pound) was employed in the identification of the carbamate residue. Benzyl carbamate crystallized from the reaction mixture and was identified by Kjehldahl analysis for nitrogen and a mixed melting point with an authentic sample.

The semicarbazone of III melted at 197–201°, dec., while that of an authentic sample of 2-ethylindanone melted at 202°, dec. The 2,4-dinitrophenylhydrazones, respectively, melted at 173–175° and 172–174°, while a mixed melting point of the two was 172–174°.

2-Ethylindanone.—A sample of 2-ethylindanone was prepared from α-ethyl-β-phenylpropionic acid by cyclization in 85% sulfuric acid according to the method of Speight, *et al.*[5] The acid was made as follows: one-tenth mole of sodium was added to 75 ml. of absolute ethanol in a 250-ml. reflux flask. Eastman Kodak Co. grade diethyl ethylmalonate (18.8 g.) was added in several portions, with stirring, and the mixture heated on the steam-bath. Benzyl chloride (12.7 g.) was then added dropwise, the system refluxed for five hours, whereupon it was no longer alkaline to litmus. Excess alcohol was removed under vacuum. The solution was treated with 20 ml. of dilute acetic acid. The oil which separated was refluxed with an excess of 3 *N* potassium hydroxide for six hours and then neutralized with dilute sulfuric acid. The α-ethyl-β-phenylpropionic acid was obtained by distillation at 270–273° (765 mm.) and weighed 11.6 g. (58%).

Summary

1. Crotonaldehyde and cinnamaldehyde have been shown to form products with isopropyl and benzyl carbamate in which the molar ratio is one aldehyde to two carbamate molecules.

2. The reaction of α-ethylcinnamaldehyde and carbamates is in a one to one molar ratio and is attended by ring closure to form substituted indanone derivatives. The identity of the products has been established by comparison with authentic samples.

NEWARK, NEW JERSEY RECEIVED APRIL 20, 1948

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[5] E. A. Speight, A. Stevenson and J. F. Thorpe, *J. Chem. Soc.*, **125**, 2185 (1924).

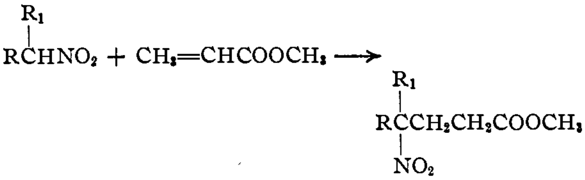
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DEPAUW UNIVERSITY AND THE RESEARCH DIVISION OF COMMERCIAL SOLVENTS CORPORATION]

Reactions of Nitroparaffins. II. Addition of Nitroparaffins to Unsaturated Esters

BY MILTON C. KLOETZEL[1]

Addition of nitromethane, as the sodio derivative, to esters of benzalmalonic, cinnamalmalonic and benzoylacrylic acids has been described by Kohler, *et al.*[2,3] When piperidine and other feebly basic condensing agents were employed, uncrystallizable colored oils were obtained, which could not be purified.

Triethylamine has now been found to be an effective catalyst for the Michael type condensation of methyl acrylate with nitroparaffins (Table I).[4]

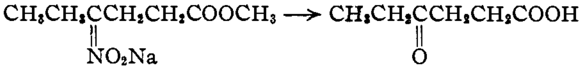


$$\mathrm{R\overset{R_1}{\overset{|}{C}}HNO_2 + CH_2{=}CHCOOCH_3 \longrightarrow R\underset{\underset{NO_2}{|}}{\overset{\overset{R_1}{|}}{C}}CH_2CH_2COOCH_3}$$

I, R = CH_3; R_1 = H
II, R = C_2H_5; R_1 = H
III, R = R_1 = CH_3

Treatment of methyl acrylate with three moles of 1-nitropropane and one-half mole of triethylamine at 30° afforded 57% and 80% yields of methyl 4-nitrohexanoate (II) after two and seven days, respectively. Extension of the reaction period to fourteen days did not increase the yield. Methyl crotonate and methyl methacrylate gave no evidence of reaction with 1-nitropropane under similar conditions, even after standing for seven days. Likewise, methyl cinnamate was recovered quantitatively after standing at 30° for fourteen days with three moles of 2-nitropropane and one mole of triethylamine. A comparable hindering effect resulting from substitution on either the α- or the β-carbon of the acceptor has been observed[5] in other Michael condensations.

Properties of the 4-ketohexanoic acid (V) obtained by acidification of the aci-nitro ester sodium salt (IV) from II[6] corresponded to those previously described for this keto acid.[7] This transformation therefore established the structure of II.



$$\mathrm{CH_3CH_2\underset{\underset{NO_2Na}{\|}}{C}CH_2CH_2COOCH_3 \longrightarrow CH_3CH_2\underset{\underset{O}{\|}}{C}CH_2CH_2COOH}$$

IV V

Methyl acrylate reacted with nitroethane and with 2-nitropropane within four days, under conditions similar to those described for preparation of II, to yield 66% and 81% of methyl 4-nitropentanoate (I) and methyl 4-methyl-4-nitropentanoate (III), respectively.

