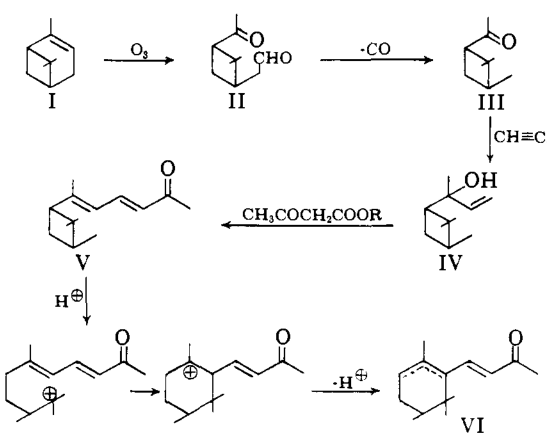
We wish to report a new synthesis of irones from α-pinene involving five steps: α-Pinene (I) was ozonized to yield 65–70% *cis*-pinonic aldehyde (II), b.p. 92° (1.5 mm.); $n^{20}D$ 1.4610; $\alpha^{25}D + 40°$; purity 96% by oximation, and a small amount of pinonic acid.

Decarbonylation of (II) by means of palladium catalyst[6] at about 200° afforded the new ketone, pinonone, 1-acetyl-2,2,3-trimethylcyclobutane (III), (*cis* and *trans* mixture) in 80% yield, b.p. 53° (9 mm.); $n^{20}D$ 1.4410; semicarbazone of probable *cis*-isomer, m.p. 197–198°. (Found: C, 60.92; H, 9.84; N, 21.40); 2,4-dinitrophenylhydrazone, m.p. 201–202° (Found: C, 56.36; H, 6.38; N, 17.63).

Pinonone (III) and acetylene in the presence of sodium acetylide in liquid ammonia gave 3-(2,2,3-trimethylcyclobutyl)-but-1-yn-3-ol (IV) (*cis* and *trans* mixture) in almost quantitative yield, b.p. 74° (8 mm.); $n^{20}D$ 1.4667; $\alpha^{25}D -4°$. *Anal.* Calcd. $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.76; H, 11.02.

The butynol (IV) and ethyl acetoacetate[7] at 178–180° afforded cyclobutyl isomers of irone, 2-(2,2,3-trimethylcyclobutyl)-hepta-2,4-dien-6-one, referred to as cyclobutirones (V) in 65% yield, b.p. 95–105° (0.5 mm.); $n^{20}D$ 1.5080–1.5280. At least four main isomers were identified by gas-liquid partition chromatography. The most stable of the isomers was isolated from the mixture as the semicarbazone, m.p. 202–203° (ethanol). (Found: C, 67.92; H, 9.11; N, 15.87). 2,4-Dinitrophenylhydrazone, m.p. 198–199° (ethanol). (Found: C, 62.16; H, 6.62; N, 14.47).

The mixture of cyclobutirones (V) was rearranged to irone isomers (VI) by treatment for several hours with 85% phosphoric acid at 25° in over 50%



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(1) F. Tiemann and P. Krüger, *Ber.*, **26**, 2679 (1893).

(2) L. Ruzicka, C. F. Seidel and H. Schinz, *Helv. Chim. Acta*, **16**, 1143 (1933); L. Ruzicka and H. Schinz, *ibid.*, **23**, 959 (1940).

(3) Y. R. Naves, A. V. Grampoloff and P. Bachmann, *ibid.*, **30**, 599 (1947).

(4) H. Grütter, R. Helg and H. Schinz, *ibid.*, **35**, 771 (1952).

(5) W. Kimel, J. D. Surmatis, J. Weber, G. O. Chase, N. W. Sax and A. Ofner, *J. Org. Chem.*, **22**, 1611 (1957).

(6) H. E. Eschinazi, *Bull. Soc. Chim. France*, 967 (1952).

(7) M. F. Carroll, *J. Chem. Soc.*, 704, 1266 (1940); 507 (1941).

yield, b.p. 74–83° (0.3 mm.); n^{20}D 1.5002; α^{25}D −15°. The irone mixture was shown by infrared and gas–liquid partition chromatography to consist of about 57% α-neoisoirone[8] (4-phenylsemicarbazone,[9] m.p. 174–175° from ethanol. (Found: C, 74.02; H, 8.43.)), 10.5% α-irone; 8.2% β-irone, 8.4% lights and 16% high boiling isomer (4-phenylsemicarbazone, m.p. 144° from ethanol (Found: C, 74.03; H, 8.18)). The structure of the latter isomer is being elucidated.

[8] The structure of α-neoisoirone was established by Y. R. Naves and P. Ardizio, *Bull. Soc. Chim. France*, 1479 (1955).

[9] Pseudoirone from Hoffmann-La Roche, Inc.,[5] Nutley, N. J., gave upon cyclization with 85% phosphoric acid 16% α-irone, 10.5% β-irone, 7% lights, and 66.5% α-neoisoirone (4-phenylsemicarbazone, m.p. 174° from ethanol). Mixed melting point with 4-phenylsemicarbazone of α-neoisoirone from cyclobutirone, 174°. Both derivatives show identical infrared spectra in KBr pellets.

