0.40 to 3.24 mm. In only three attempts was any decrease in pressure whatsoever observed and the average of these three decreases was only 0.02 mm. It may be concluded that no rapid polymerization occurs during the period 3 seconds-45 minutes after the gas leaves the discharge. It was not possible to detect any long-time (one or two days) pressure changes arising from slow decomposition, because of insufficient stability of the Bourdon gage over long periods.

The results of several measurements of the pressure change resulting from the decomposition of the monoxide to sulfur and SO_2 are summarized in Table I.

TABLE I

PRESSURE DECREASE ON DECOMPOSING SULFUR MONOXIDE

Initial P(mm.)	Final P(mm).	Decrease, %
0.14	0.09	36
.26	.21	19
.44	.32	18
.56	.38	32
.63	.57	10
.64	.44	31
.70	.64	9
.70	.54	23
.71	.62	13
.94	.63	33
1.15	.48	58
	Average	26

To ensure that the changes were really due to the presence of sulfur monoxide, seven measurements were made on SO_2 alone, three on SO_2 passed through the discharge in the absence of sulfur vapor, and one on SO_2 to which was added sulfur vapor in the absence of the discharge. The average change for these eleven experiments was a decrease of 0.1% with a probable error of 1%.

The large variation between samples in the observed pressure changes is mainly the result of variation in sulfur monoxide content. Qualitatively it was noted that when the deposit in F was more intensely colored, the pressure decrease was greater. Also the relative proportion of molecular species in the gas might be quite variable in a mixture suddenly withdrawn from the reaction zone and "frozen" in a metastable condition. Thus the average decrease of 26% has no quantitative significance other than to show that the change is far greater than the experimental error of the control experiments and to demonstrate that a considerable part of the gas is responsible for the effect. From the average sulfur monoxide content it may be estimated that a typical gas sample contains about 70% monomeric SO, but a wide variation from this typical value is probable.

It is strongly indicated by these experiments that the product from the discharge is a mixture of SO and S_2O_2 which undergoes no appreciable further dimerization after removal from the discharge tube and holding at room temperature 45 minutes. It is not surprising that Kondrat'ev's contention of complete dimerization is contradicted; his arguments rest almost entirely upon experiments conducted in the presence of H_2S and O_2 at total pressures as high as 100 mm. and catalysis of the dimerization may be very important. The existence of monomeric SO should not be considered established, however, until the uncertainties in the analytical methods for the gas mixture and decomposition products are entirely removed and until the question of the absence of a characteristic infrared absorption is solved.

Experiments upon the paramagnetism of the gas would be instructive, if such measurements could be carried out on a compressed sample before it underwent decomposition. Such experiments are projected for the near future.

Acknowledgment.—We are indebted to the Research Corporation for generous support of this project, to T. M. Cromwell, who carried out some of the preliminary experiments, and to Dr. E. N. Marvell, who originally suggested this problem.

DEPARTMENT OF CHEMISTRY
OREGON STATE COLLEGE
CORVALLIS, OREGON

A New Approach to δ-Phenylvaleric Acids

BY PETE D. GARDNER, W. J. HORTON, GRANT THOMPSON[1]
AND ROBERT R. TWELVES[2]

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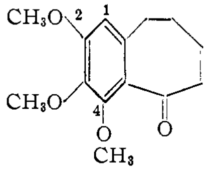
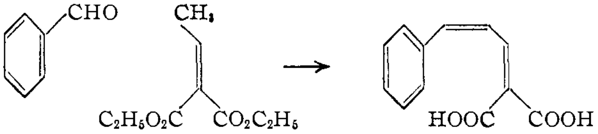
Investigations in progress in this Laboratory on the synthesis of compounds having the carbon ring system of colchicine have encouraged us to seek a method for the preparation of 2,3,4-trimethoxybenzosuberone (I) a needed intermediate. The original synthesis[3,4] was found laborious and a more recent method[5] gave us a mixture of products.



