(Fig. 1B) at 5.06, 6.61, 8.65 and 9.14 p.p.m. are 2:3:2:15. Ratios found were 1.8 ± 0.1:3.0 (assumed):2.0 ± 0.1:14.9 ± 2.7. It is noted (Fig. 1B) that peaks at 8.65 and 9.14 p.p.m. overlap; therefore a somewhat arbitrary manual separation must be made.

N.m.r. Peak Assignments. 2,2,5,5-Tetramethyl-3-hexanol (Fig. 2A).—The characteristic shift of one peak (6.13 p.p.m.) with dilution of the samples marked it as the hydroxyl group. The other low field multiplet (6.73 p.p.m.) must therefore be the proton attached to the hydroxylated carbon. It is well known that such protons have a peak in this region.[17] The two sharp peaks (9.06 and 9.15 p.p.m.) represent the methyl protons because of their position, intensity and sharpness. This leaves the other multiplet (in the region of 8.68 p.p.m.) to be assigned to the protons attached to the 4-carbon. As noted above, the spin coupling pattern is entirely consistent with this assignment if it is assumed that the two protons on the 4-carbon couple unequally with the proton on the 3-carbon.

2,2,5,5-Tetramethyl-1,4-hexanediol (Fig. 2B).—The hydroxyl peak was identified by the disappearance of the peak at 5.06 p.p.m. after exchange of the diol with D_2O. The other low field peak (6.61 p.p.m.) must therefore be due to the protons attached to the hydroxylated carbon. The methyl groups were assigned to the sharp peak at high field (9.14 p.p.m.) for the same reasons as noted for the monoalcohol. This leaves the doublet at 8.65 p.p.m. to be assigned to the remaining two internal methylene protons. As noted above, area measurements of the peaks are in good agreement with this assignment.

Acknowledgments.—The authors are indebted to Dr. W. L. Courchene for infrared interpretations, Dr. C. H. Orr for gas chromatographic analyses, and to Mr. R. H. Lindahl for X-ray powder pattern data.

CINCINNATI 39, OHIO

---

[17] Correlations of chemical shift with proton type have been published by N. F. Chamberlain, *Anal. Chem.*, **31**, 56 (1959).

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF THE WILLIAM MARSH RICE AND YALE UNIVERSITIES]

Heats of Hydrogenation. VII. The Cycloheptatrienylium (Tropylium) Ion

BY RICHARD B. TURNER, H. PRINZBACH AND W. VON E. DOERING

RECEIVED OCTOBER 22, 1959

The heat of hydrogenation of tropylium chloride in acetic acid is −86.2 kcal./mole. Its heat of formation in the same solvent is +19.8 kcal./mole and may be compared with estimations of +19.6 and +23.8 kcal./mole for the heat of formation of the covalently bonded isomer. The heat of solvation in water of gaseous tropylium ion is estimated to lie between −50 and −68 kcal./mole. An attempt is made to compare the heat of formation of tropylium ion with that of its isomer, the benzylcarbonium ion.

As the parent of the heptagonal aromatic system, the cycloheptatrienylium ion occupies the same relative position as benzene in the hexagonal system and the cyclopentadienide anion in the pentagonal. Paralleling a perennial concern with the energy content and aromaticity of benzene, today's interest in the experimental and theoretical energy content of tropylium arises from wonder at the very existence of this stable carbonium ion and at the high π-electron delocalization energy of 3.0 β Hückel[1] calculated for it by his molecular orbital treatment. Unlike benzene, where three times the heats of hydrogenation of cyclohexene[2] or of ethylene minus corrections[3] serve as convenient models for comparison with a theoretical π-electron delocalization energy of 2.0 β, tropylium ion has no adequate, localized model.

To obtain a fundamental thermodynamic datum from which heats of formation and solvation may be estimated, the heat of hydrogenation of tropylium ion has been determined. The hydrogenation experiments employ the technique described in the first paper of this series.[4] Tropylium bromide[5] was hydrogenated in stock acetic acid at 25° to cycloheptane and hydrogen bromide. On the basis of hydrogen absorbed, which was about 97% of theory for four molar equivalents of hydrogen calculated from the weight of sample employed, the heat of hydrogenation is −89.06 ± 0.17 kcal./mole (see Table I).

