(1.1 moles) of redistilled epichlorohydrin and the reaction mixture was stirred for 7 hours at the reflux temperature of liquid ammonia. Ammonium chloride (118 g., 2.2 moles) was then added in 3 portions followed by 1 liter of ether and stirring maintained while the ammonia was allowed to evaporate overnight. The ethereal solution was filtered, the solid residue was washed with ether and then dissolved in water, and the aqueous solution was extracted with ether. The combined ether solution was dried over anhydrous magnesium sulfate, filtered, and the ether removed at room temperature using a water aspirator. Approximately 0.8 mole of phenylacetylene was next recovered by distillation using an oil-pump and products obtained by distillation using a mercury vapor pump. Two fractions were isolated. (1) α-Benzylfuran, 55.2 g., 34.7% yield, b.p. 50–52° (10^{-3} mm.), n^{25}D 1.5411 (lit.[5] b.p. 70–72° (1 mm.), n^{16}D 1.5459, 6.7% yield; from α-bromomethylfuran,[6] b.p. 114–116° (23 mm.), n^{19}D 1.5451).

Anal. Calcd. for $C_{11}H_{10}O$: C, 83.51; H, 6.37; mol. wt., 158.17. Found: C, 83.23; H, 6.38; mol. wt., cryoscopic in benzene, 157.

(2) 5-Phenyl-2-penten-4-yn-1-ol, 58.6 g., 36.8% based on epichlorohydrin, b.p. 92–97° (10^{-3} mm.), n^{25}D 1.6158 (lit.[5] b.p. 94–96° (10^{-3} mm.), n^{24}D 1.6173); yield 24% based on half of the phenylacetylene taken.

The ultraviolet spectrum of the α-benzylfuran showed an unconjugated phenyl group. The infrared spectrum showed the absence of acetylene and hydroxyl groups and confirmed the presence of the phenyl.

5-Phenyl-2-penten-4-yn-1-al (III).—A solution of 15.8 g. (0.158 mole) of chromic anhydride and 25.3 g. of concd. sulfuric acid diluted with water to a total volume of 79 ml. was added dropwise with stirring to 17.9 g. (0.113 mole) of 5-phenyl-2-penten-4-yn-1-ol dissolved in 70 ml. of acetone during 1 hour while keeping the temperature at about 15°. The reaction mixture was stirred for an additional hour at 15°, poured on crushed ice and extracted thoroughly with ether. The ethereal solution was washed with water, extracted with sodium bicarbonate solution, dried over anhydrous magnesium sulfate, filtered, and the ether removed at room temperature. 5-Phenyl-2-penten-4-yn-1-al was distilled under high vacuum, b.p. 62° (10^{-3} mm.), n^{25}D 1.6422, yield 9.7 g. (55%). Light absorption properties (solvent, 95% ethanol): $\lambda_{\max}$ 229 mμ, $\epsilon_{\max}$ 13,600; $\lambda_{\max}$ 238 mμ, $\epsilon_{\max}$ 13,900; $\lambda_{\text{shoulder}}$ 243 mμ, ε 11,850; $\lambda_{\max}$ 249 mμ, $\epsilon_{\max}$ 13,200; $\lambda_{\text{shoulder}}$ 274 mμ, ε 12,000; $\lambda_{\max}$ 289.5 mμ, $\epsilon_{\max}$ 13,800; $\lambda_{\max}$ 308–318 mμ, $\epsilon_{\max}$ 15,950. The infrared spectrum had an exceptionally strong acetylene peak at 2195 cm.$^{-1}$. The expected carbonyl, olefin and phenyl absorption bands were present.

Anal. Calcd. for $C_{11}H_8O$: C, 84.59; H, 5.16. Found: C, 84.29; H, 5.19.

From the sodium bicarbonate solution was isolated phenylpropiolic acid, 0.4 g., m.p. 130–133° (no depression with an authentic sample). None of the acid IV could be obtained.

