

combined organic layers, after washing with water, were distilled to dryness. The residue after digestion with petroleum ether (60–90°) weighed 29.4 g. (0.0717 mole, 90.4%), m.p. 138–150°. Repeated purification from ethyl acetate–petroleum ether (65–110°) gave colorless needles, m.p. 152–153°.

Anal. Calcd. for $C_{20}H_{27}NO_9$: C, 56.46; H, 6.39. Found: C, 56.82; H, 6.40.

α -Acetamido- β -3,4,5-trimethoxybenzoylpropionic Acid.—A solution containing 8.5 g. (0.02 mole) of the alkylation product in 100 cc. of 10% potassium hydroxide and 30 cc. of ethanol was refluxed for 3 hours. After distillation of the alcohol at 20 mm. pressure and extraction with ether, the alkaline layer was acidified with dilute hydrochloric acid. The solid obtained (VIII) weighed 6.6 g. (0.018 mole, 89%) and melted at 132–134° (dec.). It decomposed during attempted recrystallization.

By heating at 160° under nitrogen, 6.0 g. (0.016 mole) of the malonic acid gave 5.0 g. (0.015 mole, 95%) of solid, m.p. 168.5–170°. By treatment with charcoal and recrystallization from water, colorless needles were obtained, m.p. 169.5–170.5°.

Anal. Calcd. for $C_{15}H_{19}NO_7$: C, 55.38; H, 5.88. Found: C, 55.27; H, 5.69.

α -Acetamido- γ -3,4,5-trimethoxyphenylbutyric Acid (IX).—Reduction of 9.0 g. (0.028 mole) of the above keto acid in 75 cc. of acetic acid with 3.0 g. of 5% palladium–carbon⁸ at 30 lb. pressure and 55° gave 7.5 g. (0.024 mole, 87%) of the butyric acid, m.p. 174–176°. After five crystallizations from water, the compound melted at 175–176.5°.

Anal. Calcd. for $C_{15}H_{19}NO_8$: C, 57.86; H, 6.80. Found: C, 58.06; H, 6.58.

A mixture with the keto acid melted at 152–162°.

α -Acetamido- α -carboisopropoxy- γ -hydroxy- γ -3,4,5-trimethoxyphenylbutyric Acid Lactone (X).—A solution containing 5.3 g. (0.012 mole) of VII in 20 cc. of isopropyl alcohol was added to a solution of aluminum isopropoxide (from 0.5 g. of aluminum) in 10 cc. of isopropyl alcohol. After 18.5 hours of refluxing, no additional acetone formation could be detected.¹⁷ The residue after distillation of the solvent at 20 mm. pressure was acidified with dilute hydrochloric acid. The solid which precipitated and material obtained by benzene extraction of the filtrate were combined and recrystallized from ethyl acetate. The first crop, m.p. 181–184° (2.95 g.), and a second, m.p. 180–183° (0.55 g.), brought the yield to 73%. Six recrystallizations from ethyl acetate gave colorless plates, m.p. 183–184.5°.

(17) Reference 9, p. 203.

The compound was insoluble in cold 5% sodium hydroxide but dissolved on warming.

Anal. Calcd. for $C_{19}H_{25}NO_8$: C, 57.71; H, 6.37. Found: C, 58.13; H, 6.44.

α -Acetamido- α -carboisopropoxy- γ -3,4,5-trimethoxyphenylbutyric Acid (XI).—Hydrogenation of 1.0 g. (0.0025 mole) of the lactone (X) with 5% palladium–carbon as above gave 0.9 g. (0.0023 mole, 89%) of colorless crystals, m.p. 136–138° dec. After four recrystallizations from aqueous ethanol, colorless plates, m.p. 141–142° dec., were obtained. The compound was soluble in aqueous sodium bicarbonate.

Anal. Calcd. for $C_{19}H_{27}NO_8$: C, 57.42; H, 6.85. Found: C, 57.52; H, 7.27.

α -Acetamido- γ -3,4,5-trimethoxyphenylbutyric Acid (IX).—A solution containing 0.7 g. (0.0018 mole) of the malonic half-ester in 10 cc. of 5% sodium hydroxide was refluxed for 1 hour. On acidification 0.4 g. (0.0011 mole, 64%) of the malonic acid (XII), m.p. 80–85° dec., was obtained.

