Chesebro[12] first showed its importance in oxidation reactions. Taylor and Lavin[5] and others[5] found that potassium chloride would not recombine hydrogen atoms but would cause recombination of hydroxyl radicals. Pease[13] also showed that potassium chloride surfaces decreased the rate greatly and eliminated peroxide in the hydrogen–oxygen reaction. Frost and Alyea[14] observed a higher explosion limit at a given temperature for the hydrogen–oxygen reaction when a potassium chloride-coated container was used. The effect of different salt-coated surfaces has also been shown by von Elbe and Lewis.[15] In addition to these observations, many others of a similar nature have been made. All of these results indicate that the specific action of potassium chloride or other salt is that of a dry surface. In the present experiments it was found that surfaces of lithium, sodium and potassium chlorides prepared in the same way gave essentially identical result. In addition, a fresh Pyrex surface resulted in approximately halving both the peroxide and water formed (results in Figs. 3 and 4 were obtained with an essentially wet Pyrex surface).

An interesting observation was made in regard to the effect of oxygen on the chemiluminescence occurring on some of the surfaces. With a clean Pyrex surface a very faint green-blue luminescence occurred on the surface of the main reaction trap at temperatures of 150° and higher. With a potassium chloride coated surface the luminescence was much more pronounced. No surface luminescence was observed with phosphoric acid as the coating. When the oxygen flow was cut off, the luminescence disappeared completely for the Pyrex surface and was many times less intense for the potassium chloride surface. The reaction accompanying luminescence cannot be a reaction leading to water or peroxide since the luminescence was strongest when the peroxide and water were formed in least quantity.

Summary

1. In the low-temperature reaction (−196°) between atomic hydrogen produced by electrical discharge and molecular oxygen the rate of peroxide and water formation is proportional to the oxygen concentration at low oxygen concentrations.

2. At temperatures slightly above −196° water formation increases at the expense of a decrease in peroxide formation.

3. A mechanism involving initial formation of the unstable intermediate complex $[\mathrm{HO{-}OH}]^*$ is proposed to account for both water and peroxide formation.

4. Hydrogen and oxygen both present in the discharge lead to similar results.

5. The effect of Pyrex, phosphoric acid and potassium chloride surfaces at higher temperatures has been studied. The effects have been attributed to the relative amounts of water present on the three surfaces. Surfaces of lithium, sodium and potassium chloride gave essentially similar results.

6. This effect of the surface in leading to a decrease in peroxide and water has been attributed to destruction of OH (or possibly HO_2) in addition to H recombination to give molecular hydrogen and oxygen.

7. The chemiluminescence occurring on the chloride coated surfaces is dependent on oxygen and is strongest when peroxide and water are formed in least amounts.

PRINCETON, N. J. RECEIVED MAY 10, 1948

[12] R. N. Pease and P. R. Chesebro, *Proc. Nat. Acad. Sci.*, **14**, 472 (1928).

[13] R. N. Pease, THIS JOURNAL, **52**, 5106 (1930).

[14] A. A. Frost and H. N. Alyea, *ibid.*, **55**, 3227 (1933).

[15] G. von Elbe and B. Lewis, *J. Chem. Phys.*, **10**, 366 (1942).

[CONTRIBUTION FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

Studies on Carbon Black. II. Grignard Analysis[1]

BY D. S. VILLARS[2]

Introduction

Analysis by means of Grignard reagent, developed by Kohler, Stone and Fuson,[3] has found extensive application in problems of organic chemistry. It was suggested by Dr. R. H. Gerke that this technique might be of value if applied to a study of oxygen on carbon black. In the present paper a report is given of the results of such a study.

It is well-known that commercial carbon blacks contain varying amounts of volatilizable matter. Some of this is loosely bound, being held by van der Waals (unactivated) adsorption and comes off on heating to 110°. The remainder is tightly bound, being held by activated adsorption and requires heating to around 1000° for liberation. This tightly bound portion of the volatilizable matter is conventionally called "volatile matter" in the carbon black and rubber industry. The present discussion concerns only the latter, chemically adsorbed material. About two-thirds of the tightly bound volatilizable matter is oxygen, the bulk of the remainder being attributable to

[1] For Part I, see THIS JOURNAL, **69**, 214–217 (1947).

[2] Present address: Jersey City Junior College, Jersey City 4, N. J.