5-Phenyl-2-penten-4-ynoic acid (IV) was prepared by adding 12.1 g. (0.0775 mole) of 5-phenyl-2-penten-4-yn-1-al in ethanol to a mixture of freshly-prepared, thoroughly-washed silver oxide (from 52.7 g. of silver nitrate and 12.4 g. of sodium hydroxide) in 400 ml. of water and shaking for 22 hours. The silver salt of the acid was converted to the sodium salt with aqueous sodium hydroxide and the free acid liberated with diluted sulfuric acid. The acid was readily soluble in ether or alcohol but relatively insoluble in water; it was recrystallized from pentane as a white solid, m.p. 147–148.6°. Light absorption properties (solvent, 95% ethanol): $\lambda_{\max}$ 220 mμ, $\epsilon_{\max}$ 11,250; $\lambda_{\max}$ 225 mμ, $\epsilon_{\max}$ 11,000; $\lambda_{\max}$ 237 mμ, $\epsilon_{\max}$ 8,100; $\lambda_{\text{shoulder}}$ 250 mμ, ε 9,100; $\lambda_{\max}$ 296 mμ, $\epsilon_{\max}$ 24,300. The infrared spectrum was taken in a potassium bromide disk; it had a strong internal acetylene absorption at 2190 cm.$^{-1}$ and displayed the usual carboxyl, olefin and phenyl absorptions.

Anal. Calcd. for $C_{11}H_8O_2$: C, 76.73; H, 4.68. Found: C, 76.54; H, 4.47.

Phenylcoumalin (V).—A solution of 0.3 g. of 5-phenyl-2-penten-4-ynoic acid in 4.46 g. of glacial acetic acid and 4.46 g. of concentrated sulfuric acid was warmed for 5 hours on a steam-bath, then left overnight at room temperature. Addition of water gave an oil which solidified on cooling and did not dissolve when aqueous sodium carbonate solution was added until the mixture was basic to litmus. The solid was taken up in ether, and the solution was washed with water and dried over anhydrous magnesium sulfate. Evaporation of the ether gave 0.28 g. of white crystals, m.p. 61–66° (93% yield). The product was recrystallized from pentane, m.p. 66–67° (lit.[13] m.p. 68°). Light absorption properties (solvent, 95% ethanol): $\lambda_{\text{shoulder}}$ 221 mμ, ε 7,100; $\lambda_{\text{shoulder}}$ 229 mμ, ε 8,860; $\lambda_{\max}$ 233.5 mμ, $\epsilon_{\max}$ 9850; $\lambda_{\text{shoulder}}$ 243 mμ, ε 8,070; $\lambda_{\max}$ 332 mμ, $\epsilon_{\max}$ 14,100. The infrared spectrum showed the absence of the carboxylic acid group; a strong carbonyl band centered about 1700 cm.$^{-1}$, somewhat lower than less unsaturated δ-lactones.

4-Phenyl-1-buten-3-yne-1,1-dicarboxylic Acid (IX).—Kalff's directions were followed to prepare the so-called "soluble" compound which we obtained with a m.p. of 200–218°. The infrared spectrum of this solid in a potassium bromide disk showed strong absorption at 2190 cm.$^{-1}$ indicative of the acetylenic group. A neutral equivalent in 95% alcohol showed 1.74 carboxyl groups per molecule.

6-Phenylcoumalin-3-carboxylic acid (X) was prepared by refluxing IX in *p*-xylene for 18 hours.[13] The product melted at 218° and its infrared spectrum in a potassium bromide disk showed no absorption in the 2000–2300 cm.$^{-1}$ region. A neutral equivalent indicated 0.96 carboxyl group per molecule.

LOS ANGELES 24, CALIFORNIA

[CONTRIBUTION NO. 1012 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

The Chemistry of Allenic Acids. III.[1] The Acid Behavior of Highly Branched Unsaturated Malonic Acids Prepared by a Novel Method

BY J. H. WOTIZ[2] AND H. E. MERRILL[3]

RECEIVED OCTOBER 9, 1957

The reaction of butylbutadienoic acid with Grignard reagents results in a complex which on hydrolysis yields 2-butyl-3-alkyl-3-butenoic acids, and which on carbonation followed by hydrolysis gives butyl-(1-alkylvinyl)-malonic acids in high yields. They titrate as monobasic acids in 50% ethanol. Butyl-(1-*t*-butylvinyl)-malonic acid has the K_1/K_2 ratio of 57,600,000, which is the highest known.

It has been shown previously[4,5] that Grignard reagents add to allenic acids and α,β-olefinic acids to yield an adduct, which upon hydrolysis gives the corresponding β-substituted acid in high yield. The present paper reports the reaction of various Grignard reagents (I) (R = CH_3, C_2H_5, *i*-C_3H_7, *t*-C_4H_9, $CH_2C_6H_5$ and C_6H_5) with butylbutadienoic acid (II) to give a complex (III) which on hydrolysis results in high yields of 2-butyl-3-alkyl-3-butenoic acids (IV). Reaction of this complex with CO_2 results in

---

[1] The Chemistry of Allenic Acids. II, J. H. Wotiz and N. C. Bletso, *J. Org. Chem.*, **19**, 403 (1954).