The crude malonic acid (0.2 g., 0.00056 mole) after 15 minutes at 140° (20 mm.) gave a glassy solid which dissolved in hot water. On cooling, 0.12 g. (0.00039 mole, 68%) of colorless needles was obtained, m.p. 156–168°. Further crystallization from water gave material, m.p. 169–172°, which melted at 172.5–175.5° when mixed with IX above.

α -Amino- γ -3,4,5-trimethoxyphenylbutyric Acid.—A solution containing 3.0 g. (0.0096 mole) of IX in 15 cc. of 3 *N* hydrochloric acid was refluxed for 1 hour. The ice-cold solution was adjusted to pH 6 by addition of ammonia. The colorless precipitate which then appeared weighed 2.1 g. (0.0078 mole, 78%), m.p. 223–226° dec. After further purification from water colorless needles were obtained, m.p. 225.5–227.5° dec.

Anal. Calcd. for $C_{13}H_{19}NO_5$: C, 57.98; H, 7.11. Found: C, 58.20; H, 7.15.

α -Phthalimido- γ -3,4,5-trimethoxyphenylbutyric Acid.—A mixture of 2.0 g. (0.0074 mole) of the amino acid and 1.1 g. of phthalic anhydride was heated for 15 minutes in a bath at 145°. The residue (2.8 g., 0.0070 mole, 94%) melted at 190–196° and after four recrystallizations from ethanol, at 197.5–199°.

Anal. Calcd. for $C_{21}H_{21}NO_7$: C, 63.15; H, 5.30. Found: C, 63.41; H, 5.41.

The phthalimidobutyric acid was submitted to the Arndt–Eistert reaction⁸ analogous to the model compound above. After saponification, the expected valeric acid could not be purified.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DE PAUL UNIVERSITY]

Unsymmetrical Quaternary Carbon Compounds. II. The Comparative 1,4-Additions of Grignard Reagents to Several Conjugated Systems¹

BY FRANKLIN S. PROUT, ELIZABETH P.-Y. HUANG, ROBERT J. HARTMAN AND CHARLES J. KORPICIS

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The reactions of *n*-alkyl, aryl and benzyl organometallic reagents with five isopropylidene conjugated systems have been compared. The 1,4-addition products were major products in all cases except one. Grignard additions to ethyl isopropylidene cyanoacetate were most dependable. Additions with organocadmium compounds were poor with alkyl and aryl reagents but excellent with dibenzylcadmium.

The work of Alexander, McCollum and Paul² and the results reported in the first paper of this series³ implied that the *sec*-alkylidene cyanoacetic esters were the most effectively alkylated of this class of compounds.⁴ In order to test this conclusion we

(1) Abstracted in part from the thesis for Master of Science of Elizabeth P.-Y. Huang, June, 1953, and from the theses for Bachelor of Science of Robert J. Hartman and Charles J. Korpics, June, 1952.

(2) E. R. Alexander, J. D. McCollum and D. E. Paul, *THIS JOURNAL*, **72**, 4791 (1950).

(3) F. S. Prout, *ibid.*, **74**, 5915 (1952).

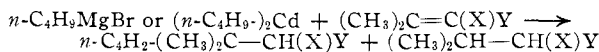
(4) See reference 3 for a bibliography of examples of this reaction.

have examined the 1,4-addition to five conjugated isopropylidene compounds—ethyl isopropylidene cyanoacetate, ethyl isopropylidene malonate, isopropylidene malonitrile, isopropylidene cyanoacetic acid and potassium isopropylidene cyanoacetate—with *n*-butylmagnesium bromide, phenylmagnesium bromide, benzylmagnesium chloride and some organocadmium compounds. Furthermore, the addition reactions of ethyl *sec*-butylidene cyanoacetate were extended to aryl and benzyl Grignard reagents.

The results obtained from reaction of these conjugated compounds with *n*-butylmagnesium bromide and di-*n*-butylcadmium are assembled in Table I. While the Grignard reagent gave substantially the same yield in all comparative cases, the yields of addition product were markedly reduced when di-*n*-butylcadmium was used. Only the preparations for the malonic⁵ and cyanoacetic² esters have previously been reported.

