Coloration and Decarboxylation of the Aniline Salts of 2, 4, 6-Trinitrobenzoic Acid in Ketones and Other Solvents

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Molecular compounds of aromatic polynitro compounds with aromatic hydrocarbons and with aromatic amines have been reported by many authors⁽¹⁾ and a number of molecular compounds of 1, 3, 5-trinitrobenzene⁽²⁻⁴⁾, 2, 4, 6-trinitrotoluene⁽⁵⁾, 2, 4, 6-trinitroanisole⁽⁶⁾, picric acid⁽⁷,⁸⁾, etc., have been investigated, but little has been known of 2, 4, 6-trinitrobenzoic acid (TNBA) complexes. So the present author studied TNBA complexes and found that, while several aromatic hydrocarbons and phenols form normal molecular complexes with TNBA, aniline, as expected, forms salts when one mole of aniline is added to one mole of TNBA.

The TNBA salts of anilines decompose into the complexes of 1, 3, 5-trinitrobenzene (TNB) with anilines and carbon dioxide on heating in solution or in the crystalline state, and the decarboxylation is extremely fast in ketonic solvents even at low temperatures. Moreover, a striking dark red color is produced in ketonic solvents. From the investigation of the relation

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1) Extensively reviewed by L. J. Andrews, *Chem. Revs.*, **54**, 713 (1954).

2) H. Kronberger and J. Weiss, *J. Chem. Soc.*, **1948**, 464.

3) B. R. Brown and D. L. Hammick, *J. Chem. Soc.*, **1948**, 1395.

4) H. M. Powell and G. Huse, *J. Chem. Soc.*, **1943**, 435.

5) J. Landauer and H. McConnel. *J. Am. Chem. Soc.*, **74**, 1221 (1952).

6) E. Hertel et al., *Ber.*, **61**, 1545 (1928); **63**, 2446 (1930).

7) O. L. Baril and E. S. Hauber, *J. Am. Chem. Soc.*, **53**, 1087 (1931).

8) R. Kuhn and A. Winterstein, *Helv. Chim. Acta*, **11**, 144 (1938).

between the coloration and the rates of decarboxylation in various solvents it has been found that there are two types of coloration. The color of the first type occurs immediately after the dissolution of a salt in a pure ketone, accompanying very rapid decarboxylation, its intensity decreasing rather rapidly. The color of the other type occurs some time after the dissolution of the salt in an alcohol or in a mixed solvent containing an alcohol, when the decarboxylation is completed and almost all the TNBA has decomposed, its intensity increasing gradually. The spectra of the colors of both types resemble each other in shapes but differ in the locations of the absorption maxima. The measurments of the rates of the decarboxylation of the complexes of TNBA with anilines also showed that the decarboxylation in ketones is extremely rapid.

2, 4, 6-Trinitrobenzoates of Aniline and Substituted Anilines and their Decomposition into Corresponding Trinitrobenzene Complexes on Fusion. — A colorless crystalline substance was obtained when one mole of aniline and one mole of TNBA, both in cold acetone solution, were mixed, while a red mass was obtained from one mole of TNBA and two moles of aniline. The colorless substance was proved to be a 1 : 1 compound by analysis (Found: N, 18.09%, Calcd: N, 18.30%). The infrared absorption spectrum indicated that this compound is a salt[9]; namely it showed no absorption near 1725 cm^{-1} (carbonyl stretching frequency of the carboxyl group), and 1270 cm^{-1}, but absorption bands at 1600 cm^{-1} and 1380 cm^{-1} (antisymmetric and symmetric stretching frequencies of the carboxylate ion). (See Fig. 1 for the infrared spectra of the TNBA salts of aniline and pyridine.) The molecular compounds[10] of TNBA with benzene, naphthalene and chrysene have acid type carbonyl absorptions near 1730 and 1270 cm^{-1}. The 2 : 1 compound also showed no absorption near 1730 cm^{-1} but more experiments are required for further information.