When attempts were made to effect condensation of nitroparaffins with methyl acrylate, methyl methacrylate or methyl crotonate by means of the more active catalyst diethylamine,[8] the prod-

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[1] Present address: University of Southern California, Los Angeles 7, California.

[2] Kohler and Engelbrecht, THIS JOURNAL, **41**, 764 (1919).

[3] Kohler and Darling, *ibid.*, **52**, 424 (1930).

[4] While this investigation was in progress, Bruson, U. S. Patents 2,342,119 and 2,390,918 [*C. A.*, **38**, 4619 (1944): *ibid.*, **40**, 2456 (1946)] reported the condensation of simple nitroparaffins with methyl and ethyl acrylate, under the catalytic influence of benzyltrimethylammonium hydroxide.

[5] Connor and McClellan, *J. Org. Chem.*, **3**, 570 (1939).

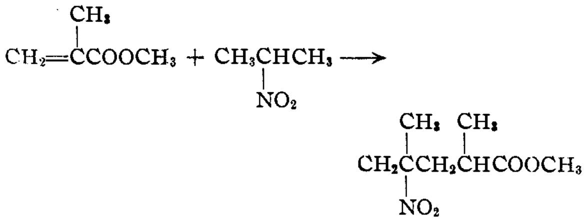
[6] Compare Nef, *Ann.*, **280**, 263 (1894); Hass and Riley, *Chem. Revs.*, **32**, 398 (1943).

[7] Maire, *Bull. soc. chim.*, [4] **3**, 285 (1908).

[8] Compare Kloetzel, THIS JOURNAL, **69**, 2271 (1947).

ucts were largely or exclusively basic substances. It is not unlikely that these products resulted from the addition of the diethylamine itself to the unsaturated esters. Diethylamine has been reported to add to methyl acrylate at room temperature.[9]

Methyl 2,4-dimethyl-4-nitropentanoate (VI), accompanied by a considerable quantity of basic byproduct, was produced in 35% yield when methyl methacrylate was allowed to react with 2-nitropropane at 30° under the catalytic influence of diethylamine.



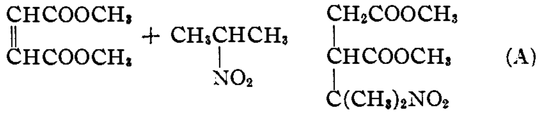
$CH_2{=}C(CH_3)COOCH_3 + CH_3CH(NO_2)CH_3 \longrightarrow CH_3C(CH_3)(NO_2)CH_2CH(CH_3)COOCH_3$

VI

Under similar conditions, methyl crotonate yielded a basic substance exclusively. As might have been predicted from steric considerations, substitution of a methyl group on the β-carbon of methyl acrylate (*i. e.*, methyl crotonate) appears to offer greater hindrance to nitroparaffin addition than does the substitution of a methyl group on the α-carbon (methyl methacrylate).

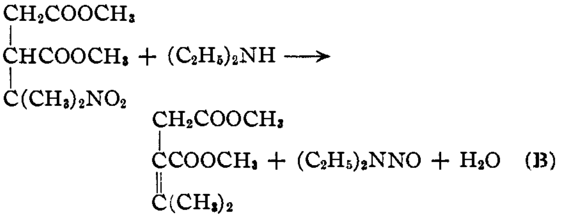
Extension of these studies to fumaric acid esters has disclosed respective advantages attending the use of either diethylamine or triethylamine as catalyst.

Dimethyl fumarate reacted with 2-nitropropane at 30° in the presence of diethylamine to give a mixture of dimethyl 3-methyl-3-nitro-1,2-butanedicarboxylate (VII), dimethyl teraconate (VIII) and N-nitrosodiethylamine. A sample of pure nitro ester VII was also converted to VIII independently, in 83–88% yield, by the action of diethylamine at 30°. It is evident that formation of VII is the result of a normal Michael condensation (A) and that VIII is the product of the subsequent action (B) of diethylamine upon VII.



$CHCOOCH_3{=}CHCOOCH_3 + CH_3CH(NO_2)CH_3 \longrightarrow CH_2COOCH_3{-}CHCOOCH_3{-}C(CH_3)_2NO_2$ (A)

VII



$CH_2COOCH_3{-}CHCOOCH_3{-}C(CH_3)_2NO_2 + (C_2H_5)_2NH \longrightarrow CH_2COOCH_3{-}C(COOCH_3){=}C(CH_3)_2 + (C_2H_5)_2NNO + H_2O$ (B)

VIII

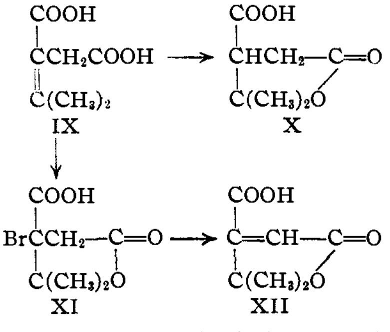
The proportion of VII and VIII produced is dependent upon the concentration of diethylamine employed. Utilization of 0.2 mole of the amine per mole of ester yielded 80% of VII and 15% of VIII, whereas one mole of diethylamine per mole of ester yielded 11% of VII and 85% of VIII. These experiments represent the most practical conditions for the preparation of VII and VIII, respectively. Concentrations of catalyst less than 0.2 mole per mole of ester were found to be ineffective in causing condensation within reasonable periods of time.