TABLE I

THE REACTION OF ISOPROPYLIDENE COMPOUNDS WITH *n*-BUTYLMAGNESIUM BROMIDE AND DI-*n*-BUTYLCADMIUM



<i>n</i> -Butyl reagent (0.3 mole)	Isopropylidene cpd. (0.25 mole)		Products, yield, %	
	-X	-Y	1,4-Addition	Reduction
Mg	-CN	-COOC ₂ H ₅	40 ^{a,b}	15
Cd	-CN	-COOC ₂ H ₅	15	23
Mg	-COOC ₂ H ₅	-COOC ₂ H ₅	40 ^{a,c}	20
Cd	-COOC ₂ H ₅	-COOC ₂ H ₅	28 ^a	34
Mg	-CN	-CN	35 ^d	19
Cd	-CN	-CN	5 ^d	39
Mg	-CN	-COOH	41 ^{e,f}	6
Mg	-CN	-COOK	17 ^f	..

^a Average of two runs. ^b Alexander, McCollum and Paul² report a 42% yield. ^c Wideqvist⁵ reported a 30% yield. ^d In these runs 0.15 mole of bromide and 0.125 mole of isopropylidenemalononitrile were used. ^e Three-quarters of a mole of *n*-butylmagnesium bromide was used. ^f The product was 3,3-dimethylheptanenitrile.

The more effective additions with phenylmagnesium bromide and benzylmagnesium chloride (Ta-

TABLE II

THE REACTION OF *sec*-ALKYLIDENE COMPOUNDS WITH PHENYL AND BENZYL ORGANOMETALLIC COMPOUNDS

Alkylation agent (0.3 mole)	<i>sec</i> -Alkylidene cpd. (0.25 mole)	Addn. prod. yield, %
C ₆ H ₅ MgBr	(CH ₃) ₂ C=C(CN)COOC ₂ H ₅	63 ^a
(C ₆ H ₅) ₂ Cd	(CH ₃) ₂ C=C(CN)COOC ₂ H ₅	12
C ₆ H ₅ MgBr	(CH ₃) ₂ C=C(COOC ₂ H ₅) ₂	40 ^b
C ₆ H ₅ MgBr	(CH ₃) ₂ C=C(CN) ₂	5.5 ^{c,d}
C ₆ H ₅ MgBr	(CH ₃) ₂ C=C(CN)COOH	60 ^{e,f}
C ₆ H ₅ MgBr	(CH ₃) ₂ C=C(CN)COOK	30 ^e
C ₆ H ₅ MgBr	C ₂ H ₅ (CH ₃)C=C(CN)COOC ₂ H ₅	79 ^g
(C ₆ H ₅) ₂ Cd	C ₂ H ₅ (CH ₃)C=C(CN)COOC ₂ H ₅	26 ^g
<i>p</i> -Cl-C ₆ H ₄ MgBr	C ₂ H ₅ (CH ₃)C=C(CN)COOC ₂ H ₅	73 ^g
C ₆ H ₅ CH ₂ MgCl	(CH ₃) ₂ C=C(CN)COOC ₂ H ₅	85 ^h
(C ₆ H ₅ CH ₂) ₂ Cd	(CH ₃) ₂ C=C(CN)COOC ₂ H ₅	92
C ₆ H ₅ CH ₂ MgCl	(CH ₃) ₂ C=C(COOC ₂ H ₅) ₂	60 ⁱ
C ₆ H ₅ CH ₂ MgCl	(CH ₃) ₂ C=C(CN) ₂	76
C ₆ H ₅ CH ₂ MgCl	(CH ₃) ₂ C=C(CN)COOH	68 ^{i,j}
C ₆ H ₅ CH ₂ MgCl	(CH ₃) ₂ C=C(CN)COOK	33 ^{i,k}
C ₆ H ₅ CH ₂ MgCl	C ₂ H ₅ (CH ₃)C=C(CN)COOC ₂ H ₅	88 ^{b,c}
(C ₆ H ₅ CH ₂) ₂ Cd	C ₂ H ₅ (CH ₃)C=C(CN)COOC ₂ H ₅	93 ^c

^a The literature reports 60%. ^b Average of two runs. ^c These runs used 0.6 mole of halide and 0.5 mole of alkyldene compound. ^d See Experimental. ^e The product here was 3-methyl-3-phenylbutanenitrile. ^f Six-tenths mole of phenylmagnesium bromide was used. ^g Here 0.40 mole of *p*-bromochlorobenzene and 0.30 mole of the alkylidene ester were employed. ^h The literature² reports 49% yield. ⁱ The product was 3-benzyl-3-methylbutanenitrile. ^j Six-tenths mole of benzylmagnesium chloride was used. ^k Average of four runs.

