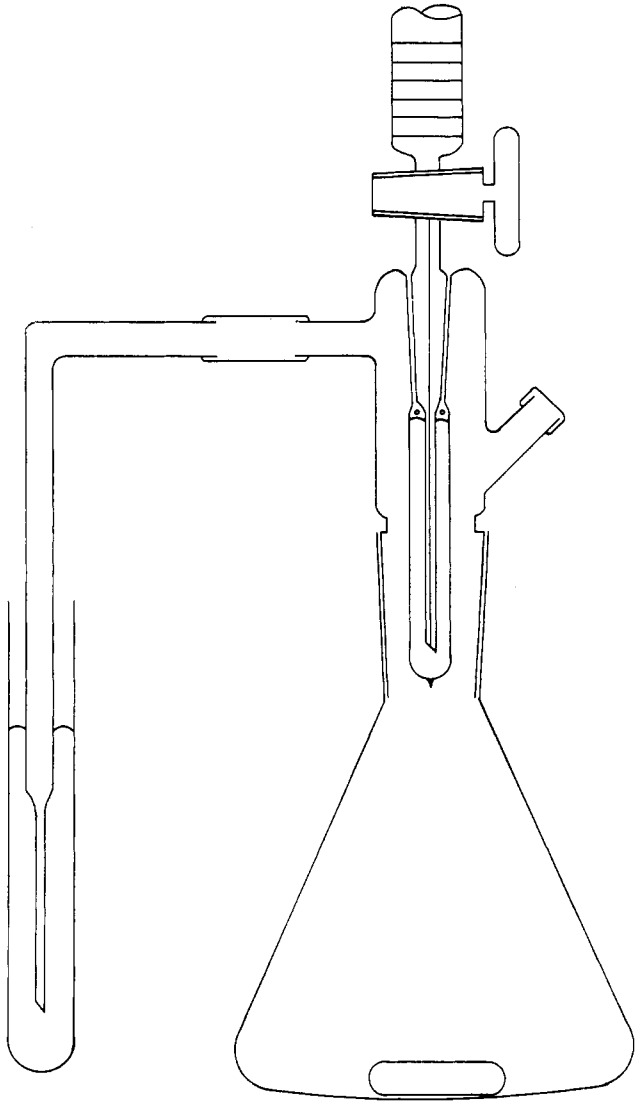


Fig. 1.—Apparatus for the quantitative hydrogenation of unsaturated compounds.

The precision and accuracy appear highly satisfactory It should also be pointed out that the five successive determinations were made consecutively with the same preparation of catalyst. Each determination required only 1–2 minutes for completion. Consequently, this apparatus and procedure appear to provide a highly convenient, precise analysis for unsaturation in organic compounds.

Experimental

Procedure.—A stock solution of sodium hydroxide in ethanol (0.100 *M*) was prepared by dissolving 4.00 g. of sodium hydroxide in 50.0 ml. of water and diluting to 1.0 l. with absolute ethanol. The standard sodium borohydride solution was prepared by adding 3.95 g. of sodium borohydride (Metal Hydrides Incorporated, 98%) to 100.0 ml. of this ethanolic solution and stirring magnetically until solution of the salt was complete. If the solution was not clear, it was filtered through a plug of glass wool. The solution was standardized by injecting 10.00 ml. with a hypodermic syringe into aqueous acetic acid and measuring the hydrogen evolved. The 0.250 *M* and 0.100 *M* sodium borohydride solutions were prepared by diluting aliquots of the 1.00 *M* solution with the sodium hydroxide–ethanol solution.

In the 125-ml. flask of the apparatus (Fig. 1) was placed 1.00 g. of Darco K-B carbon, 40.0 ml. of absolute ethanol, 1.00 ml. of 0.02 *M* chloroplatinic acid solution, and a Teflon-covered magnetic bar. The apparatus was assembled with a rubber stopple in the injection port. The flask was immersed in a beaker of water maintained at 25°. Injection of 5.00 ml. of 1.00 *M* sodium borohydride with a syringe into the vigorously stirred solution produced the catalyst. After about 1 min., 2.00 ml. of concentrated hydrochloric acid was injected, destroying the excess borohydride and providing a hydrogen atmosphere. A small quantity of 1-octene was injected to bring the apparatus to equilibrium.

The analysis was carried out by injecting either the pure liquid olefins or standard solutions of the olefin in ethanol with a syringe. Hydrogenation proceeded rapidly to completion. Generally, but 1 to 2 min. proved adequate for each individual determination. A total of 5 to 10 successive analyses could be carried out before the flask became inconveniently full.