[3] Kohler, Stone and Fuson, THIS JOURNAL, **49**, 3181 (1927); **52**, 3736 (1930).

carbon coming off with the oxygen as carbon oxides. A study of the distribution of this oxygen among the different possible types of bonds would appear to be of great fundamental importance to the understanding of the behavior of carbon black in rubber.

Experimental Technique

The Grignard analysis is accomplished by adding a measured quantity of standardized Grignard reagent (MeMgI) to a weighed sample, in the absence of oxygen and of moisture. The apparatus was a copy of Fig. 1 of Kohler and Richtmyer.[4] The gas evolved during the reaction of the carbon black with Grignard reagent is collected and measured in a gas buret. The Grignard reagent taken up irreversibly by the carbon can be quantitatively estimated by difference on measuring the methane evolved from the unused Grignard reagent after the latter has been treated with an excess of water. Throughout the present work it is assumed that each hydroxyl and each carbonyl group on the carbon black surface behaves like similar groups in (small) organic molecules. The gas liberated during the reaction between carbon black and Grignard reagent is thus taken to be a measure of hydroxyl oxygen and the amount of Grignard irreversibly taken up is considered to be a measure of the number of carbonyl groups. This neglects the possibility of steric effects preventing reaction of some carbonyl groups which might conceivably be too close together.

In view of descriptions already published of the apparatus and its operation, it will not be necessary to recount here the details of operation in the present work. Instead, attention will merely be called to a few precautions that were found necessary because of the fact that measurements are made on a suspension of a finely divided solid in an inert liquid (xylene) and not on a true solution.

a. **Solubility of Methane in Xylene.**—In order to achieve adequate contact between the Grignard reagent and the carbon black it was necessary to suspend the latter in an inert liquid. The solubility of the evolved methane in that liquid had therefore to be taken into consideration. It was found that methane has an appreciable solubility in xylene. Standardizations with xylene present were always lower than when no xylene was present, the discrepancy being proportional to the amount of xylene used. Assuming Henry's law, an absorption coefficient, α, was determined experimentally from a series of runs where the amount of xylene was varied.

$$\alpha = \frac{(a - x)/V_l}{x/V_g} \qquad (1)$$

In equation (1)

a = total milliequivalents (mq.) methane liberated
x = mq. methane remaining undissolved in xylene
V_l = volume of liquid
V_g = total volume of gas.

The solubility of methane in the xylene can now be corrected for by multiplying the observed (apparent) volume of methane liberated by a correction factor, F, given by

$$F \equiv a/x = 1 + \alpha V_l/V_g \qquad (2)$$

The value of α found experimentally was 0.803—some 60% higher than a value interpolated from Landolt–Börnstein (IIa, 487). Our high value might be partly due to a higher solubility of methane in xylene in the presence of isoamyl ether, which was used as the solvent for the Grignard reagent.

b. **Adsorption of Nitrogen on the Black.**—The apparatus was regularly dried by sweeping out with purified nitrogen. It was found that a small amount of this nitrogen would adsorb through the xylene onto the carbon black suspended in it. This adsorbed nitrogen was subsequently liberated, on boiling the suspension, bringing about high apparent values of hydroxyl oxygen.[5] The maximum amount adsorbed by standard MPC black (*i. e.*, a channel black with average diameter about 300 Å.) was about 2 ml. (standard conditions) per gram of black. Much greater amounts were adsorbed by ink blacks. To obviate this error, the suspension had to be boiled vigorously and returned to room temperature immediately before establishing the "zero" volume from which to start computations. (In general, it was not necessary to determine the volume before boiling unless one desired data on the amount of adsorption.) The temperature was adjusted to 26° by surrounding the reaction flask with a water-bath. A rigid time schedule was adhered to in all steps of the procedure. The volume readings had to be reproducible within 0.1 ml. with no drift during a five-minute interval before the next step of the analysis was undertaken. Columns 4 and 5 of Table I list some data obtained on nitrogen adsorption during investigation (d) below. Nitrogen was driven off by boiling the black suspension after installing the sample flask on the Grignard apparatus. The suspension was then allowed to stand a measured length of time under nitrogen. This time is listed in column 5 as "Diffusion Time." The suspension was then boiled again to drive off the nitrogen which had adsorbed

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[4] Kohler and Richtmyer, This Journal, **52**, 3737 (1930).

