yield which when recrystallized from ethanol afforded cream-colored prisms, m.p. 147–147.5°.

Anal. Calcd. for $C_{23}H_{25}O_5N$: C, 69.85; H, 6.37; N, 3.54. Found: C, 69.90; H, 6.34; N, 3.52.

4a-(β-Hydroxyethyl)-1,2,3,4,4a,9(and 2,3,4,4a,9,10)-hexahydrophenanthrene (XIII and Isomer).—A solution of 4.18 g. of the preceding diol *p*-nitrobenzoate (XI) in 30 ml. of pyridine was treated dropwise while cooling with 5 ml. of phosphorus trichloride and the solution warmed to 50° for 2 hours. The mixture was poured on crushed ice and extracted with chloroform and the extract washed with dilute hydrochloric acid and water and finally dried and evaporated to yield a crystalline mass. Recrystallization from acetone–methanol gave cream-colored blades, m.p. 124–130°. Further purification failed to raise or sharpen the m.p.

Anal. Calcd. for $C_{23}H_{23}O_4N$: C, 73.19; H, 6.14; N, 3.71. Found: C, 73.15; H, 6.11; N, 3.73.

Saponification was accomplished by heating under reflux for 2 hours a solution of 2.50 g. of the product in 150 ml. of methanol containing 5 g. of potassium hydroxide. Most of the methanol was evaporated, water was added and the product extracted with ether and the extract washed with water, then dried and evaporated. Crystallization of the residue from ether–petroleum ether (b.p. 30–60°) gave 1.033 g. (68% yield) of crystals (XIII), m.p. 84–90°. Three additional recrystallizations from ether–petroleum ether afforded fine colorless needles, m.p. 93–100°. Further recrystallizations did not alter this m.p.

Anal. Calcd. for $C_{16}H_{20}O$: C, 84.16; H, 8.82. Found: C, 84.29; H, 8.81.

4a-(β-Hydroxyethyl)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (XIV).—Of the above unsaturated alcohol mixture, 933 mg. was dissolved in 50 ml. of glacial acetic acid and hydrogenated over 200 mg. of platinum oxide under a pressure of 15 lb. p.s.i. of hydrogen. After 20 min. 105% of the theoretical amount of hydrogen was absorbed. The catalyst was removed by filtration and the filtrate evaporated to dryness *in vacuo*. The residue was dissolved in 50 ml. of methanol containing 5 g. of potassium hydroxide and after standing for one hour the solution was diluted with water and extracted with ether. The ether, after one water-wash, was dried and evaporated to yield an oil which resisted all attempts at crystallization. It was distilled *in vacuo* to give 808 mg. of a viscous and colorless oily distillate, b.p. 185–190° (1.5 mm.).

Anal. Calcd. for $C_{16}H_{22}O$: C, 83.42; H, 9.62. Found: C, 83.15; H, 9.76.

It gave a crystalline *p*-**nitrobenzoate (XV)** which after numerous recrystallizations from acetone melted at 120–128°. This m.p. was not significantly altered by additional recrystallization from acetone or other solvent mixtures. Chromatography on alumina was not more successful, all the fractions having similar diffuse m.p.

Anal. Calcd. for $C_{23}H_{25}O_4N$: C, 72.77; H, 6.64; N, 3.69. Found: C, 72.75; H, 6.63; N, 3.72.

***trans*-4a-(β-Dimethylaminoethyl)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (XVI).**—Seven hundred and fifteen milligrams of the preceding alcohol (XIV) was dissolved in 10 ml. of dry benzene and one ml. of redistilled phosphorus tribromide added. After standing for 3 hours the solution was warmed to 60° for 30 min. and poured into ether which was washed with dilute aqueous sodium hydroxide and water and finally dried and evaporated to yield 517 mg. of an oil which gave a strongly positive Beilstein test for halogen. This was dissolved in 50 ml. of pure anhydrous dioxane and the solution saturated with anhydrous dimethylamine. The mixture was heated to 100° in a sealed tube for 44 hours after which time it was concentrated to a small volume *in vacuo* and poured into ether. The ether extract was washed with dilute aqueous sodium hydroxide and water and then extracted with dilute hydrochloric acid. The acid extract was made alkaline with aqueous sodium hydroxide and extracted with ether. The ether extract was washed with water and finally dried and evaporated to yield 245 mg. of a yellowish oil. This was treated in a little methanol with 200 mg. of picric acid whereupon 344 mg. of yellow crystals, m.p. 160–180°, deposited. Five additional recrystallizations from large volumes of ethanol afforded 96 mg. of large yellow blades with a constant m.p. of 191.5–193°. [Reported[5] for N-methylisomorphinane dihydrodesbase picrate: 191–192.5° (cor.)]. It caused no depression of the m.p. of an authentic sample[12] of N-methylisomorphinane dihydrodesbase picrate upon admixture.