It was anticipated that reaction B might be inhibited by the use of a tertiary amine or an amine salt as catalyst, instead of diethylamine. This result was realized when triethylamine (0.3 mole) afforded an 85% yield of VII without significant formation of VIII, but the reaction was slow (forty-three days). Diethylamine acetate likewise promoted a slow condensation, yielding 69% of VII within thirty days at 30°.

Dimethyl maleate is also converted to dimethyl 3-methyl-3-nitro-1,2-butanedicarboxylate (VII) by the action of 2-nitropropane and diethylamine. This condensation, however, is preceded by an isomerization of the maleate to dimethyl fumarate.

The reaction of diethyl fumarate with 2-nitropropane proceeded in a manner similar to that described for the methyl ester. With 0.2 mole of diethylamine at 30°, a 90% yield of diethyl 3-3-methyl-3-nitro-1,2-butanedicarboxylate (XVI) was obtained, while the use of 1.25 moles of the amine afforded an 83% yield of diethyl teraconate.

Dimethyl and diethyl teraconate were hydrolyzed to teraconic acid (IX) which was identified by conversion to terebinic acid (X) according to the method of Fittig and Frost.[10] Our teraconic acid also reacted with bromine to yield bromoterebinic acid (XI), m. p. 170.5–171° dec., which, upon being heated, lost hydrogen bromide to form terebilenic acid (XII). Fittig and Frost[10] reported the m. p. of bromoterebinic acid to be 151°. In our hands, however, an authentic sample of teraconic acid[11] likewise yielded the bromo acid XI melting at 170.5–171° dec.



Finally, the N-nitrosodiethylamine which was produced by the action of diethylamine upon VII was identified by reaction with dry hydrogen chloride to yield diethylammonium chloride.[12]

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(9) Morsch, *Monatsh.*, **63**, 220 (1933).

(10) Fittig and Frost, *Ann.*, **226**, 365 (1884).

(11) Stobbe, *Ber.*, **26**, 2312 (1893); *Ann.*, **282**, 280 (1894); *Ber.*, **36**, 197 (1903); Fittig and Petkow, *Ann.*, **304**, 208 (1899).

(12) Compare Geuther, *Ann.*, **128**, 154 (1863).

TABLE I

NITRO ESTERS FROM METHYL ACRYLATES AND NITROPARAFFINS

Methyl ester	Reaction time, days	Yield, %	B. p., °C.	Mm.	n^{20}_D	d^{20}_{20}	Nitrogen, % Calcd.	Nitrogen, % Found
4-Nitropentanoate (I)	4	66[a]	88–89	2	1.4359	1.1398	8.69	8.84
4-Nitrohexanoate (II)	7	80	97	2	1.4371	1.1050	7.99	8.06
4-Methyl-4-nitropentanoate (III)	7	86[b,c]	77–78.5[d]	1.3	1.4419	1.1166	7.99	8.07
2,4-Dimethyl-4-nitropentanoate (VI)	20[e]	35	72	1.3	1.4388	1.0849	7.40	7.26

[a] Bruson[4] reported a 44% yield of this nitro ester. [b] When the condensation of methyl acrylate (17.2 g.) and 2-nitropropane (89 g.) was effected with diethylamine (7.3 g.) as catalyst, there was obtained 13.0 g. (37%) of III, b. p. 125–130° at 17 mm., and 8.3 g. of practically colorless oil (probably methyl β-diethylaminopropionate), b. p. 85–90° at 17 mm., which was moderately soluble in water and fumed strongly in the presence of hydrogen chloride. [c] Bruson[4] reported an 86% yield of this nitro ester. [d] The blue color is not readily removed from this ester by distillation, but shaking with dilute acidified (sulfuric acid) potassium permanganate is effective. [e] Diethylamine was employed as catalyst instead of triethylamine. The crude product was extracted with 10% hydrochloric acid to remove basic impurities before fractionation.

TABLE II

ALKYLIDENESUCCINIC ESTERS FROM REACTION OF NITROPARAFFINS (3 MOLES) WITH FUMARATES (1 MOLE) AT 30° IN PRESENCE OF DIETHYLAMINE (1 MOLE)

Ester	Reaction time, days	Yield, %	B. p., °C.	Mm.	n^{20}_D	d^{20}_{20}	Analyses, % Calcd. C	Calcd. H	Found C	Found H
Dimethyl itaconate	5	22–43[a]	56–58	1.3	1.4457[b]	1.1246	53.15[c]	6.37	53.15	6.41
Dimethyl ethylidenesuccinate	6	77	73–74	1.5	1.4553	1.1058	55.80	7.02	55.80	7.10
Dimethyl *n*-propylidenesuccinate	14	86	78.5–80	1.3	1.4555	1.0746	58.04	7.57	58.02	7.66
Dimethyl teraconate	14	85[d]	77–78	1.5	1.4581	1.0788	58.04	7.57	58.06	7.02
Diethyl itaconate	11	45	68–69	1.3	1.4398[e]	1.0459	58.04[c]	7.57	57.91	7.49
Diethyl ethylidenesuccinate	11	88	82	1.3	1.4484	1.0437	59.98	8.05	59.93	8.04
Diethyl *n*-propylidenesuccinate	10	95	88–90	1.3	1.4491	1.0171	61.66	8.46	61.58	8.53
Diethyl teraconate	18	83	87	1.3	1.4537	1.0261	61.66[c]	8.46	61.54	8.49