TABLE I. INFRARED SPECTRA OF TNBA AND ITS SALTS

Compound	Infrared absorption by carboxyl group, cm^{-1} $\nu_{C=O}$	$\nu_{CO_2^-}$		ν_{C-O} or δ_{O-H}
TNBA	1737			1272
Sodium salt		1603	1310	
Aniline salt		1603	1370	
N-Methylaniline salt		1600	1348	
N, *N*-Dimethylaniline salt		1600	1326	
p-Toluidine salt		1597	1366	
p-Anisidine salt		1605	1366	
p-Bromoaniline salt		1603	1372	
Pyridine salt		1602	1353	

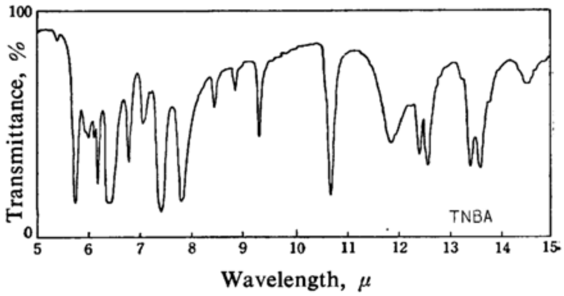

Fig. 1a.

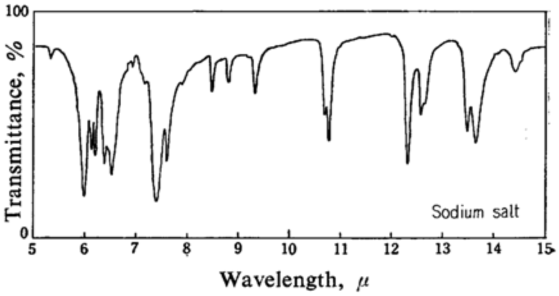

Fig. 1b.

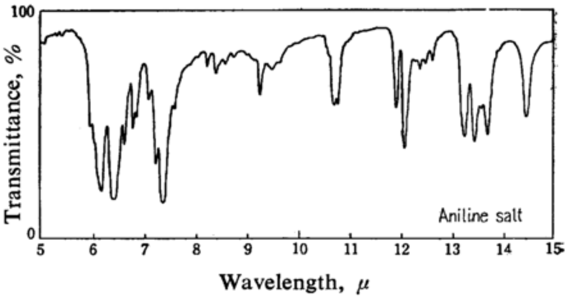

Fig. 1c.

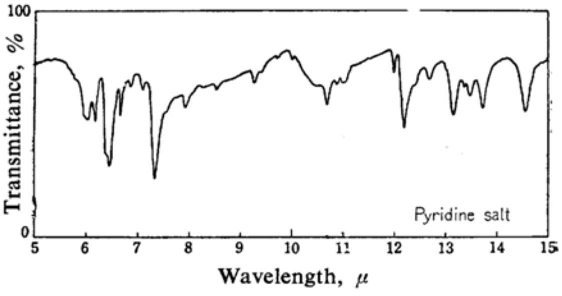

Fig. 1d.

Fig. 1. Infrared spectra of 2, 4, 6-trinitrobenzoates.

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9) The salt form is proved mainly by the absence of the bands at 1730 and 1270 cm^{-1}, because the bands at 1600 and 1360 cm^{-1} overlap with the strong bands of the nitro group.

10) These molecular compounds will be described later.

2, 4, 6-Trinitrobenzoates of substituted anilines were also prepared and compared in the infrared spectra with the sodium and ammonium salts of TNBA (Table I and Fig. 1), which showed that all of these colorless 1:1 compounds are salts.

The 2, 4, 6-trinitrobenzoates decomposed at their melting points and changed into an orange-yellow or red liquid. The orange-yellow crystalline substance melting at 127°C, obtained from the melt of the aniline salt, was identified with the TNB-aniline complex. Other salts also gave the corresponding TNB complexes.

TABLE II. COLORATION OF ANILINE SALTS OF TNBA IN VARIOUS SOLVENTS

Solvents	2, 4, 6-Trinitrobenzoate of Aniline	*N*-Monoethyl-aniline	*N, N*-Diethyl-aniline
Acetone	+	+	+
Methyl ethyl ketone	+	+	+
Acetophenone	+	+	+
Benzophenone	+	+	+
Cyclohexanone	+	+	+
Ethyl acetoacetate	+	+	+
Benzaldehyde	+	+	+
Acetaldehyde*	−	−	
Pinacolone	+	+	+
p-Ethylacetophenone	+	+	+
Ethanol	−	−	−
Amyl alcohol	−	−	−
Ethylene chlorohydrin		−	
Allyl alcohol	−	−	
Triethylene glycol	±	±	±
Glycerol	−	−	−
Diethylene glycol monoethyl ether	±	±	±
Ethylene bromide	−	−	−
Chloroform	−	−	−
Benzyl chloride	−	−	
Chlorobenzene	−	−	
Nitrobenzene	+	+	+
Nitromethane	+	+	+
Ether	−	−	−
Dioxane**	+	+	+
Anisole	−	−	−
Petroleum ether	−	−	−
Benzene	−	−	−
Acetic anhydride	−	−	−
Carbon disulfide	−	−	−

