yield, b.p. 74–83° (0.3 mm.); $n^{20}\text{D}$ 1.5002; $\alpha^{25}\text{D}$ −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

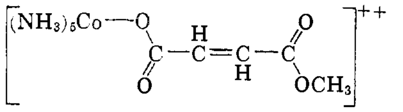
RECEIVED APRIL 1, 1959

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.

GEORGE HERBERT JONES LAB.
UNIVERSITY OF CHICAGO
CHICAGO, ILL.
R. T. M. FRASER
D. K. SEBERA
H. TAUBE

RECEIVED FEBRUARY 27, 1959

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[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

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

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

approximately 6 cycles on the high field side from benzene. The spin–spin splitting is about 24 cycles. The fluorine resonance spectrum consists of two broad bands arising from spin–spin coupling of the fluorine nuclei with the proton. The high field member of this doublet was measured at 2100 cycles on the low field side of trifluoroacetonitrile.

The vapor pressure of difluoroamine was measured and can be expressed by a Clausius–Clapeyron equation

$$\log P(\text{mm.}) = -1298/T + 8.072$$

The boiling point of difluoroamine is −23° and the heat of vaporization is estimated to be 5940 cal./mole. The melting point is approximately −131° and its critical temperature measured by the Cagniard de la Tour tube method is 130°. From an extrapolation of the vapor pressure data a critical pressure of 93 atmospheres was calculated.

A material thought to be difluoroamine has been reported previously by Ruff and Staub[3] and Staub.[4] They found it to be a product of the electrolysis of ammonium bifluoride and reported a boiling point "ostensibly about −100°,"[4] an approximate b.p. −65°, and m.p. −125°.[3] These figures are somewhat different from those reported herein, b.p. −23° and m.p. −131°. We have failed in many attempts to obtain difluoroamine by the electrolysis of ammonium bifluoride. Burg[5] has pointed out the uncertainty of the identification of difluoroamine by Ruff.

Caution should be used in working with difluoroamine. We have had occasional explosions with both solid and liquid difluoroamine. Difluoroamine has been stored at room temperature in glass vessels for long periods of time with no apparent decomposition.

The authors wish to express their appreciation to Dr. Keith S. McCallum for the n.m.r. and infrared spectra of difluoroamine.

[3] O. Ruff and L. Staub, *Z. anorg. allgem. Chem.*, **198**, 32–38 (1931).

[4] Lisbeth Staub, Thesis, Breslau, 1932.

[5] A. B. Burg in Simons, "Fluorine Chemistry," Vol. I, Academic Press, New York, N. Y., 1950, p. 88.

ROHM AND HAAS COMPANY
REDSTONE ARSENAL
RESEARCH DIVISION
HUNTSVILLE, ALABAMA

AL KENNEDY
CHARLES B. COLBURN

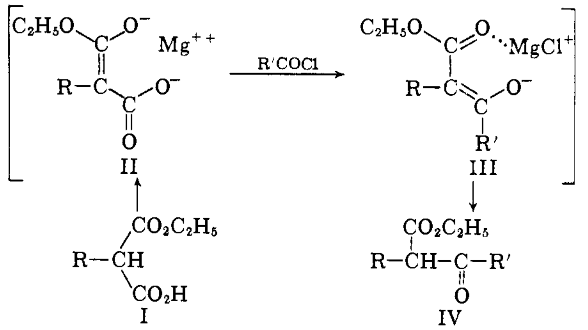
RECEIVED MARCH 24, 1959

A NEW SYNTHETIC METHOD FOR THE PREPARATION OF α-SUBSTITUTED β-KETOESTERS

Sir:

During the course of a synthetic program directed toward polycyclic terpenes, we had need of substantial quantities of the β-ketoester, ethyl 5-(*o*-methoxyphenyl)-3-keto-2-methylvalerate (IV, R = CH_3, R′ = *o*-$CH_3OC_6H_4CH_2CH_2$). One approach (methylation of the pyrrolidine enamine of the unsubstituted β-ketoester, obtained *via* partial hydrolysis[1] of the corresponding malonate) led to the desired product in only 31% yield from *o*-methoxyhydrocinnamic acid. In an effort to find a more rewarding synthesis we turned to the acylation of the magnesium salt of ethyl hydrogen methylmalonate and have been able to develop this method into a very convenient one-step synthesis of α-substituted β-ketoesters.