THE GIVAUDAN CORPORATION
DELAWANNA, NEW JERSEY H. E. ESCHINAZI

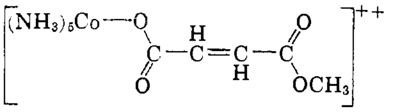
RECEIVED APRIL 1, 1959

SUBSTITUTION COUPLED TO ELECTRON TRANSFER[1]

Sir:

Rate comparisons[2] made for a series of pentamminecobaltic complexes reacting with Cr^{++} aq. suggest that when appropriate bridging groups are associated with Co(III), electron transfer takes place by remote attack of Cr^{++}, the electron flowing through the bond system of the bridging group. The results reported now seem to constitute definite proof for this conclusion.

The ion



(to be subsequently represented as $RFCH_3^{++}$) reacts with Cr^{++}aq. at almost the same rate as does the corresponding complex with fumaric acid in place of the half-ester. In both systems, good stoichiometry for the oxidation–reduction process is observed, one Co^{++}aq. (and $5NH_4^+$) being formed for each Cr^{++}aq. which reacts.

Now it should be noted that remote attack by Cr^{++}aq. on the half-ester will leave both Cr(III) and CH_3 attached to the remote carboxyl. The resulting structure would not be stable, so that ester hydrolysis may be expected to ensue on electron transfer. We cite evidence that this reaction does indeed take place. When Cr^{++}aq. in equivalent amount is added to 0.01 *M* $RFCH_3^{++}$ in the presence of 0.1 *M* $HClO_4$, and the solution immediately after reaction is titrated to *p*H 4.5 with standard alkali, we observe that acid has been produced equivalent in amount to the complex which has reacted. When such mixtures after reaction are distilled at 4°, variable amounts of CH_3OH are detected in the distillate, but comprising only 2 to 7% of the total CH_3OH. In a blank experiment, similar in every respect except that Cr^{+++}aq. is used in place of Cr^{++}aq., no CH_3OH is found in the distillate. Free CH_3OH added to a synthetic mixture containing the metal ions and acid is recovered almost quantitatively under the same conditions for distillation.

When pyrophosphate in excess is added to the mixture after reaction and the solution is subjected to continuous extraction with ether, in 6 hours 60–70% of the fumaric acid is recovered, this recovery being identical to that observed when RFH^{++} rather than $RFCH_3^{++}$ is the oxidant. The extract however contains very little alcohol (it should be noted that the half-ester would respond to the test for CH_3OH). If the reaction mixture then is refluxed to complete the complexing by pyrophosphate, the alcohol can be recovered essentially quantitatively on distillation.

From these and related observations, we conclude that ester hydrolysis accompanies electron transfer (to account for the appearance of acid and the extractability of fumaric acid) and that the CH_3OH is left coördinated to Cr(III) (to account for the holdback of alcohol by the solution). Blank experiments prove that CH_3OH in solution does not become associated with chromium when Cr^{++}-aq. reacts with RFH^{++}. Thus we conclude further that transfer of alcohol to chromium must be direct, and therefore that Cr^{++} attacks the ester end of the fumarato ligand.

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UNIVERSITY OF CHICAGO D. K. SEBERA
CHICAGO, ILL. H. TAUBE

RECEIVED FEBRUARY 27, 1959

[1] This work is supported by the Atomic Energy Commission under Contract AT(11-1)-378.

[2] D. K. Sebera and H. Taube, to be published (described in part in *Can. J. Chem.*, **37**, 129 (1959)).

DIFLUOROAMINE[1]

Sir:

During the reaction of nitrogen trifluoride with arsenic at elevated temperatures (250–300°) to produce tetrafluorohydrazine[2] small amounts of difluoroamine were produced.

The identity of difluoroamine has been established. Its molecular weight by vapor density measurements is 52 (calculated 53). The mass spectrum of difluoroamine given in Table I was obtained on a Consolidated Electrodynamics Model 620 Mass Spectrometer and is consistent with the formula HNF_2.

TABLE I

FRAGMENTATION PATTERN OF HNF_2

m/e	Ion	Pattern, %
53	HNF_2^+	100
52	NF_2^+	8.7
34	HNF^+	99.5
33	NF^+	47.4
20	HF^+	4.0
19	F^+	5.2
15	NH^+	8.7
14	N^+	23.0

The infrared absorption spectrum of difluoroamine consists of strong doublets at 7.0, 7.8, 10.2 and a triplet at 11.2μ. The n.m.r. proton spectrum consists of a triplet as would be expected from a proton spin–spin coupling with two equivalent fluorine nuclei. The center of the triplet is

[1] Army Ordnance Contract DA-01-021-ORD-5135.

[2] C. B. Colburn and A. Kennedy, THIS JOURNAL, **80**, 5004 (1958).