of water containing 20 g. of sodium hydroxide was refluxed with 24.2 g. (0.256 mole) of chloroacetic acid for three hours. The solution was acidified with hydrochloric acid, and the precipitate was stirred with sodium bicarbonate solution. The insoluble sodium salt of the monoacetic acid derivative was filtered from the solution. Acidification of the filtrate and the subsequent crystallization of the precipitate from dilute ethanol yielded 12.3 g. (33%) of the bis-(oxyacetic acid) monohydrate, m.p. 143–144°.

Anal. Calcd. for $C_{16}H_{22}O_6 \cdot H_2O$: C, 58.52; H, 7.37. Found: C, 58.35; H, 7.60.

3-Hydroxy-4(or 6)-*n*-hexylphenoxyacetic Acid.—This compound occurred as a by-product in the synthesis of the above bis-(oxyacetic acid). With equal moles of chloroacetic acid and hexylresorcinol in alkaline solution, poor yields of the monoacetic acid derivative were obtained. Accordingly, the following method was developed.[19] Sodium granules (11.5 g.) in 500 ml. of xylene, 5 g. of activated charcoal and 105 g. of 4-*n*-hexylresorcinol were mixed, allowed to stand at room temperature for two hours, and finally refluxed for one hour. Then 62.5 g. of ethyl chloroacetate was added and the mixture refluxed for one hour. Sodium hydroxide solution (500 ml. of 2.5 *N*) was added and the xylene was removed by distillation, the volume of the aqueous layer being kept constant by the addition of water. The solution was diluted with water, filtered, and poured into cold hydrochloric acid. The precipitate was stirred with sodium bicarbonate solution and the insoluble sodium salt was filtered off. After the solution was acidified to precipitate the free acid, the sodium bicarbonate treatment and acidification was repeated again. The product was crystallized from benzene. Concentration of the benzene mother liquor yielded additional product, which received the treatment just described; yield 49.0 g. (36%), m.p. 178–180°. It gave a positive test for a phenol with 2% phosphomolybdic acid and ammonium hydroxide.[20]

Anal. Calcd. for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99. Found: C, 66.40; H, 7.89.

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[19] By Donald L. Wright of Pitman–Moore Company.

[20] G. H. Stillson, D. W. Sawyer and C. K. Hunt, THIS JOURNAL, **67**, 306 (1945).

RESEARCH DEPARTMENT, PITMAN–MOORE COMPANY
DIVISION OF ALLIED LABORATORIES, INC.
INDIANAPOLIS, INDIANA H. ELDRIDGE FAITH

RECEIVED APRIL 30, 1952

Thiosemicarbazones of 5-Substituted Isatins[1]

5-Bromoisatin Thiosemicarbazone.—Addition of 10.5 g. (0.0465 mole) of 5-bromoisatin[2] dissolved in 150 ml. of glacial acetic acid to a warm solution of 4.25 g. (0.0465 mole) of thiosemicarbazide in 175 ml. of water and 10 ml. of glacial acetic acid gave an immediate precipitate. The mixture was heated under reflux for 30 minutes, cooled, and the yellow crystals recrystallized from ethyl acetate to give 10.0 g. (75%) of 5-bromoisatin thiosemicarbazone which decomposes at 273–275° (considerable darkening before decomposition).

Anal. Calcd. for $C_9H_7N_4OSBr$: N, 18.72. Found: N, 18.43.

5-Nitroisatin Thiosemicarbazone.—Nine grams (0.047 mole) of 5-nitroisatin[3] dissolved in 200 ml. of absolute ethanol was added to a warm solution of 4.3 g. (0.047 mole) of thiosemicarbazide in 125 ml. of water and 10 ml. of glacial acetic acid and the mixture refluxed for one hour. The aqueous ethanol solution upon cooling gave 11.5 g. (92%) of yellow crystals which did not melt below 350° despite considerable darkening at approximately 300°. An analytical sample was obtained by recrystallization from a water–pyridine solvent pair.

Anal. Calcd. for $C_9H_7N_5O_3S$: N, 26.32. Found: N, 26.15.

