such small amounts would have had a negligible effect on the dielectric constant. The distillate was deiodized with copper and fractionally distilled with absolute alcohol to separate the isomers. Runs 25 and 26 were made with the *trans* isomer so obtained. The apparent slightly higher percentage of *cis* in the final equilibrium mixture in run 26 may be due to some impurity. The runs from the *cis* side are probably more reliable, and the others agree sufficiently to indicate that the state reached in these reactions was indeed an equilibrium between the two isomers as was assumed.

The changes in free energy, entropy, and heat content on isomerization are all zero within experimental error. As good an estimation as can be made is to say that the equilibrium constant, K, for the reaction *trans*-$C_2H_2Br_2 \rightleftarrows$ *cis*-$C_2H_2Br_2$ is 0.984 at 145° and 0.975 at 170°. The changes in thermodynamic quantities on isomerization at 158° become $\Delta F^0 = 17 \pm 40$ cal./mole. $\Delta H^0 = -130 \pm 300$ cal./mole. $\Delta S^0 = -0.34 \pm 0.8$ cal./mole degree.

So little is known about the vibration frequencies of the isomers that it is impossible to make a statitstical mechanical treatment of the equilibrium as was done by Wood and Stevenson.[2]

Summary

The gaseous equilibrium of *cis* and *trans* dibromoethylenes catalyzed by iodine has been studied in the range from 144 to 178° and has been found to correspond to equal amounts of the two isomers over the entire interval within the experimental error in analysis. Hence the standard free energy, entropy and heat content changes are all zero for the isomerization.

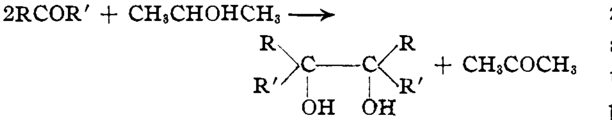
PASADENA, CALIFORNIA RECEIVED APRIL 27, 1943

NOTES

Photochemical Pinacolization

BY FELIX BERGMANN AND YEHUDA HIRSHBERG

In a previous paper from this Laboratory,[1] pinacolization of ketones under the influence of ultraviolet light was studied with the aim of elucidating the elementary process in the mutual oxidation and reduction of ketones and secondary alcohols, according to the scheme



$$2RCOR' + CH_3CHOHCH_3 \longrightarrow \underset{R'}{\overset{R}{>}}\underset{OH}{C}-\underset{OH}{C}\underset{R'}{\overset{R}{<}} + CH_3COCH_3$$

We have now extended this investigation and found very narrow structural limits for the applicability of this type of reaction.

1. The fact that benzophenone and acetophenone are pinacolized quantitatively according to the above scheme would indicate that at least one aryl group is necessary to activate the carbonyl group. However, neither α- nor β-acetyl-naphthalene gave any reaction, and, likewise, α-naphthyl phenyl ketone and di-α-naphthyl ketone remained unchanged. Also, phenyl *p*-biphenylyl ketone, like its *o*-isomer, was not attacked, although the *m*-compound has been reported to yield the pinacol.[2] It is apparent that a change in the type of the aromatic substituent both in benzophenone and acetophenone nearly always impairs the photochemical reactivity.

2. Systematic changes were now applied to the non-aromatic part of acetophenone. Desoxybenzoin yielded the (higher-melting) α-pinacol in about 80% yield; no trace of the β-form was detected. The next higher homolog, benzyl-acetophenone, was inactive, but 1,4-diphenylbutanone-1 yielded a small amount of a liquid pinacol, which perhaps represents a mixture of both stereoisomers. It is very significant that the same behavior was encountered in the cyclic analogs of the last two ketones: α-indanone (I), comparable to $C_6H_5COCH_2CH_2C_6H_5$, was not pinacolized, but yielded, instead, the condensation product II: α-tetralone corresponding to $C_6H_5COCH_2CH_2CH_2$-C_6H_5 yielded the pinacol in yields up to 75%.

3. On the principle of vinylogy, the styryl group was presumed to behave like the phenyl

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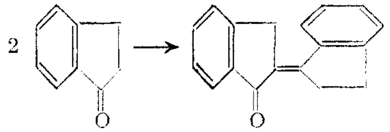
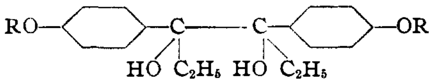
[1] Weizmann, E. Bergmann and Hirshberg, THIS JOURNAL, **60**, 1530 (1938).