Anal. Calcd. for $C_{24}H_{30}O_7N_4$: N, 11.51. Found: N, 11.56.

Because of the small amount of material obtained, attempts at the isolation of an isomeric picrate from the mother liquors have not been successful thus far.

QUEBEC, QUEBEC

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

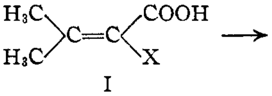
The Decarboxylation of α,β-Unsaturated Malonic Acid Derivatives *via* β,γ-Unsaturated Intermediates. II. The Effect of α-Substituents upon Product Composition and Rate

BY ELIAS J. COREY

RECEIVED AUGUST 18, 1952

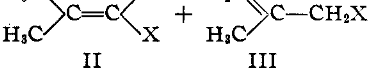
The variation in the relative amounts of α,β- and β,γ-unsaturated products formed by the decarboxylation of each of ten malonic acid derivatives (IA-E, IVA-E) in pyridine has been determined. The malonic acids afford the highest proportion of β,γ-unsaturated decarboxylation product (over 90%) and appear to be the most satisfactory precursors for the synthesis of β,γ-unsaturated acid derivatives by decarboxylation. Evidence has been obtained from rate data for participation of the carboxyl function in isomerization of α,β- to β,γ-unsaturated malonic acid derivatives. Both steric inhibition and copper(II) ion catalysis of decarboxylation *via* β,γ-unsaturated intermediates have been observed and are discussed.

It has been shown recently[1] that the decarboxylation of ethyl hydrogen isopropylidenemalonate (IC) in pyridine occurs *via* the β,γ-unsaturated isomer and affords a mixture of α,β- and β,γ-unsaturated products (25% IIC and 75% IIIC) both of which are stable under the reaction conditions. Since a knowledge of the relationship between the substituent X in compounds of type I (X = CN, $CONH_2$, COOH, $CON(CH_3)_2$) and product composition is necessary for the evaluation of decarboxylation as a synthetic route to β,γ-unsaturated acids and acid derivatives, we have investigated the change in the ratio of α,β- to β,γ-unsaturated decarboxylation product for the series IA-IE. In addition, a parallel series of β,γ-



I

A, X = CN
B, X = $CONH_2$
C, X = $COOC_2H_5$
D, X = COOH
E, X = $CON(CH_3)_2$



II III

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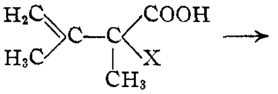
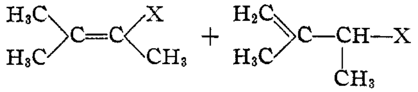
[1] E. J. Corey, This Journal, 74, 5897 (1952).

unsaturated acid derivatives of type IV has been studied. The effect of the group X upon both product composition and rate of decarboxylation is obviously also of interest from a theoretical viewpoint.



IV

A, X = CN
B, X = CONH$_2$
C, X = COOC$_2$H$_5$
D, X = COOH
E, X = CON(CH$_3$)$_2$



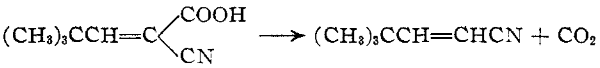
V VI

The substances obtained by decarboxylation of compounds of types I and IV under standard conditions are indicated in Table I together with the approximate first-order rate constants for decarboxylation. All decarboxylation products were found to be stable under the reaction conditions. Analyses of products were performed by refractometry or by infrared spectroscopy, as specified.

The reactions used for the synthesis of the compounds which were subjected to decarboxylation and certain of the decarboxylation products are outlined in Fig. 1.