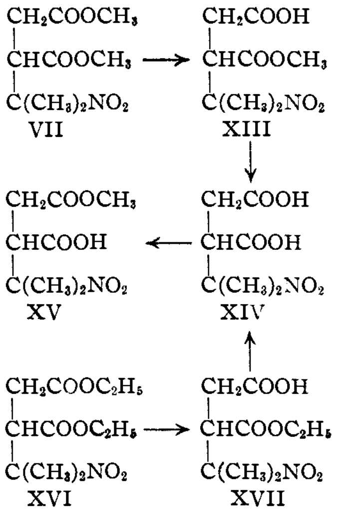
[a] Viscous polymer of the itaconate also obtained, thereby accounting for the low yield of pure ester. [b] Knops, *Ann.*, **248**, 200 (1888), reported 1.444125. [c] Not a new compound; analysis employed for identification. [d] There was also obtained 11% of dimethyl 3-methyl-3-nitro-1,2-butanedicarboxylate. [e] Knops, *Ann.*, **248**, 201 (1888), reported $n^{20.2}_D$ 1.438762.

Dimethyl 3-methyl-3-nitro-1,2-butanedicarboxylate (VII) was hydrolyzed to the corresponding dicarboxylic acid (XIV) in 91% yield by prolonged heating with 1% hydrochloric acid. This acid (XIV) was easily converted, in quantitative yield, to a monomethyl ester for which structure XV is proposed. This suggestion is in harmony with Menschutkin's observation[13] that primary carboxyl groups are more readily esterified than are secondary carboxyl groups.

Dimethyl 3-methyl-3-nitro-1,2-butanedicarboxylate (VII) was partially hydrolyzed by refluxing for two hours with 1% hydrochloric acid. Structure XIII is ascribed to the resulting monomethyl ester, since the sterically hindered secondary carbomethoxyl group is probably resistant to hydrolysis. Moreover, XIII and XV were found not to be identical. Esterification of XIII yielded VII.

Diethyl 3-methyl-3-nitro-1,2-butanedicarboxylate (XVI) likewise was first hydrolyzed to a half ester (XVII) by the action of dilute hydrochloric acid, and finally yielded a nitro dicarboxylic acid identical with that obtained from dimethyl ester VII.

Alkaline hydrolysis of esters VII and XVI took place rapidly, with concurrent loss of the nitro group by a process simulating reaction B, to yield teraconic acid (IX). Even the use of the relatively weak base barium hydroxide for the hydrolysis failed to prevent entirely the splitting out of the elements of nitrous acid, although this cleavage was suppressed and a mixture of teraconic acid and XIV was obtained.



When the diethylamine-catalyzed reaction of other nitroparaffins with dimethyl and diethyl

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(13) Menschutkin, *J. Chem. Soc.*, **40**, 883 (1881).

fumarate was investigated, elimination of the elements of nitrous acid from the initial condensation product proved to be a common phenomenon. This reaction therefore constitutes a new and convenient method for the synthesis of alkylidenesuccinic acids and esters. In Table II are described the esters which were obtained when the fumarate was allowed to react at 30° with three moles of nitroparaffin and one mole of diethylamine.

Dimethyl and diethyl ethylidenesuccinate were identified by hydrolysis to the same solid dicarboxylic acid, the properties of which corresponded to those described for ethylidenesuccinic acid by Fittig and Fraenkel.[14] In addition, hydrolysis of the saturated ester obtained by catalytic hydrogenation of diethyl ethylidenesuccinate yielded the known ethylsuccinic acid.

The identity of dimethyl *n*-propylidenesuccinate was established by hydrolysis to the corresponding unsaturated acid, which in turn yielded the characteristic dibromide.[15] Catalytic hydrogenation of diethyl *n*-propylidenesuccinate and subsequent hydrolysis yielded the known *n*-propylsuccinic acid.

Experimental[16]

Condensation of Methyl Acrylates with Nitroparaffins.—A mixture of the appropriate methyl acrylate (1 mole), nitroparaffin (3 moles) and triethylamine (0.5 mole) was allowed to react at 30° for a suitable period of time and the mixture was then subjected to reduced pressure distillation to remove unreacted reagents (to 50° at 13 mm.). Two fractionations in vacuum generally sufficed to yield the pure nitro esters as colorless oils having camphoraceous or similar pleasant odors. Properties of these esters are indicated in Table I.

Characterization of Methyl 4-Nitrohexanoate (II).—A solution of 9.72 g. of methyl 4-nitrohexanoate in 60 cc. of water containing 3.88 g. of sodium hydroxide was added to an ice-cooled, mechanically stirred solution of 12.2 cc. of concentrated sulfuric acid in 55 cc. of water at such a rate that the temperature of the reaction mixture remained at 5–7°. Extraction of the green-yellow solution with ether yielded 4.7 g. (65%) of crude 4-ketohexanoic acid (V) which crystallized upon cooling and scratching. Crystallization from ether–petroleum ether yielded colorless rectangular plates, m. p. 37–39°. Maire[7] reported a m. p. of 36–37° for this acid.