In order to obtain the number of millimoles of double-bonds in the samples, it is necessary to add to the number of mmoles of "hydride" in the borohydride solution (1.00 *M* $NaBH_4$ = 4.00 *M* "hydride") the number of mmoles of hydrogen displaced by the volume of the sample introduced plus the volume of the borohydride solution used. Since 1 mmole of hydrogen at ordinary temperatures and pressures occupies a volume of very nearly 25 cc., this free space equivalent (F. S. E. of Table I) may be conveniently estimated by multiplying the sum of the added volumes by 0.04.

It should be pointed out that an alternative procedure in which hydrogen is generated in one flask and is utilized in a second provides a slightly modified method which may have advantages in some special cases.[2]

Presently we are exploring the applicability of this automatic hydrogenation procedure to the analysis of micro quantities of unsaturated compounds.

Acknowledgment.—We wish to acknowledge the financial support of the Esso Research and Engineering Co. which made this study possible.

Chelation as a Driving Force in Organic Reactions. V.[1] The Preparation of α-Nitro Esters through the Carboxylation of Nitroparaffins

HERMAN L. FINKBEINER AND GEORGE W. WAGNER

General Electric Research Laboratory, Schenectady, New York

Received August 16, 1962

The synthetic utility of α-nitro esters dates almost from Steinkopf's[2] first synthesis of nitroacetic acid by the self-condensation of nitromethane. Reduction of the nitro group leads to α-amino esters,[3] reaction with Mannich bases provides a synthesis of δ-keto esters,[4] and treatment with sodium nitrite provides a synthesis of α-oximino esters.[5] However, the preparation of the nitro ester itself has not been simple, and, consequently, a number of techniques have been developed for their synthesis. Steinkopf used the nitration of diethyl methylmalonate in the preparation of α-nitropropionic acid.[6] Kornblum has developed a modification of the Victor Meyer reaction to convert α-halo esters to α-nitro esters.[7] The activity of the acidic α-hydrogen in ethyl nitroacetate has been utilized in a Michael addition to acrylonitrile and ethyl acrylate.[8]

(1) Previous paper in this series: H. L. Finkbeiner and M. Stiles, *J. Am. Chem. Soc.*, in press.
(2) W. Steinkopf, *Ber.*, **42**, 2026 (1909).
(3) D. A. Lyttle and D. I. Weisblatt, *J. Am. Chem. Soc.*, **69**, 2118 (1947).
(4) A. Dornow and A. Frese, *Ann.*, **581**, 211 (1953).
(5) N. Kornblum and J. H. Eicher, *J. Am. Chem. Soc.*, **78**, 1494 (1956).
(6) W. Steinkopf and A. Supan, *Ber.*, **43**, 3239 (1910).
(7) N. Kornblum, R. K. Blackwood, and J. Powers, *J. Am. Chem. Soc.* **79**, 2507 (1957).
(8) R. N. Boyd and R. Leshin, *ibid.*, **74**, 2675 (1952).

Aldehydes have been condensed with ethyl nitroacetate to synthesize diethyl 1,3-dinitro-2-alkylglutarates.[9]

In connection with our interest in chelation as a driving force in organic reactions, we have established that primary nitro compounds can be carboxylated with magnesium methyl carbonate to give α-nitro acids.[1,10] The purpose of this paper is to demonstrate that this carboxylation provides a facile preparative method for the synthesis of α-nitroesters.

The pale yellow magnesium methyl carbonate (MMC) solution which results from the saturation of a magnesium methoxide suspension in dimethylformamide with carbon dioxide is a reagent for the introduction of the carboxyl group into active hydrogen compounds such as primary nitro alkanes[10] and ketones,[11] as shown in equation 1. This product can then be esterified.

$$R{-}CH_2NO_2 \xrightarrow[2)\ HCl]{1)\ MMC} R{-}\underset{\displaystyle NO_2}{\overset{|}{C}}H{-}COOH \xrightarrow[CH_3OH]{HCl} RCHNO_2COOCH_3 \quad (1)$$

Previous work has shown that an excess of magnesium methyl carbonate is necessary to obtain a maximum conversion of the nitroalkane to the magnesium chelate of the nitro acid.[1] Therefore, a magnesium methyl carbonate nitroalkane ratio of 2 was used in carrying out the present preparative scale work. In general, when sufficient nitroalkane was available, one mole of the nitro compound was added to a liter of 2 *M* magnesium methyl carbonate at 60°. The product was then converted to the ester by either of two methods. The reaction mixture was hydrolyzed with cold aqueous hydrochloric acid, the nitro acid was extracted with ether, and after drying and removing the ether, the acid was esterified with cold methanolic hydrogen chloride. Alternatively, the magnesium chelate was precipitated from the dimethylformamide solution by pouring the reaction mixture into ether, and then esterifying the nitro acid by dissolving the chelate directly in methanolic hydrogen chloride. The yields and physical properties of a number of methyl esters of α-nitro acids prepared by carboxylation followed by esterification are given in Table I.