Discussion

The Nitriles, Amides and Esters.—Both the nitriles studied (IA and IVA) yield the same high proportion of β,γ-unsaturated isomer upon decarboxylation. If the only route available for the decarboxylation of IA is *via* the β,γ-isomer IA′, it is apparent that the presence of an α-methyl substituent in IVA instead of a hydrogen (as in IA′) is not sufficient to affect product composition. Since the structural considerations which argue against the possibility of facile direct decarboxylation of α,β-unsaturated malonic esters, amides, etc., do not apply in the case of the nitriles,[2] the decarboxylation of pivalylidenecyanoacetic acid (VII) which is incapable of isomerization to a β,γ-unsaturated intermediate was studied to determine the ease of *direct decarboxylation*. The rate constant for the decarboxylation of VII in pyridine at 111° is 0.14 times that of IA and the product of reaction is *trans*-β-*t*-butylacrylonitrile (VIII) (also formed by heating VII alone).[3] It is possible, therefore, that IA decarboxylates to a small extent by a direct mechanism



$$(CH_3)_3CCH{=}C\begin{matrix}\diagup COOH\\ \diagdown CN\end{matrix} \longrightarrow (CH_3)_3CCH{=}CHCN + CO_2$$

VII VIII

to give IIA.

Table I

Compound	Product (% β,γ-isomer in α,β + β,γ-mixture)	Rate constant, k_1, min.$^{-1}$	Temp., °C.
IA	80[a,b]	0.028	111.0
IB	80[b]	.024	
IC	75[a,d]	.02	
ID	93[a]	.067[c]	
IE	28[b]	.001	
IVA	80[b]	3.0	95.0
IVB	72[b]	0.5	
IVC	50[a,d]	.05	
IVD	95[a]	.092[c]	
IVE	90[b]	.02	

[a] Analyzed by refractive indices. [b] Analyzed by infrared spectra. [c] Uncorrected for statistical effect of two carboxyl groups. [d] *Cf.* ref. 1.

Neither the amides IB and IVB nor the esters IC and IVC can be regarded as more satisfactory precursors than the corresponding nitriles for the production of β,γ-unsaturated acid derivatives. It is worthy of note, however, that decarboxylation of the α,β-unsaturated half amides and half esters IB and IC leads to a higher proportion of β,γ-unsaturated product than does decarboxylation of the β,γ-unsaturated derivatives IVB and IVC.

The Acids ID and IVD.—It is clear from Table I that the malonic acids ID and IVD afford relatively more of the β,γ-decarboxylation product than do their derivatives. Hence, α,β-unsaturated malonic acids appear to be the most satisfactory precursors of β,γ-unsaturated acids and acid derivatives.

A second point of significance emerges from the rate data. The rate constant for the decarboxylation of the α,β-unsaturated malonic acid ID (allowing for a statistical factor of 2) is *larger* than those for the α,β-unsaturated derivatives IA, IB and IC, whereas the rate constant for the decarboxylation of the β,γ-unsaturated malonic acid IVD (allowing for a statistical factor of 2) is *smaller* than those for any of the other β,γ-unsaturated compounds IVA, IVB and IVC. This fact suggests the possibility that a statistical factor of 2 is operative not only in the decarboxylation of the β,γ-unsaturated acids, but also in the conversion of the α,β-unsaturated compound ID to the β,γ-isomer. In turn, the operation of a statistical factor for the isomerization signifies participation by the carboxyl function in this step. A reasonable interpretation of the isomerization factor may be derived on the basis of the finding in previous work[1] that the rate-determining step for the $\alpha,\beta \rightarrow \beta,\gamma$-isomerization of IC is the abstraction of a proton from the γ-carbon of *un-ionized* IC. If the assumption is made that migration of a proton from the carboxyl function of compounds IA–E to the α-carbon atom occurs simultaneously with the removal of a proton from the γ-carbon, as indicated, the origin of the isomerization factor for the diacid ID becomes clear. In ID each of two carboxyl groups can participate in isomerization.

The high proportion of β,γ-unsaturated decarboxylation product formed from ID and IVD may be due to similar participation by the remain-

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[2] In theory the cyano group can play a more important role than do the carbonyl functions in stabilizing the transition state for direct decarboxylation of α,β-unsaturated malonic acid derivatives. In the case of cyano derivatives two orbitals on the cyano carbon are available for overlapping in the transition state, whereas the carbonyl functions provide only one orbital (insufficient for overlapping with both the α,β-ethylenic linkage and the orbital made available by the departing carbon).

[3] R. M. Ross and M. L. Burnett, This Journal, 71, 3562 (1949).

