308. *Studies in Qualitative Organic Analysis. Part II. Identification of Alkyl Halides, Aromatic Nitroso-compounds, Aromatic Hydrocarbons, and* cyclo*Pentadiene Compounds.*

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Methods are given for the identification of alkyl halides as *S*-alkyl*iso*thiourea picrates and of aromatic *C*-nitroso-compounds as 3-arylimino-2-phenylindolenines and *p*-bromoazobenzenes. Tests are recommended for the detection of aromatic hydrocarbons and these tests are shown to be characteristic, as they are given even by highly purified compounds. A colour test for compounds containing the *cyclo*pentadiene nucleus is described.

(i) It was shown (Brown and Campbell, J., 1937, 1699) that alkyl bromides and iodides can be satisfactorily identified as alkyl*iso*thiourea picrates, and we have now improved and extended the method so that tertiary compounds and chlorides are included. The melting points of the derivatives are more convenient than those of the *N*-alkylsaccharins used by Merritt, Levey, and Cutter (*J. Amer. Chem. Soc.*, 1939, **61**, 15) for the same purpose. Ethyl*iso*thiourea picrate was obtained from *tert.*-butyl and *iso*valeryl halides owing to interaction with the solvent, as shown by the formation of methyl*iso*thiourea picrate when methyl alcohol replaced ethyl alcohol as solvent. Methyl and ethyl chloroformates gave methyl- and ethyl-*iso*thiourea picrates respectively.

(ii) Various reagents were investigated for the identification of aromatic *C*-nitroso-compounds by condensing them with compounds containing reactive methylene groups. The methylene group in 2 : 7-dibromofluorene (Sieglitz, *Ber.*, 1920, **53**, 1232) is very reactive and condenses readily with *C*-nitroso-compounds, but on the small scale the products were difficult to purify, probably owing to formation of both anils and nitrones (cf. Schönberg and Michaelis, J., 1937, 627; Bergmann, *ibid.*, p. 1628; Thorneycroft, Thesis, London, 1927; Barrow and Thorneycroft, this vol., p. 770). 2-Phenylindole in presence of alkali condenses readily with nitroso-compounds (Angeli and Morrelli, *Centr.*, 1908, **12**, 605) to form anils, and these are suitable for identifying nitrosobenzene and its *m*- and *p*-substituted derivatives. The azo-compounds formed by condensation of nitroso-compounds with *p*-bromoaniline (Ingold, J., 1925, **127**, 516) were found to be the most suitable derivatives for identification.

(iii) 2 : 4 : 5-Trinitrotoluene is a valuable reagent for the alkylamines (Brown and Campbell, *loc. cit.*), but not for aromatic amines. The more easily accessible 2 : 3 : 5-trinitro-*p*-xylene is not so reactive with aliphatic amines.

(iv) The fluorescence of many organic compounds (*e.g.*, fluorene) is due to traces of impurities. In view of the use of fluorescence in qualitative work, we purified several aromatic hydrocarbons by chromatographic adsorption to find if thorough purification diminished or removed the fluorescence. This was necessary in view of Dutt's claim (*J. Indian Chem. Soc.*, 1930, **7**, 505) that extensive purification of certain aromatic and heterocyclic compounds removed their fluorescence, which returned only when the compounds were exposed to air. In no case did we observe any change in fluorescence even when some of the compounds studied by Dutt were purified several times by the chromatographic method. Dutt's conclusions seem improbable in the light of other investigations; *e.g.*, he claimed to have obtained pure anthracene which did not fluoresce in ultra-violet light, but Weigert and Jäckh (*Naturwiss.*, 1927, **15**, 124) showed that anthracene is converted into dianthracene in ultra-violet light, the increase in reaction velocity being inversely proportional to the decrease in fluorescence.

(v) The colours obtained by the addition of sulphuric acid, or of sulphuric acid and benzylidene chloride (Lippmann and Pollak, *Monatsh.*, 1902, **23**, 670), to aromatic hydrocarbons were given when the latter were highly purified, and these tests, together with the fluorescence in benzene solution, are valuable aids for detection and identification.