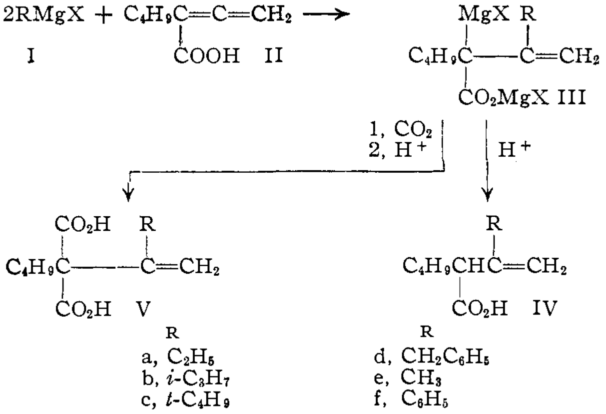
[2] Research Center. Diamond Alkali Co., Painesville, Ohio.

[3] Abstracted from a portion of the Ph.D. dissertation of H. E. M., Univ. of Pittsburgh, 1957.

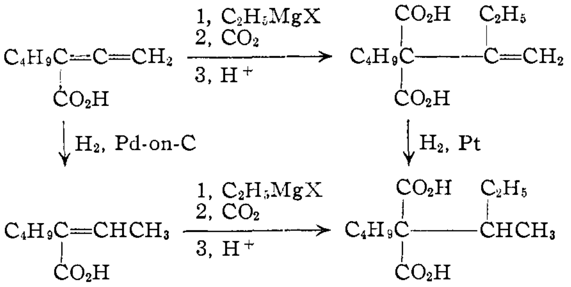
[4] J. H. Wotiz and J. S. Matthews, THIS JOURNAL, **74**, 2559 (1952).

[5] J. H. Wotiz, J. S. Matthews and H. Greenfield, *ibid.*, **75**, 6342 (1953).

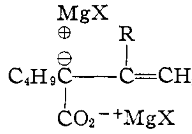
essentially quantitative yields of butyl-(1-alkylvinyl)-malonic acids (V). The over-all course of the reactions may be represented as



The structure of products IV and V was established by elementary analyses, infrared spectra, neutralization equivalents, esterification and hydrogenation equivalents with the formation of known hydrogenated products, and ozonolysis with the identification of fragments. Compounds V were quantitatively decarboxylated to IV. The structures of Va and c were also confirmed by their proton nuclear magnetic resonance spectra. The presence of two free carboxy groups in Va was also unequivocally established by the sequence of reactions



Mechanism of Addition.—In the reaction product of the Grignard reagent I and the allenic acid II, several resonance forms can be recognized which involve the polarization of the carbonyl group and/or the α,β-double bond. The carbonation of the adduct III and the isolation of the corresponding substituted malonic acid V in high yields favor the formulation of the adduct as VI. Evidence for such a 3,4-addition is also found in the work of Blicke and Zinnes[6,7] in which, for example, the adduct formed by reaction of isopropylmagnesium chloride with crotonic acid was treated with cyclohexanone and phenyl isocyanate to give α-(1-hydroxycyclohexyl)- and α-(phenylcarbamyl)-β-isopropylbutyric acid, respectively.



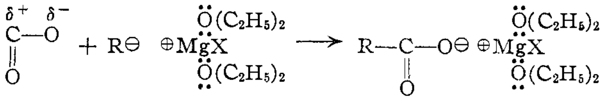
VI

The effect of changing the R-group in the Grignard reagent seems to have little effect (except in the case where R = methyl) in the ease of formation of III, since hydrolysis of the adduct gives high yields of the β-substituted acid.

The effect of changing the groups attached to the α,β-double bond in the acid seems to have a much more pronounced effect upon the ease of formation of the adduct. A comparison of the yields of β-substituted acids obtained in the reaction of Grignard reagents with allenic acids and with α,β-olefinic acids[5] show that much higher yields are obtained with the allenic acids.