[2] Hatt, Pilgrim and Stephenson, *J. Chem. Soc.*, 478 (1941).



I II



III

nucleus. However, benzalacetophenone and benzalacetone, the vinylogs of benzophenone and acetophenone, respectively, were not affected.

4. In a further set of experiments the influence of aromatic substitution on the pinacolization of acetophenone was studied with the view of synthesizing the pinacol III, which could serve as a suitable starting material for stilboestrol.[3] *p*-Methoxypropiophenone did not react at all, and the *p*-acetoxy-, propoxy- and butyroxyacetophenone only suffered partial deacylation to *p*-hydroxypropiophenone; the acetoxy compound yielded also traces of pinacol III (R = CH_3CO–).

Finally, it was found that under our experimental conditions benzoin undergoes a reverse Cannizzaro reaction, giving benzaldehyde as the only reaction product.

Experimental Part

Under the conditions used, benzophenone in 6.7% solution gave 100% of pinacol after fifteen hours of irradiation, acetophenone 70%.

(1) **α-Indanone.**—The ketone (20 g.) in isopropanol (150 cc.) was irradiated for ten hours and the mixture fractionated. The residue was triturated with toluene. From isopropanol it gave prisms of II, m. p. 142–143°.

Anal. Calcd. for $C_{18}H_{14}O$: C, 87.8; H, 5.7. Found: C, 87.0; H, 5.7.

When the same reaction was carried out in sunlight (30 days), a small amount of another product was obtained, which crystallized from nitrobenzene or pyridine in beautiful brown rods, m. p. 352–353°. With concd. sulfuric acid a violet color appears which turns slowly to red-brown; no reaction with bromine. No method was found for determining the molecular weight.[4]

Anal. Calcd. for $C_{36}H_{26}O(2 \times C_{18}H_{14}O - H_2O)$: C, 91.1; H, 5.5. Found: C, 92.8, 93.1; H, 5.65, 5.5.

(2) ***α*-Tetralone.**—After evaporation of the solvent, the pinacol crystallized only partially, most of it was obtained in solid form only after distillation, b. p. 220° (4 mm.); from butyl acetate as beautiful prisms, m. p. 192°.[5] Ten grams of tetralone yielded 7.5 to 8 g. of pinacol. For identification the product was converted into the diene by dehydration in acetic acid–acetic anhydride mixture. From high-boiling petroleum ether the diene gave prismatic blocks, m. p. 141–142°.

Pinacolization of the tetralone was favored by dilution, mainly because the formation of a brown film around the quartz lamp was thereby avoided. Thus, using 50 g. of tetralone in 100 cc. of either isopropanol or isopropanol and benzene, there was obtained a 3% yield of pinacol in ten hours; using 20 g. and 5 g. in 150 cc. of isopropanol, there were obtained in ten and twenty hours, 10 and 80% yields of pinacol, respectively. Ten grams of tetralone in 10 cc. of isopropanol after thirty days in sunlight gave a 40% yield of pinacol.

(3) **Desoxybenzoin.**—The residue from the distillation of unreacted ketone was recrystallized from butanol, m. p. 214°, and identified with an authentic sample of the pinacol.

(4) **1,4-Diphenylbutanone-1.**—This ketone was prepared by a Grignard reaction between benzonitrile (18 g.) and γ-phenylpropylmagnesium bromide (one-sixth mole). On working up the mixture with dilute sulfuric acid, the ketimine was hydrolyzed in the cold and the ketone obtained directly, b. p. 180° (6 mm.),[6] 155° (0.2 mm.), yield 50%. The irradiation yielded a small amount of a high-boiling sirup, b. p. 190° (0.25 mm.), which could not be induced to crystallize.

Anal. Calcd. for $C_{32}H_{34}O_2$: C, 85.3; H, 7.6; mol. wt., 450. Found: C, 85.8; H, 7.45; mol. wt., 395.

(5) ***p*-Acetoxypropiophenone.**—The sirup which was left after distillation of the starting material was distilled in a high vacuum. Crystallization from butyl acetate gave beautiful prisms, m. p. 214° (III, R = $COCH_3$).[7]

Anal. Calcd. for $C_{22}H_{26}O_6$: C, 68.4; H, 6.7. Found: C, 68.5; H, 6.6.