TABLE I

Nitro compound	Yield of $R{-}CHNO_2{-}COOCH_3$	$n^{20}D$	B.p., °/mm.
CH_3NO_2	58	1.4253[a]	68/2
$CH_3CH_2NO_2$	47	1.4216	79/5
$CH_3CH_2CH_2NO_2$	44	1.4249	77/2.5
$CH_3(CH_2)_2CH_2NO_2$	43	1.4281	68/1
$CH_3(CH_2)_3CH_2NO_2$	45	1.4308	80/0.75
$(CH_3)_2CHCH_2NO_2$	40	1.4275	73/1
$CH_3(CH_2)_4CH_2NO_2$	47	1.4333	80/0.5
$C_6H_5CH_2CH_2NO_2$	40	1.5100	110/0.01

[a] Lit. $n^{20}D$ 1.4245; N. Feuer, H. B. Hass, and K. S. Warren, *J. Am. Chem. Soc.*, **71**, 3079 (1949).

To establish the identity of the esters, they were converted to the corresponding ammonium salts and analyzed for carbon, hydrogen and nitrogen. These analyses and melting points are given in Table II.

TABLE II

ANALYSES AND M.P. OF $[RCNO_2COOCH_3]^-NH_3^+$

R	M.p.	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
H	138–140°	26.5	5.9	20.6	27.2	6.2	20.1
CH_3	126–127°	32.0	6.7	18.7	32.2	6.8	19.2
CH_3CH_2	109–110°	36.6	7.4	17.1	36.6	7.2	17.4
$CH_3CH_2CH_2$	116–118°	40.4	7.9	15.7	40.5	7.8	15.8
$CH_3(CH_2)_3$	105–106°	43.7	8.4	14.6	44.0	8.3	15.0
$CH_3(CH_2)_4$	104–105°	46.6	8.8	13.6	46.0	8.8	14.0
$C_6H_5CH_2$	122–123°	53.1	6.2	12.4	53.5	6.1	12.6

A few of the α-nitro esters were also converted to the α-amino ester hydrochloride by catalytic reduction with hydrogen in methanol. When reduction was complete, hydrogen chloride was added to the filtered solution to convert the aminoester to its salt. After evaporation of the methanol, the solid residue was recrystallized. In this fashion methyl α-nitrobutyrate and methyl α-nitrovalerate were converted to methyl α-aminobutyrate hydrochloride and methyl valinate hydrochloride, respectively. The Nef reaction was used to convert small samples of methyl nitropropionate and methyl nitrobutyrate to methyl pyruvate and methyl α-ketobutyrate. The α-ketoesters were isolated and identified as their 2,4-dinitrophenylhydrazones.

The carboxylation of primary nitro compounds offers a method of preparing nitro acids and esters on a synthetic scale, under mild conditions, through a method essentially free of side reactions. The high purity products can easily be reduced by catalytic methods at atmospheric pressure to give α-amino esters.

Experimental

Nitromethane, nitroethane, 1-nitropropane, 1-nitropentane, and 1-nitrohexane are commercially available materials which were redistilled before use. The remaining nitro compounds, except 2-phenylnitroethane, were prepared by the method developed by Kornblum[12] from the corresponding primary alkyl bromides. Phenylnitroethane was prepared by reducing ω-nitrostyrene with lithium aluminum hydride at −40° using the procedure developed by Schecter,[13] *et al.*

Magnesium Methyl Carbonate.—Eight liters of anhydrous methanol was placed in a 12-l. flask equipped with a reflux condenser, stirrer, and provisions for passing gas over the liquid. After the reaction of magnesium and methanol had been initiated using a few grams of magnesium, a total of 480 g. (20 moles) of magnesium turnings was added at a rate to maintain a constant, but controlled, reflux. After the magnesium had completely reacted, the excess methanol was stripped off at water pump vacuum. A 50° water bath was used to heat the mixture, and stirring was continued as long as possible to aid in removing the methanol. However, it is essential that some methanol remain in the solid mass or redissolution becomes extremely slow. When the pressure in the system dropped to the minimum that the water pump was capable of (approximately 20 mm.), enough dimethylformamide was added to the flask to give a total volume of 10 l. Then carbon dioxide was admitted to the stirred system as rapidly as it could be taken up. A bubble counter was used at the outlet of the system to maintain a positive pressure.