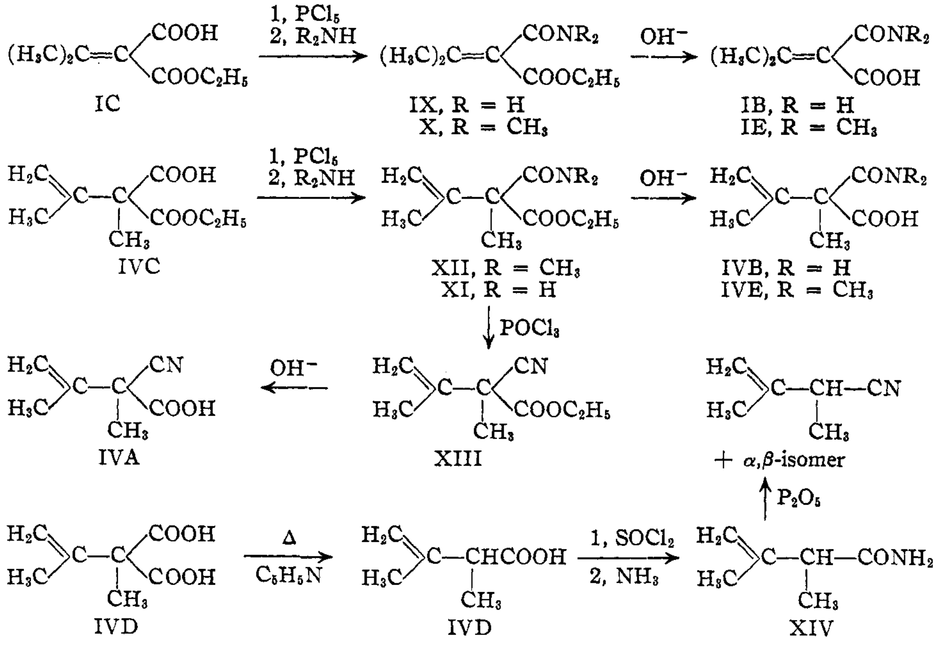
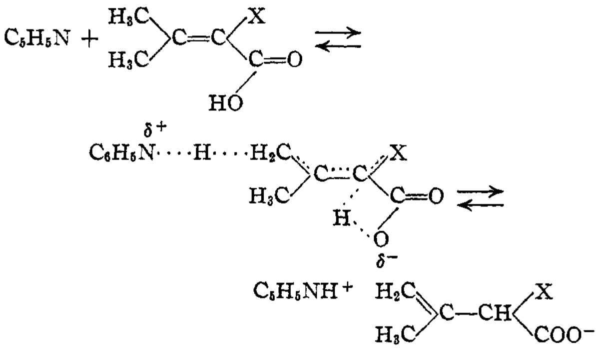


Fig. 1.

ing carboxyl group (at Cα) in the decarboxylation step.[4]



The Dimethylamides IE and IVE.—There are striking differences between the dimethylamides IE and IVE and the corresponding amides IB and IVB both in rate of decarboxylation and product composition. As is evident from Table I, the rate constants for the decarboxylation of IE and IVE are approximately one twenty-fifth as large as those for IB and IVB, respectively. The increased stability of IE and IVE toward decarboxylation is almost certainly a consequence of the relatively large size of the dimethylamido grouping. Inspection of scale models reveals the inability of the dimethylamido group to assume without large steric interactions a position in which it can stabilize the transition state (a) for the isomerization of IE to the β,γ-unsaturated acid or (b) for decarboxylation of the β,γ-unsaturated dimethylamido acid. The low proportion of β,γ-unsaturated product formed from IE appears to indicate that decarboxylation *via* a β,γ-unsaturated intermediate has been retarded to such an extent that it is less important than direct decarboxylation.

Catalysis of Decarboxylation.—Observation of a unique characteristic of the cyano acids IA and IVA has been made in connection with an attempt to induce catalysis of decarboxylation in pyridine by the addition of copper(II) acetate. In the case of IA a strong catalytic influence was indeed observed. The half-life of IA at 111° is reduced from a value of 32 minutes in pyridine alone to less than one minute in 0.03 *M* copper(II) acetate in pyridine. The product ratio is also influenced by copper(II) acetate which heavily favors the formation of the α,β-unsaturated isomer. The product of decarboxylation of IA in 0.03 *M* copper(II) acetate consists of 89% of the α,β-unsaturated isomer IIA and only 11% of the β,γ-unsaturated isomer IIIA.