I

Ethylidenemalonic ester (II) has previously been condensed with several aromatic aldehydes by means of concentrated sulfuric acid.[6] Saponification of the condensation products gave cinnamylidenemalonic acids. We have found that potassium hydroxide in absolute alcohol, benzyltrimethylammonium hydroxide in methanol or choline in methanol may replace sulfuric acid in this



II III

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[1] Public Health Service Research Fellow of the National Cancer Institute.

[2] From the Master's Dissertation of R. R. Twelves.

[3] R. D. Haworth, B. P. Moore and P. L. Pauson, *J. Chem. Soc.*, 1045 (1948).

[4] The Haworth procedure has been improved by A. G. Anderson, Jr., and H. F. Greef, THIS JOURNAL, **74**, 2923 (1952).

[5] E. C. Horning, M. G. Horning, J. Koo, M. S. Fish, J. A. Parker, G. N. Walker, R. M. Horowitz and G. E. Ullyot, *ibid.*, **72**, 4840 (1950).

[6] L. Higginbotham and A. Lapworth, *J. Chem. Soc.*, **121**, 2823 (1922).

TABLE I

R	Yield, % Method A	Yield, % Method B	M.p., °C. Crude	Method B Purified[a]	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Cinnamylidenemalonic Acids, R—CH=CH—CH=C(COOH)$_2$									
C_6H_5	..	98	183–186[b]						
2-$CH_3OC_6H_4$	42	94	187–188	201–201.5	$C_{13}H_{12}O_5$	62.90	62.49	4.88	4.75
4-$CH_3OC_6H_4$	26	66[c]	165–168[d]	187–188					
2,3-$(CH_3O)_2C_6H_3$	40	56[e]	181–186	185–186.5	$C_{14}H_{14}O_6$	60.43	60.45	5.07	5.00
3,4-$(CH_3O)_2C_6H_3$	26	63	208–209	212.5–213.5	$C_{14}H_{14}O_6$	60.43	60.39	5.07	5.13
3,4-$(CH_2O_2)C_6H_3$	43	60[f]	206–209						
3,4,5-$(CH_3O)_3C_6H_2$	50	86	187–191.5	195–196.5	$C_{15}H_{16}O_7$	58.44	58.19	5.23	5.43
$C_6H_5CH{=}CH$	35	77	168–179	190–192.5	$C_{14}H_{12}O_4$	68.84	68.68	4.95	5.02
γ-Phenylpropylmalonic acids, R(CH$_2$)$_3$CH(COOH)$_2$									
C_6H_5	84[g]								
2-$CH_3OC_6H_4$	Quant.		115–116		$C_{13}H_{16}O_5$	61.89	61.39	6.39	6.50
4-$CH_3OC_6H_4$	Quant.		108–109.5[h]		$C_{13}H_{16}O_5$	61.89	61.64	6.39	6.39
2,3-$(CH_3O)_2C_6H_3$			Oil[i]						
3,4-$(CH_3O)_2C_6H_3$	Quant.		110–112		$C_{14}H_{18}O_6$	59.57	59.01	6.43	6.44
3,4-$(CH_2O_2)C_6H_3$	Quant.		144–145		$C_{13}H_{14}O_6$	58.64	58.32	5.30	5.40
3,4,5-$(CH_3O)_3C_6H_2$	Quant.		115–117 (gas)		$C_{15}H_{20}O_7$	57.68	57.51	6.46	6.24
$C_6H_5CH_2CH_2$	96		112–115		$C_{14}H_{18}O_4$	67.18	66.78	7.25	7.37
δ-Phenylvaleric acids, R(CH$_2$)$_4$COOH									
C_6H_5	84		55–58[j]						
2-$CH_3OC_6H_4$	Quant.		79–81		$C_{12}H_{16}O_3$	69.21	69.61	7.75	7.75
4-$CH_3OC_6H_4$	94		113–114.5[k]						
2,3-$(CH_3O)_2C_6H_3$	(70)[i]		41–44		$C_{13}H_{18}O_4$	65.53	65.25	7.61	7.85
3,4-$(CH_3O)_2C_6H_3$	82		75–76[l]						
3,4-$(CH_2O_2)C_6H_3$	Quant.		94–95[m]						
3,4,5-$(CH_3O)_3C_6H_2$	80		66–68[n]						
$C_6H_5CH_2CH_2$	90		B.p. 142–144 (0.6 mm.)[o]						
Benzosuberones									
1,2-$(CH_3O)_2$	67		49–50.5		$C_{13}H_{16}O_3$	70.89	70.85	7.32	7.22
Oxime	97		137.5–142		$C_{13}H_{17}NO_3$	66.36	66.73	7.29	7.34
2,3-$(CH_3O)_2$	74		64–65[p]						
Oxime	Quant.		147–149.6		$C_{13}H_{17}NO_3$	66.36	66.04	7.29	7.17
2,3-(CH_2O_2)	Polymer								
2,3,4-$(CH_3O)_3$	Quant.		99–100[q]						
Oxime	91		165–167 (sealed tube)		$C_{14}H_{19}NO_4$	63.38	63.60	7.22	7.14

