Triphenylgermanyltriethylgermanium, $(C_6H_5)_3Ge-Ge(C_2H_5)_3$, has been prepared by the action of triethylgermanium bromide on sodium triphenylgermanide in benzene solution.

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The Reactivity of Atoms and Groups in Organic Compounds. XIV. The Influence of Substituents on the Thermal Stability of Certain Derivatives of Malonic Acid

BY JAMES F. NORRIS AND HELEN F. TUCKER[1]

It has been shown in this Laboratory[2] that the substitution products of malonic acid begin to lose carbon dioxide at different temperatures and that there is a relationship between these temperatures and the radicals present in the acids. The results indicated the relative effects of the several radicals on the lability toward heat of a carbon to carbon bond in compounds of this type. Other investigations have shown that the rates vary at which these acids decompose in solutions at a fixed temperature and with change of solvent.[3,4,5,6] Hinshelwood[7] has studied the effect of temperature on the rate at which solid malonic acid decomposes.

As it seemed probable that an extension of the work would lead to results of value in interpreting pyrolytic reactions in general, a large number of compounds were studied.

Some time after the appearance of the paper by Norris and Young and when further work was in progress in this Laboratory, Marshall[8] reported a repetition, with slightly modified apparatus, of the published work and the results obtained by him in the study of some additional compounds. With the exception of two acids, which will be considered later in this paper, the temperatures checked within three degrees or less those given in the earlier papers.

The results published from this Laboratory were obtained by heating the acid in a tube connected with a long capillary tube, which contained a bead of mercury. The temperature of the acid was raised at the rate of one degree per minute and the position of the bead and the temperatures noted. The results were plotted and a line drawn through the points. The

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[1] From the thesis of Helen F. Tucker presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1933.

[2] Norris and Young, THIS JOURNAL, **52**, 5066 (1930).

[3] Lindner, *Monatsh.*, **28**, 1041 (1908).

[4] Bernoulli, Wege and Jakubowicz, *Helv. Chim. Acta*, **2**, 511 (1919); **4**, 1018 (1921).

[5] Jakubowicz, *Z. anorg. Chem.*, **121**, 113 (1922).

[6] Burk and Davis, *J. Phys. Chem.*, **35**, 146 (1931).

[7] Hinshelwood, *J. Chem. Soc.*, **17**, 156 (1920).

[8] Marshall, *Rec. trav. chim.*, **51**, 233 (1932).

change from a straight line to an upward curve showed the point at which decomposition began to take place. To check the result obtained in this way malonic acid was heated and a stream of air free from carbon dioxide was passed over the acid and then through a solution of barium hydroxide. The temperature at which a precipitate was first formed agreed within two degrees with the temperature found with the use of the expansion method.

In obtaining the results reported in this paper the two methods, improved and made more accurate, were applied to a number of compounds. The method based on expansion (called the physical method) was found to be more delicate than the one based on the detection of carbon dioxide (the chemical method). The former gave cracking temperatures from one to three degrees lower than the latter in the eleven cases in which the two methods were used. The detection of the first appearance of barium carbonate was rendered more certain by the use of a specially constructed nephelometer.

The following conclusions can be drawn from the results. (1) All the twelve monosubstitution products studied began to crack below the decomposition temperature of malonic acid (129°). The least effective group in lowering the cracking temperature was phenyl (123°) and the most effective *sec*-butyl (98°). The order of the primary alkyl group was as follows: methyl, isobutyl, ethyl, *n*-butyl, isoamyl, *n*-propyl, allyl.

(2) The introduction of a side chain in the α-position increased to some extent lability toward heat of the C–C bond: C_2H_5 110°, iso-C_3H_7 103°; C_3H_7 99°, *sec*-butyl 98°; $(CH_3)(C_2H_5)$ 123°, (CH_3) (iso-C_3H_7) 110°. Comparisons in β-and γ-positions are limited to single cases. In the β-position there was decreased lability—*n*-C_3H_7 99°, iso-C_4H_9 115°; in the γ-position increased lability—*n*-C_4H_9 108°, iso-C_5H_{11} 101°. A similar alternation in chemical reactivity of the hydrogen atom in alcohol has been shown to take place when side chains are introduced in these positions.[9]

(3) All the five di-substituted malonic acids containing one kind of radical which have been studied decompose at higher temperatures than the corresponding monosubstituted acids: $(CH_3)_2$ 150°, CH_3 120°, $(C_2H_5)_2$ 126°, C_2H_5 110°; (*n*-$C_3H_7)_2$ 143°, *n*-C_3H_7 99°; (iso-$C_3H_7)_2$ 182°, iso-C_3H_7 103°; (iso-$C_4H_9)_2$ 140°, iso-C_4H_9 115°.