Tropylium chloride has the disadvantage of being more hygroscopic and more unstable than tropylium bromide. Pure samples, obtained by cyrstallization from dilute solution in acetonitrile in the complete absence of air, remain colorless if stored under prepurified nitrogen at −60°. The material rapidly becomes sticky and turns yellow on exposure to air. Carefully prepared samples absorbed 90.2% of the required amount of hydrogen. Calculated on the basis of hydrogen actually absorbed, the heat of hydrogenation is 86.20 ± 0.33 kcal./mole.[6] This absorption is appreciably greater than that obtained with a sample prepared and handled in the usual way.[5] This latter sample, despite absorbing only 74.3% of the required hydrogen, gave a heat of hydrogenation of −86.23 ± 0.77 kcal./mole. The excellent agreement can be rationalized by assuming the impurity in the samples of tropylium chloride to be water.

The difference of 2.9 kcal./mole in the heats of hydrogenation of the chloride and bromide is noteworthy since the reaction observed in both cases is the hydrogenation of tropylium ion to cycloheptane and a proton. Although the discrepancy can be attributed in part to variation in

---

[1] (a) E. Hückel, "Grundzüge der Theorie ungesättigter und aromatischer Verbindunge," Verlag Chemie, Berlin, 1938, pp. 71–85; (b) J. D. Roberts and A. Streitwieser, Jr., THIS JOURNAL, **74**, 4579 (1952); (c) J. L. Franklin and F. H. Field, *ibid.*, **75**, 2819 (1953).

[2] G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, *ibid.*, **58**, 146 (1936).

[3] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959).

[4] R. B. Turner, W. R. Meador and R. E. Winkler, THIS JOURNAL, **79**, 4116 (1957).

[5] W. von E. Doering and L. H. Knox, *ibid.*, **76**, 3203 (1954).

[6] For reasons noted below, the solvent indicated by aq. AcOH consisted of 225 ml. of stock acetic acid to which 0.3 ml. of water was added.

the water content of the solvent, it seems more likely that the effect is due to incomplete dissociation of ions.

A heat of hydrogenation to liquid cycloheptane and gaseous hydrogen chloride may be derived from the following heats combined as indicated.

$C_7H_7{}^+Cl^-(\text{aq. AcOH}) + 4H_2(g) \longrightarrow C_7H_{14}(\text{aq. AcOH}) + HCl(\text{aq. AcOH})$ -86.2

$C_7H_{14}(\text{aq. AcOH}) \longrightarrow \text{Aq. AcOH} + C_7H_{14}(l)$ -1.5

$HCl(\text{aq.}) \longrightarrow HCl(g) + H_2O$ $+16.9$

$HCl(\text{aq. AcOH}) \longrightarrow HCl(\text{aq.}) + HOAc$ -17.9

$H_2O + HOAc \longrightarrow \text{aq. AcOH}$ $+9.1$

$HCl(\text{aq. AcOH}) \longrightarrow HCl(g) + \text{aq. AcOH}$ $+8.1$

$C_7H_7{}^+Cl^-(\text{aq. AcOH}) + 4H_2(g) \longrightarrow C_7H_{14}(l) + HCl(g)$ -79.6

The heat of solution of liquid cycloheptane (+1.5 kcal./mole) was measured in the acetic acid–water mixture of the hydrogenation. The heat of solution of gaseous hydrogen chloride in water to give aqueous hydrochloric acid of the appropriate concentration (−16.9 kcal./mole) is known.[7] The heat of diluting aqueous hydrogen chloride in the appropriate amount of acetic acid (+17.9 kcal./mole) and the heat of mixing the appropriate amounts of water and acetic acid (+9.1 kcal./mole) were determined experimentally. The resultant heat of solution of gaseous hydrogen chloride in the acetic acid–water mixture is −8.1 kcal./mole. The heat of hydrogenation of dissolved tropylium chloride (in the acetic acid–water mixture of the experiments) to liquid cycloheptane and gaseous hydrogen chloride is thus −79.6 kcal./mole.

The heat of formation of tropylium chloride can now be derived from known quantities. The heat of formation of gaseous hydrogen chloride[7] is −22.1 kcal./mole and that of liquid cycloheptane is −37.7 kcal./mole.[8] Consequently, the heat of formation of dissolved tropylium chloride is +19.8 kcal./mole.

