of tetracycline by twenty-fold or greater are 2-carboxamide to nitrile, epimerization at C.4, epimerization at C.5a, and dehydrogenation at C.5a(11a).

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RECEIVED AUGUST 18, 1958

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## STUDIES[1] INVOLVING ISOTOPICALLY LABELLED FORMIC ACID AND ITS DERIVATIVES. IV. DETECTION OF CYANIDE ($CN^-$) IN A MIXTURE OF FORMIC ACID AND NITROGEN IN THE MASS SPECTROMETER

*Sir:*

During mass spectrometric studies of formic acid,[1] a research spectrometer[2] was modified for examining ion-molecule reactions. An essentially field-free region was set up between the ionization chamber and the first accelerating plate. Ions produced from one gas in the ionization chamber are passed at low energy through neutral molecules of another gas introduced into the field-free space. As the 10-fold higher pressure[3] in the chamber permits little back diffusion from the field-free region, it is possible to determine which of two species furnishes the ion in an ion-molecule reaction by inverting the mode of addition of two gases and noting the effect on the relative abundance of a production.

Ionization of formic acid in the chamber by electrons having an indicated energy[4] of 2.3 e.v. produced $HCOO^-$ ions[1] and essentially no positive ions.[5]

With nitrogen gas in the field-free region, a negative ion of mass 26 was detected. Its mass was not affected by substitution of DCOOH for the formic acid. Substitution of either $HC^{13}OOH$ for formic acid or nitrogen-$N^{15}$ for nitrogen shifted the mass of this ion to 27. Use of both $HC^{13}OOH$ and nitrogen-$N^{15}$ in the same experiment caused mass 28 to appear. When carbon monoxide or carbon dioxide was substituted for formic acid the ion of mass 26 failed to appear. We conclude that this negative ion is $CN^-$. Since the positive peaks known to arise from hydrogen cyanide and cyanogen[6] were absent even with the electron energy raised to 75 e.v., neither of these substances is a likely precursor. Inversion of the mode of addition—that is introduction of nitrogen into the ionization chamber and formic acid into the field-free region—resulted in a 10-fold reduction in abundance of the $CN^-$ ion.

When, in a subsequent experiment, an equimolar mixture of nitrogen and formic acid at 2 mm. pressure was subjected to a spark discharge, 1% hydrogen cyanide was found in the product mixture.

In the mass spectrometric study, some active species produced from formic acid in the ionization chamber apparently reacts with nitrogen molecules to give rise to the $CN^-$ ions. The active species is probably the negative ion,[7] $HCOO^-$, although we cannot rule out all other possibilities. Were the present reaction between $HCOO^-$ and $N_2$ molecules, this would presumably be the first mass-spectrometric observation of a negative[8] ion-molecule reaction of this type.

The present results indicate some similarity between the reactions produced by the electric discharge and those effected by the 2.3 e.v. electrons in the mass spectrometer. The results also may be significant because of a current interest in nitrogen fixation by ionizing radiations.

Helpful discussions with Russell Baldock, John Burns and P. S. Rudolph are acknowledged.

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[1] Previous study, G. A. Ropp and C. E. Melton, THIS JOURNAL, **80**, 3509 (1958).

[2] C. E. Melton, G. A. Ropp and P. S. Rudolph, *J. Chem. Phys.*, in press (October, 1958).

[3] G. F. Wells and C. E. Melton, *Rev. Sci. Instr.*, **28**, 1065 (1957).

[4] C. E. Melton and G. F. Wells, *J. Chem. Phys.*, **27**, 1132 (1957); previous experience indicates that the actual electron energy does not differ by more than ±3 e.v. from the indicated energy.

[5] T. Mariner and W. Bleakney, *Phys. Rev.*, **72**, 792 (1947).

[6] C. A. McDowell and J. W. Warren, *Trans. Faraday Soc.*, **48**, 1084 (1952); K. E. Dorsch and H. Kallman, *Z. physik.*, **60**, 376 (1930); J. T. Tate, P. T. Smith and A. L. Vaughan, *Phys. Rev.*, **48**, 525 (1935).

[7] The low energy of the ionizing electrons makes it improbable that a positive ion is the precursor of the $CN^-$ ion. A free-radical precursor is unlikely at the low pressures employed since a three-step process would be required: (a) electron impact with formic acid to produce a radical, (b) reaction of the radical with nitrogen, and (c) conversion of the resulting species to $CN^-$.