(4) All the di-substituted acids containing two unlike radicals decompose below the temperature of malonic acid. The most striking effect of lack of symmetry on cracking temperatures is shown in the case of the (CH_3) (iso-C_3H_7) derivative (110°). The dimethyl derivative breaks at 150° and the di-isopropyl at 182°. These results and those summarized in paragraph 3 will be of service in interpreting the cracking of paraffin hydrocarbons containing straight and branched chains.

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(9) Norris and Cortese, THIS JOURNAL, **49**, 2640 (1927).

(5) The order of the effect of the introduction of alkyl radicals into methylmalonic acid, as far as determined, is the same as that obtained when these same radicals are introduced into malonic acid, namely: CH_3, C_2H_5, n-C_4H_9, iso-C_3H_7, n-C_3H_7, $CH_3CH{=}CH_2$.

(6) The order of the effect of the introduction of C_2H_5, n-C_4H_9 and n-C_3H_7 into chloromalonic acid is the same as in paragraph 5.

(7) Only three compounds which contained a benzene ring have as yet been studied. In phenylmalonic acid (123°) the radical had less effect than methyl (120°) on the lability toward heat of the C–C bond. The introduction of a chlorine in the ortho position changed the cracking temperature from 123 to 102°. Benzyl (115°) had a slightly greater labilizing effect than CH_3 (120°).

Some preliminary observations were made of the influence of the presence of a variety of substances on the cracking temperature of malonic acid with the expectation of finding catalysts that lower the temperature at which the carbon to carbon bond breaks in this compound. It was shown that malonic acid could be held for at least three hours in a stream of air at 115–116° without the formation of carbon dioxide. Mixtures of the acid (0.5 g.) and the contact substance (0.25 g.) were held at this temperature for one-half hour or less and air free from carbon dioxide was drawn over the mixture and then through a solution of barium hydroxide. If any decomposition occurred, the time required to yield a precipitate of barium carbonate was noted. The most efficient substances and the time in minutes required to produce decomposition were as follows: water (3), acetic acid (3), $KHSO_4$ (5), Mg powder (8), Al powder (10), zinc chloride (10). When the acid was slowly heated in the presence of calcium oxide free from carbonate, carbon dioxide was formed at 90°.

The acids were prepared by using the methods described in the literature. The determination of the melting points in the usual way of most of these acids is not a test of purity because they decompose, in many cases, before they begin to melt. The neutralization equivalents were accurately determined.

Since the melting points obtained in capillary tubes are dependent on the rate of heating and the rate of decomposition of the acids, determinations of melting points on a Dennis[10] bar were made. The temperatures obtained were reproducible. When the melting point was below the cracking temperature, the two methods gave similar results. When the acids began to decompose before melting, the melting point in a capillary tube was below that found with the use of the bar. The greatest difference was shown by phenylmalonic acid (cracking temperature 122.8°). In the tube it melted at 139–140° with much decomposition, and on the bar at 169°.

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(10) Dennis and Shelton, THIS JOURNAL, **52**, 3128–3132 (1930).

Experimental Details

Preparation of Malonic Acid Derivatives.—The alkyl substitution products were made by methods based on the work of Conrad.[11] The aryl derivatives were made by the method of Rising and Stieglitz.[12] Advantage was taken of the fact that monoalkylated malonic esters are saponified in two hours or less by a hot 50% aqueous solution of potassium hydroxide, whereas the disubstituted esters require concentrated alcoholic potash and ten or more hours of refluxing. It was possible therefore to separate largely a monoalkyl acid from a dialkyl derivative formed simultaneously. The ethyl esters formed in the syntheses were fractionated under diminished pressure before hydrolysis. The disubstituted esters were prepared from the purified monosubstituted esters. The acids were crystallized several times before use. The neutralization equivalent of the acids is the best criterion of purity that can be used. The melting points on the Dennis bar were determined on two occasions and the results obtained checked.

The results obtained with the acids prepared for this investigation are given in Table I.