Benzyl chloride, an isomer of tropylium chloride, has a heat of formation of −7.8 kcal./mole as the liquid.[9] The heat of solution in the solvent of the hydrogenation experiments is +0.4 kcal./mole, and the heat of formation in the dissolved state is therefore −7.4 kcal./mole. By adding the stabilization in the benzene ring (36 kcal./mole), the heat of formation of non-resonating benzyl chloride is obtained (+28.6 kcal./mole). This value may be taken as approximate for a non-resonating, covalently bonded tropylium chloride. Corrected for the stabilization energy of tropilidene (about 9.0 kcal./mole),[10] the heat of formation of covalently bonded tropylium chloride becomes 19.6 kcal/mole. An alternate way of deriving the heat of formation of covalently bonded tropylium chloride involves the assumption that the difference in the heat of formation of toluene and tropilidene (+31.2 kcal./mole) can be taken as an estimate of the difference in the heat of formation of benzyl chloride (−7.4 kcal./mole) and covalently bonded tropylium chloride. This approximation gives a heat of formation of +23.8 kcal./mole for the model. The balance between the ionized salt (+19.8 kcal./mole)[11] and th e covalently bonded molecule (19.6; 23.8 kcal./mole) emerges as a delicate one in agreement with two properties of the tropylium ion. One is the ease of sublimation of tropylium salts. Surprising at first sight, this property may find consistent explanation in the existence of appreciable concentrations of the volatile, covalent tropilidene derivative in equilibrium with the non-volatile tropylium salt. The second property is the well-recognized dependence of the existence of the tropylium ion on the nature of the accompanying Lewis base. If the bases are weak like chloride, bromide, perchlorate and fluoroborate, the compounds are salts, whereas stronger bases like acetate, cyanate and cyanide afford covalent tropilidene derivatives.

The heat of formation of the isomeric, unknown benzylcarbonium chloride can be approximated by taking the activation energy of the acetolysis of benzyl chloride as a maximum value for the difference in heat content of covalent and ionic forms. We wish to emphasize that this procedure is valid only to the extent that the transition state in the solvolysis is proceeding toward an ionized state that closely resembles, in association and solvation, tropylium chloride in the hydrogenation solvent. Winstein[12] reports 24.0 kcal./mole as the heat of activation, whence the maximum heat of formation of benzylcarbonium chloride is +16.6 kcal./mole. Assuming the validity of this approach and granting further that the difference in heat content may be equated with the difference in free energy, the benzylcarbonium ion is more stable, thermodynamically, than tropylium ion by at least 3.2 kcal./mole. This result is the more interesting in view of the contrary conclusion recently considered by Meyerson, Rylander, Eliel and McCollum.[13] Although the heat of formation of benzylcarbonium ion, estimated in this way, is lower than that of tropylium ion, the contribution of benzene resonance to the heat of formation of benzyl chloride is so large that benzylcarbonium salts are highly unstable thermodynamically relative to their covalent derivatives, in contrast to the tropylium–tropilidene situation.

The heat of solvation of aqueous tropylium ion is of interest. In this ion, the charge is spread evenly over a regular heptagonal ring of carbon atoms in a way that may lend itself to theoretical calculation. Expressed in general terms, which permit continual correction of uncertain heats as they may be changed in the future, the heat of solvation, assuming complete dissociation of tropylium chloride in water, is given by

---

[7] "Selected Values of Chemical Thermodynamic Properties," Circular 500 of the National Bureau of Standards, U. S. Printing Office, Washington, D. C., 1958, pp. 22–23.

[8] H. L. Finke, D. W. Scott, M. E. Gross, J. F. Messerly and G. Waddington, THIS JOURNAL, **78**, 5469 (1956).

[9] F. W. Kirkbride, *J. Appl. Chem.* (*London*), **6**, 11 (1956).

[10] R. B. Turner, W. R. Meador, W. von E. Doering, L. H. Knox, J. R. Mayer and D. W. Wiley, THIS JOURNAL, **79**, 4127 (1957).

[11] The heat of solution of the solid sample in the acetic acid–water mixture of the hydrogenation was determined to be +2.1 kcal./mole, whence the heat of formation of solid tropylium chloride is at least as low as +17.7 kcal./mole.

[12] Professor S. Winstein, private communication.