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[3] Dodds, Golberg, Lawson and Robinson, *Proc. Roy. Soc.* (London), **B127**, 140 (1939).

[4] It is very probable, that this substance is impure bouxene, $C_{27}H_{18}$, the m. p. of which is given as 369–370° by Stobbe, *Ber.*, **60**, 457 (1927). We thank Dr. Ernst Bergmann for this suggestion.

[5] Barnett and Lawrence, *J. Chem. Soc.*, 1104 (1935).

[6] Stoermer and Schenck, *Ber.*, **61**, 2320 (1928).

[7] Dodds and co-workers (ref. 3) report a m. p. of 200°. Their pinacol may represent the other stereoisomer, although it was converted into the high-melting form of hexoestrol.

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REHOVOTH, PALESTINE

RECEIVED NOVEMBER 6, 1942

The Iodination of Tyrosine by Iodine Monochloride

BY PAUL BLOCK, JR., AND GARFIELD POWELL

Tyrosine was first iodinated to diiodotyrosine by Wheeler and Jamieson[1] who added solid iodine to a solution of tyrosine in sodium hydroxide. Oswald[2] improved the yield by performing the reaction at 0°. More recently Harington[3] and also Savitskii[4] have described the iodination of tyrosine in ammonia using iodine dissolved in potassium iodide. Bauer and Strauss[5] used iodine

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[1] Wheeler and Jamieson, *Am. Chem. J.*, **33**, 365 (1905).

[2] Oswald, *Z. physiol. Chem.*, **59**, 320 (1909).

[3] Harington, *Biochem. J.*, **22**, 1434 (1928).

[4] Savitskii, *Chem. Abs.*, **34**, 741 (1940).

[5] Bauer and Strauss, *Ber.*, **69**, 245 (1936).

monochloride vapor to synthesize diiodotyrosine in 38.5% yield. The following method gives 80 to 85% of a product that can more easily be rendered absolutely white than diiodotyrosine iodinated by the method of Oswald.

Five grams of tyrosine was suspended in 20 cc. of acetic acid, and 10 g. of iodine monochloride in 20 cc. of acetic acid added. The tyrosine immediately went into solution. The reaction mixture was warmed to 60° and 80 cc. of water added in three portions, warming the solution to 60° after each addition. The total time of heating was thirty minutes. Sodium bisulfite was added to destroy the excess iodine monochloride, and ammonia to precipitate the diiodotyrosine. One reprecipitation from dilute hydrochloric acid gave an entirely colorless product, decomposing with evolution of iodine at 201° (cor.), heated at 10° per minute.

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK CITY

RECEIVED APRIL 23, 1943

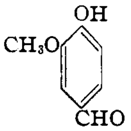
Some Derivatives of Creosol

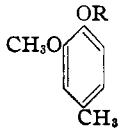
BY JOHN H. FLETCHER AND D. S. TARBELL

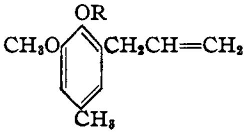
It was recently necessary to prepare 3,4-dimethoxy-5-propenyltoluene (VI) in connection with some other work. It seems worth while to report the observations and new compounds which resulted from the synthetic work.

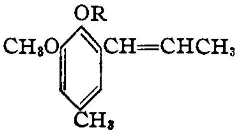
The starting material was vanillin (I) from which creosol (II) was prepared by a Clemmensen reduction. This reaction has been reported by Kawai and Sugiyama,[1] but neither yields nor experimental details were given. These workers also carried out the synthesis of the allyl ether of creosol (III) and its subsequent rearrangement to 6-allylcreosol (IV); our work checks theirs. Methylation of IV followed by alkali-induced isomerization of the allyl side-chain in diethylene glycol solution produced 3,4-dimethoxy-5-propenyltoluene (VI). If IV was first isomerized and then methylated, VI was obtained but in poorer yield than by the former method. Compound VII, 6-propenylcreosol, is a solid, m. p. 61–62°; all the other derivatives described above are high-boiling liquids.