[5] That the gas liberated on addition of Grignard was methane and not more of this adsorbed nitrogen was demonstrated by qualitative tests kindly undertaken by G. S. Buettner and R. R. Hampton of these laboratories. Unfortunately, no analysis was made of the gas evolved during the actual runs in the present work. Accordingly, the hydroxyl content of the carbon black deduced in the present work must, strictly speaking, be considered as merely an upper limit of the true value. However, the ease with which nitrogen could be rapidly removed by boiling xylene and the fact that "hydroxyl" oxygen, as determined by Grignard, correlates well with water liberated at 950° make it unlikely that the gas evolved during the run was contaminated with any appreciable amount of adsorbed nitrogen. Also, if the gas evolved contained appreciable amounts of nitrogen released by selective adsorption of Grignard, the latter should have come back into solution during the subsequent titration with water. Chances would have been high, under such circumstances, that some of the blacks of the wide range investigated, would have given negative carbonyl values. This never occurred.

during this period. The volume, per gram, reduced to standard conditions, driven off from the sample of weight given in column 3 is listed in column 4. In the run where no heating nor topping of xylene was applied, ∞ is used to signify that in this particular case the diffusion time of the nitrogen was not controlled by the preliminary boiling in the apparatus before the usual one used to establish the volume zero of the determination.

TABLE I

EFFECT OF DRYING AND BOILING PROCEDURE ON GRIGNARD ANALYSIS OF STANDARD MPC BLACK

Xylene boiling time, min.	Run	Sample, g.	Cc. N_2 liberated S. C. per gram black	Diffusion time, hours	μq.[a]/gram		
					OH	O	Total
No oven dehydration							
0	17	1.3057	3.38	∞	592	98	690
5	7	1.2100	1.50	3.9	247	293	540
10	16	1.9116	1.64	18.8	165	223	388
20	3	1.2102	1.98	282	179	268	447
60	2	1.2861	1.88	139	193	215	408
70° Oven							
0	13	1.6800	1.95	120	266	219	485
5	5	2.2419	0.99	4	192	168	360
10	12	1.8071	1.11	3.8	180	220	400
20	14	1.6068	0.80	3.1	157	247	404
60	19	1.3186	1.11	3.5	192	235	427
105° Oven							
0	6	1.0544	2.08	288	280	261	541
5	18	1.0496	2.07	4.8	336	332	668
10	11	1.1471	2.08	18.5	194	246	440
20	4	1.0854	0.85	3.2	166	326	492
60	15	1.0413	2.04	18.3	188	264	452
140° Oven							
0	1	1.0866	2.22	144	328	292	620
5	20	1.8259	1.53	18.3	174	198	372
10	10	1.5268	1.07	4.1	185	240	425
20	9	0.9916	1.77	18.3	211	247	458
60	8	2.3143	0.71	3	145	197	342

[a] μq = microequivalents.

c. Rate of Liberation of Active Hydrogen.—A longer time of boiling with Grignard reagent was found to be necessary when analyzing a suspension of carbon black than when analyzing a soluble substance. Tests at varying lengths of time showed maximum liberation of methane on twenty minutes boiling.

d. Drying and Boiling Procedure.—Ordinarily, carbon black samples hold about 3% of loosely bound moisture. Such water, if not removed, would react with Grignard reagent and register an equivalent amount of hydroxyl oxygen. It was therefore desirable to investigate effects on the Grignard analysis of details of the drying procedure. Samples of standard MPC black were dried sixteen hours at the three different temperatures, 70, 105 and 140°. An undried control was also included.

The xylene used to suspend the sample was always topped in a stream of purified nitrogen (with the sample present) before attaching the sample flask to the Grignard apparatus. In the present exploratory experiment, time of boiling the xylene was also varied from zero to sixty minutes. The order of carrying out the temperature-time combinations was carefully randomized to accord with the principles enumerated by R. A. Fisher for a factorial experiment[6] and the conclusions were checked by variance and covariance analysis.

Table I gives the results of this factorial experiment. The computations may be illustrated by those for hydroxyl oxygen for run 2. In this run 6.15 cc. of methane was evolved from 1.2861 g. of black. Correcting for methane solubility, this becomes 7.27 cc. Reduction to standard conditions gives 6.58. From this was subtracted the reduced volume of gas observed during the corresponding (blank) step in the standardization run, 1.0 cc. The difference, 5.56, divided by the weight of black, 1.2861, and by 0.0224 cc./μq gives 193 μq/g., the value recorded for hydroxyl oxygen for this run. If per cent. oxygen is desired the number of μq/g. is multiplied by 0.0016.