The increased proportion of α,β-unsaturated nitrile in the copper(II)-catalyzed reaction is not due to catalysis of the direct decarboxylation of IA, since the rate of decarboxylation of pivalylidenecyanoacetic acid (VII) is not increased by the presence of copper(II) acetate (0.03 *M*). Thus, one may conclude that copper(II) catalyzes the conversion of IA into the β,γ-unsaturated isomer and possibly also the decarboxylation of the latter, but not the direct decarboxylation. A plausible interpretation of such catalysis may be made on the basis of complex formation between copper(II) acetate and the nitrogen of the cyano function which should facilitate proton transfer and also anionic decarboxylation.[5]

The product obtained by the copper(II) ion-catalyzed decarboxylation (0.03 *M* copper(II) ion) of the β,γ-unsaturated nitrile IVA consists of 75% of the β,γ-unsaturated isomer and only 25% of the α,β-unsaturated isomer, which indicates that the effect of copper(II) ion upon product com-

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[4] For evidence indicating participation of a carboxyl group in the decarboxylation of β,γ-unsaturated acids (at Cγ) see R. T. Arnold, O. C. Elmer and R. M. Dodson, THIS JOURNAL, 72, 4359 (1950).

[5] For an example of copper(II) ion catalysis of proton transfer in the bromination of ethyl acetoacetate and 2-carbethoxycyclopentanone see K. J. Pedersen, *Acta Chem. Scand.*, 2, 252, 385 (1948).

position is smaller in the case of IVA than with IA. This difference may be due to the fact that the rate of combination of the substrate IVA with the catalyst is not fast enough to prevent a considerable amount of uncatalyzed decarboxylation from occurring.

In contrast to the catalysis of the decarboxylation of IA and IVA by copper(II) ion which appears to be specific for cyano acids, the addition of N-ethylpiperidine increases the rates of decarboxylation in pyridine of the acids IVA, B, C, D and E without exception. From this fact it is clear that the rate constant for anionic decarboxylation of such compounds is considerably greater than that for decarboxylation *via* the un-ionized acid.

Experimental[5a]

Ethyl Isopropylidenemalonamate (IX).—To a solution of 17.2 g. (0.1 mole) of ethyl hydrogen isopropylidene malonate (IC)[1] in 30 ml. of benzene was added 20.9 g. (0.1 mole) of phosphorus pentachloride in five portions. The clear solution was concentrated under reduced pressure to remove benzene and phosphorus oxychloride and the residual liquid was added dropwise with stirring to 75 ml. of concentrated ammonium hydroxide at *ca.* −20°. The mixture was stored for two hours at 0° and then filtered. From the filtrate by extraction with ether there was obtained an oil which crystallized upon storage at 0° overnight. Recrystallization from chloroform–petroleum ether yielded 9.45 g. (55%) of the amide-ester IX as fine, colorless needles, m.p. 108–108.5°. After two recrystallizations the product melted at 109–110°.

Anal. Calcd. for $C_8H_{13}NO_3$: C, 56.12; H, 7.65; N, 8.18. Found: C, 56.36; H, 7.56; N, 8.00.

The corresponding **dimethylamide X** was prepared in the same way using 25% aqueous dimethylamine and was isolated by distillation, b.p. 94° (0.3 mm.), $n^{20}\mathrm{D}$ 1.4780, yield 69%.

Anal. Calcd. for $C_{10}H_{17}NO_3$: C, 60.28; H, 8.60; N, 7.03. Found: C, 60.24; H, 8.73; N, 6.98.

Isopropylidenemalonamic Acid (IB).—A solution of 6.8 g. of ethyl isopropylidenemalonamate (IX) and 2.2 g. of potassium hydroxide in 30 ml. of water and 6 ml. of ethanol was allowed to stand at 25° until neutral to litmus (20 hours). The solution was concentrated under reduced pressure to 20 ml., acidified with 5 ml. of 12 *N* hydrochloric acid and extracted with three 15-ml. portions of ether to remove ether-soluble impurities. Distillation of the aqueous solution under reduced pressure, trituration of the residue with acetone and filtration yielded, after evaporation of the filtrate, 6.0 g. of a viscous sirup which crystallized upon storage. Recrystallization of the crude solid from acetone–chloroform (Darco) and then from acetone alone afforded 4.05 g. (71.5%) of IB as colorless needles, m.p. 158.5–159° (dec.), *pKa* 3.95 (25°).

Anal. Calcd. for $C_6H_9NO_3$: C, 50.34; H, 6.34; N, 9.79. Found: C, 50.22; H, 6.40; N, 9.69.