Ethyl 4-ketohexanoate, obtained by refluxing the acid with ethanol and sulfuric acid for five hours, yielded a semicarbazone which crystallized from ethanol in colorless leaflets, m. p. 106–107°. Maire[7] reported 106°.

Characterization of Methyl 4-Methyl-4-nitropentanoate (III).—A 5.0-g. sample of the ester (III) was refluxed for ten minutes with 2.0 g. of potassium hydroxide and 10 cc. of water. When the cooled decolorized solution was acidified with 18% hydrochloric acid, 4.1 g. of 4-methyl-4-nitropentanoic acid was deposited as a green oil. This acid yielded a *p*-toluidide[17] which separated from 50% ethanol in colorless needles, m. p. 115–116°.

Anal. Calcd. for $C_{13}H_{18}N_2O_3$: N, 11.19. Found: N, 11.00.

Attempted Condensation of Methyl Crotonate with 2-Nitropropane.—When a mixture of methyl crotonate (80 g.), 2-nitropropane (214 g.) and diethylamine (29.2 g.) was allowed to stand at 30° for sixteen days and was then worked up in the usual manner, there was obtained 41.1 g. of colorless oil boiling at 62–63° at 1.8 mm. This material, evidently formed by the addition of diethylamine to methyl crotonate, fumed strongly in the presence of hydrogen chloride, and dissolved completely in 10% hydrochloric acid with the evolution of considerable heat.

Preparation of Alkylidenesuccinic Esters.—A mixture of dimethyl or diethyl fumarate (1 mole), the nitroparaffin (3 moles) and diethylamine (1–1.1 moles) was allowed to stand at 30° in a stoppered flask. When dimethyl fumarate was employed, the suspension was swirled frequently until all of the ester had dissolved (several hours). In most instances the mixture became warm from heat of reaction.

After standing for an appropriate period (see Table II) the orange or red solution was subjected to reduced pressure distillation to remove diethylamine, nitroparaffin and water. Fractionation of the residue, employing a ten-inch Vigreux column, yielded yellow N-nitrosodiethylamine (b. p. 72–75° at 12 mm.) followed by the higher-boiling alkylidenesuccinic ester. Removal of traces of basic impurities from the esters was effected by extraction with 10% hydrochloric acid. A final vacuum distillation yielded pure products with properties shown in Table II.

The N-nitrosodiethylamine produced in these reactions was identified by conversion to diethylammonium chloride by means of anhydrous hydrogen chloride, according to the method of Geuther.[12] The chloride separated from anhydrous ethanol–ether in large colorless transparent plates, m. p. 222–223°.

Identification of Alkylidenesuccinic Esters.—**Dimethyl ethylidenesuccinate** (8.8 g.) was refluxed for forty minutes with 4.5 g. of sodium hydroxide and 45 cc. of water. Acidification of the decolorized solution with 36% hydrochloric acid deposited 5.2 g. of ethylidenesuccinic acid, which crystallized from water in colorless prisms, m. p. 165–167° (with previous sintering). Hydrolysis of **diethyl ethylidenesuccinate** yielded the identical acid. Fittig and Fraenkel[14] reported a m. p. of 166–167° for this acid.

Diethyl ethylidenesuccinate (27.1 g.) was dissolved in a mixture (300 cc.) of anhydrous ethanol (95%) and benzene (5%), Raney nickel (10 g., washed in the same solvent mixture) was added and hydrogenation was carried out for two hours at 100° under a pressure of 200 lb. per sq. in. Distillation of the product yielded 25 g. (91%) of diethyl ethylsuccinate, b. p. 93–97° at 2–4 mm. Hydrolysis of this ester with 20% potassium hydroxide and subsequent acidification yielded ethylsuccinic acid which, after recrystallization from chloroform–petroleum ether, melted at 98–99°. Huggenberg[18] reported 98°.

Dimethyl *n*-propylidenesuccinate was hydrolyzed in the aforedescribed manner to give ***n*-propylidenesuccinic acid** (85% yield) which separated from ether in colorless prisms, m. p. 163–166° (with previous sintering). Fittig and Glaser[15] reported 162–167°. When 5.0 g. of the acid was heated with 5.0 g. of bromine and 10 cc. of chloroform for seven and one-half hours at 100° in a sealed tube, and the solution was concentrated, there was first obtained 0.6 g. of a compound, m. p. 172–174° dec., of unknown composition. The mother liquor was then diluted with benzene and the solution was allowed to stand at 5°. 2,3-Dibromopentane-1,2-dicarboxylic acid (0.6 g.) slowly separated and was recrystallized from ether-petroleum ether; colorless prisms, m. p. 153–154° dec. Fittig and Glaser reported 153–154° dec.

Anal. Calcd. for $C_7H_{10}O_4Br_2$: C, 26.43; H, 3.17. Found: C, 26.46; H, 3.19.

Diethyl *n*-propylidenesuccinate was hydrogenated over Raney nickel in the manner previously described; yield,

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[14] Fittig and Fraenkel, *Ann.*, **255**, 36 (1889).