[a] All of the cinnamylidenemalonic acids melt with gas evolution. [b] Reported[6,8] m.p. 212°, 208°. [c] Using choline and recrystallization from methanol–water, 80% yield, m.p. 168–170° (dec.). [d] Reported[6,9] m.p. 189° (dec.), 203° in a hot-bath; 182° (dec.). [e] Using choline and recrystallization from aqueous methanol. [f] Yield is after treating the crude, m.p. 180–190° (95%), with hot water and filtering from piperic acid; reported[6,10] m.p. 200–204°, 205–206°. [g] Melts at 87–91° after recrystallization, reported[11] 95°. [h] Reported[12] m.p. 144–145°. [i] Decarboxylated and the product distilled, b.p. 148–149° (0.6 mm.); from petroleum ether (30–60°), m.p. 37–44°, 70% from the malonic acid. [j] Reported[11,13] m.p. 58°; 56–58°. Melts undepressed with an authentic sample.[14] [k] Reported[12] m.p. 65°; also[15,16] 114–114.5° and 116–118°. [l] Reported[17] m.p. 72°. [m] Reported[18] m.p. 100–101°. [n] Reported[3,4,17] m.p. 70°, 68–69°, 68°. [o] Reported[19] b.p. 205–210° (17 mm.). Amide, m.p. 87–89°; reported[19] 89°. [p] Reported[17] m.p. 63–64°, oxime, m.p. 152°. [q] Reported,[3,17] m.p. 102°.

reaction to give cinnamylidenemalonic acids. The use of these alkaline reagents in the reaction greatly shortened the process and gave satisfactory to excellent yields (Table I). The use of benzyltrimethylammonium hydroxide greatly increased the yield in several cases. When the quaternary bases were used, a period of refluxing of the aqueous alcohol solution of the reaction product increased the yield, presumably by saponification of the ester.

The orange or yellow cinnamylidenemalonic acids were rapidly reduced to colorless γ-phenylpropylmalonic acids and the latter gave δ-phenylvaleric acids when heated (Table I). Cyclization using polyphosphoric acid[7] gave benzosuberones except in the case of δ-2-methoxy-, δ-4-methoxyphenylvaleric acids and ζ-phenylenanthic acid. The acid chlorides of the first two did not cyclize when aluminum chloride in nitrobenzene was used. Difficulties might be expected in these two

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(7) W. J. Horton and F. E. Walker, THIS JOURNAL, **74**, 758 (1952).

(8) C. Liebermann, *Ber.*, **28**, 1438 (1895).

(9) D. Vorlander and K. Giesler, *J. prakt. Chem.*, [2] **121**, 247 (1929).

(10) M. Scholtz, *Ber.*, **28**, 1187 (1895).

(11) E. C. S. Jones and F. L. Pyman, *J. Chem. Soc.*, **127**, 2588 (1925).