[8] A number of positive ion-molecule reactions are known: see H. S. Johnston in *Annual Reviews of Physical Chemistry*, **8**, 252–3 (1957). However, see E. E. Muschlitz, Jr., *J. Appl. Phys.*, **28**, 1414 (1957).

[9] Operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

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RECEIVED JULY 25, 1958

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## A NOVEL SYNTHESIS OF METAL CARBONYLS USING TRIETHYLALUMINUM AS THE REDUCING AGENT[1]

*Sir:*

We wish to report a novel method for preparing transition metal carbonyls, one that is of particular value for the less accessible metal carbonyls. The method consists essentially of a reductive carbonylation[2] reaction of an appropriate salt of the transition metal with triethylaluminum and carbon monoxide. The reaction generally is carried out in an ether solvent at elevated temperature and pressure. The triethylaluminum appears to function in this reaction as a selective reducing agent for the transition metal, permitting carbonylation to occur at a rate greater than the rate of reduction to the free metal.

The method differs from the conventional Grignard methods[3–7] in that (1) it is applicable to the

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[1] Reductive Carbonylation Synthesis of Metal Carbonyls. I.

[2] The term "reductive carbonylation" as used here denotes overall reduction and carbonylation of the transition metal in a compound or intermediate in which the metal has a formal positive charge of one or greater.

[3] A. Job and A. Cassal, *Compt. rend.*, **183**, 392–4 (1926).

[4] A. Job and J. Rouvillois, *Bull. soc. chim.*, **41**, 1041 (1927).

[5] W. Hieber and E. Romberg, *Z. anorg. Chem.*, **221**, 321 (1935).

[6] K. A. Kocheskov, A. N. Nesmeyanov, N. M. Nadj, I. M. Rossinskaya and L. M. Borissova, *Compt. rend. acad. sci.*, **26**, 54 (1940).

[7] B. B. Owen, J. English, Jr., H. G. Cassidy and C. V. Dundon, THIS JOURNAL, **69**, 1723 (1947).

synthesis of a greater variety of metal carbonyls, (2) little or no free metal is formed as a by-product, (3) the yields generally are higher, and more sensitive to variations in reaction conditions such as solvent, temperature and pressure, and (4) the product is formed directly as the carbonyl and does not require treatment with water to liberate it.

The method may be exemplified by the synthesis of chromium hexacarbonyl: To a suspension of 4.75 g. (0.030 mole) of anhydrous chromic chloride in 50 ml. of anhydrous diethyl ether was added dropwise a solution containing 28 ml. (0.19 mole) triethylaluminum and 60 ml. of anhydrous diethyl ether over a period of 30 minutes at 0° under Seaford grade nitrogen. The mixture then was charged into a 250-ml. Magne-Dash autoclave in a dry nitrogen box. The autoclave was purged twice with 600 p.s.i.g. C.P. grade carbon monoxide and pressurized with 3500 p.s.i.g. of carbon monoxide. The autoclave then was heated with stirring at 100–115° for 5.5 hours. After the autoclave had cooled overnight to room temperature, it was vented slowly at −80°. The reaction mixture was quenched carefully at 0° under a Dry Ice condenser with a methanol–benzene solution, water, and hydrochloric acid in succession. Finally, the mixture was steam distilled with stirring, and 5.0 g. (76% yield) of chromium hexacarbonyl, m.p. 154–155° (uncor.), was obtained.

Details of this method as it applies to the synthesis of various metal carbonyls will be reported in a future paper.

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RECEIVED AUGUST 20, 1958

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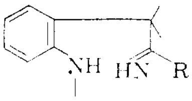
## SIX-MEMBERED RING FORMATION DURING FISCHER INDOLE SYNTHESIS

*Sir:*

The Robinson mechanism for the Fischer indole synthesis[1] has received strong confirmation recently. Carlin, *et al.*,[2] have presented convincing evidence for the detailed intermediates involved in the rearrangement and, in particular, the existence of an intermediate of type I has been established by its isolation in two instances.

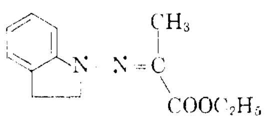


I

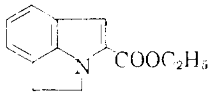
Plieninger[3] obtained such an intermediate from the Fischer reaction with α-keto-γ-butyrolactone phenylhydrazone, and Suvorov, *et al.*,[4] trapped the intermediate aniline in the rearrangement of butanone phenylhydrazone.