[15] Fittig and Glaser, *ibid.*, **304**, 181 (1899).

[16] Nitroparaffins used in this investigation were obtained from Commercial Solvents Corporation and were employed without further purification. Melting points are uncorrected. Nitrogen analyses and physical constants are by the Analytical Department of Commercial Solvents Corporation, Terre Haute, Indiana; carbon and hydrogen analyses by Dr. E. W. D. Huffman, Denver, Colorado.

[17] Shriner and Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 132.

[18] Huggenberg, *Ann.*, **192**, 149 (1878).

86% of diethyl *n*-propylsuccinate, b. p. 112–117° at 7–9 mm. Hydrolysis of the hydrogenated ester yielded *n*-propylsuccinic acid which melted at 91–92° after one crystallization from chloroform–petroleum ether. Melting points of 91°, 91–92°, 91–92.5°, 92–93° and 95° for this acid have been reported by Waltz,[19] Fittig and Glaser,[15] Walden,[20] Demarçay[21] and Salzer,[22] respectively.

Hydrolysis of dimethyl and diethyl teraconate yielded teraconic acid (IX) which separated from water in colorless columnar needles, m. p. 165–166° dec. alone and also when mixed with authentic teraconic acid prepared according to Stobbe.[11]

When 0.9 g. of the presumed teraconic acid (IX) was heated for one and three-quarters hours on a steam-bath with a mixture of 9 cc. of water and 9 cc. of concentrated sulfuric acid and the cooled solution was diluted with 18 cc. of water, 0.5 g. of terebinic acid (X) crystallized in colorless transparent prisms, m. p. 173–174° alone and also when mixed with a sample prepared from authentic teraconic acid.

To a mixture of 1.58 g. of finely powdered presumed teraconic acid and 4 cc. of water was added dropwise with continuous shaking 1.6 g. of bromine. Decolorization of the bromine took place quickly and the reaction mixture formed a mass of very small colorless crystals. After cooling in ice, the bromoterebinic acid (XI) was filtered and twice recrystallized from anhydrous ether; colorless transparent prisms, m. p. 171–172° with vigorous evolution of hydrogen bromide. The m. p. was not depressed by admixture with bromoterebinic acid, m. p. 170.5–171°, prepared in the aforedescribed manner from authentic teraconic acid.

Anal. Calcd. for $C_7H_9O_4Br$: Br, 33.71. Found: Br, 34.33.

When a sample of bromoterebinic acid was heated to 172° until no further evolution of hydrogen bromide occurred and was then allowed to solidify, it remelted at 166–167° without decomposition (terebilenic acid, XII). Fittig and Frost[10] reported a m. p. of 168° for pure terebilenic acid prepared in this manner.

Preparation of Dialkyl 3-Methyl-3-nitro-1,2-butanedicarboxylates VII and XVI.—A suspension of 36 g. of dimethyl fumarate in 66.8 g. (3 moles) of 2-nitropropane and 3.65 g. (0.2 mole) of diethylamine was allowed to stand at 30° for six days. The ester dissolved completely within thirty-three hours. When the green reaction mixture was fractionated, employing a six-inch Vigreux column, there was obtained 1.8 g. of crude yellow N-nitrosodiethylamine, 7.2 g. (15.5%) of nearly colorless dimethyl teraconate and 46.5 g. (80%) of faintly green **dimethyl 3-methyl-3-nitro-1,2-butanedicarboxylate** (VII), b. p. 118–120° at 1.8 mm. The nitro ester crystallized completely upon cooling, and separated from ether–petroleum ether (60–75°) in colorless rectangular plates, m. p. 35.5–36°.

Anal. Calcd. for $C_9H_{15}NO_6$: C, 46.34; H, 6.48; N, 6.00. Found: C, 46.58; H, 6.08; N, 6.38.

A similar run in which reaction was allowed to proceed for thirty days at 3° yielded 82% of dimethyl 3-methyl-3-nitro-1,2-butanedicarboxylate.

When triethylamine (0.3 mole) was employed as catalyst instead of diethylamine, 85% of VII was obtained after forty-three days at 30°. Diethylamine acetate (0.3 mole) as catalyst yielded only 69% of VII after thirty days at 30°. Use of 1 mole of diethylamine acetate resulted in the formation of 67% of VII within six days at 30°. An attempt to speed the reaction by refluxing resulted in extensive decomposition.

A solution of 14.4 g. of dimethyl maleate and 0.73 g. of diethylamine in 9.3 g. of 2-nitropropane became hot and began to deposit colorless crystals of dimethyl fumarate after standing at 30° for twenty minutes. After seven hours, 11.6 g. of dimethyl fumarate, m. p. 102–103°, was obtained by filtration, and a second crop (0.3 g.), obtained by concentrating and cooling the mother liquor, brought the total yield in this isomerization to 83%. When the precipitated dimethyl fumarate was allowed to remain in contact with the 2-nitropropane and diethylamine it slowly redissolved, and VII was produced in the usual manner.