The number of μq/g. being 44.6 times the standard conditions volume of methane evolved, one may compare, if he wishes, the volume of methane evolved with the amount of nitrogen desorbed on boiling by dividing the μq./g. figure listed in column 6 of Table I by 44.6. (Similarly, the volume of methane per gram of black may be computed from per cent. hydroxyl oxygen in Table II by dividing by 0.0714.)

According to the data of Table I, there is no dependence of result on size of sample and it is unnecessary to dry the black in an oven if the suspension is boiled ten minutes in the xylene. Accordingly, in the investigation reported below, the practice was followed of boiling undried samples ten minutes in the xylene in the presence of a stream of purified nitrogen.

Results

Various commercial and experimental blacks (see Part I) were compared, not only by Grignard analysis, but also by analysis of the gases volatilized at 1000°. Column 1 of Table II designates the blacks investigated, in accordance with the standard terminology recently introduced (see Part I and note at bottom of present Table II).

Column 2 of Table II lists the specific surface of each black in square meters per gram as determined by the Emmett method.[7] We are indebted to Prof. P. H. Emmett for determining those values designated by *c*. Prof. Emmett used nitrogen. The other values designated by *b* were de-

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[6] R. A. Fisher, "The Design of Experiments," 2nd Ed., Oliver and Boyd, London, 1937; F. Yates, "Design and Analysis of Factorial Experiments," Imperial Bureau of Soil Science, England, Technical Communication No. 35 (1937); see also ref. 7, Part I.

[7] Brunauer, Emmett and Teller, THIS JOURNAL, 60, 309–319 (1938).

Table II

Oxygen Distribution, %

		By Grignard analysis		By diff.	By sweeping with N_2 at 1000°			
(1) Black[a]	(2) Sp. S. sq. m./g.	(3) -OH	(4) =O	(5) -O-	(6) H_2O	(7) CO_2	(8) CO	(9) Total
Thermal	21.3[c]	0.09	0.11	0.09				0.29
Exptl. 1	110[b]	.00	.03	0.057	0.009	0.03	0.05	0.087
EPC 1	100[c]	.27	.34	3.32	.54	1.36	2.02	3.93
MPC 1	112[c]	.33	.37	3.16	.55	1.40	1.92	3.86
MPC 2	118[c]	.40	.39	2.27	.24	1.55	1.28	3.06
MPC 3	122[c]	.25	.34	2.32	.28	0.92	1.67	2.91
MPC 4	122[c]	.30	.33	2.96	.29	1.41	1.89	3.59
MPC 5	134[c]	.33	.40	1.39	.19	1.25	0.69	2.12
MPC 6	140[c]	.33	.41	3.23	.41	1.50	2.07	3.97
Exptl. 2	147[b]	.46	.40	2.51	.06	1.53	1.79	3.37
Mean		.28	.31					
MPC 7	126[b]	.27	.29	2.62	.28	1.20	1.64	3.18
HPC 1	197[b]	.24	.29	2.49	.06	1.32	1.59	3.02
EPC 2	103[b]	.28	.32	3.70	.52	1.49	2.20	4.30
HPC 2	175[b]	.18	.26	1.90				2.34
MPC 8	119[b]	.21	.29	3.12				3.62
MPC 9	122[b]	.24	.34	2.49				3.07
Mean		.23	.30					
Color	422[b]	.60	.63	2.70	.009	1.38	2.29	3.93

[a] Following standard terminology, EPC blacks are easy processing channel blacks differing in manufacturer and lot; MPC, medium processing channel; HPC, hard processing channel. See L. H. Cohan, *Chem. Eng. News*, 23, 2078–85 (1945). See part I, first paragraph under "Results," for further description of blacks. [b] Determined using butane. [c] Determined using nitrogen.

termined in this laboratory by means of butane. They have been corrected to nitrogen by multiplying our butane values by 1.5 (see note (1) of Table II of ref. 1).