(vi) Vanscheidt (*Chem. Abs.*, 1935, **29**, 2160) gives a test for *cyclo*pentadiene and compounds, such as indene and fluorene, containing the *cyclo*pentadiene nucleus. We have found this test to be somewhat untrustworthy, but if *p*-dinitrobenzene is added to Vanscheidt's reagent (methyl-alcoholic potassium hydroxide and acetone or pyridine) characteristic green or blue colours are obtained with *cyclo*pentadiene, etc. The mere presence of a methylene group is insufficient to give the test, as negative results were obtained with diphenylmethane, acenaphthene, etc. It was first thought that the test was due to the formation of a potassium salt, but this in itself is insufficient, since indene, phenylacetylene, and 9-phenylfluorene all have the same degree of acidity (Conant and Wheland, *J. Amer. Chem. Soc.*, 1932, **54**, 1216) but only indene gives a positive test. Of special interest is truxene, the structure of which has not yet been established. It gives a positive test with our reagent, and this confirms the structure assigned in Beilstein's "Organische Chemie" (cf. Stobbe and Zschoch, *Ber.*, 1927, **60**, 457).

EXPERIMENTAL.

Unless otherwise stated, compounds were prepared by standard methods and had the properties given in the literature. M. p.'s were determined in Kofler's apparatus (*Mikrochem.*, 1934, **15**, 242). Most of the analyses were done by Mr. W. Brown, Edinburgh.

Preparation of S-*Alkyl*iso*thiourea Picrates.*—Finely powdered thiourea (1 g.), alkyl halide (1 g.), and ethyl alcohol (10 c.c.) were refluxed for a period depending on the nature of the alkyl halide (see following table). Picric acid (1 g.) was then added, and the mixture heated until a clear solution was obtained and cooled. If no precipitate separated, a few drops of water were added. The picrates crystallised from alcohol in yellow needles or prisms. In the majority of cases the method can easily be applied with 0·2 g. of alkyl halide.

S-*Alkyl*iso*thiourea Picrates.*

Alkyl halide.	Formula.	M. p.	Time.	N, %, found.	N, %, calc.
Methyl iodide		224°	5 mins.		
Ethyl iodide		188	5 mins.		
Ethylene dibromide		260	15 mins.		
n-Propyl bromide		177	5 mins.		
n-Propyl chloride *	$C_{10}H_{13}O_7N_5S$	176	5 hrs.	19·9	20·2
*iso*Propyl bromide		196	3 hrs.		
Propylene dibromide *	$C_{11}H_{15}O_7N_7S_2$	232	40 mins.	23·2	23·3
n-Butyl bromide		177	5 mins.		
n-Butyl chloride	$C_{11}H_{15}O_7N_5S$	177	2 hrs.	19·5	19·4
*iso*Butyl iodide		167	10 mins.		
sec.-Butyl iodide *		166	10 mins.		
tert.-Butyl iodide †	$C_{11}H_{15}O_7N_5S$	188	3 hrs.	20·8	21·0
*iso*Butylene dibromide *	$C_{12}H_{17}O_7N_7S_2$	223	1 hr.	22·1	22·5
n-Amyl bromide		154	20 mins.		
n-Amyl chloride	$C_{12}H_{17}O_7N_5S$	154	2 hrs.	19·0	18·7
*iso*Amyl bromide		173	20 mins.		
*iso*Amyl chloride *	$C_{12}H_{17}O_7N_5S$	173	2 hrs.	19·0	18·7
sec.-Amyl bromide		157	40 mins.		
*iso*Valeryl chloride †	$C_9H_{11}O_7N_5S$	187	3 hrs.	21·0	21·0
n-Hexyl bromide		157	20 mins.		
n-Heptyl bromide	$C_{14}H_{21}O_7N_5S$	142	20 mins.	17·4	17·4
n-Octyl bromide	$C_{15}H_{23}O_7N_5S$	134	20 mins.	16·5	16·8
Cetyl iodide	$C_{23}H_{39}O_7N_5S$	137	3 hrs.	13·4	13·2
Allyl chloride	$C_{10}H_{11}O_7N_5S$	155	5 mins.	20·5	20·3
Trimethylene dibromide	$C_{11}H_{15}O_7N_7S_2$	229	5 mins.	23·1	23·3
a-Phenylethyl bromide	$C_{15}H_{15}O_7N_5S$	167	5 mins.	17·4	17·1
β-Phenylethyl bromide	$C_{15}H_{15}O_7N_5S$	139	5 mins.	16·9	17·1
o-Bromobenzyl bromide	$C_{14}H_{12}O_7N_5BrS$	222	5 mins.	15·1	14·8
m-Bromobenzyl bromide	$C_{14}H_{12}O_7N_5BrS$	205	5 mins.	14·9	14·8
p-Bromobenzyl chloride	$C_{14}H_{12}O_7N_5BrS$	219	5 mins.	14·8	14·8
o-Chlorobenzyl bromide	$C_{14}H_{12}O_7N_5ClS$	213	5 mins.	15·6	16·3
m-Chlorobenzyl bromide	$C_{14}H_{12}O_7N_5ClS$	200	5 mins.	16·3	16·3
p-Chlorobenzyl bromide	$C_{14}H_{12}O_7N_5ClS$	194	5 mins.	16·4	16·3
Methyl chloroformate ‡		224	30 mins.		
Ethyl chloroformate †		187	30 mins.		