[13] S. Meyerson, P. N. Rylander, E. L. Eliel and J. D. McCollum, THIS JOURNAL, **81**, 2606 (1959).

$$\Delta H_{\text{solv}}\ C_7H_7^+ = \Delta H_f\ C_7H_7^+Cl^-(\text{aq.}) - \Delta H_f\ Cl^-(\text{aq.}) - \Delta H_f\ C_7H_7^+(\text{g})$$

where $\Delta H_f\ C_7H_7^+Cl^-$(aq) is +17.6 kcal./mole and $\Delta H_f Cl^-$(aq), the heat of formation of aqueous chloride ion, is presently accepted as −147 kcal./mole.[14] $\Delta H_f\ C_7H_7^+$(g), the heat of formation of gaseous tropylium ion, has been sought extensively and ingeniously, but without definitive result.[15] If one assumes the mass peak 91 in the mass spectrum of tropilidene to be tropylium ion, then the appearance potential of this mass combined with the heat of formation of tropilidene vapor[8] corresponds to a heat of formation of gaseous tropylium ion of $+230.4 \pm 2.3$ kcal./mole.[15c] This figure is maximal to the extent that activation energy is required for the dissociation of tropilidene molecule ion to a hydrogen atom and tropylium ion, that excess kinetic energy may be present in these products, or that the products may be in excited electronic levels. Combining this value for the heat of formation of tropylium ion in the gas phase with the figure given above, the heat of solvation in water becomes −64 to −68 kcal./mole. Quite recently, it has been shown[13] that all carbon atoms in the mass 91 fragment from benzyl halides are identical and that the mass number is likewise to be associated with the tropylium structure. Combining the appearance potentials of $C_7H_7^+$ (223.0 ± 1.2 kcal./mole) from benzyl bromide [15a] with the heat of formation of benzyl bromide vapor determined by Benson and Buss[16] (20.0 kcal./mole and the most reliable value in our opinion) and taking ΔH_f Br· to be 26.7 kcal./mole, the heat of formation of tropylium ion in the gas phase becomes 216.3 ± 1.2 kcal./mole and the heat of solvation −50.5 to −53.0 kcal./mole. It is not worth trying to assign a more precise value at this time. Attention has been directed at the doubtful points on which the assignment depends and as these become resolved and more precisely defined in the future, more reliable values may be given to the heat of solvation.

Let it be sufficient to indicate that the heat of solvation of tropylium ion is relatively small (Li^+, 121.2; Na^+, 94.6; K^+, 75.8; Rb^+, 69.2 and Cs^+, 62.0 kcal./mole[14b]). Were it a spherical ion, the approach of Latimer, Pitzer and Slansky[14b] could be used to calculate the heat of solvation. The highest value is obtained by assuming a diameter equal to that of the thickness of the benzene ring. This is given as 3.40 Å.[17] and leads to a heat of solvation of −66 kcal./mole. By taking the diameter of the tropylium ring (assuming C–C, 1.41 Å.; C–H, 1.10 Å., van der Waals radius of H, 1.20 Å.) to be 7.70 Å., a heat of solvation of −35 kcal./mole is obtained. Finally, roughly approximating an elipsoid by taking $[(3.85 + 0.85)^2\ (1.70 + 0.85)]^{1/3}$ as the radius leads to a heat of solvation of −43 kcal./mole. The lowest evaluation of the heat of formation of tropylium ion vapor, +207 kcal./mole,[13] leads to a heat of solvation of −43 kcal./mole.

An abnormally high heat of solvation (100–150 kcal./mole) might have encouraged the assumption of significant covalent bonding of water molecules to tropylium ion functioning as a type of Lewis acid. The fact that both theory and experiment fall in the same low range affords sufficient grounds for excluding special bonding between tropylium ion and water as the source of its stability.

Horst Prinzbach warmly acknowledges the generous support of the International Co-operative Administration under a program administered by the National Academy of Sciences. Thanks are due Dr. J. L. Franklin, Humble Oil and Refining Co., Baytown, Tex., for his valuable counsel.

Tropylium Chloride—sample A—was prepared according to Doering and Knox.[5] A solution of about 3 g. of this sample in 12 cc. of acetonitrile, which had been dried by distillation from phosphorus pentoxide and then from anhydrous potassium carbonate, was cooled to −60°. The chloride crystallized in needles, sufficiently heavy to permit simple decantation of the solvent under a nitrogen atmosphere. The yield of essentially colorless material recrystallized twice in this manner (**sample B**) was about 0.1 g.

The acetic acid employed in these experiments was prepared by prereduction over platinum oxide and distillation. The forerunner was discarded, but no attempt was made to ascertain the residual water content of the solvent.

Heats of hydrogenation given in Table I were measured by the previously described procedure.