TABLE I

PROPERTIES OF THE MALONIC ACID DERIVATIVES USED

(For Chloromalonic Acids, see Table II)

Radical	Neutralization equivalent Calcd.	Neutralization equivalent Found		Melting point, °C. Cap. tube observed	Melting point, °C. Dennis bar	Melting point, °C. Literature	Av. decomp. temp., phys. method, °C.
None	52.01	51.99	52.18	129–131	134	130.5–135.6	129
iso-C_3H_7	73.04	73.07	73.02	87–91	88	87	103
$CH_3CH{=}CH_2$	72.03	71.74	72.08	97–101	95	102–105	99
sec-C_4H_9	80.05	80.30	80.44	75–76	76	76	98
iso-C_5H_{11}	87.05	86.86	86.99	95–96	96	93	101
C_6H_5	90.03	89.93	90.14	139–141	169	152–153	123
o-ClC_6H_4	107.28	107.2	107.4	128–130	133	139	101
$C_6H_5CH_2$	97.04	97.09	97.26	119–120	120	117–121	116
CH_3, CH_3	66.03	66.09	66.11	193–194	195	186–193	150
C_2H_5, C_2H_5	80.05	80.17	80.11	126–127	126	121–125	126
CH_3, C_2H_5	73.04	73.05	72.90	121–122	121	117.5–122	123
CH_3, *n*-C_3H_7	80.05	80.18	79.90	102–106	105	106–107	98
CH_3, iso-C_3H_7	80.05	79.86	79.54	120–124	126	124	110
CH_3, $CH_3CH{=}CH_2$	79.04	78.84	79.14	89–91	85	134	96
CH_3, *n*-C_4H_9	87.05	86.97	87.36	98–99	98	99–101	109
C_6H_5, C_2H_5	104.05	104.5	104.9	153–155	182	...	117

Determination of Decomposition Temperatures.—The so-called *physical method* was based on the same principle used in the earlier work but the apparatus was improved. The tube to contain the material was made of Pyrex glass tubing 14 cm. in length and 1 cm. in diameter. It was connected with a long horizontal capillary tube (internal diameter 2 mm.) enclosed in a larger glass tube carrying a meter stick which served to measure the position of a mercury bead as it moved when the temperature of the reaction tube was raised. In order to avoid the possible irregular adhesion of the bead to the tube the latter was furnished with a tapper (a door bell buzzer) which was set in motion thirty seconds before a reading was made. The decomposition tube was placed in a large tube containing Nujol and this into a short-necked liter flask containing the same liquid and surrounded by asbestos paper. A calibrated thermometer was placed in the inner bath. The horizontal capillary tube was first made level. This was accomplished by moving the tube to such a position that the mercury bead did not move when the tube was tapped at intervals of about 5 cm.

A volume of the acid to be investigated equivalent to about 0.5 g. of malonic acid

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(11) Conrad, *Ann.*, **204**, 127 (1880).

(12) Rising and Stieglitz, THIS JOURNAL, **40**, 723(1918).

was placed in the decomposition tube, which had been disconnected from the capillary tube. The tube was closed by a rubber stopper and the temperature of the bath raised rapidly to about 50° below the decomposition temperature, and thereafter at the rate of one degree in two minutes. At about 25° below the decomposition temperature the side arm of the reaction tube was connected with the capillary tube. After equilibrium was established the position of the bead was recorded for every two degrees rise in temperature. Before decomposition the position of the bead plotted against temperature gave a straight line. As soon as decomposition began a smooth upward curve was obtained. The inclination of this curve to the straight line varied with the different acids.

The position of the mercury bead, after pyrolysis began, was determined by the volume of the carbon dioxide and of the vapor of the organic acid produced. Since the latter varied with the acid used, the curves cannot be used to determine the relative rates of decomposition. The differences between the curves in certain cases were so great, however, that they indicated markedly different rates of decomposition. The number of divisions on the scale over which the bead moved as the acid was heated from its cracking temperature to 5° above this temperature was determined. A few of the results were as follows: $(C_6H_5)(C_2H_5)$ 26, $(CH_3)(C_2H_5)$ 24, $(C_6H_5)(CH_3)$ 20, malonic acid 12, iso-C_5H_{11} 5, $CH_3CH{=}CH_2$ 5, $(CH_3)(C_3H_7)$ 3. It is evident that the first three acids decomposed much more rapidly than the last three. There appears to be no direct relationship between the cracking temperatures, melting points and rates of decomposition.

In the *chemical method* of determining the cracking temperature the same apparatus and procedure were used, except that the capillary tube was replaced by a nephelometer and a stream of air was drawn through the entire length of the reaction tube and the nephelometer. The air before use was passed through three spiral wash bottles which contained a strong solution of sodium hydroxide, a trap, a similar wash bottle containing concentrated sulfuric acid, a train containing cotton wool to remove traces of spray and finally through a tube containing phosphorus pentoxide and glass wool. A small plug of cotton wool was placed between the decomposition tube and the nephelometer to prevent any of the solid acid from being carried along with the stream of air.