* Small yield. † *S*-Ethyl*iso*thiourea picrate. ‡ *S*-Methyl*iso*thiourea picrate.

Two compounds were further analysed: m-*chlorobenzyl*iso*thiourea picrate* (Found: C, 39·3; H, 3·4. $C_{14}H_{12}O_7N_5ClS$ requires C, 39·1; H, 2·8%), and o-*bromobenzyl*iso*thiourea picrate* (Found: C, 35·8; H, 2·7. $C_{14}H_{12}O_7N_5BrS$ requires C, 35·4; H, 2·5%).

Preparation of 3-Arylimino-2-phenylindolenines.—The nitroso-compound (0·5 g.) and 2-

phenylindole (0·5 g.) were dissolved in alcohol, the solution cooled, and a few drops of alcoholic potassium hydroxide added; a violent reaction occurred. The condensation product which separated was crystallised from alcohol. All formed orange needles, except the nitrosobenzene compound, which formed vermilion prisms.

3-Arylimino-2-phenylindolenines.

Nitroso-compound.	Formula.	M. p.	N, %, found.	N, %, calc.
Nitrosobenzene	$C_{20}H_{14}N_2$	154°	10·5	9·9
o-Chloronitrosobenzene	$C_{20}H_{13}N_2Cl$			
m-Chloronitrosobenzene	,,	148	9·25	8·85
p-Chloronitrosobenzene	,,	157	9·16	8·85
o-Bromonitrosobenzene	$C_{20}H_{13}N_2Br$			
m-Bromonitrosobenzene	,,	169	7·88	7·74
p-Bromonitrosobenzene	,,	154	7·93	7:74
o-Nitrosotoluene	$C_{21}H_{16}N_2$			
m-Nitrosotoluene	,,	136	9·64	9·46
p-Nitrosotoluene	,,	146	9·53	9·46

The following *compounds* were further analysed: nitrosobenzene derivative (Found: C, 84·5; H, 4·9. $C_{20}H_{14}N_2$ requires C, 85·1; H, 5·0%); *p*-chloronitrosobenzene derivative (Found: C, 76·1; H, 4·1. $C_{20}H_{13}N_2Cl$ requires C, 75·8; H, 4·1%); *p*-nitrosotoluene derivative (Found: C, 84·5; H, 5·7. $C_{21}H_{16}N_2$ requires C, 84·5; H, 5·6%).

p-Nitrosotoluene gave rise, not only to the anil, but also to a high-melting compound formed by the action of the potassium hydroxide used as condensing agent; this was separated from the anil by its insolubility in ether. Tedious separations with benzene gave three fractions, m. p. above 350°, m. p. 209—250°, and m. p. 190—245°. The middle fraction was crystallised several times from benzene and then melted at 215° with the exception of a very small quantity which melted at 250°. Analysis of the compound, m. p. 215° (Found: C, 72·03; H, 5·51; N, 11·77%), is not in good agreement with the results of Reissert (*Ber.*, 1909, **42**, 1371), who had isolated this compound and suggested the termolecular formula $C_{21}H_{19}O_2N_3$ (Calc.: C, 73·01; H, 5·55; N, 12·17%).