* 50% aqueous solution

** The color is much paler than in ketonic solvents.

The sign + is for rapid coloration, the sign ± is for slow coloration (about one hour after heating) and the sign − is for no coloration.

Coloration and Decarboxylation of the Aniline Salts of TNBA in Various Solvents. — The aniline salt of TNBA could be recrystallized from boiling benzene without coloration, but a dark red color appeared when boiling acetone was used as the solvent for recrystallization, an orange crystalline substance being obtained from the colored solution after spontaneous evaporation of acetone and was again identified with the TNB-aniline complex by the melting point and by the X-ray diffraction pattern (Table IV). On the other hand, the free TNBA could be recrystallized from boiling acetone without decomposition; and, therefore, the aniline salt form is essential for the unusual

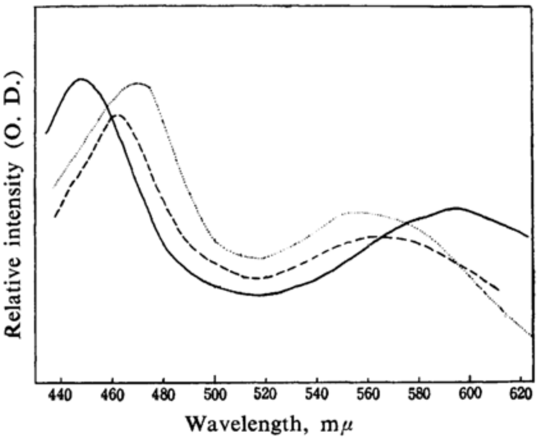

Fig. 2a.

Aniline salt of TNBA
- in acetone ——
- in triethylene glycol ……
- in a mixture of 60% acetone and 40% ethanol ----

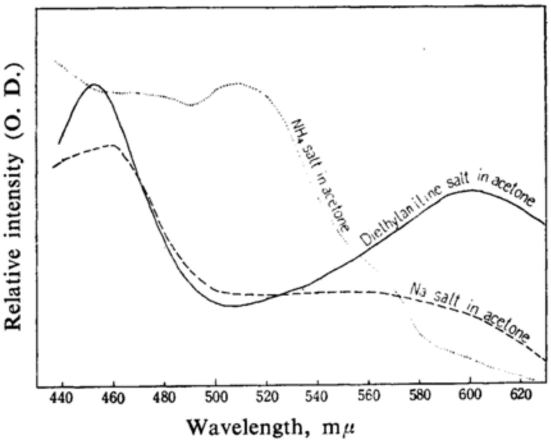

Fig. 2b.

Dimethylaniline salt ——
Ammonium salt ……
Sodium salt ----
} in acetone.

Fig. 2. The visible spectra of TNBA salt in various solvents.

TABLE III. ABSORPTION SPECTRA OF THE ANILINE SALTS OF TNBA

Compound	Solvent*	Absorption maxima, mμ		
TNBA-aniline	A	447.5	595	
	MEK	450	595	
	Dioxane	442.5	595	
	Triethylene glycol	470	552	
	Nitromethane	448	590	
	Ethanol	475	550(sh)	
	A90%-E10%	464	570	
	A80%-E20%	463	565	
	A40%-E60%	465	560	
TNBA-*N*-monomethylaniline	MEK	447	598	
	Ethanol	465	555(sh)	
	MEK75%-E25%	464	560	
TNBA-*N*, *N*-diethylaniline	MEK	452	605	
Na salt of TNBA	MEK	456	560(sh)	
NH_4 salt of TNBA	MEK	470	505	520(sh)
		560(sh)		

* "A" is for acetone, "MEK" for methyl ethyl ketone and "E" for ethanol.