TABLE I

HEATS OF HYDROGENATION, 25°

Compound, tropylium	H_2 absorbed, mmoles	Theory, %	$-\Delta H$, kcal./mole
Bromide[a]	3.912	98.0	88.92
Bromide[a]	3.904	96.0	89.20
		Average	89.06
Chloride[b] (sample A)	3.192	74.3	86.17
Chloride[b] (sample A)	3.064	74.3	86.29
		Average	86.23 ± 0.08
Chloride[b] (sample B)	3.500	90.4	86.57
Chloride[b] (sample B)	3.993	89.9	85.62
		Average	86.10 ± 0.48

[a] Solvent is 225 ml. of stock acetic acid. [b] Solvent is 225 ml. of stock acetic acid with 0.3 ml. of water added.

Heats of solution were obtained by breaking scaled samples of the various compounds into the appropriate solvents in the hydrogenation calorimeter at 25°.

The heat of solution of tropylium chloride in the hydrogenation solvent was obtained for sample A just prior to the hydrogenation runs. The average of the two determinations was $+2.06 \pm 0.09$ kcal./mole. Since the tropylium chloride did not absorb the theoretical amount of hydrogen, the heat of solution was calculated on the basis of tropylium chloride actually present in the samples, this value being obtained from the hydrogen uptake data. The heat of solution of tropylium chloride in water was determined to be +0.10 kcal./mole (calculated on the basis of 90.2% of purity) by dissolving a 96.2-mg sample in 200 ml. of water.

Samples of 4.01 *N* aqueous hydrochloric acid containing 1.16 mmoles of hydrogen chloride gave a value of $+17.9 \pm 0.31$ kcal./mole of hydrogen chloride for the heat of solution in stock acetic acid. The particular concentration of acid chosen gives a solution containing approximately the same amount of hydrogen chloride and of water as that present at the conclusion of the hydrogenation experiments. In order to obtain the heat of transfer of hydrogen chloride from the aqueous solution to solution in the hydrogenation solvent

(14) (a) J. L. Franklin, *Trans. Faraday Soc.*, **48**, 443 (1952); (b) W. M. Latimer, K. S. Pitzer and C. M. Slansky, *J. Chem. Phys.*, **7**, 108 (1939).

(15) (a) F. P. Lossing, K. U. Ingold and I. H. S. Henderson, *ibid.*, **22**, 1489 (1954); (b) F. H. Field and J. L. Franklin, *ibid.*, **22**, 1895 (1954); (c) S. Meyerson and P. N. Rylander, *ibid.*, **27**, 901 (1957); (d) P. N. Rylander, S. Meyerson and H. M. Grubb, THIS JOURNAL, **79**, 842 (1957).

(16) S. W. Benson and J. H. Buss, *J. Phys. Chem.*, **61**, 104 (1957).

(17) D. J. Cram, N. L. Allinger and H. Steinberg, THIS JOURNAL, **76**, 6132 (1954); see especially footnote 14.

(and hence, the heat of solution of gaseous hydrogen chloride in the latter medium), the heat of mixing of water with acetic acid is required. Two samples of water (282.8 and 255.1 mg.) were therefore dissolved in 225 ml. of stock acetic acid. The heat of mixing obtained from these experiments was found to be +9.1 ± 0.01 cal./11.8 mmoles of water, which is the amount transferred per millimole of hydrogen chloride when 4.01 *N* aqueous chloride is employed.

The heat of solution of cycloheptane in 225 ml. of the hydrogenation solvent, obtained from two determinations (220.3 and 226.4 mg. of cycloheptane), is +1.52 ± 0.09 kcal./mole. The heat of solution of benzyl chloride in the same solvent (two determinations, 385.8 and 297.7 mg.) is +0.42 ± 0.06 kcal./mole.

HOUSTON, TEXAS
NEW HAVEN, CONN.

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF THE UNIVERSITY OF NORTH DAKOTA AND HOFSTRA COLLEGE]

A Simple Method for the Direct Oxidation of Aromatic Amines to Nitroso Compounds[1]

BY RICHARD R. HOLMES AND RAYMOND P. BAYER

RECEIVED OCTOBER 15, 1959

A convenient method for the direct oxidation of a number of 2,6-dichloro- and 2,6-dibromo- aromatic amines to the corresponding nitroso compounds is described. The reagent is a mixture of glacial acetic acid and ordinary 30% aqueous hydrogen peroxide, with or without addition of catalytic amounts of sulfuric acid. The procedure consists of simply allowing the reactants to stand at room temperature (or warming slightly) and then filtering off the crystalline product. Use of the same reagent under more vigorous conditions is shown (two examples described in detail) to produce nitro compounds in good yield.