The **dimethylamido** acid IE was prepared in a similar way from X and recrystallized from acetone, m.p. 175–176° (dec.), yield 59%.

Anal. Calcd. for $C_8H_{13}NO_3$: C, 56.12; H, 7.65; N, 8.18. Found: C, 56.27; H, 7.67; N, 8.13.

Ethyl Isopropenylmethylmalonamate (XI).—This substance was prepared from ethyl hydrogen isopropenylmethylmalonate (IVC)[1] using the procedure described for IX. The yield of XI obtained as a colorless liquid, $n^{20}\mathrm{D}$ 1.4763, by evaporative distillation at 100° (0.5 mm.) was 75.5%.

Anal. Calcd. for $C_9H_{15}NO_3$: C, 58.36; H, 8.16; N, 7.56. Found: C, 58.59; H, 8.36; N, 7.71.

The corresponding **dimethylamide (XII)**, b.p. 94–96° (1.5 mm.), $n^{20}\mathrm{D}$ 1.4670 was prepared in the same way.

Anal. Calcd. for $C_{11}H_{19}NO_3$: C, 61.95; H, 8.98; N, 6.57. Found: C, 61.68; H, 8.77; N, 6.87.

Isopropenylmethylmalonamic Acid (IVB).—The hydrolysis of XI was conducted as described for the preparation of IB with a reaction time of 12 days. The pure acid IVB, m.p. 97° (dec.), pK_a 3.42 (25°) was obtained in 65% yield after two recrystallizations from acetone–carbon tetrachloride.

Anal. Calcd. for $C_7H_{11}NO_3$: C, 53.49; H, 7.06; N, 8.91. Found: C, 53.32; H, 6.97; N, 8.89.

The dimethylamido acid IVE, m.p. 75–76°, was obtained by a similar procedure.

Anal. Calcd. for $C_9H_{15}NO_3$: C, 58.36; H, 8.16; N, 7.56. Found: C, 58.38; H, 8.30; N, 7.84.

Ethyl Isopropenylmethylcyanoacetate (XIII).—A mixture of 11.1 g. of the amide-ester XI and 35 ml. of phosphorus oxychloride was heated to reflux for 55 minutes. The phosphorus oxychloride was removed under reduced pressure, ice was added to the residue and the product was extracted with ether. Distillation of the crude product afforded 8.4 g. (82.7%) of pure XIII, b.p. 48° (0.8 mm.), $n^{20}\mathrm{D}$ 1.4372.

Anal. Calcd. for $C_9H_{13}NO_2$: C, 64.65; H, 7.84; N, 8.38. Found: C, 64.48; H, 8.06; N, 8.40.

Hydrolysis of the ester function in XIII occurred readily in aqueous potassium hydroxide at 25° and afforded the cyano acid IVA, $n^{20}\mathrm{D}$ 1.4570 (purified by evaporative distillation at 75–85° (0.1 mm.)) in 88% yield.

Anal. Calcd. for $C_7H_9NO_2$: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.33; H, 6.48; N, 10.11.

Decarboxylation Products.—All decarboxylations were carried out at 111° until reaction was complete using 3 ml. of pure pyridine for each g. of acid.

The decarboxylation of **isopropylidenemalonic acid (ID)**[6] (40-minute heating period) furnished, after pouring the reaction mixture into cold hydrochloric acid, extracting with ether, drying the extract and distilling through a Holzman semi-micro column, an 83% yield of a mixture of β,β-dimethylacrylic acid (IID) and β-methyl-β-butenoic acid (IIID),[7] b.p. 83–85° (12 mm.), $n^{20}\mathrm{D}$ 1.4362. Esterification of the mixture of acids with a twice-distilled solution of diazoethane[8] in ether and distillation afforded a 94% yield of the corresponding mixture of ethyl esters, b.p. 67–69.5° (58 mm.), $n^{20}\mathrm{D}$ 1.4298 (lit.[1] ethyl β,β-dimethylacrylate: b.p. 76.0–76.5° (57.8 mm.), $n^{20}\mathrm{D}$ 1.4360; ethyl β-methyl-β-butenoate: b.p. 67.5–68.5 (57.8 mm.), $n^{20}\mathrm{D}$ 1.4185). On the basis of refractive indices the mixture of esters contains 93% of the β,γ-isomer and 7% of the α,β-isomer.