Mechanism of Carbonation.—It was reported by Wotiz and Matthews[4] that when the adduct III, formed by the addition of ethylmagnesium bromide to II, was added to a slurry of Dry Ice and ether and the resultant mixture hydrolyzed, only 2-butyl-3-ethyl-3-butenoic acid (IVa) was isolated. In the present work this reaction was repeated and upon long standing in a small amount of petroleum ether a small amount (*ca.* 9%) of crystalline butyl-(1-ethylvinyl)-malonic acid (Va) was isolated. When the reaction was repeated and the carbonation was carried out at room temperature under a carbon dioxide gas pressure of about three atmospheres Va was isolated in 90% yield. In the preparation of butyl-(1-*t*-butylvinyl)-malonic acid (Vc), however, the yield of isolated acid was 87% when the carbonation was carried out at −70° and atmospheric pressure. These findings are exactly the reverse of those expected on the basis of the steric interferences of the groups in the product. One would expect that the larger *t*-butyl group would interfere sterically with the incoming carbon dioxide molecule and that more drastic conditions would be necessary to carbonate the adduct VIc than the adducts VIa.

Consideration of the mechanism of carbonation, however, suggests a possible explanation for the relative yields of the various acids obtained. Although for the sake of simplicity the Grignard reagent is usually written unsolvated, it is helpful to the present mechanism to include the ethers of solvation. The accepted mechanism of carbonation of the Grignard reagent involves the attack of the carbanion portion of the solvated Grignard reagent upon the positive carbon in the polarized form of a carbon dioxide molecule. The success of such reactions should be dependent upon the degree of polarization or ionic character of the carbon–magnesium bond.



$$\overset{\delta^+}{C}(=O)-\overset{\delta^-}{O} + R^{\ominus}\ \ ^{\oplus}\underset{\ddot{O}(C_2H_5)_2}{\overset{\ddot{O}(C_2H_5)_2}{MgX}} \longrightarrow R-\underset{\|\atop O}{C}-O^{\ominus}\ ^{\oplus}\underset{\ddot{O}(C_2H_5)_2}{\overset{\ddot{O}(C_2H_5)_2}{MgX}}$$

A study of the Fisher–Taylor–Hirschfelder atomic models of the compounds represented by structures VIc and VIa, shows that a carboxy group may be introduced in the α-position of either molecule without introducing significant steric strains (although there is not freedom of rotation of the carboxy group). The much larger dietherated halomagnesium ion, however, cannot be brought into close proximity to the α-carbon of structure VIc because of the prohibitive steric interference of the *t*-butyl group. In the case of structure VIa the smaller

---

(6) F. F. Blicke and H. Zinnes, This Journal, **77**, 5399 (1955).

(7) F. F. Blicke and H. Zinnes, *ibid.*, **77**, 6051 (1955).

ethyl group permits a much closer approach of the solvated halomagnesium ion to the α-carbon. It seems reasonable then that there will be a greater separation of charge in the carbon–magnesium bond in structure VIc than in structure VIa. This steric enhancement of ionic character could account for the yields of acid obtained. Thus the more ionic nature of the carbon–magnesium bond in structure VIc would permit carbonation at much milder conditions (−70° and one atmosphere pressure), while the more covalent nature of structure VIa would require more drastic conditions (25° and three atmospheres pressure) to bring about carbonation.

The Acid Behavior.—The highly branched malonic acids V titrated as strong monobasic acids in 50% ethanol. Similarly, Cookson and Trevett[8] in the study of reactions of delphinium alkaloids, have isolated a dicarboxylic acid which titrates as a monobasic acid in a 50% ethanol solution. The use of this solvent mixture was necessitated by the insolubility of the acids in water. The explanation of this behavior may lie in either or both of the following considerations. The basicity of the solvent and/or the possibility of very strong internal hydrogen bonding. Both of these considerations have been discussed recently by Brown and McDaniel.[9,10] They point out that in changing from water to solvents of lower dielectric constants (such as 50% alcohol) the apparent strength of carboxylic acids decreases. In the present work one of the substituted malonic acids studied was found to be water soluble. Butyl-(1-ethylvinyl)-malonic acid (Va), was titrated in both water and in 50% alcohol (Fig. 1). The pK_1 observed when water was used as a solvent was 2.91, while when the solvent was 50% alcohol the pK_1 found was 3.32. Likewise the pK_2 values were 8.40 and 10.39 in water and 50% alcohol, respectively. It should be noted that in water the second break in the titration curve is obvious, but that it is not in evidence in the case of the water–alcohol mixture. This may be due in part to the insensitivity of the glass electrode in such basic solution.