The results of duplicate Grignard determinations are listed in columns 3 and 4. All values are calculated to per cent. (grams oxygen per 100 grams black). The standard deviation, together with the number of degrees of freedom upon which it is based, is a quantitative measure of the reproducibility of the determination.[8] As estimated from variance analysis of the first group of ten blacks run in duplicate, the standard deviation (with 11 degrees of freedom), per individual determination is 0.051 and 0.037% absolute for columns 3 and 4, respectively. Per mean of two it is 0.036 and 0.026% absolute respectively. These standard errors include sampling fluctuations as well as errors of measurement. Among the latter are included a grouping correction for the fact that the gas buret could only be read within 0.1 cc. Except for the first two low oxygen blacks in the Table, correction for the latter is of negligible importance, however, only amounting to one to two per cent relative.

Columns 6, 7, 8 and 9 of Table II give the results of single determinations of total oxygen content. In the latter analysis, the black was heated to 1000° in the presence of a stream of purified nitrogen and the amounts of liberated water, carbon dioxide and carbon monoxide were determined by the usual procedure of successive absorption of water and of carbon dioxide, before and after passing the effluent gas over heated copper oxide. The proportionate amount of oxygen in each constituent is recorded as grams oxygen per hundred grams black. Column 9 gives the sum of columns 6, 7 and 8. The standard deviation of the total oxygen content, column 9, as estimated from another series of determinations with 21 degrees of freedom, is 0.23% absolute. This includes sampling variability of the carbon black.

Column 5 records the amount of oxygen not accounted for by Grignard analysis. The values are the differences between the figures in column 9 minus those of columns 3 and 4. The values in column 5 are subject to greater absolute error than those in columns 3 and 4 not only because they are *differences* between measurements which have error but because the samples upon which the total oxygen determinations were made were different from those upon which the Grignard analyses were performed. The sampling variability of total oxygen content, however, is not great enough to invalidate our conclusions in regard to the relative amount of active and inactive oxygen.

The data of columns 3 and 4 in the table show that the amount of carbonyl oxygen is greater than hydroxyl oxygen. This conclusion is supported as being statistically significant by Fisher's procedure of variance analysis.

Discussion

It is to be concluded from the present results that only about 26% of the tightly bound oxygen (*i. e.*, by activated adsorption) on the black is reactive toward methylmagnesium iodide. Estimates of the area occupied per oxygen atom lead one to infer that the surface of ordinary channel black is covered by one unimolecular layer of oxygen. Since ether oxygen is not reactive toward Grignard, the implication is strong that most of the oxygen on this layer is tied down by different carbon atoms by such bonds. Dr. Hugh M. Smallwood suggests the possibility that these ether oxygen atoms may constitute bridges between the edges of the graphite planes where they jut into the surface of the particle.

Although the great majority of the oxygen is unreactive toward Grignard, the minor reactive part may well be of importance to the behavior of carbon black in rubber.

Comparison of the different types of oxygen liberated on heating to 1000° (columns 6, 7 and 8 of Table II) with the types existent on the surface at room temperature (columns 3, 4 and 5) show order of magnitude correlation between oxygen liberated as water above 950° and hydroxyl oxygen. There is no correlation among the other

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(8) For those not used to quantitative statistical measures, it may be of help to point out that the mean range within sub-groups of three to ten replicated (repeated) samples—"range" is the difference between the maximum and minimum values within a group—lies within 4% of the standard deviation of the totals of the sub-groups. The standard deviation of a total of *n* being equal to the square root of *n* multiplied by the standard deviation per individual observation, the mean range for groups of four would thus be twice the standard deviation per individual observation. See R. G. Newton, *Chemistry & Industry*, Oct. 20 (1945), pp. 322–323.

types of oxygen. This is confirmed in another group of data not recorded here, in which the volatile oxygen analyses were carried out on the same samples of black as those on which the Grignard analyses were run. We therefore seem to be justified in concluding that the distribution of oxygen (other than hydroxyl) obtained from the analysis at 1000° is defined by the pyrolytic equilibrium obtaining at the temperature at which the bulk of the gases come off. It has no relationship to the distribution of bonds prevailing naturally upon the black before it is heated. The observed ratio of $CO:CO_2$ corresponds to an equilibrium temperature between 600 and 800°. Actually, the gases come off in differing ratios as the temperature is increased. Most of the carbon dioxide is evolved between 500 and 600° and most of the monoxide comes off between 600 and 700°. This is in accord with what one should expect from the equilibria prevailing at these different temperatures.