(5) S. Wideqvist, *Arkiv. Kemi Mineral. Geol.*, **B23**, No. 4 (1946).

ble II) occurred *without* reduction and thus in higher yields. The yields were highest with the cyanoacetic esters. However, it was noted that additions to isopropylidenecyanoacetic acid fur-

TABLE III

PROPERTIES OF CYANOACETIC ESTERS, R'R''(CH₃)C-CH(CN)COOC₂H₅

R'	R''	B.p. °C.	Mm.	<i>n</i> _D ²⁰	Sapn. eq. Calcd.	Nitrile, % Found	Nitrile, % ^a
CH ₃	<i>n</i> -C ₄ H ₉ ^a	120-124	7	1.4389	211.3	210	78 ^b
CH ₃	C ₆ H ₅ ^b	185-192	28	1.5038	231.3	231	70
CH ₃	C ₆ H ₅ CH ₂ ^c	180-186	15	1.5012	245.3	248	74
C ₂ H ₅	C ₆ H ₅ ^d	178-180	11	1.5053	245.2	247	71
C ₂ H ₅	<i>p</i> -ClC ₆ H ₄ ^e	203-205	13	1.5179	280.7	281	56
C ₂ H ₅	C ₆ H ₅ CH ₂ ^f	195-197	11	1.5052	259.3	259	91

^a The literature² gives b.p. 109° (2 mm.), *n*_D²⁰ 1.4392. ^b The literature² gives b.p. 155° (0.5 mm.), *n*_D²⁰ 1.5062. ^c The literature² gives b.p. 142-143° (0.4 mm.), *n*_D²⁰ 1.5032. ^d *Anal.* Calcd. for C₁₅H₁₃NO₂: N, 5.71. Found: N, 5.68; *d*₄²⁵ 1.049. ^e *Anal.* Calcd. for C₁₅H₁₃ClNO₂: N, 5.01. Found: N, 4.94; *d*₄²⁵ 1.132. ^f *Anal.* Calcd. for C₁₆H₂₁NO₂: N, 5.40. Found: N, 5.22; *d*₄²⁵ 1.037. ^g Cyanoacetic esters were hydrolyzed and decarboxylated according to the procedure in reference 3. The properties of the nitriles are given in Table V. ^h This value refers to the yield of acid, 3,3-dimethylheptanoic acid (Table VI).

TABLE IV

PROPERTIES OF MALONIC ESTERS, R(CH₃)₂C-CH(COOC₂H₅)₂

R	<i>n</i> -C ₄ H ₉ ^a	C ₆ H ₅	C ₆ H ₅ CH ₂
B.p. { °C.	134-135	177-178	185-186
{ Mm.	10	18	8
<i>n</i> _D ²⁰	1.4429	1.4939	1.4890
<i>d</i> ₄ ²⁵	1.001	1.062	1.043
Carbon, %	Calcd.	69.07	69.83
	Found	69.26	69.51
Hydrogen, %	Calcd.	7.97	8.27
	Found	8.07	8.26
Acid, % ^b	70	66	70

^a Wideqvist⁵ reported 129.5° (8 mm.). ^b Malonic esters hydrolyzed for two hours with potassium hydroxide in ethylene glycol, decarboxylated and distilled to give the monobasic acid. The properties are given in Table VI.

TABLE V

MALONONITRILES AND ACETONITRILES

R(CH ₃) ₂ C-CH(CN) ₂ ^a	B.p. °C.	Mm.	<i>n</i> _D ²⁰	<i>d</i> ₄ ²⁵	Nitrogen, % Calcd.	Nitrogen, % Found	Acid ^d %
<i>n</i> -C ₄ H ₉	123-125	15	1.4371	0.8951	17.06	17.30	69
C ₆ H ₅	138-143	1	1.5183	1.039	15.21	15.01	..
C ₆ H ₅ CH ₂	153-154	6	1.5122	1.017	14.13	14.23	90
R(CH ₃) ₂ C-CH ₂ CN ^b							
<i>n</i> -C ₄ H ₉	95-97	25	1.4251	0.8179	10.05	9.55	80
C ₆ H ₅	146-147	20	1.5146	0.9775	8.80	9.01	93
C ₆ H ₅ CH ₂	148-149	17	1.5078	0.9565	8.08	8.00	90
R(CH ₃)(C ₂ H ₅)-CH ₂ CN ^c							
C ₆ H ₅	149-151	16	1.5149	0.9742	8.08	8.04	88
<i>p</i> -Cl-C ₆ H ₄	180-183	14	1.5289	1.087	6.74	6.80	64
C ₆ H ₅ CH ₂	161-165	15-18	1.5110	0.9592	7.48	7.68	91