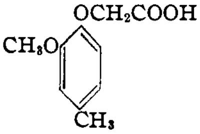
Two solid derivatives were prepared and analyzed as checks. Oxidation of III gave 2-methoxy-4-methylphenoxyacetic acid (VIII); both V and VI gave 2,3-dimethoxy-5-methylbenzoic acid (IX) when treated with aqueous permanganate.

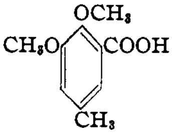

I


II, R = H
III, R = $CH_2CH{=}CH_2$


IV, R = H
V, R = CH_3


VI, R = CH_3
VII, R = H


VIII


IX

Experimental[2]

Creosol (II).—The modified procedure of Martin[3] was used with the following amounts: 200 g. of mossy zinc, 150 cc. of water, 350 cc. of concentrated hydrochloric acid, 200 cc. of toluene, and 90 g. of vanillin (Eastman Kodak Company). This mixture was refluxed for twenty-four hours. The yield of creosol was 51.7 g. (63%), b. p. 105–106° (15 mm.), $n^{23}D$ 1.5355.[4]

Creosol Allyl Ether (III).—To a solution of 50 g. (0.36 mole) of creosol in 180 cc. of acetone was added 90 cc. of water containing 18 g. (0.45 mole) of sodium hydroxide; after mixing well, 54.5 g. (0.45 mole) of allyl bromide was added and the mixture refluxed for one hour. Dilution was made with 500 cc. of water and the solution was extracted with three 90-cc. portions of petroleum ether (b. p. 60–70°). The ether extract was washed twice with 5% alkali, twice with water, and was dried over calcium chloride. The solvent was distilled and the residual oil subjected to vacuum distillation; yield, 55.4 g. (86%), b. p. 128–130° (15 mm.), $n^{24}D$ 1.5270.

2-Methoxy-4-methylphenoxyacetic Acid (VIII).—A solution of 4.7 g. (0.03 mole) of potassium permanganate in 200 cc. of water was prepared. To this were added 1.3 g. (0.01 mole) of sodium carbonate monohydrate and 1.8 g. (0.01 mole) of creosol allyl ether (III). The mixture was shaken at intervals for fifteen minutes; heat was evolved and a brown solid separated. After standing overnight the mixture was filtered; the filtrate was acidified with hydrochloric acid and evaporated to 50 cc. On cooling, white crystals were obtained; yield, 0.6 g. (31%), m. p. 111–113°. The product was recrystallized from water; m. p. 115–116°.

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.2; H, 6.2. Found: C, 61.3; H, 6.0.

6-Allylcreosol (IV).—Fifty-five grams of creosol allyl ether (III) was heated in an oil-bath to 210° whereupon gentle boiling set in and the liquid darkened. After five minutes the material was allowed to cool. It was distilled

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[1] Kawai and Sugiyama, *Ber.*, **72B**, 367 (1939).

[2] Analyses by Mr. Robert W. King.

[3] Martin, THIS JOURNAL, **58**, 1438 (1936).

[4] de Vries, *Rec. trav. chim.*, **28**, 283 (1909), gives for creosol $n^{25}D$ 1.5353.

at diminished pressure giving 46.2 g. (84%) of colorless liquid, b. p. 135–138° (18 mm.), $n^{23}\text{D}$ 1.5344.

An alcoholic solution of the product gave a deep blue-green color with ferric chloride. The **α-naphthylurethan** of 6-allylcreosol was prepared in 70% yield; after one recrystallization from ligroin it melted at 132–132.5°.

Anal. Calcd. for $C_{22}H_{21}O_3N$: C, 76.1; H, 6.1. Found: C, 76.1; H, 6.3.

3,4-Dimethoxy-5-allyltoluene (V).—To 130 cc. of 2 *N* sodium hydroxide solution in a glass-stoppered bottle was added 46.2 g. (0.26 mole) of 6-allylcreosol (IV) and one-third of a portion of 32.8 g. (0.26 mole) of dimethyl sulfate; the mixture was shaken vigorously at intervals for five minutes, after which another third of the dimethyl sulfate was added; the final addition was made after a similar period. An oily layer separated and was extracted with ether. The ether extract was washed twice with water and dried over calcium chloride. After removal of the ether, distillation at diminished pressure gave 43.0 g. (86%) of colorless liquid, b. p. 125–135° (12 mm.), $n^{23}\text{D}$ 1.5240.