The isolation and analysis of the decarboxylation products of **isopropenylmethylmalonic acid (IVD)**[9] were performed as described above for ID. The mixture of acids obtained upon decarboxylation of IVD (82% yield), $n^{20}\mathrm{D}$ 1.4410, yielded by esterification with diazoethane a 95% yield of the corresponding mixture of ethyl esters, b.p. 75–77° (48 mm.), $n^{20}\mathrm{D}$ 1.4220 (lit.[10] ethyl trimethylacrylate: b.p. 169° (733 mm.), $n^{20}\mathrm{D}$ 1.4430; ethyl α,β-dimethyl-β-butenoate: b.p. 151° (735 mm.), $n^{20}\mathrm{D}$ 1.4210) which consists of 95% of the β,γ-isomer and 5% of the α,β-isomer.

A mixture of the two isomeric decarboxylation products of **isopropylidenemalonamic acid (IB)** was isolated by two sublimations (at 0.5 mm.) of the solid which remained after the removal of pyridine from the reaction mixture. The solid mixture, m.p. 74–106.5° (unchanged by further sublimation), obtained in 87% yield, consisted of 80% of the β,γ-isomer (IIIB) and 20% of the α,β-isomer (IIB) as determined by infrared analysis. The transmittance of the mixture[11] was found to be 0.537. The composition of the mixture was calculated using molecular extinction coefficients (ε) determined for pure samples of IIB and IIIB at 905 cm.$^{-1}$ of 0.0 and 55.8, respectively. The infrared

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[5a] We are indebted to Miss Emily Davis, Mrs. Katherine Pih, Mrs. Esther Fett and Mr. Joseph Nemeth for the microanalyses and to Mrs. Rosemary Hill and Miss Helen Miklas for the infrared determinations.

(6) A. Meyerberg, *Ber.*, **28**, 786 (1895).

(7) A. Mooradian and J. B. Cloke, THIS JOURNAL, **68**, 785 (1946); A. A. Morton, M. L. Brown, M. E. T. Holden, R. L. Letsinger and E. E. Magat, *ibid.*, **67**, 2224 (1945).

(8) A. L. Wilds and A. L. Meader, *J. Org. Chem.*, **13**, 763 (1948).

(9) G. A. R. Kon and E. Speight, *J. Chem. Soc.*, 2727 (1926).

(10) R. C. Huston and G. L. Goerner, THIS JOURNAL, **68**, 2504 (1946).

(11) At 905 cm.$^{-1}$, concn. = 30 mg./ml. in chloroform, cell thickness = 0.020 cm.

spectrum of a synthetic 80–20 mixture of IIIB and IIB was identical with that of the mixture obtained by decarboxylation.

The two isomeric decarboxylation products VB and VIB from **isopropenylmethylmalonamic acid** were isolated and determined in the same way. A 90% yield was obtained of the solid mixture, m.p. 92–100°, transmittance[11] 0.605 72% VIB, 28% VB. At 905 cm.$^{-1}$ ϵ for VB is 0 and ϵ for VIB is 57.5.

The products of decarboxylation of **isopropylidene-N,N-dimethylmalonamic acid (IE)** were obtained by direct distillation of the reaction mixture through a Holzman semi-micro column, b.p. 69–70.5° (4.5 mm.), n^{20}D 1.4768, transmittance[11] 0.842, yield 86%. Using the average of the extinction coefficients (56.5) for the amides IIIB and IVB at 905 cm.$^{-1}$ as the value of ϵ for the dimethylamide IIIE at 905 cm.$^{-1}$ and 0 as the value of ϵ for IIE, the calculated composition of the mixture is 28% β,γ-isomer IIIE and 72% α,β-isomer IIE. The mixture was also subjected to elemental analysis.

Anal. Calcd. for $C_7H_{13}NO$: C, 66.10; H, 10.30; N, 11.01. Found: C, 65.86; H, 10.38; N, 11.11.

The decarboxylation of **isopropenylmethyl-N,N-dimethylmalonamic acid (IVE)** afforded 89% of a mixture, b.p. 51–54° (1.5 mm.), n^{20}D 1.4642, transmittance[11] 0.597 which was found by calculation to contain 90% of the β,γ-dimethylamide VIE (ϵ assumed to be 56.5 for pure VIE at 905 cm.$^{-1}$) and 10% of the α,β-dimethylamide VE (ϵ assumed to be 0 for pure VE at 905 cm.$^{-1}$).