Attempts to obtain α-nitrosonaphthalene by the method of Willstätter and Kubli (*Ber.*, 1908, **41**, 1938) gave unsatisfactory results (cf. Neunhoeffer and Liebich, *Ber.*, 1938, **71**, 2247).

Preparation of Substituted p-*Bromoazobenzenes.*—These were obtained from *p*-bromoaniline and the various nitroso-compounds by Ingold's method (*loc. cit.*) and were purified from glacial acetic acid. 0·1 G. of nitroso-compound can easily be identified by this method.

Nitroso-compound.	Formula.	M. p.	N, %, found.	N, %, calc.
Nitrosobenzene		88°		
o-Chloronitrosobenzene	$C_{12}H_8N_2ClBr$	110	9·74	9·48
m-Chloronitrosobenzene	,,	119	9·46	9·48
p-Chloronitrosobenzene	,,	190	9·67	9·48
o-Bromonitrosobenzene	$C_{12}H_8N_2Br_2$	104	8·58	8·23
m-Bromonitrosobenzene	,,	126	8·16	8·23
p-Bromonitrosobenzene	,,	205		
o-Nitrosotoluene	$C_{13}H_{11}N_2Br$			
m-Nitrosotoluene	,,	82	10·3	10·2
p-Nitrosotoluene	,,	152	10·4	10·2

Preparation of 4 : 6-*Dinitro*-N-*aryl*-m-*toluidines.*—Prepared from aromatic amines and 2 : 4 : 5-trinitrotoluene by the method of Brown and Campbell (*loc. cit.*), these separated from alcohol as orange or yellow needles. Derivatives were obtained from the following amines (m. p.'s in parentheses): aniline (145°), *m*-toluidine (150°), *m*-xylidine (186°), and *p*-anisidine (139°). The method is not recommended, as amines such as *o*-toluidine did not yield derivatives.

Preparation of 3 : 5-*Dinitro*-N-*alkyl*-p-*xylidines.*—Difficulty was experienced in preparing 2 : 3 : 5-trinitro-*p*-xylene, for the purchased *p*-xylene contained considerable quantities of the *m*-compound. On oxidation of the xylene with potassium permanganate and esterification of the product with methyl alcohol, methyl terephthalate (m. p. 140°) was obtained, but the alcoholic filtrate after some time deposited the *iso*phthalic ester (m. p. 66°). Nitration of the xylene afforded a mixture which, crystallised from ethyl alcohol, yielded trinitro-*m*-xylene (m. p. 180°), whereas the filtrate on standing gave trinitro-*p*-xylene (m. p. 139°). In testing xylenes it is therefore advisable to use both oxidation and nitration.

2 : 3 : 5-Trinitro-*p*-xylene reacted in the same way as 2 : 4 : 5-trinitrotoluene towards aliphatic amines, the 2-nitro-group being replaced; *e.g.*, methylamine gave 3 : 5-*dinitro*-N-*methyl*-p-*xylidine* (Found: N, 18·7. $C_9H_{11}O_4N_3$ requires N, 18·7%). The reagent does not react

readily with many aliphatic amines, and is therefore not to be recommended for this class of compound.

Fluorescence and Colour Tests of Aromatic Hydrocarbons.—All fluorescence observations were made with ultra-violet light from a Hanovia mercury lamp provided with a filter to eliminate visible waves.