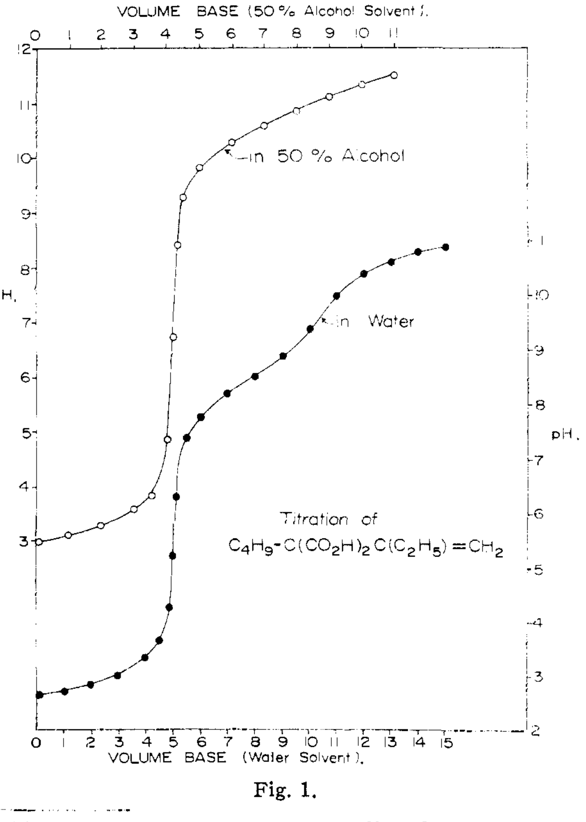
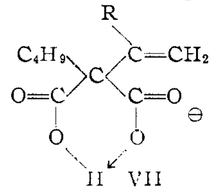


Fig. 1.

Brown and McDaniel[9,10] have discussed hydrogen bonding as a factor in the ionization of dicarboxylic acids. They cite as experimental confirmation the work of Gane and Ingold[11] on the ionization of alkylated malonic acids. Westheimer and Benfey[12] subsequently have shown a semi-quantitative relationship between the degree of hydrogen bonding and the ratio of the first ionization constant of the dibasic acid to the ionization constant of the corresponding monomethyl ester.

In the present work a series of malonic acids (and their monomethyl esters) of structure V were titrated in 50% alcohol and their pK values were determined. The results are given in Table I. Since the titrations were run in a mixture of solvents, no attempt was made to correct the observed pK values to thermodynamic values. It is at once evident that the substituents attached to the malonic acid skeleton have much greater steric requirements than any previously reported. If the proposed hydrogen bonding does occur in substituted malonic acids and is enhanced by steric effects in the substituents, then it will be expected that evidence for hydrogen bonding will be found in the present series of acids in the form of greatly increased K_1/K_2 and K_1/K_E ratios. This is indeed the case as is shown in Table I. Also it should be noted that the greater the steric requirements of the group R the larger are the K_1/K_2 and K_1/K_E values. The apparent exception is the case where R is benzyl and in this case there is no way of determining what electronic or electrostatic effect the presence of the phenyl ring may have upon the ionization of the acid. It is realized that the K_1/K_2 ratios in water will be lower than those recorded in 50% alcohol, but even if they were reduced by a factor of ten they would still be higher than any such values reported in the literature. In the light of such evidence for hydrogen bonding, a possible explanation for the failure to observe the second break in the titration curve might be that in the more acidic alcohol solution the cyclic hydrogen bonded acid anion VII cannot be broken by the used base to free the second proton.



VII

---

[8] R. C. Cookson and M. E. Trevet, *J. Chem. Soc.*, 3864 (1956).

[9] H. C. Brown, D. H. McDaniel and O. Hafliger in Braude and Nachod, "Determination of Organic Structures by Physical Methods," Academic Press, Inc., New York, N. Y., 1955, p. 628.

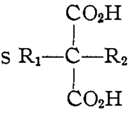
[10] D. H. McDaniel and H. C. Brown, *Science*, **118**, 370 (1953).

[11] R. Gane and C. K. Ingold, *J. Chem. Soc.*, 2153 (1931).

[12] F. H. Westheimer and O. T. Benfey, This Journal, **78**, 5309 (1956).