The nephelometer, which was contained in a closed box, was so arranged that observations were made of two half circles of reflected light which touched and each of which had passed through a tube containing a solution of barium hydroxide. When the solutions were placed in the tubes the presence of carbon dioxide was avoided. The temperature at which the tube connected with the rest of the apparatus first showed a cloudy appearance was taken as the cracking temperature. Before making a measurement air was drawn through the complete apparatus with the acid in place and the absence of carbon dioxide demonstrated. Before use the acids were crystallized from appropriate solvents and heated overnight in a vacuum oven at about 35°.

In Table II are given the results obtained by us and, for use in the comparison of the effect of the nature of the radicals on cracking temperatures, those of Norris and Young and of Marshall.

The purified chloromalonic acids were furnished us by Mr. E. B. Hershberg of this Laboratory. The melting points determined in the usual way were as follows: Cl, C_2H_5, 110.2°, Cl, n-C_3H_7 98.8–99.3; Cl, n-C_4H_9 90.7–91.8°.

It will be seen from Table II that the chemical method gave results slightly higher than the physical method. The latter responds more quickly to decomposition since the movement of the mercury bead is brought about by both the carbon dioxide and the vapor of the acid formed.

TABLE II

CRACKING TEMPERATURES OF MALONIC ACID DERIVATIVES

The letter after the temperatures recorded refers to the measurements of Norris and Young. The solvents listed are those used in this Laboratory.

Substituent	Solvent for recrystallization	Decomposition temperatures, °C. Physical method	Decomposition temperatures, °C. Chemical method	Physical method by Marshall
None	Benzene	128 Y		
None	Acetone and toluene	128.8, 128.2	131	133.7
None	Water	117.4, 117.1	127	
CH_3	Benzene	120 Y		117
C_2H_5	Benzene	110 Y		112
n-C_3H_7	Benzene	99		102
iso-C_3H_7	Benzene	90 Y, 103.5, 102	104	108
$CH_3CH{=}CH_2$	Benzene	99, 98.6		
n-C_4H_9	Benzene	108 Y	109	
iso-C_4H_9				115
sec-C_4H_9	Carbon tetrachloride	99.6, 97.2	99.5	
iso-C_5H_{11}	Benzene and pet. ether	101.4, 101.0	103	
CH_3, CH_3	Acetone and toluene	149.4, 150		
CH_3, CH_3	Water	153, 153.5	155	171
CH_3, C_2H_5	Ether and pet. ether	122.6, 123.6		
C_2H_5, C_2H_5	Chloroform	125.8, 125.5		130
CH_3, *n*-C_3H_7	Benzene	97.8, 97.6		
CH_3, iso-C_3H_7	Benzene	109.6, 110	111	
CH_3, $CH_3CH{=}CH_2$	Ether and pet. ether	96.5, 95.8		
CH_3, *n*-C_4H_9	Benzene and pet. ether	109.3–108.5	111	
n-C_3H_7, *n*-C_3H_7				143
iso-C_3H_7, iso-C_3H_7				182
iso-C_4H_9, iso-C_4H_9				140
C_6H_5	Acetone and toluene	122.8	125	
o-ClC_6H_4	Benzene	101.2, 103.2	102	
$C_6H_5CH_2$	Benzene	116.4, 114.6	118	
$C_6H_5C_2H_5$	Furfural, benzene and pet. ether	116.8	119	
Cl, C_2H_5	Benzene	97.2, 95		
Cl, *n*-C_3H_7	Benzene	76.4, 75.7		
Cl, *n*-C_4H_9	Benzene	83.6, 82.8	87	

It is necessary, however, to remove the last traces of solvent from the acids before they are used. It is probable that the difference between the results obtained by the use of the two methods with malonic acid crystallized from water is due to the fact that all the solvent had not been removed.

It is possible that the presence of a trace of solvent may act catalytically and thus lower the cracking temperature. Notwithstanding these sources of error, which were guarded against, we believe the results obtained by the physical method are the more reliable. The relationship between the cracking temperatures of the acids is independent of the method used.

The difference between the results of Marshall and those of Norris and Young in the case of malonic acid (5.7°) and isopropyl malonic acid (18°) led to a re-study of these compounds. In the case of malonic acid by the physical method the average of the new determinations is 128.5°. Norris and Young reported 128° and Marshall obtained 133.7° with what was considered the best sample of his acid. A re-investigation of the sample of isopropylmalonic acid used in the earlier investigation (cracking temperature 90°) gave 92° by the physical and 104–105° by the chemical method. The acid apparently had not been freed from the solvent. A new sample of the acid gave by the physical method 103.5 and 102° and by the chemical method 104°. These results are in closer agreement with Marshall's determination—108°.