(12) E. Fourneau and P. M. Baranger, *Bull. soc. chim. France*, **49**, 1161 (1931).

(13) R. G. Kadesch, THIS JOURNAL, **66**, 1207 (1944).

(14) J. W. Cook, R. Philip and A. R. Somerville, *J. Chem. Soc.*, 164 (1948).

(15) J. M. van der Zanden, *Rec. trav. chim.*, **57**, 233 (1938).

(16) D. Papa, E. Schwenk and H. Hankin, THIS JOURNAL, **69**, 3018 (1947).

(17) D. Caunt, W. D. Crow, R. D. Haworth and C. A. Vodoz, *J. Chem. Soc.*, 1631 (1950).

(18) W. Borsche, *Ber.*, **44**, 2942 (1911).

(19) J. v. Braun, *ibid.*, **44**, 2867 (1911).

cases since ring closure is to a position meta to a methoxy group.[19a]

The monomolecular cyclization of ζ-phenylenanthic acid would produce benzocyclononanone, a ring system which could not be found in the literature. Polyphosphoric acid converted the enanthic acid to a nearly colorless solid, insoluble in most solvents. The solid exhibited no tendency toward distillation at 280° (0.01 mm.) in a micro-sublimation apparatus with a cold finger condenser and was abandoned as polymeric.

The polyphosphoric acid cyclization of δ-3,4,5-trimethoxyphenylvaleric acid was distinguished by the fact that colorless crystals could be obtained in quantitative yield simply by diluting with water and cooling after the heating period in polyphosphoric acid was over.

This work was assisted by a Frederick Gardner Cottrell grant for which the authors are greatly indebted. A fellowship grant from the University Research Committee was greatly appreciated. The gifts by Rohm and Haas Company of quaternary ammonium bases and of polyphosphoric acid by Victor Chemical Works are gratefully acknowledged.

Experimental[20]

3,4,5-Trimethoxycinnamylidenemalonic Acid.—The following illustrates the procedure used on all of the aldehydes in Table I. **Method A**: 3,4,5-Trimethoxybenzaldehyde, purified by means of the bisulfite compound followed by recrystallization from cyclohexane or from petroleum ether (60–70°) (4.9 g., 0.025 mole) melting at 74–76° was added to 14 cc. of ethyl ethylidenemalonate[21,22] and 35 cc. of absolute ethyl alcohol. After swirling to dissolve as much as possible of the aldehyde, 10 g. of potassium hydroxide pellets was added and the stoppered flask was swirled under the tap so that room temperature was maintained. Solid separated usually before the last of the alkali had dissolved. The reaction was then set aside for 24–48 hours at room temperature. The mixture was then cooled in ice-water and acidified by the addition of a cold solution of 20 cc. of concentrated hydrochloric acid in 140 cc. of water. After standing overnight at 5°, the yellow crystals were filtered and washed with cold water. The product was then dried in air or in a vacuum desiccator overnight. **Method B**: 3,4,5-Trimethoxybenzaldehyde (0.025 mole) was combined with 9.3 cc. of ethylidenemalonic ester as above and treated with 55 cc. of 35% methanolic benzyltrimethylammonium hydroxide. An equivalent amount (26 cc. per 0.025 mole of aldehyde) of 50% methanolic choline was substituted for benzyltrimethylammonium hydroxide in two experiments. In all cases only a slight amount of heat was noted on mixing. After standing as above, a clear dark red solution was obtained. The ester was saponified by the addition of 120 cc. of water and refluxing for 30–60 minutes. After cooling, 40 cc. of 1:1 hydrochloric acid was added and the precipitated crystals were cooled at 5° overnight. The product was dried as before.

The cinnamylidenemalonic acids were purified by recrystallization from methanol. Recrystallization by dissolving in a small amount of warm ethanol, addition of benzene and distillation to remove the alcohol gave excellent recoveries and was superior to methanol where the crude products contained oil.