Although the direct oxidation of aromatic amines to nitroso compounds has been carried out successfully many times[2] with Caro's acid, the simple procedure described in the present communication is new. Emmons[3] has recently described a somewhat similar, though experimentally more complex, procedure for the direct oxidation of cyclohexylamine to bisnitrosocyclohexane. This was the only example of an aliphatic amine which could be oxidized directly to the nitroso compound. All other examples cited by Emmons were prepared *via* oxazirane intermediates. In the present method a solution of the amine in a mixture of glacial acetic acid and 30% aqueous hydrogen peroxide, with or without a catalytic amount of sulfuric acid, was warmed slightly (or allowed to stand at room temperature) for several hours. During this time crystals of the (dimeric) nitroso compound gradually separated from solution, and the product was isolated (in most cases) by simply filtering off the crystals. The method required a minimum of experimental manipulation, the simplest apparatus, and was well-suited for production of the nitroso compounds on a large scale.

The experimental results are summarized in Table I. No attempt was made to determine the optimum conditions for nitroso compound production, and no doubt the yields listed in the table could be substantially improved.

The advantage of the direct oxidation procedure is well illustrated by the example of tribromonitrosobenzene. Our simple method produced the compound from tribromoaniline in one step and in 80.8% yield. The crude product was of good quality even before recrystallization. The only method previously described in the literature, that of von Pechman and Nold,[4] involved five steps from the same starting material and proceeded *via* the diazonium salt, tribromobenzene, tribromonitrobenzene and tribromophenylhydroxylamine. The over-all yield was very low.

It was also found possible to oxidize tribromoaniline directly to the nitroso compound with Caro's acid, but the yield was only about one-third that obtained with the acetic acid–hydrogen peroxide reagent.

The direct oxidation of amines to aromatic *nitro* compounds by means of peroxy acids has been described many times,[5] most recently in a series of studies by Emmons[6] of the oxidizing action of peroxytrifluoracetic and peroxyacetic acids. It is therefore interesting that under the mild conditions used in the present study one can stop the reaction at the nitroso stage.

Under more vigorous conditions and by extending the reaction time it was possible to prepare nitro compounds directly from the amines by use of the 30% hydrogen peroxide–acetic acid reagent. An advantage of this reagent over those recommended for the same purpose by Emmons is that it does not involve preformed peracetic acid or use of the potentially hazardous 90% hydrogen peroxide.[7] Although the oxidation of several amines[8] to the corresponding nitro compounds has been successfully carried out in these laboratories using the acetic acid–30% peroxide reagent, the oxidation of only two—3,5-dibromo-4-amino-benzonitrile and 3,5-dichloro-4-aminobenzonitrile—is described in detail. The yield of pure nitro compound from the former amine was 68%, and from the latter, 83%. In each case the oxidation proceeded *via* the nitroso compound, which was not isolated. These nitroso compounds were prepared and characterized but,

---

[1] Abstracted in part from the M.S. Thesis of Raymond P. Bayer, University of North Dakota, 1957.

[2] A. von Baeyer, *Ber.*, **33**, 124 (1900); **34**, 855 (1901); H. H. Hodgson and J. S. Wignall, *J. Chem. Soc.*, 2216 (1927); W. D. Langley, *Org. Syntheses*, **22**, 44 (1942).

[3] W. D. Emmons, THIS JOURNAL, **79**, 6523 (1957).

[4] H. von Pechmann and A. Nold, *Ber.*, **31**, 562 (1898).

[5] J. D'Ans and A. Kneip, *ibid.*, **48**, 1144 (1915); F. P. Greenspan, *Ind. Eng. Chem.*, **39**, 847 (1947); E. Bamberger and F. Tschirmer, *Ber.*, **32**, 1675 (1899); W. D. Langley, *Org. Syntheses*, **22**, 44 (1942).

[6] W. D. Emmons, THIS JOURNAL, **79**, 5528 (1957); **76**, 3470 (1954).

[7] The referee has kindly pointed out that it is standard safety practice to work with an explosion proof shield when handling any quantity of *either* 30 or 90% peroxide.

[8] 2,4,6-Tribromoaniline, 2,4,6-trichloroaniline and 2,6-dichloroaniline: unpublished work, present authors.