TABLE I

ACID PROPERTIES OF SOME MALONIC ACIDS



$R_1-\overset{CO_2H}{\underset{CO_2H}{C}}-R_2$

R_1	R_2	pK_1	pK_2	pK_E[d]	K_1K_2	K_1/K_E
C_4H_9[b]	$C(CH_2C_6H_5)=CH_2$	3.53	10.20[c]	4.90	4,700,000	23.5
C_4H_9[b]	$C(C_2H_5)=CH_2$	3.32	10.39[c]	5.14	11,800,000	66.1
C_4H_9[a]	$C(C_2H_5)=CH_2$	2.91	8.40	3.65	3,240,000	5.9
C_4H_9[b]	$C[CH(CH_3)_2]=CH_2$	3.25	10.70[c]	5.22	28,000,000	93.3
C_4H_9[b]	$C[C(CH_3)_3]=CH_2$	3.39	11.15[c]	5.34	57,600,000	89.3

[a] Water solvent. [b] 50% ethanol solvent. [c] Taken at three-halves neutralization even though a second break in the titration curve was not observed. [d] Half methyl ester.

Additional evidence for the strongly hydrogen bonded structure VII may be found in two experiments with butyl-(1-benzylvinyl)-malonic acid (Vd). In an attempt to confirm the presence of two carboxy groups in the acid a Zerewitinoff determination was run and only one mole of gas was evolved per mole of acid. Two interpretations may be placed upon this experiment. The monoanion may be so highly hydrogen bonded (structure VII) that the second proton will not react with the second mole of Grignard reagent. This would be consistent with the titration behavior. The other possibility arises from the formation of an insoluble oil during the determination. It has been noted[13] in the reaction of Grignard reagents with a number of polycarboxybenzenes in ether that less than the calculated volume of gas was collected, presumably due to the insolubility of the monohalomagnesium salts in the solvent.

The Infrared Spectrum.—The monosodium salt of butyl-(1-benzylvinyl)-malonic acid also was prepared and its infrared spectrum taken. The spectrum shows very weak absorption over the range 3600–2400 cm.$^{-1}$ (with the exception of the strong C–H stretch at 2900 cm.$^{-1}$). The O–H stretching frequency of carboxylic acids in solutions dilute enough so that the acid is all in the monomeric form lies near 3600 cm.$^{-1}$ (similar to alcohols and phenols), while in the liquid or solid state, where acids exist entirely in hydrogen bonded dimers, broad absorption occurs over the range between 3000 and 2500 cm.$^{-1}$.[14] If structure VII correctly represents the acid anion one would expect to find an OH absorption similar to that found in β-hydroxyaldehydes, ketones and esters.[15,16] The infrared spectrum also shows the presence of the ionized carboxyl by absorption at 1610 cm.$^{-1}$ and a terminal double bond by the weak absorption at 905 cm.$^{-1}$.

Experimental

1. **Preparation of 2-Butyl-3-alkyl-3-butenoic Acids (IV).**—To a solution of 0.25 mole of the appropriate Grignard reagent dissolved in 250 ml. of ether was added 14 g. (0.1 mole) of II dissolved in 250 ml. of dry ether, and this reaction mixture was stirred two hours. After hydrolysis with a saturated solution of ammonium chloride followed by dilute hydrochloric acid, the ether solution was extracted with sodium carbonate. Acidification of the sodium carbonate extracts with cold dilute hydrochloric acid liberated the organic acids IV which were isolated by extraction with ether and removal of the solvent under reduced pressure. The crude acids were distilled under vacuum. The yields and analytical data of acids IV are given in Table II.

2. **Preparation of Butyl-(1-alkylvinyl)-malonic Acids (V).** **a.**—To a solution of 0.25 mole of the appropriate Grignard reagent dissolved in 200 ml. of ether was added 14.0 g. (0.1 mole) of II dissolved in 200 ml. of dry ether. After stirring for two hours, the reaction mixture was poured onto a Dry Ice–ether slurry and allowed to come to room temperature. After hydrolysis with saturated ammonium chloride solution and then by dilute cold hydrochloric acid, the ether solution was extracted with sodium carbonate. Acidification of the sodium carbonate extracts with cold dilute hydrochloric acid liberated the organic acids V which were isolated by extraction with ether and removal of the solvent under reduced pressure. Upon standing, the viscous oil crystallized. Recrystallization from a mixture of ether and petroleum ether brought the product to a constant melting point (with decomposition and gas evolution). Yields and analytical data are given in Table III.