TABLE IV. X-RAY DIFFRACTION PATTERNS OF THE DECARBOXYLATION PRODUCTS

Compounds	Diffraction angles, 2θ (Relative intensities)*
TNB-Aniline:	13.10(1.00), 14.26(0.22), 14.96(0.17), 18.54(0.55), 22.02(0.13), 22.75(0.11), 24.43(0.17), 25.48(0.28), 27.82(9.34), 30.55(0.15)
The decarboxylation products of TNBA salt of aniline	13.60(1.00), 14.30(0.29), 14.95(0.19), 18.60(0.82), 22.05(0.26), 22.40(0.25), 24.54(0.35), 25.52(0.50), 27.82(0.58), 30.58(0.30)

* Relative intensities to the strongest diffracted beams are in parentheses.

TABLE V. RESULTS OF THE ELEMENTARY ANALYSES OF 2, 4, 6-TRINITROBENZOATES

Compounds	m. p. °C	N calcd.	N found
Aniline salt	156	16.00	16.19
p-Anisidine salt	155~6	14.73	14.88
p-Bromoaniline salt	129	13.43	13.2
p-Toluidine salt	158	15.38	15.22
N-Methylaniline salt	148	15.38	15.33
N, *N*-Dimethylaniline salt	158	14.81	14.75
Pyridine salt	174	16.67	16.95

facility of decarboxylation of TNBA in ketones.

In order to investigate what kind of solvent produces the particular red color, 5 mg. of a salt was added in 2 ml. of a solvent (if insoluble, the salt was suspended in the solvent), and then the whole was heated for 5 sec. on a water bath of 60°C. If the red did not appear markedly immediately after heating, the

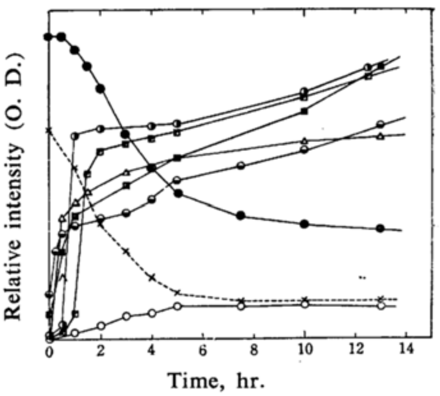

Fig. 3. Intensity change of the color produced by dissolving the aniline salt of TNBA in acetone-ethanol mixture. (at 38°C) *

—◓— 90%, 460 mμ	—◪— 20%, 460 mμ
—■— 80%, 460 mμ	—○— 0% (ethanol), 460 mμ
—△— 60%, 460 mμ	—●— 100%, 450 mμ
—◐— 40%, 460 mμ	---×--- 100%, 600 mμ

* This figure shows the changes of the absorption intensities of the solutions. Time after dissolution of the salt is plotted on the horizontal axis; while the relative intensity at constant wavelength (mostly at 460 mμ) on the vertical axis. The percentages in this figure indicate volume percentages of acetone in ethanol: for example, "90%, 460 mμ" means that a mixed solvent consists of 90% of acetone and of 10% of ethanol is used for the measurement of the intensity change, and the measurement is done at 460 mμ.

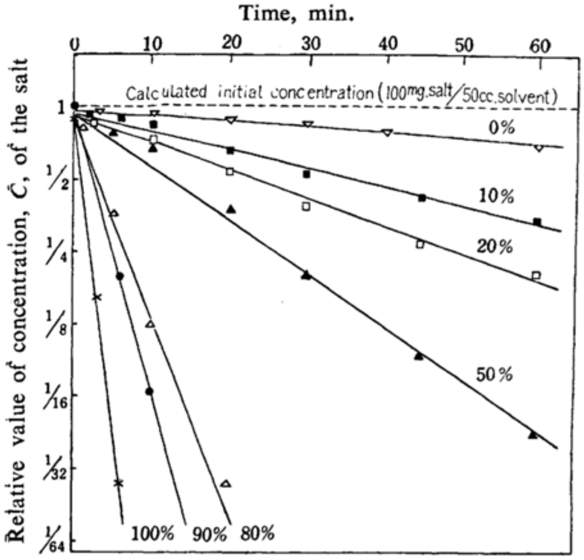

Fig. 4. Rates of decarboxylation of aniline salt of TNBA in acetone-ethanol mixed solvent.*

* The logarithmic value of relative concentration referred to the calculated initial concentration is plotted on the vertical axis. The percentages on the figure indicated acetone content in the mixture, the remainder is ethanol only.