In the aforedescribed manner, diethyl fumarate yielded 90% of **diethyl 3-methyl-3-nitro-1,2-butanedicarboxylate** (XVI) which distilled at 130–136° at 1.8 mm. The nitro ester was shaken with 10% hydrochloric acid to remove traces of basic impurities and was then redistilled; colorless oil, b. p. 117–117.5° at 1.3 mm., $n^{20}\text{D}$ 1.4480, $d^{20}{}_{20}$ 1.1384.

Anal. Calcd. for $C_{11}H_{19}NO_6$: N, 5.36. Found: N, 4.97.

Acid Hydrolysis of Dialkyl 3-Methyl-3-nitro-1,2-butanedicarboxylates VII and XVI.—The solution obtained by refluxing 26.1 g. of diethyl 3-methyl-3-nitro-1,2-butanedicarboxylate (XVI) and 225 cc. of 1% hydrochloric acid for twenty-four hours was decolorized and filtered hot. Upon cooling, the solution deposited 12.2 g. (52%) of crystalline **3-carboethoxy-4-methyl-4-nitropentanoic acid** (XVII), m. p. 90–94°. The monoethyl ester separated from ether–petroleum ether in colorless cubes, m. p. 94–95.5°. Neutral equivalent calculated, 233.2; found, 229.7.

Anal. Calcd. for $C_9H_{15}NO_6$: N, 6.06. Found: N, 5.91.

The aqueous mother liquor from crystallization of the monoethyl ester was allowed to evaporate to dryness and the residue was crystallized from ether–petroleum ether; yield, 5.5 g. (27%) of **3-methyl-3-nitro-1,2-butanedicarboxylic acid (XIV)**; colorless opaque prisms, m. p. 142–144° dec. Neutral equivalent calculated, 102.6; found, 103.6.

Anal. Calcd. for $C_7H_{11}NO_6$: N, 6.82. Found: N, 6.51.

Monoethyl ester XVII was hydrolyzed to crude dicarboxylic acid XIV in 91% yield upon refluxing for four and one-half days with 1% hydrochloric acid.

A mixture of 50 g. of dimethyl 3-methyl-3-nitro-1,2-butanedicarboxylate and 500 cc. of 1% hydrochloric acid was refluxed until all of the ester had dissolved (one and three-quarters hours) and then for an additional fifteen minutes. Upon cooling, **3-carbomethoxy-4-methyl-4-nitropentanoic acid (XIII)** separated as an oil which later crystallized. Concentration of the mother liquor to a volume of 150 cc. yielded an additional quantity of monomethyl ester; total yield, 42.8 g. (91%) of colorless crystals, m. p. 104–108°. The pure ester separated from water or ether–petroleum ether in needles, m. p. 108–110° (with previous sintering).

Anal. Calcd. for $C_8H_{13}NO_6$: N, 6.38; neut. equiv., 219.2; Found: N, 6.08; neut. equiv., 221.7.

When the aqueous mother liquor (150 cc.), from which the monomethyl ester had separated, was allowed to evaporate to dryness and the residue was crystallized from ether-petroleum ether, there was obtained 1.8 g. (4%) of 3-methyl-3-nitro-1,2-butanedicarboxylic acid (XIV).

Monomethyl ester XIII was converted to the crude dicarboxylic acid XIV in 91% yield upon being refluxed for three days with 1% hydrochloric acid.

3-Carbomethoxy-4-methyl-4-nitropentanoic acid (XIII, 2.19 g.) was refluxed for five hours with 5 cc. of anhydrous methanol containing two drops of concentrated sulfuric acid. Evaporation of the reaction mixture, dilution with 15 cc. of water and extraction with ether yielded 2.10 g. (90%) of **dimethyl 3-methyl-3-nitro-1,2-butanedicarboxylate** (VII), m. p. 35–36° alone and also when mixed with VII from dimethyl fumarate and 2-nitropropane.

A 1.0 g. sample of 3-methyl-3-nitro-1,2-butanedicarboxylic acid (XIV) was esterified by refluxing for two hours with 5 cc. of methanol containing two drops of sulfuric acid; yield, 1.0 g. (93%) of **1-carbomethoxy-3-methyl-3-nitro-2-butanecarboxylic acid (XV)** which separated from

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[19] Waltz, *ibid.*, **214**, 59 (1882).

[20] Waldon, *Ber.*, **24**, 2036 (1891).

[21] Demarçay, *Ann. chim. phys.*, [5] **20**, 491 (1880).

[22] Salzer, *J. prakt. Chem.*, [2] **61**, 166 (1900).

ether–petroleum ether in colorless prisms, m. p. 73.5–75°. Neutral equivalent calculated, 219.2; found, 220.6.

Anal. Calcd. for $C_8H_{13}NO_6$: N, 6.38. Found: N, 6.26.

Alkaline Hydrolysis of Dialkyl 3-Methyl-3-nitro-1,2-butanedicarboxylates VII and XVI.—Dimethyl 3-methyl-3-nitro-1,2-butanedicarboxylate (10 g.) was refluxed for thirty minutes with 10 g. of potassium hydroxide and 40 cc. of water. When the cooled solution was acidified with 20% hydrochloric acid, there was a vigorous evolution of oxides of nitrogen and 3.2 g. (47%) of teraconic acid (IX) was precipitated, m. p. 161–163° dec. This acid was identified as previously described. An attempt to obtain a further quantity of teraconic acid from the acidified mother liquor was unsuccessful.