γ-Phenylpropylmalonic Acids.—The above acids were dissolved or suspended in absolute ethyl alcohol and shaken with 0.5–5.0% platinum oxide under hydrogen at a pressure slightly above atmospheric. Reduction proceeded rapidly and indicated the presence of two double bonds (Table I).

δ-Phenylvaleric Acids.—The colorless malonic acids were heated at 18 mm. in a large test-tube immersed in an oil-bath. Gas was evolved at 170–180° and the reaction was complete in 15 minutes.

Benzosuberones.—The method used was that reported,[6] using 6.0 g. of polyphosphoric acid per 0.001 mole of the valeric acid and a 30-minute heating period at 95°.

δ-2-Methoxyphenyl-, δ-4-methoxyphenylvaleric acids and ζ-phenylenanthic acid gave high melting neutral compounds insoluble in the common solvents and not distillable at low pressures. These are probably the products of intermolecular condensation. Cyclization of the acid chlorides of the first two with aluminum chloride in nitrobenzene (room temperature overnight) gave only the starting acid.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF UTAH
SALT LAKE CITY 1, UTAH

A Reinvestigation of the Structure of Difluoromethane by Electron Diffraction

BY WALTER C. HAMILTON AND KENNETH HEDBERG

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An early electron-diffraction investigation[1] of the structure of difluoromethane led to the parameter values C–F $\doteq$ 1.36 ± 0.02 Å., ∠ F–C–F = 110 ± 1°, C–H = 1.06 Å. (assumed) and ∠ H–C–H = 109° 28′ (assumed). Recently, an analysis of the infrared spectrum[2] of this substance, based upon the approximate symmetric top character of the molecule, led to two rotational constants and the parameter values C–F = 1.32 ± 0.01 Å., ∠ F–C–F = 107.0 ± 0.5°, C–H = 1.094 Å. (assumed) and ∠ H–C–H = 110° (assumed). Because of the serious discrepancies between the results of these two methods for the principal parameters (which cannot, of course, be explained by the difference between the assumed values for the remaining parameters), it seemed that a reinvestigation of the structure was in order.

The sample of difluoromethane, supplied by the Jackson Laboratory of the du Pont Co., contained 0.2–0.3% fluoroform and 0.05% chlorodifluoromethane. The camera distance was 10.91 cm. and the electron wave length 0.06056 Å. The methods used in the structure determination have been described elsewhere.[3]

Theoretical intensity curves were calculated over the shape parameter range C–F/F···F = 1.36/2.14 to 1.36/2.23, assuming C–H/C–F = 1.09/1.36 and ∠ H–C–H = 109°28′. All terms except H···H were included, and in the factor exp $(-a_{ij}q^2)$, a was given the values 0.00016 and 0.00030 for the C–H and H···F distance, respectively, in accord with our experience, and zero elsewhere.[4]

It is our conclusion that the best agreement with the appearance of the photographs is given by a curve slightly closer to J than I (Fig. 1). The factors of particular importance for this decision are the characters of the doubled maxima 3–4,

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[19a] Numerous examples of the decreased yield in cyclization to a position meta to a methoxy group have been collected. W. S. Johnson, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 120.

[20] Melting points are uncorrected.

[21] F. R. Goss, C. K. Ingold and J. F. Thorpe, *J. Chem. Soc.*, **123**, 3342 (1923). Ethyl ethylidenemalonate can be prepared in 86% yield in a hydrogenation bomb provided that the entire reaction mixture is distilled at 20 mm.

[22] I. Vogel, *ibid.*, **130**, 1985 (1927).

[1] L. O. Brockway, *J. Phys. Chem.*, **41**, 747 (1937).

[2] H. B. Stewart and H. H. Nielsen, *Phys. Rev.*, **75**, 640 (1949).

[3] K. Hedberg and A. J. Stosick, THIS JOURNAL, **74**, 954 (1952).

[4] Some curves were calculated using values of $a_{F...F}$ different from zero, however. It was concluded that $a_{F\cdots F}$ might be as large as about 0.00005 relative to $a_{C-F} = 0$, but that use of the value zero caused no error in the values of determined parameters.