Acknowledgment.—Thanks are expressed to Dr. Hugh M. Smallwood for helpful advice during the prosecution of this investigation. The author is also greatly indebted to G. S. Buettner and R. R. Hampton for the proof that the gas liberated on addition of Grignard was actually methane.

Abstract

Different types of tightly bound oxygen on carbon black have been distinguished by Grignard analysis. Carbonyl oxygen tends to be from 13 to 30% greater in amount than hydroxyl oxygen for all blacks. About 26% of the total content of tightly bound oxygen is accounted for by Grignard analysis. The greater part of the oxygen on the black is thus more or less chemically inert.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF TORONTO]

The Reaction between Formaldehyde and Ammonia

BY H. H. RICHMOND, G. S. MYERS AND GEORGE F WRIGHT

Although it is accepted that the final condensation product of formaldehyde and ammonia is hexamine, there have been several opinions concerning other substances which may form from these reagents and which may be intermediates in the hexamine synthesis. Thus Duden and Scharf[1] believed that formaldehyde and ammonia condensed to methylolamine, I, or methyleneimine, then trimerized to cyclotrimethylenetriamine, II. Further methylolation of this intermediate would then produce trimethylolcyclotrimethylenetriamine, III, which on condensation with ammonia would form hexamine, IV. These opinions have been endorsed by Baur and Ruetschi[2] who carried out kinetic studies on hexamine formation and designated it as a third order reaction.

Duden and Scharf found that freshly-prepared formaldehyde–ammonia mixtures did not act like aqueous hexamine solution. Thus their equimolar mixture of alkali-neutralized ammonium chloride and formaldehyde would not form 1,5-endomethylene-3,7-di-[*m*-nitrobenzenediazo]-1,3,5,7-tetrazacyclooöctane, V, as does hexamine, by reaction with diazotized *m*-nitroaniline. Furthermore this ammonia–formaldehyde solution gave, with benzoyl chloride, 1,3,5-tribenzoyl-1,3,5-triazacyclohexane, VI, and only a trace of the 1,3,5-tribenzoyl-1,3,5-triazapentane, VII, which this acid chloride gave with hexamine. Both hexamine, IV, and the Duden–Scharf solution, II, gave 1,3,5 - trinitroso - 1,3,5 - triazacyclohexane, VIII, when treated with an excess of nitrous acid, but the yield[3] from IV was only 24% and that from the solution assumed to contain II was 47% on the formaldehyde basis.[3a] We found the work of Duden and Scharf to be completely reproducible, but we have increased their yield of VI from II to 23% of theoretical, by a fortunate crystallization separation from the 12% of other product, methylene dibenzamide, IX.

Duden and Scharf believed formaldehyde–ammonia solution to consist essentially of cyclotrimethylenetriamine II. Henry,[4] on the other hand, considered that the liquid he obtained by drying an equimolar solution of aqua ammonia and formaldehyde with potassium carbonate was pure trimethylolamine, X. We have found it impossible that he could have had a pure compound, since rigorous drying with potassium carbonate removes formaldehyde and ammonia as well as water, and hexamine, IV, eventually is formed. Actually Table I shows that his solutions varied from 20–50% in water. Indeed, we found, by analysis for formaldehyde and ammonia[5] of what we shall for convenience call Henry solution, that, instead of an excess of formaldehyde, as predicted by formula X, the molar ratio of formaldehyde to ammo-

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[1] P. Duden and M. Scharf, *Ann.*, **288**, 218 (1895).

[2] E. Baur and W. Ruetschi, *Helv. Chim. Acta*, **24**, 754 (1941).

[3] F. Mayer, *Ber.*, **21**, 2883 (1888).

[3a] This latter contrast may not be entirely valid since Duden and Scharf, unlike Mayer, skimmed off the unstable trinitroso compound before it could decompose. The difference in manipulation does not, however, in our experience, account for the entire yield difference.

[4] L. Henry, *Bull. acad. roy. méd. Belg.*, 721 (1902).

[5] Hans Meyer, "Nachweis und Bestimmung organischer Verbindungen," Springer, Berlin, 1933, p. 51. We are indebted to Drs. Carmack, Kuehl and Leavitt, University of Pennsylvania, for advice on applicability of this method to our compounds.