After all the magnesium methoxide had dissolved, a short bubble cap fractionating column was put on the flask and the temperature was raised to distill any remaining methanol. The reaction mixture was stirred under a slow stream of carbon dioxide during this distillation. The distillation was continued until the head temperature reached approximately 150°. Then the mixture was cooled to room temperature under carbon dioxide to assure saturation.

(9) A. Dornow and H. Menzel, *Ann.*, **588**, 40 (1954).
(10) M. Stiles and H. L. Finkbeiner, *J. Am. Chem. Soc.*, **81**, 505 (1959).
(11) M. Stiles, *ibid.*, **81**, 2598 (1959).
(12) N. Kornblum, H. O. Larson, R. K. Blackwood, D. P. Mooberry, E. P. Oliveto, and G. E. Graham, *ibid.*, **78**, 1497 (1956).
(13) H. Schecter, D. E. Ley, and E. B. Roberson, Jr., *ibid.*, **78**, 4984 (1956).

The molarity of the solution with respect to magnesium was determined by adding a known volume to excess standard sulfuric acid, heating to dispel carbon dioxide, and back-titrating with sodium hydroxide. The carbon dioxide content of the reagent could be determined gasometrically; however, the interpretation of the result is not straightforward.[1] A magnesium methyl carbonate solution prepared in this fashion was used for seven months with no detectable change in its effectiveness. All the methyl esters were prepared in an identical fashion. The preparation of methyl α-nitrobutyrate is given as an illustration.

Methyl α-Nitrobutyrate. (a) **Carboxylation of Nitropropane.**—One liter of 2 *M* magnesium methyl carbonate was placed in a 2-l. flask equipped with a stirrer, a gas inlet tube, and a combination condenser and gas outlet. The reagent was heated, while stirring, to 60° under a carbon dioxide stream. When the temperature of the magnesium methyl carbonate solution had stabilized at approximately 60°, 89 g. of 1-nitropropane was added, and the carbon dioxide stream was replaced by a slow nitrogen stream.

After stirring for 6 hr. at 60°, the reaction mixture was cooled to 10° with an ice bath, and then either hydrolyzed or the magnesium chelate precipitated.

(b) **Hydrolysis and Esterification.**—The carboxylation mixture was poured with vigorous stirring into a mixture of 600 ml. of concentrated hydrochloric acid and 750 g. of ice that had been overlayed with 100 ml. of ether. The ether was separated and the aqueous layer extracted four times with 100-ml. portions of ether. The ether extracts were combined and given a preliminary drying for 15 min. with powdered anhydrous magnesium sulfate. After filtering off the magnesium sulfate, the drying was completed with phosphorus pentoxide. The essentially colorless ether solution was evaporated on a rotary film evaporator at room temperature or slightly below. While the ether was evaporating, 200 ml. of 2 *M* methanolic hydrogen chloride was cooled to −50°. This was poured into the flask containing the α-nitrobutyric acid and the mixture was allowed to warm spontaneously to room temperature and stand overnight. Approximately 100 ml. of the methanol was removed at room temperature, under vacuum, and the remaining reaction mixture was poured into 200 ml. of water. The aqueous solution was extracted five times with 50-ml. portions of ether, the ether dried over magnesium sulfate and distilled. The yield of methyl α-nitrobutyrate was 64.7 g. (44%), b.p. 77°/2.5, $n^{20}D$ 1.4249.

(c) **Precipitation and Esterification.**—The carboxylation mixture was poured with vigorous stirring into 2 l. of ether to precipitate the magnesium chelate of α-nitrobutyric acid and unchanged magnesium methyl carbonate. After decanting the supernatant liquid phase, 1 l. of methanol containing 200 g. of hydrogen chloride cooled to −50° was added to the solid precipitate. This mixture was allowed to warm spontaneously to room temperature and stand overnight. Approximately 600 ml. of methanol was distilled at room temperature under vacuum, and the remaining mixture was poured into 800 ml. of water. The aqueous system was extracted eight times with 50-ml. portions of ether. After drying the ether solution with magnesium sulfate, the product was distilled. The yield was 67 g. (45.5%) of methyl α-nitrobutyrate.

Preparation of Ammonium Salts.—Approximately 1.0 g. of the α-nitro ester was added to 25 ml. of 1 *M* ammoniacal methanol, and the reaction mixture was placed in the refrigerator overnight. The crystals were filtered off and recrystallized from 0.5 *M* ammoniacal methanol. The products were dried over potassium hydroxide in an ammonia atmosphere. All melting points were taken in sealed tubes. An analogous procedure gave the sodium salts of the methyl nitro esters when sodium methoxide was used in place of ammonia.