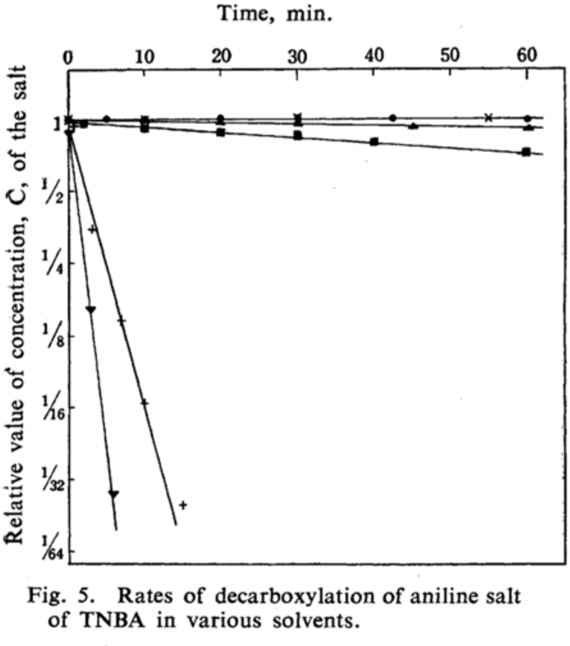

Fig. 5. Rates of decarboxylation of aniline salt of TNBA in various solvents.

—×— in water
—■— in ethanol
—●— in dioxane
—+— in methyl ethyl ketone
—▲— in methanol
—▼— in acetone

color was observed after heating at 50°C for 3 up to 60 min.

Dark red coloration was instantly observed when a carbonyl or nitro compound was used as the solvent. Some alcohols and ethers also produced a red color on longer heating. The color in ketones is so intense immediately after heating that very small amounts of a ketone and the aniline salts are needed for the color reaction and it gives a method for the qualitative detection of ketones. Nevertheless, this method requires ketones of high purity, so the utilization is limited. Some nitro compounds, ethers and alcohols also produced coloration, but the greenish red color in ketones and nitro compounds seemed to be different from the red color in alcohols. Results of the color reaction in various solvents are summarized in Table II.

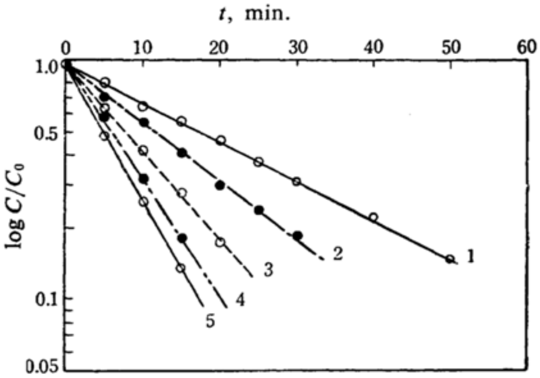

Fig. 6. The rates of decarboxylation of *p*-substituted aniline of TNBA in acetone 30°C.

C_0: intial concentration (about 0.004 mol./l.)
C: concentration at time t.
t: time after the beginning of the reaction.
1: *p*-Br, 2: *p*-NO_2, 3: *p*-Me,
4: H, 5: *p*-MeO

Then, the absorption spectra of the aniline salts in various solvents were measured. Some of the spectra are illustrated in Fig. 2 and the locations of the absorption maxima are given in Table III. The spectra of the aniline salt of TNBA in a pure ketone or nitromethane, measured immediately after dissolution and warming, had absorption maxima at 447.5 and 595 mμ, and their intensities (extinction coefficients) decreased as time passed. On the other hand, the spectra of the salt in alcohols had absorption maxima at 465 and 565 mμ and their intensities gradually increased as time passed. From these experimental results it was certain that there were two types of coloration, so the time dependence of the absorption intensity was measured with the results given below.