^a The malononitriles were formed by addition to isopropylidenemalononitrile. ^b These nitriles were prepared by additions to isopropylidenecyanoacetic acid and by partial hydrolysis of the product from addition to ethyl isopropylidenecyanoacetate. ^c These nitriles were prepared by partial saponification of the alkylation product from ethyl *sec*-butylidenecyanoacetate. ^d Nitriles were heated under brisk reflux with potassium hydroxide in ethylene glycol for 6-36 hours to effect hydrolysis. The properties of the acids are given in Table VI.

TABLE VI
 PROPERTIES OF *t*-ALKYLACETIC ACIDS, $R(\text{CH}_3)_2\text{C}-\text{CH}_2\text{COOH}$ AND $R(\text{CH}_3)(\text{C}_2\text{H}_5)\text{C}-\text{CH}_2\text{COOH}$

$R(\text{CH}_3)_2\text{C}-\text{CH}_2\text{COOH}$ R	B.p. °C.	Mm.	n_D^{25}	d_4^{25}	Neut. equiv.		Carbon, %		Hydrogen, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
<i>n</i> -C ₄ H ₉	133–134	18	1.4319	0.9059	158.23	157.9	68.31	68.18	11.46	11.67
C ₆ H ₅	172–175	18 ^a	1.5182	178.22	178.7	74.13	74.32	7.91	8.05
C ₆ H ₅ CH ₂	181–182	18	1.5140	1.036	192.25	192.5	74.96	74.76	8.39	8.35
$R(\text{CH}_3)(\text{C}_2\text{H}_5)\text{C}-\text{CH}_2\text{COOH}$ R										
C ₆ H ₅	180–182	14	1.5183	1.050	192.25	191.6	74.96	74.88	8.39	8.45
<i>p</i> -ClC ₆ H ₄	203–205	16 ^b	226.70	226.8	63.57	63.39	6.67	6.71
C ₆ H ₅ CH ₂	153–156	0.1	1.5160	1.035	206.28	206.3	75.69	75.93	8.79	8.96

^a Crystallizes as diamonds from hexane, m.p. 58–59°, f.p. 58°. ^b Rapidly solidifies. Crystallizes as heavy prisms from ethanol–water, m.p. 72–74°.

nished the nitriles, $R(\text{CH}_3)_2\text{C}-\text{CH}_2\text{CN}$, in yields better than those obtained by the additions to ethyl isopropylidenecyanoacetate followed by hydrolysis to the nitrile. The reaction of isopropylidenemalononitrile with phenylmagnesium bromide revealed that the polymerization of the alkylidene compounds can be a serious side reaction. The properties of the purified alkylation products are summarized in Tables III–V.

The partial hydrolyses of the *t*-alkylcyanoacetic esters in Table III in a mixture of ethylene glycol and a limited amount of potassium hydroxide gave the nitriles in 56–82% yields.³ These nitriles had the same properties as those resulting from additions to isopropylidenecyanoacetic acid and potassium isopropylidenecyanoacetate.

These mononitriles and the *t*-alkylmalononitriles from butyl and benzyl additions (Table V) were converted to the *t*-alkylacetic acids by long hydrolysis in a mixture of ethylene glycol and potassium hydroxide in 64–93% yields. The *t*-alkylmalonic esters (Table IV) were similarly, but more easily, hydrolyzed and decarboxylated to give acids in 66–70% yields. The properties of the six purified acids resulting from these hydrolyses are assembled in Table VI.