By treatment of ethyl hydrogen methylmalonate[2] (I, R = CH_3) with two equivalents of magnesium ethoxide, then removal of the ethanol formed,[3] or, better, with two equivalents of isopropylmagnesium bromide in tetrahydrofuran, the half-ester was converted to the tetrahydrofuran-soluble magnesium chelate (II, R = CH_3).[4] Addition of acetyl chloride to this solution at 0° led to the rapid evolution of carbon dioxide and the formation of the new magnesium chelate (III, R = CH_3, R′ = CH_3). Removal of most of the solvent, and hydrolysis of the residue with dilute aqueous ammonium chloride afforded a 62% yield of ethyl α-methylacetoacetate (IV, R = CH_3, R′ = CH_3), b.p. 70° (13 mm.).[5] Similarly we have prepared ethyl 3-keto-2-methylcaproate (IV, R = CH_3, R′ = C_3H_7), b.p. 86–89° (10 mm.),[6] in 69% yield from butyryl chloride; ethyl α-methylbenzoylacetate (IV, R = CH_3, R′ = C_6H_5), b.p. 90–94° (0.2 mm.),[7] in 52% yield from benzoyl chloride; and diethyl 3-keto-2-methyladipate (IV, R = CH_3, R′ = $CH_2CH_2CO_2C_2H_5$), b.p. 80–82° (0.08 mm.) C, 57.45; H, 7.66), in 71% yield from β-carbethoxypropionyl chloride. Application of this method to the formation of the desired β-ketoester (IV, R = CH_3, R′ = *o*-$CH_3OC_6H_4CH_2CH_2$), b.p. 117° (0.1 mm.) (C, 68.04; H, 7.53) led to a 63% yield from *o*-methoxycinnamic acid without isolation of the acid chloride.



When ethyl hydrogen phenylmalonate[8] was employed, acetylation of the resulting magnesium chelate (II, R = C_6H_5) afforded a 60% yield of ethyl α-phenylacetoacetate (IV, R = C_6H_5, R′ = C_6H_5), b.p. 128–134° (8 mm.)[9] Diethyl 3-keto-2-phenyladipate (IV, R = C_6H_5, R′ = $CH_2CH_2CO_2C_2H_5$), b.p. 137–138° (0.25 mm.) (C,

[1] B. R. Baker, R. E. Schaub and J. H. Williams, *J. Org. Chem.*, **17**, 116 (1952).

[2] J. R. Roland and S. M. McElvain, THIS JOURNAL, **59**, 132 (1937).

[3] The procedure reported for the preparation of diethyl ethoxymagnesiomalonate was used, J. A. Price and D. S. Tarbell, *Org. Syn.*, **37**, 20 (1957).

[4] *Cf.* a similar magnesium chelate prepared by carboxylation of nitroalkanes with methylmagnesium carbonate, R. M. Stiles and H. Finkbeiner, THIS JOURNAL, **81**, 505 (1959).

[5] K. Folkers and H. Adkins, *ibid.*, **53**, 1416 (1931).

[6] C. Glacet, *Ann. chim.*, [12] **2**, 293 (1947).

[7] J. B. Dorsch and S. M. McElvain, THIS JOURNAL, **54**, 2960 (1930).

[8] E. J. Corey, *ibid.*, **74**, 5903 (1952).

[9] R. H. Kimball, J. D. Jefferson and A. B. Pike, *Org. Syn.*, Coll. Vol. II, 284 (1955).