In a similar manner, hydrolysis of 10 g. of diethyl 3-methyl-3-nitro-1,2-butanedicarboxylate (two and one-half hours) with 9 g. of potassium hydroxide yielded 3 g. (50%) of teraconic acid.

A mixture of 10 g. of dimethyl 3-methyl-3-nitro-1,2-butanedicarboxylate, 14 g. of barium hydroxide octahydrate and 50 cc. of water was refluxed for forty-five minutes. The mixture of solid barium salts which had precipitated was suspended in a small quantity of water and decomposed with 36% hydrochloric acid. Several fractional crystallizations from ether–petroleum ether were required to separate the precipitated mixture of acids (3.5 g.) into 0.6 g. of teraconic acid and 1.6 g. of 3-methyl-3-nitro-1,2-butanedicarboxylic acid.

Reaction of Dimethyl 3-Methyl-3-nitro-1,2-butanedicarboxylate with Diethylamine.—A solution of 23.3 g. of nitro ester VII and 7.3 g. (1 mole) of diethylamine in 20 cc. of 2-nitropropane (or benzene) was allowed to stand at 30° for fourteen days. Fractionation of the reaction mixture yielded N-nitrosodiethylamine, 15.5–16.4 g. (83–88%) of dimethyl teraconate and 1.7 g. of unchanged nitro ester which crystallized upon cooling.

Summary

1. Triethylamine has been found to be an effective catalyst for the Michael-type condensation of methyl acrylate with nitroparaffins.

2. Alkylidenesuccinic esters are produced in good yield when dimethyl or diethyl fumarate reacts at 30° with three moles of nitroparaffin and one mole of diethylamine

3. In the presence of a smaller concentration (0.2 mole) of diethylamine, dimethyl and diethyl fumarate condense with 2-nitropropane to yield dimethyl 3-methyl-3-nitro-1,2-butanedicarboxylate and diethyl 3-methyl-3-nitro-1,2-butanedicarboxylate, respectively. Some reactions of these new nitro esters are described.

LOS ANGELES, CALIFORNIA RECEIVED APRIL 26, 1948

[CONTRIBUTION FROM DIVISION OF FOOD TECHNOLOGY, UNIVERSITY OF CALIFORNIA]

Deterioration of Dried Fruits. I. The Effect of Sugars and of Furfurals[1]

BY VICTORIA A. HAAS, E. R. STADTMAN, F. H. STADTMAN AND G. MACKINNEY

A wide variety of darkened foods, including dried apricots, orange and lemon concentrates, sulfited dried cabbage and some trade caramels show a characteristic absorption band in aqueous media, *ca.* 285 mμ (Fig. 1.) Studies with dried apricots have shown that the band at 285 mμ is absent in undarkened fruit and that its development is usually concurrent with browning. Since a similar band was observed in some though not in all commercial caramels, it was a logical inference that sugars were involved in the formation of the compounds responsible for this absorption. Moreover, it seemed possible that these compounds were involved in browning. It is the purpose of this paper to test these hypotheses.

Experimental

Apricot concentrates were used in preference to dried fruit. Qualitatively, concentrates behave in the same manner as dried fruit and they possess the following advantages: they are homogeneous and smaller samples may be used without introducing large sampling errors; their composition may be readily modified by the addition or removal of substances and chemical changes can be followed readily.

Preparation of Concentrates.—To test the possible role of sugar in the deterioration, it was desirable to have for comparison a natural concentrate and one from which the sugar had been removed. A natural concentrate was prepared from 10 kg. of fresh apricots which were steam-treated for ten minutes to inactivate enzymes, cooled and blended in a Waring Blendor for five minutes and filtered through a thin layer of celite. The filtered juice was then concentrated at 2–3 cm. pressure, below 35° to a thick sirup, *ca.* 50% solids. To obtain sugar-free concentrate part of the filtered juice was fermented with Peerless bakers' yeast prior to concentration. It required twenty-four hours at 30° to effect a maximum decrease in reducing value, 98% of the original being destroyed. The yeast was then filtered out, and the fermented samples were concentrated to the same extent by volume as the unfermented sample. The composition of the unfermented and fermented concentrate, in grams per 100 g. concentrate, was

	Unfermented	Fermented
Total solid[a]	48.4	17.7
Kjeldahl nitrogen	0.0041	0.0025
Reducing value[b]	33.0	0.65

[a] By vacuum oven. [b] Computed as glucose after acid inversion.

It is of course not to be supposed that the elimination of sugar by fermentation is the sole change undergone by the fermented sample, nor can it be expected that the two concentrates will be exactly comparable except for the sugar.

Measurement of Deterioration.—Deterioration was determined by the increase in darkening, as a measure of which the optical density[1a] was determined on samples

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[1] The subject matter of this series of papers (I–IV) has been undertaken in coöperation with the Committee on Food Research of the Quartermaster Food and Container Institute for the Armed Forces under contract with the University. The opinions and conclusions contained in these reports are those of the authors. They are not to be construed as necessarily reflecting the views or endorsement of the War Department.

[1a] Measurements of optical densities were made on two different instruments in these papers. To avoid confusion, measurements on the photoelectric colorimeter are designated by the term 2 − log