b.—In separate experiments 0.125 mole of Grignard reagent was allowed to react for two hours with 7 g. (0.05 mole) of II. The reaction mixture was placed in a shaking bottle and subjected to a carbon dioxide pressure of 44 p.s.i.g. overnight. The products were hydrolyzed and isolated as in method a. Acids V, c and d were prepared by method **a** and Va and b by method **b**. The yield of Va was 10% by method a and 90% by method **b**.

c.—Acid Vc also was prepared in 13% yield by the reaction of the Grignard reagent prepared from 35 g. (0.2 mole) of 1-bromo-2-heptyne with Dry Ice,[17] in a flask protected from the atmosphere. After the reaction mixture had come to room temperature it was heated for one hour and to it was added 0.22 mole of *t*-butylmagnesium chloride (IIc) in 100 ml. of ether. The reaction mixture was stirred for two hours, poured onto a slurry of Dry Ice and ether and allowed to stand overnight. Upon hydrolysis and isolation as in method **a**, 6.2 g. (13%) of recrystallized Vc was obtained.

3. **Preparation of Butyl (*sec*-butyl)-malonic Acid.**—A sample of II was hydrogenated to 110% of theory for the uptake of one equivalent of hydrogen, using a 5% palladium-on-charcoal catalyst. The product was 2-butylcrotonic acid, $C_4H_9C(CO_2H)=CHCH_3$, b.p. 112° at 1.5 mm. Its infrared spectrum showed among other bands, a strong absorption band near 1680 cm.$^{-1}$ (C=C stretch) and the absence of an absorption band near 900 cm.$^{-1}$, characteristic of a terminal double bond, and 1950 and 1930 cm.$^{-1}$ characteristic of the allene bond.[18] The reaction of 2-butylcrotonic acid with Ia and carbonation at room temperature at 41 lb./in.^{2} for 16 hours yielded butyl-(*sec*-butyl)-malonic acid in 75% yield. The m.p., 115–117°, was not depressed when mixed with the reduction product of Va. The compounds prepared by the two methods had identical infrared spectra.

Characterization of Products. Table II and III.—Acids

---

[13] M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, p. 1171.

[14] L. J. Bellamy, "The Infrared-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, Chapters 6 and 10 and references therein.

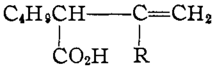
[15] R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, THIS JOURNAL, **71**, 1068 (1949).

[16] M. St. C. Flett, *J. Chem. Soc.*, 1441 (1948).

[17] J. H. Wotiz, THIS JOURNAL, **72**, 1639 (1950).

[18] J. H. Wotiz and D. E. Mancuso, *J. Org. Chem.*, **22**, 207 (1957).

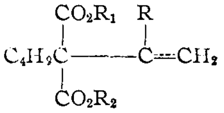
TABLE II



$C_4H_9CH(CO_2H)—C(R)=CH_2$

R	Yield, %	B.p. °C.	B.p. Mm.	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Neut. equiv. Calcd.	Neut. equiv. Found	H_2 absorbed, ml. Calcd.	H_2 absorbed, ml. Found
CH_3	18	108	12	..	69.2	69.3	10.2	10.3	156	157	34.4	33.9
t-C_4H_9	95	127	1	46	72.7	72.6	11.1	11.2	198	198	31.8	30.8
C_6H_5	79	155	1.3	..	77.1	77.1	8.3	8.1	218	224	80.4	72.0
$C_6H_5CH_2$	96	175	6	..	77.7	77.1	8.6	8.4	232	228	20.9	19.0

TABLE III



$C_4H_9C(CO_2R_1)(CO_2R_2)—C(R)=CH_2$

			$R_1 = R_2 = H$				$R_1 = H, R_2 = CH_3$			$R_1 = R_2 = CH_3$	
R	Yield, %	M.p., °C.	Carbon, % Calcd. Found	Hydrogen, % Calcd. Found	Neut. equiv.[a] Calcd. Found	H_2 absorbed, ml. Calcd. Found	Carbon, % Calcd. Found	Hydrogen, % Calcd. Found	Neut. equiv. Calcd. Found	Carbon, % Calcd. Found	Hydrogen, % Calcd. Found
C_2H_5	90	77–78	61.7	8.4	107	31.3	62.2	8.8	228	64.5	9.1
			62.1	7.5	216[b]	33.4	62.9	9.0	225	65.0	10.0
i-C_3H_7	55	107–108	63.3	8.8	114	26.4	64.5	9.1	242	65.7	9.4
			63.2	8.6	226	27.1	64.5	9.0	253	65.2	9.5
t-C_4H_9	88	127–128	64.5	9.0	121	29.5	65.6	9.4	256	66.7	9.6
			65.0	9.1	245	39.5	65.2	9.4	262	66.8	9.9
$C_6H_5CH_2$	54	128–131	69.6	7.2	138	35.0	70.4	7.6	290	71.2	7.9
			70.9	7.2	278	36.1	70.6	7.6	290[c]	71.9	7.8