Difficulty was encountered in determining the cracking temperature of isopropylmalonic acid by the physical method. The acid melted about 15° below the temperature at which it decomposed. While the acid was melting the movement of the mercury bead either stopped or was greatly reduced. Before cracking began the normal movement set in. As a result of this behavior the plotted points before cracking did not lie on a continuous straight line but on two straight lines at the same inclination, connected by a horizontal or slightly inclined curve. The extent to which this phenomenon is noticeable is determined by the rapidity of heating between the melting and cracking points. Too rapid heating leads to an apparent cracking temperature that is too low. Similar behavior was shown by the allyl and the methyl-*n*-butyl compounds.

We have no explanation to offer for the difference between our result and that of Marshall in the case of dimethylmalonic acid. Marshall modified the method of Norris and Young by replacing mercury in the capillary tube by an organic liquid that wet the tube. This change does not appear to us to be advantageous and may be the reason why Marshall obtained figures in most cases slightly higher than ours.

Effect of the Presence of Certain Substances on the Cracking Temperature of Malonic Acid.—The method used has been outlined in the first part of this paper. Since the experiments were of a preliminary nature

TABLE III

EFFECT OF CONTACT SUBSTANCES ON THE DECOMPOSITION OF MALONIC ACID

The times noted are those required to produce carbon dioxide

Contact substance	Observation	Contact substance	Observation
None	No test in 3 hours	$ZnCl_2$	10 min.
Al powder	10 min.	CaO	Test at 90°
Sb powder	No test in 1/2 hr.	Fe_2O_3	No test in 1/2 hr.
Cu powder	No test in 1/2 hr.	PtO	Slight test in 15 min.
Fe filings	No test in 1/2 hr.	$KHSO_4$	5 min.
Zn dust	No test in 1/2 hr.	H_2O (2 drops)	3 min.
Mg powder	8 min.	CH_3COOH (2 drops)	3 min.
Ni powder	Slight test 15 min.	None	Satd. soln. of acid test at 92°
S	Slight test in 1/2 hr.		
I_2	No test in 1/2 hr.	Satd. soln. of acid + $AlCl_3$ + HCl in H_2O	Test at 86°
$AlCl_3$	No test in 3/4 hr.		

to find what substances should be carefully studied, ordinary C. P. materials were used without further purification. The oxides used were shown to yield no carbon dioxide when treated with an acid. All the substances were dried overnight in a vacuum oven at 30° and kept in a vacuum desiccator until used. About 0.5 g. of the acid and 0.25 g. of the substance were ground together and placed in the reaction tube. The chemical method was used. The temperature of the bath was 115–116°. The results are given in Table III.

Summary

1. The temperatures have been determined at which a number of substituted malonic acids first begin to show evidence of decomposition when they are heated so that the temperature is increased at the rate of two degrees per minute.

2. The relationship is discussed between the composition, structure and the number of radicals present and the cracking temperatures so determined.

3. The results are of value in showing the effect of structure on the lability toward heat of a carbon to carbon bond in these compounds.

4. It is shown that certain contact substances lower the temperature at which this bond is broken by heat.

CAMBRIDGE, MASSACHUSETTS

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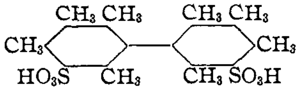
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Stereochemistry of Diphenyls. XXXIV.[1] Preparation and Properties of 2,2',4,4',5,5',6,6'-Octamethyldiphenyl-3,3'-disulfonic Acid and Diphenyl-3,3'-disulfonic Acid

BY A. E. KNAUF[2] AND ROGER ADAMS

The resolution of 2,2',4,4,'5,5',6,6'-octamethyldiphenyl-3,3'-disulfonic acid (I) into optical antipodes has been accomplished. The active forms could not be racemized by any of the usual methods. On the other hand, attempts to resolve the corresponding diphenyl 3,3'-disulfonic acid (II) have been unavailing.



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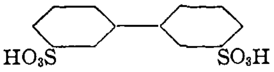

II

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[1] For the previous paper in this field see VanArendonk, Becker and Adams, THIS JOURNAL, **55**, 4230 (1933). See also Adams and Yuan, *Chem. Rev.*, **12**, 261 (1933).

[2] Submitted as a thesis for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.