Anal. Calcd. for $C_8H_{15}NO$: C, 68.04; H, 10.71; N, 9.92. Found: C, 67.83; H, 10.69; N, 9.81.

The procedure for the isolation of the decarboxylation products of **isopropylidenecyanoacetic acid (IA)**[12] was essentially the same as that employed with the diacid ID. The yield was 84% of a mixture of the α,β-nitrile IIA and the β,γ-nitrile IIIA, b.p. 73.5–75° (89 mm.), n^{20}D 1.4220, transmittance[11] 0.462 (lit.[13] senecionitrile (IIA): b.p. 141.6–141.8° (757 mm.), n^{20}D 1.4372; lit.[14] β-methyl-β-butenonitrile (IIIA); b.p. 134.5–136.5°, n^{20}D 1.4180). The composition of the mixture calculated either from refractive indices or infrared data (ϵ at 905 cm.$^{-1}$ for IIIA equals 57.5) is 80% β,γ-nitrile IIIA and 20% of the α,β-nitrile IIA.

In the same way there was obtained from **isopropenylmethylcyanoacetic acid (IVA)** in 84% yield a mixture of VA and VIA, b.p. 69–73° (52 mm.), n^{20}D 1.4268, transmittance[11] 0.513 (lit.[13] trimethylacrylonitrile (VA): b.p. 157.0–157.4° (766 mm.), n^{20}D 1.4455). The composition of the mixture on the basis of the infrared data (assuming ϵ at 905 cm.$^{-1}$ for VIA is 57.5) is 80% β,γ-nitrile VIA and 20% α,β-nitrile VA.

Anal. Calcd. for C_6H_9N: C, 75.74; H, 9.54; N, 14.72. Found: C, 75.55; H, 9.44; N, 14.40.

α,β-Dimethyl-β-butenoamide (XIV).—α,β-Dimethyl-β-butenoic acid was prepared as described above from 1.95 g. of isopropenylmethylmalonic acid and was converted to the acid chloride by heating with 1.5 g. of purified thionyl chloride for 30 minutes. Dry benzene (25 ml.) was added and the solution was treated with excess anhydrous ammonia at +5°. The resulting mixture was evaporated to dryness under reduced pressure, the residue was triturated with acetone and the slurry filtered. The acetone solution was evaporated and the oily solid was purified by sublimation (90°, 0.5 mm.), recrystallization from carbon tetrachloride and a final sublimation. The yield of pure product, m.p. 104.5–105.0°, ϵ (905 cm.$^{-1}$) 57.5, was 0.95 g. (68%).

Anal. Calcd. for $C_6H_{11}NO$: C, 63.68; H, 9.80; N, 12.38. Found: C, 63.86; H, 9.83; N, 12.38.

Dehydration of XIV by distillation from phosphorus pentoxide at 100 mm. yielded a mixture of the α,β- and β,γ-unsaturated nitriles, n^{20}D 1.4335.

β-Methyl-β-butenoamide was prepared by essentially the same procedure from isopropylidenemalonic acid in 58% over-all yield, m.p. 118–119°, ϵ (905 cm.$^{-1}$) 55.8 (lit.[7] m.p. 119–120°).

Trimethylacrylamide, m.p. 133–134° (lit.[13] m.p. 130.5°) and β,β-dimethylacrylamide, m.p. 108.5–109.5 (lit.[15] m.p. 108°) were prepared from the corresponding acids *via* the acid chlorides and were found to have no absorption bands at or near 905 cm.$^{-1}$.

Pivalylidenecyanoacetic Acid VII.—This substance was best prepared by the method of Ross and Burnett[3] which involves condensation of pivalaldehyde with sodium cyanoacetate in aqueous solution. The yields of VII were much poorer when the aldehyde and cyanoacetic acid were allowed to react in pyridine or triethanolamine solution.

The decarboxylation of VII in boiling pyridine afforded *trans-t*-butylacrylonitrile (VIII) as the sole product, b.p. 83–84° (52 mm.), n^{20}D 1.4349 (lit.[3] b.p. 59–60° (28 mm.), n^{20}D 1.4344). The infrared spectrum of VIII possessed a strong band at 975 cm.$^{-1}$ indicative of a *trans* arrangement of the hydrogens attached to the double bond.

Measurements.—Rates of decarboxylation were measured by the technique described previously.[1]

The infrared spectra were obtained by means of a Perkin-Elmer model 21 double beam spectrophotometer.

URBANA, ILL.

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