[a] Titrated in 50% ethanol. [b] 105 when titrated in H_2O. [c] M.p. 123–125° dec. from petroleum ether.

IV and V were *titrated* with 0.02809 N NaOH in a solvent mixture composed of 25 ml. of water and 25 ml. of ethanol and followed with a Beckman model M pH meter. Throughout the titration no effort was made to keep the alcohol concentration constant. In this solvent mixture acids of both type IV and V titrated as monobasic acids although Va when titrated in water exhibited its true dibasic nature.

Semi-quantitative hydrogenation of the acids IV and V was carried out in an all-glass apparatus at pressures slightly above atmospheric using an absolute alcohol solvent and a prereduced platinum oxide or palladium-on-charcoal catalyst. In all cases, except Vc (very slow uptake probably due to steric interference), near quantitative results were obtained.

The β,γ-unsaturation in 2-butyl-3-benzyl-3-butenoic acid (IVd) is **rearranged** by heating at 200° for two hours into the α,β-position (2-butyl-3-benzylcrotonic acid (VIII)). The position of the unsaturation in acids IV, Vd and VIII was determined by **ozonolysis** carried out in the following manner. A mixture of ozone and oxygen was passed through an acetic acid solution of the acid until absorption was complete as indicated by liberation of iodine from an acidified solution of potassium iodide. The ozonide was decomposed with zinc and acetic acid and the liberated aldehyde was trapped in alcoholic dimedon solution. The dimedon derivative of formaldehyde (m.p. 182.5–183.8°) was isolated from ozonolysis of IVc, d, f and Vd. Decomposition of the ozonide of VIII with 30% hydrogen peroxide gave a neutral liquid. Treatment of this product with 2,4-dinitrophenylhydrazine gave a solid melting at 150–151° which did not depress the melting point of the 2,4-dinitrophenylhydrazone of benzyl methyl ketone. Attempts to rearrange other acids failed.

Decarboxylations of the acids V were carried out by heating either the acid alone or an acidified benzene solution of the acid. Carbon dioxide-free dry nitrogen swept evolved carbon dioxide through a Caroxite absorption tube where it was weighed. All approach 1 mole of CO_2 per mole of acid. The decarboxylated products were identical (by infrared spectra) with the correspondingly substituted acids IV.

Esterifications of the acids V were carried out by treating a known weight of acid with a dried solution of diazomethane in ether. The nitrogen evolved was caught in a gas measuring buret. For complete esterification diazomethane was added until nitrogen evolution was complete (also the yellow color persisted). In half esterifications (only one acid group esterified) diazomethane addition was stopped when one mole of nitrogen had been evolved per mole of acid. Both the half and complete esters were oils and were characterized only by infrared spectra and elemental analysis. The half esters behaved as monobasic acids. The data are given in Table III.

The infrared spectra of both acids IV and V exhibit in addition to the bands characteristic of the carboxyl group (2600, 1700 cm.$^{-1}$) two bands associated with the double bond. The bands are centered around 1640 cm.$^{-1}$ (C=C stretch) and in the range 898–913 cm.$^{-1}$ (=CH_2 out-of-plane deformation). Hydrogenation of these acids removes the latter bands. Half esterification of the acids V caused a splitting of the carbonyl stretching frequency at 1700 cm.$^{-1}$ indicating the presence of two types of carbonyl structures (acid and ester). Complete esterification of the acids V completely removed the broad band at 2600 cm.$^{-1}$ due to the free carboxy group.

Acknowledgment.—The authors wish to thank Dr. Donald E. O'Reilly of the Gulf Research and Development Co. for the nuclear magnetic resonance analyses and interpretations; Dr. Foil A. Miller and his co-workers at the Mellon Institute for the infrared analyses and band assignments, and the National Institutes of Health for the fellowship support to H. E. M.

PITTSBURGH, PENNA.