2,3-Dimethoxy-5-methylbenzoic Acid (IX).—Two grams of 3,4-dimethoxy-5-allyltoluene was treated with aqueous permanganate as described above in the preparation of 2-methoxy-4-methylphenoxyacetic acid. The product was crystallized from petroleum ether (b. p. 60–70°) containing a little benzene; yield, 0.1 g. of white crystals, m. p. 91.5–92.5°. The product dissolved with effervescence in 5% sodium bicarbonate solution.

This compound was also obtained in 20–30% yield by the oxidation of 3,4-dimethoxy-5-propenyltoluene (VI).

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.2; H, 6.2. Found: C, 61.4; H, 6.3.

6-Propenylcreosol (VII).—Ten grams of potassium hydroxide pellets was dissolved in 100 cc. of diethylene glycol by heating to 160° in an oil-bath; to the hot solution was added 17.5 g. (0.1 mole) of 6-allylcreosol (IV). Heating (150–170°) was continued for one hour. When cool, the mixture was poured into 200 cc. of water and acidified with hydrochloric acid. The brown oily layer was extracted with petroleum ether (b. p. 60–70°), the solvent evaporated, and the residue distilled through a Widmer column. The boiling point rose gradually, and no clean-cut fractions appeared; a total of 10.5 g. of liquid, b. p. 86–120° (1 mm.), was collected. The residue from the distillation (3.5 g.) solidified upon cooling, and extraction with petroleum ether gave 1.9 g. of light tan crystals, m. p. 60–62°. The crude material was dissolved in dilute alkali, treated with Norit, and precipitated with dilute hydrochloric acid; the purified product, m. p. 61–62°, was still not white.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.1; H, 7.9. Found: C, 74.1; H, 8.0.

3,4-Dimethoxy-5-propenyltoluene (VI).—Twenty grams of potassium hydroxide pellets was dissolved in 200 cc. of diethylene glycol by heating and stirring. When the temperature of the solution had reached 165° water began to boil off; after most of this had been removed, 41.0 g. (0.213 mole) of 3,4-dimethoxy-5-allyltoluene (V) was added. For the next twenty minutes the solution was stirred and the temperature maintained at 175–185°. After cooling to 120° the dark red liquid was poured into 400 cc. of cold water, whereupon an oily layer separated. The latter was extracted with petroleum ether (b. p. 60–70°) and the ether solution dried over calcium chloride. After removal of the solvent, distillation at diminished pressure gave 16.1 g. (39%) of colorless liquid, b. p. 109–111° (1 mm.), $n^{24}\text{D}$ 1.5468.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ROCHESTER
ROCHESTER, NEW YORK

RECEIVED MARCH 1, 1943

The Heat of Polymerization of Some Vinyl Compounds

BY G. GOLDFINGER, D. JOSEFOWITZ AND H. MARK

The heat liberated in polymerization reactions is sometimes considerable and may interfere with the easy control of the process. Moreover, knowledge of the magnitude of the heat evolution may also be of use in connection with kinetic and equilibrium considerations. We have, therefore, undertaken the direct measurement of the heat of polymerization of several important substances.

Luschinsky[1] has already determined the heat of polymerization of styrene from measurements of the heats of combustion of the monomer and the polymer. These measurements can indeed be made with great accuracy, but as these heats may well be 100 times larger than the heat of polymerization, the errors in the latter may be magnified 100-fold. We have, therefore, resorted to the methods of adiabatic calorimetry and have utilized for this purpose a 100-cc. cylindrical Dewar flask submerged in a 1-liter oil-bath whose temperature could be raised uniformly by means of an insulated heater and a rapid stirrer. The flask contained 50 cc. of water in which was submerged an hermetically sealed glass tube containing 8 g. of the monomer. The adiabaticity was controlled to within ±0.25° by means of a galvanometer sensitive to 0.05°. The polymerization was initiated by heat. The temperature rise of the liquid in the Dewar flask and hence the heat evolved was measured to 0.25°.

The substances studied were purified by repeated vacuum distillation of commerical materials.

Measurements were made on four or five samples of each substance. The individual molar heats of polymerization (*H*) obtained with styrene were typical and were as follows, expressed in calories

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[1] W. V. Luschinsky, *Z. physik. Chem.*, **A183**, 384 (1938).