Experimental⁶

Isopropylidene Compounds.—Acetone was condensed with ethyl cyanoacetate,^{7,8} malononitrile^{7,9} and cyanoacetic acid⁷ using ammonium or piperidine acetates or amino acid catalyses to give the expected Knoevenagel condensation. Ethyl isopropylidenemalonate was prepared by condensation of acetone with ethyl malonate using zinc chloride as catalyst.¹⁰

Potassium isopropylidenecyanoacetate was prepared by dissolving 125 g. of isopropylidenecyanoacetic acid in 500 ml. of 95% ethanol containing 0.99 mole of potassium hydroxide. Addition of ether (400 ml. and then 700 ml.) and cooling furnished 158 g. of the salt. Upon drying in a vacuum oven at 110–120° a yield of 151 g. (93%) of the salt

(6) All melting and boiling points are uncorrected. Densities are reported as absolute density (g./cc.). All fractionations were run through a 60-cm., heated Vigreux column. The carbon, hydrogen and nitrogen analyses were performed by Micro-Tech Laboratories, Skokie, Illinois. The infrared spectra of the compounds reported in this paper and those reported in reference 3 have been taken by Samuel P. Sadtler and Son, Inc., 1517 Vine Street, Philadelphia 3, Pennsylvania.

(7) F. S. Prout, *J. Org. Chem.*, **18**, 928 (1953).

(8) A. C. Cope, C. M. Hofmann, C. W. Wyckoff and E. Hardenbergh, *THIS JOURNAL*, **63**, 3452 (1941); S. Wideqvist, *Acta Chem. Scand.*, **3**, 303 (1949).

(9) A. C. Cope and K. E. Hoyle, *THIS JOURNAL*, **63**, 733 (1941).

(10) A. C. Cope and E. M. Hancock, *ibid.*, **60**, 2901 (1938).

was obtained. (The weight loss on drying (4.6%) suggests a hemihydrate (calcd., 4.65%).) A twice-recrystallized sample was prepared for analysis.

Anal. Calcd. for C₆H₈O₂NK: N, 8.58. Found: N, 9.00.

1,4-Additions to Isopropylidene Compounds.—The procedure previously described³ was followed for the 1,4-addition reactions except for the examples noted below. The results of these reactions and characteristics of the products are assembled in Tables I–V.

Isopropylidenecyanoacetic acid (0.25 mole) was dissolved in ether and was added to the Grignard reagent prepared from 0.6–0.75 mole of halide. Potassium isopropylidenecyanoacetate (0.25 mole) was added as a powder in one portion to 0.3 mole of cold Grignard reagent in 300 ml. of ether. The poor yields by this method seem to be due to the insolubility of the salt.

The reaction of phenylmagnesium bromide (0.6 mole) with isopropylidenemalononitrile (0.5 mole) was far more exothermic than the others. Concentration of the benzene–ether extracts following the usual work-up gave 5.0 g. of solid, m.p. 218–228° dec. Four crystallizations of these soft, yellow needles from ethanol–water gave the pure product, m.p. 240–243° dec., molecular weight, 298, 283 (Rast), thus presumably the trimer of isopropylidenemalononitrile (calcd. mol. wt., 318).

Anal. Calcd. for (C₆H₈N₂)₃: C, 67.90; H, 5.70; N, 26.40. Found: C, 67.34; H, 5.82; N, 26.73.

The mother liquor was concentrated and the benzene was replaced with 95% ethanol. A total of 20.3 g. of solid was eventually collected, m.p. 162–173°. This product was crystallized three times from 95% ethanol to furnish the pure dimer as heavy, pale-yellow prisms; m.p. 169–176°, N, 26.73 (calcd., 26.40). This compound is evidently identical with the dimer of isopropylidenemalononitrile reported by Cope and Hoyle⁹ (mixed m.p. 172–175°). These two solids represent a 47.7% recovery of the starting material.

The alcoholic mother liquors remaining after removal of the crystalline polymer were diluted with water and re-extracted with benzene. After removal of solvent and forerun (8.5 g., b.p. 90–138° (13–1 mm.)) the **2-cyano-3-methyl-3-phenylbutanenitrile** was obtained: b.p. 138–143° (1 mm.), 5.1 g. (5.5%).

Hydrolyses of Alkylation Products.—The *t*-alkylcyanoacetic esters (Table III) were saponified and decarboxylated in alkaline ethylene glycol⁸ to give the nitriles (56–91% yields). However, ethyl 2-cyano-3,3-dimethylheptanoate was hydrolyzed after long heating with alkali to the acid in one step.

The malonic esters (Table IV) were saponified with potassium hydroxide in ethylene glycol after two hours heating. After decarboxylation of the crude dibasic acid obtained from the reaction mixture, the monobasic acid was obtained in 66–70% yields.

The *t*-alkylacetone nitriles were saponified according to the previously described method³ except that in most cases six hours of brisk reflux was adequate to effect the conversion. Extensive time (30 hours) was used for hydrolysis of the two malononitriles.

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