Preparation of Methyl α-Aminobutyrate Hydrochloride.—A solution of 1.47 g. (0.01 mole) of methyl α-nitrobutyrate in 40 ml. of methanol, in which was suspended 1.0 g. of 5% platinum on carbon (K&K Laboratories), was stirred, under hydrogen at 1 atm. until 670 ml. was consumed. The catalyst was filtered off, 10 ml. of 1.0 *M* methanolic hydrogen chloride was added to the filtrate, and the reaction mixture was evaporated to dryness in a film evaporator. The solid residue was recrystallized from ethanol–benzene, m.p. 136–138°, lit. 139°.[14]

Preparation of Methyl α-Ketobutyrate 2,4-Dinitrophenylhydrazone.—A sample of methyl α-nitrobutyrate (1.47 g.) was dissolved in 10 ml. of 2 *M* sodium methoxide. The mixture was poured into 20 cc. of ice cold concentrated hydrochloric acid. After filtering off the precipitated sodium chloride, the blue aqueous phase was extracted with ether and dried. After the blue color had faded, 2,4-dinitrophenylhydrazone reagent was added, the ether largely removed on the steam bath, and 10 ml. of methanol was added. The product crystallized after standing overnight in the refrigerator, m.p. 147–148°.

Anal. Calculated for $C_{11}H_{12}N_4O_6$: C, 44.90; H, 4.08; N, 19.05. Found: C, 44.9; H, 4.1; N, 19.2.

(14) T. Curtius and E. Müller, *Ber.*, **37**, 1274 (1904).

Dicyanoketenimine (Cyanoform)

S. TROFIMENKO

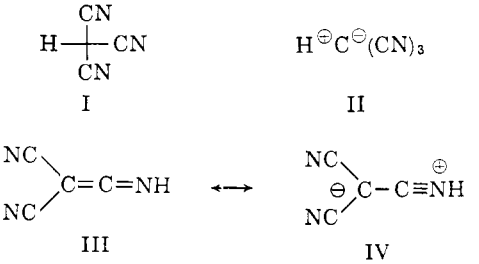
Contribution No. 807 from the Central Research Department Experimental Station, E. I. du Pont de Nemours and Company, Wilmington 98, Delaware

Received September 4, 1962

While salts and solutions of cyanoform have been known for a long time,[1] the nature of the free acid has not been established. Cox and Fontaine[2] reported the isolation of a material, m.p. 55–56°, "stable at room temperature for weeks, even when exposed to light and air," which they regarded as cyanoform. No such material could be isolated in our laboratories from aqueous or aquoethereal cyanoform solutions.

It was possible, however, to obtain by rapid evaporation of aquoethereal "cyanoform" a crystalline solid, obviously different from the material described by Cox and Fontaine. That it was indeed the anhydrous acid was established by analysis, by reaction with aqueous silver ion or *t*-butylamine to give, respectively, silver and *t*-butylammonium tricyanomethanide, and by reaction with ethanol to yield 1-amino-1-ethoxy-2,2-dicyanoethylene.

The free acid is unstable and forms an orange-red polymer on standing at room temperature, but can be purified by vacuum sublimation. The colorless, crystalline sublimate polymerizes slowly at room temperature, rapidly on heating above 70°, yet it has been stored unchanged for several days at −80°. The infrared spectra of the crude acid and of the sublimed material are essentially identical. The location of the nitrile band at 4.55 μ is sufficient to eliminate structures such as I and II and points to dicyanoketenimine, III, while the absence of ketenimine absorption[3] at 5.0–5.2 μ in conjunction with bands at 4.0, 4.4, and 5.6 μ, reminiscent of immonium bands,[4] is indicative of the



I II

III ⟷ IV

(1) (a) H. Schmidtman, *Ber.*, **29**, 1172 (1896); (b) A. Hantzsch and G. Oswald, *ibid.*, **32**, 641 (1899); (c) L. Birkenbach and K. Huttner, *ibid.*, **62B**, 153 (1929).

(2) E. Cox and A. Fontaine, *Bull. soc. chim. France*, 948 (1954).

(3) C. L. Stevens and C. J. French, *J. Am. Chem. Soc.*, **75**, 657 (1953); on the other hand, R. Dijkstra and H. J. Backer, *Rec. trav. chim.*, **73**, 569 (1954), report the ketenimine band at 4.61 μ for N-methylbisdiethylsulfonylketenimine.

(4) B. Witkop, *Experientia*, **10**, 420 (1954); *J. Am. Chem. Soc.*, **76**, 5597 (1954).