As a consequence of the existence of intermediate I, it should be possible, in any appropriately constituted molecule wherein five-membered indole ring formation is difficult and where R is a suitably reactive group, to have ring closure take an alternative course and form the six-membered ring. This result has been realized for the first time with the hydrazone (II) from 1-aminoindoline and ethyl pyruvate. On being subjected to conditions of the Fischer reaction, II formed the 3-hydroxy-2-quinolone III as the major product.[5] In addition there was isolated a small amount of the indole IV, containing the heretofore unknown pyrrolo[3,2,1-h,i] indole ring system.[6]

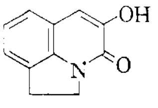
The hydrazone II (m.p. 87–87.5°) was heated for six hours in absolute ethanol containing 10 volume per cent. sulfuric acid, and cooling the reaction mixture led to crystallization of the hydroxyquinolone III (m.p. 241°. *Anal.* Found: C, 70.7; H, 4.8; N, 7.7; equiv. wt., 191). From the mother liquors, by chromatography on alumina, α-carbethoxyindole IV was isolated (m.p. 74–74.5°. *Anal.* Found: C, 72.8; H, 6.2; N, 6.3; $OC_2H_5$, 20.6).



II

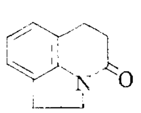


IV

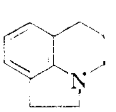


III

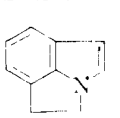
The 3-hydroxy-2-quinolone structure was assigned to III on the basis of its analysis and characteristic ultraviolet spectrum.[7] It was established beyond question by Wolff–Kishner reduction of III to the quinolone V (m.p. 112–113°. *Anal.* Found: C, 76.3; H, 6.1; N, 7.9) and reduction of the latter with lithium aluminum hydride to lilolidine (VI).[8]



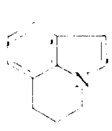
V



VI



VII



VIII

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(1) G. M. and R. Robinson, *J. Chem. Soc.*, **113**, 639 (1918); **125**, 827 (1924).

(2) R. B. Carlin and G. W. Larson, THIS JOURNAL, **79**, 934 (1957); R. B. Carlin and D. P. Carlson, *ibid.*, **79**, 3605 (1957); R. B. Carlin, W. O. Henley, Jr., and D. P. Carlson, *ibid.*, **79**, 5712 (1957).

(3) H. Plieninger, *Ber.*, **83**, 273 (1950); H. Plieninger and I. Nogradi, *ibid.*, **88**, 1964 (1955).

(4) N. N. Suvorov, N. P. Sorokina and Y. N. Scheinker, *Khim. Nauka i Prom.*, **2**, 394 (1957).

(5) Quinolones have been observed in the Diels-Reese reaction [O. Diels and J. Reese, *Ann.*, **511**, 168 (1934); E. H. Huntress, J. Bornstein and W. H. Hearon, THIS JOURNAL, **78**, 2225 (1956)] when the 1:1 adducts of hydrazobenzenes and dimethyl acetylenedicarboxylate were heated in picoline. These adducts gave pyrazolones with acid, and in two cases out of four gave indoles on heating in xylene. Although this reaction may involve intermediates similar to those in the Fischer reaction, further clarification is needed on the striking effect of solvent and the failure of two of the adducts to yield indoles.

(6) The claim of J. G. Jackson and J. Kenner, *J. Chem. Soc.*, 573 (1928), to have prepared this ring-system was shown to be incorrect by G. K. Hughes, F. Lions and E. Ritchie, *J. Proc. Roy. Soc. N. S. Wales*, **72**, 209 (1938), and H. G. Dunlop and S. H. Tucker, *J. Chem. Soc.*, 1945 (1939).

(7) R. G. Ault, E. L. Hirst and R. A. Morton, *ibid.*, 1653 (1935); K. G. Cunningham and G. G. Freeman, *Biochem. J.*, **53**, 328 (1953); A. Bracken, A. Pocker and H. Raistrick, *ibid.*, **57**, 587 (1954).

(8) B. D. Astil and V. Boekelheide, *J. Org. Chem.*, **23**, 316 (1958).