Relation between the Rate of Decarboxylation and Coloration of the Aniline Salts of TNBA in Various Solvents.—The relation between the decarboxylation and the coloration of the TNBA salt of aniline was investigated by measuring the rate of decarboxylation and the change of absorption intensity. The decarboxylation is extremely fast in ketones (Fig. 5). The rate of decarboxylation is in the order: acetone $>$ methyl ethyl ketone $>$ ethanol $>$ methanol $>$ dioxane. Measurements of the change of absorption intensity revealed that the intensity in pure ketones is reduced fast, while the color in the acetone-ethanol mixture, though not very intense at the beginning, becomes intense gradually. The more acetone the mixed solvent contains, the more promptly the coloration occurs, while, the more ethanol is present in the solvent, the more intense the absorption of the solution becomes. However the coloration is hardly observed in pure ethanol. On the other hand, since the decarboxylation of the aniline salt proceeds without any coloration in many other solvents at higher temperatures, the color is not essential for the decarboxylation, but the unusual facility of decarboxylation with simultaneous coloration in ketones suggests different mechanisms of the two types of decarboxylation.

The decarboxylation of the TNBA salts of substituted anilines were also examined with the results shown in Fig. 6.

To examine the nature of the intermediate compounds of the decarboxylation, the TNBA salts of some *p*-substituted anilines were prepared and the rates of decarboxylation were measured. The order of the decarboxylation rates is almost parallel to that of the coloration rates. Namely, ammonium salt $\ll$ *p*-nitroaniline salt $<$ *p*-bromoaniline salt $<$ aniline salt $<$ *p*-anisidine salt for the coloration, and *p*-bromoaniline salt $<$ *N, N*-dimethylaniline salt $<$ *p*-nitroaniline salt $<$ *N*-methylaniline salt $<$ *p*-toluidine salt $<$ aniline salt $<$ *p*-anisidine salt for the decarboxylation.

The order of the decarboxylation rates is not simply in the order of basicity of the anilines.

Experimental

Qualitative Tests for the Coloration. — To examine a solvent in the coloration, about 5 mg. of the aniline salt of TNBA was dissolved in 2 ml. of the solvent and the solution was heated for 30 seconds in a water bath of 60°C. If the salt was not completely dissolved, a suspension was used. All solutions in ketones produced dark red color instantly on heating. When no coloration occurred, the solution was examined after heating at 50°C for 3 minutes and 60 minutes. To test a solution in ether or other volatile solvents, the solution was heated under reflux on a water bath.

Visible Spectra of the Color. — Visible spectra were measured in the range of wavelength from 420 to 625 mμ. with a Beckman DU type quartz spectrophotometer. Determination of the band envelopes and locations of the absorption maxima were the main purpose of the spectral measurements, while the exact determination of the absolute values of intensities was less important and only relative intensities were needed for the present discussions, since the intensities of the absorption bands changed rather rapidly.

Infrared Spectra of the Salt. — The infrared spectra were determined with an Infracord infrared spectrophotometer or with a Baird Model B infrared spectrophotometer. All measurements were made in solid state; the potassium bromide pellet method was employed in most measurements, and the mull method in a few measurements. Nujol and hexachlorobutadiene were used as mulling agents, because they compensate each other, the whole wavelength region between 2.5 and 15 μ thus being covered without interference of the absorption bands of the mulling agents.

Preparation of the Materials and Determination of the Rates.—All salts were prepared by the following procedure: TNBA[12] in acetone and an equivalent amount of a base in the same solvent were mixed in an ice bath and the precipitated salt was collected by filtration as rapidly as possible, washed first with a small amount of cold acetone and then with benzene, and dried in a vacuum desiccator. The salts prepared in this way were analytically pure (Table V) and can be used in the spectral and other measurements. The rate of decarboxylation was determined by titrating the unchanged acid with a standard alkali in aqueous solution, methyl red being used as the indicator without interference by the anilines.

X-ray Diffraction Measurements.—Powder X-ray diffraction patterns were obtained with a Norelco X-ray diffractometer. Diffraction angles and relative intensities of the diffracted beams are listed in Table IV.

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[11] Similar spectra are observed with TNB and 2, 4, 6-trinitroanisole in ethanol solution containing sodium ethoxide. R. Foster, *Nature*, **176**, 746 (1955); **183**, 1042 (1959).

[12] 2, 4, 6-Trinitrobenzoic acid is prepared by the method described in "Organic Syntheses" [H. T. Clarke and W. W. Hartman, "Org. Syntheses", Col. Vol. I, p. 543 (1941)].