Sample	1	2	3	4	5	Mean
H	15600	14200	14850	14600	15400	15000 ± 475

The average deviation from the mean was therefore about ±3%; the square root of the sum of the squared deviations ±3.5%. The physical constants of the monomers and the heats of polymerization are given.

Substance	Styrene	Methyl methacrylate	Vinyl acetate
B. p., °C.	145–6	100	73
d^{20}_4	0.908	0.937	0.934
n^{20}_D	1.543	1.414	1.396
Ext. of polymerization in %	35–85	98–99	95
Temp. in °C.	70–140	60–90	80
Time, hours	$1/2$–2	$1/2$	$1/2$
H (mean), cal./mol.	15000	7900	8000
Av. dev. fr. mean	±470	±400	±400

It is a pleasant duty for the authors to express their sincerest appreciation to Mr. Dan Whyte, President of the Jay Novelty Company of New York City, whose interest in the subject enabled us to build the described calorimeter and to carry out the measurements.

POLYTECHNIC INSTITUTE OF BROOKLYN
BROOKLYN, NEW YORK
RECEIVED MARCH 4, 1943

Acid Strengths of Aliphatic Nitro Compounds

BY G. W. WHELAND AND JOHN FARR

Turnbull and Maron[1] have recently reported the measurement of the aci dissociation constants of both the nitro and the aci forms of several aliphatic nitro compounds. We had previously been making these same measurements by the same experimental method. Our provisional values of the pK's of the nitro forms at 25° are: nitromethane, 10.24; nitroethane, 8.60; 1-nitropropane, 8.98; and 2-nitropropane, 7.7–7.8. All values are corrected for salt-effect and for hydrolysis, and have probable errors of ±0.04 as judged by the internal consistency of the data. These figures are mostly in satisfactory agreement with those of Turnbull and Maron, but the discrepancy for nitroethane is somewhat larger than the probable error in either set of measurements. Under the circumstances, we have discontinued work on the problem.

The pK's of the nitro forms decrease in the unexpected order: nitromethane > nitroethane > 2-nitropropane. The opposite order might have been anticipated, since methyl groups ordinarily decrease acid strengths. Turnbull and Maron have advanced an explanation of this fact on the assumption that the ions of the nitro and aci forms are different, and are not identical with each other as they would have to be if resonance occurs between the two corresponding structures. Since this assumption seems to us to be rather improbable, we wish to call attention here to the following alternative explanation, which we consider to rest upon a more satisfactory theoretical basis. The ionizable proton in 2-nitropropane, for example, is extremely close both to the nitro group and to the methyl groups in question. Consequently, the lines of force between the large dipole moments of the nitro group and the proton must pass largely through the methyl groups—that is, through a region of relatively low dielectric constant. As a result, the electrostatic interaction, which is responsible in the main for the measurable acidities of the substances, must be greater for 2-nitropropane than for nitromethane, in which the corresponding lines of force pass largely through the solvent of high dielectric constant. Nitroethane is of intermediate acidity, as could have been predicted. The fact that the expected order of increasing pK's (nitromethane < nitroethane < 2-nitropropane) is observed in the aci forms can be related to the fact that in these aci forms the ionizable protons are farther removed from the nitro and methyl groups, so that the lines of force pass largely through the solvent in all cases. Consequently, the usual direct effects of the methyl groups in decreasing acid strengths have a chance to operate, as in the analogous carboxylic acids. Furthermore, in 1-nitropropane, the terminal methyl group is farther removed from the proton, and so it it exerts only its direct effect in making the substance less acidic than nitroethane. It is not clear to us how the explanation of Turnbull and Maron would apply to this substance.

The foregoing discussion is based upon a closely similar one given by Westheimer and Shookhoff[2] in regard to the acid constants of substituted malonic acids.

We wish to thank the Commercial Solvents Corporation for furnishing the 1-nitropropane and 2-nitropropane used in our work.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS
RECEIVED MAY 10, 1943

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[1] D. Turnbull and S. H. Maron, THIS JOURNAL, **65**, 212 (1943).

[2] F. H. Westheimer and M. W. Shookhoff, *ibid.*, **61**, 555 (1939).