Several hydrocarbons were thoroughly purified by chromatographic adsorption, a 30-in. column packed with Brockmann's aluminium oxide being used. In some cases several purifications were effected. Fluorene (0·2 g. in 200 c.c. of benzene; developer, benzene) was obtained from the filtrate as a non-fluorescing compound. Naphthalene (0·5 g. in 250 c.c. of light petroleum; developer, same solvent) was obtained in the filtrate, and had a purple fluorescence. Anthracene [0·2 g. in 750 c.c. of light petroleum (b. p. 40—60°); developer, same solvent] was obtained in the filtrate and had a purple fluorescence; from the column, dianthracene, m. p. 230°, was obtained. When the purification was performed in the dark, no dianthracene was detected. Chrysene [light petroleum (b. p. 40—60°) as solvent and developer] was isolated from the filtrate and had a bright purple fluorescence. Pyrene [0·2 g. in 10 : 1 benzene–light petroleum (b. p. 40—60°); developer, 3 : 1 benzene–light petroleum] was obtained from the filtrate as a pure white substance (cf. Clar, *Ber.*, **1936**, **69**, 1684) with a vivid light green fluorescence; from the column, a minute amount of a yellow compound was obtained which gave colour tests for anthracene. 1 : 2-Benzanthracene (benzene as solvent and developer) was obtained from the filtrate and gave a purple fluorescence. In the treatment of 2 : 3-benzanthracene (0·2 g. in 500 c.c. of benzene; developer, benzene), the column became yellow and the side exposed to the window light turned orange. The orange compound was identified as 2 : 3-naphthaquinone, m. p. 188° (lit., 194°), by the red colour it gave with concentrated sulphuric acid. When the experiment was performed in the dark, the filtrate yielded the pure hydrocarbon with a slight green fluorescence, and from the tube some of the quinone was isolated.

The colours obtained with the purified hydrocarbons and sulphuric acid, and benzylidene chloride and sulphuric acid, were the same as those given by the unpurified compounds. The latter test is reliable only when standard conditions are used : one drop of benzylidene chloride is dissolved in benzene (10 c.c.), a few mg. of the compound added, and the mixture shaken. The colours obtained were in some instances different from those observed by Lippmann and Pollak (*loc. cit.*).

Benzylidene chloride test.

Compound.	Colour.	Compound.	Colour.
Diphenylmethane	Yellow	1 : 2 : 5 : 6-Dibenzfluorene	Yellowish-green
Diphenyl	Carmine-red	Phenanthrene	Violet
Retene	Violet	Perylene	Dark purple
Fluorene	Carmine-red	1 : 2-Benzanthracene	Reddish-brown
9-Phenylfluorene	Carmine-red	9 : 10-Benzphenanthrene	Purple
1 : 2-Benzfluorene	Green	Fluoranthene	Purple
3 : 4-Benzfluorene	Emerald-green		

No characteristic colours were obtained with benzopyrene, dibenzyl, hydrindene, 2 : 3-benzanthracene, or truxene. Quinones did not respond to the test.

Detection of cyclo*Pentadiene Derivatives.*—*p*-Dinitrobenzene (0·2 g.) was dissolved in pyridine (preferably) or acetone (100 c.c.), and to 3 c.c. of this solution a little of the compound to be

Colour test for cyclo*pentadiene derivatives.*

	Solvent.	
Compound.	Acetone.	Pyridine.
*cyclo*Pentadiene	Greenish-yellow	Greenish-yellow
Di*cyclo*pentadiene	—	Emerald-green
Indene	Emerald-green	Emerald-green
Fluorene	Blue → green	Emerald-green
2-Nitrofluorene	Prussian-blue	Greenish-blue
2-Bromofluorene	Blue → green	Dark green
2 : 7-Dibromofluorene	Prussian-blue → emerald-green	Greenish-blue
7-Bromo-2-nitrofluorene	Prussian-blue	Prussian-blue
2-Bromo-3-nitrofluorene	Blue → dark green	Prussian-blue
1 : 2-Benzfluorene	—	Green
3 : 4-Benzfluorene	Dark green	Emerald-green
1 : 2 : 5 : 6-Dibenzfluorene	Emerald-green	Emerald-green
Truxene	Dirty green	Emerald-green

tested was added; 3 drops of methyl-alcoholic potash (3 c.c. of alcohol containing 3 drops of 4N-alkali) were added, the colour noted, and then more alcoholic potash was added until no further change of colour occurred.

Negative results were obtained with 9-phenylfluorene, diphenylmethane, triphenylmethane, phenylacetylene, triphenylcarbinol, and acenaphthene.

Preparation of 2 : 4-*Dinitrobenzoic Acid.*—The method given by Brown and Campbell (*loc. cit.*) is not reliable (Storrie, private communication), the yield being profoundly affected by the nature and concentration of the nitric acid. Storrie's method (J., 1937, 1746) therefore remains the best available.

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