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[1] Contribution No. 554 from the Chemistry Laboratory of Indiana University. This work was supported by a contract between the Office of Naval Research, Department of the Navy, and Indiana University.

[2] 5-Bromoisatin, m.p. 255–256°, was prepared by the method of Borsche and Jacobs, *Ber.*, **47**, 360 (1914).

[3] 5-Nitroisatin, m.p. 253–255°, was prepared by the method of Baeyer, *ibid.*, **12**, 1312 (1879).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF INDIANA E. CAMPAIGNE
BLOOMINGTON, INDIANA WESLEY LEA ARCHER

RECEIVED JULY 11, 1952

2-Alkylnaphthalimides

2-Alkyl-(or N-alkyl)-naphthalimides have been prepared by refluxing naphthalic anhydride in an excess of the amine for one hour; with dodecylamine the temperature employed was 110–120°. A stirred suspension of 5 g. of the anhydride in 35 ml. of the amine became clear on 10 minutes heating. After an hour, the excess solvent was removed by distillation *in vacuo* and the solid residue recrystallized. The five new imides are listed in Table I.

TABLE I

PROPERTIES OF 2-ALKYLNAPHTHALIMIDES

				Analyses, %					
				Calcd.			Found		
Substituent	M.p., °C.	Yield, %	Solvent	C	H	N	C	H	N
n-Amyl	84–85	78	90–120° ligroin and ethanol	76.3	6.4	5.2	76.1	6.5	4.9
n-Hexyl	74–75	74	90–120° ligroin	76.9	6.8	5.0	76.9	6.8	5.0
γ-Methoxypropyl	95–96	85	90–120° ligroin and ethanol	71.3	5.5	5.2	71.5	5.5	5.3
Cyclohexyl	224–225	85	Ethanol	77.5	6.1	5.0	78.0	6.1	5.2
n-Dodecyl	57–58	68	Methanol	78.9	8.5	3.8	79.2	8.3	4.1

EASTMAN KODAK COMPANY C. F. H. ALLEN
ROCHESTER 4, N. Y. G. A. REYNOLDS

RECEIVED JULY 14, 1952

Some Derivatives of 2-Carbomethoxycyclohexanone[1]

2-Carbomethoxymethyl-2-carbomethoxycyclohexanone and 2-β-carbomethoxyethyl-2-carbomethoxycyclohexanone were prepared by the action of methyl bromoacetate and methyl β-bromopropionate, respectively, on the sodio derivative of 2-carbomethoxycyclohexanone[2] according to procedures analogous to those used previously for the preparation of the corresponding diethyl esters.[3] The keto-diesters, b.p. 126–130° at 12 mm. and 150–155° at 15 mm., gave negative ferric and permanganate tests and were characterized as their **semicarbazones**, m.p. 222–225° and 162–165°, respectively.

Anal. Calcd. for $C_{12}H_{19}N_3O_5$: C, 50.5; H, 6.7; N, 14.7. Found: C, 50.6, 50.5; H, 7.1, 7.1; N, 15.1, 14.7.

Anal. Calcd. for $C_{13}H_{21}N_3O_5$: C, 52.2; H, 7.1; N, 14.0. Found: C, 52.4, 52.0; H, 7.4, 7.0; N, 14.3, 14.0.

2-Cyanomethyl-2-carbomethoxycyclohexanone.—The sodio derivative of 2-carbomethoxycyclohexanone was prepared by stirring and refluxing (three hours) a solution of 7.88 g. of the keto ester in 75 ml. of dry benzene, with 1.15 g. of sodium. A solution of 9.15 g. of chloroacetonitrile

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[1] This work was supported in part by a Research Corporation Grant-in-aid.

[2] W. E. Bachmann and A. S. Dreiding, *J. Org. Chem.*, **13**, 317 (1948); pyrazolone derivative, m.p. 180.5–182.5° [reported: 177° (R. Levine and C. R. Hauser, THIS JOURNAL, **66**, 1768 (1944)), 180° (H. Ruhkopf, *Ber.*, **70**, 941 (1937))].

[3] E. H. Charlesworth, J. A. McRae and H. M. MacFarlane, *Can. J. Research*, **21B**, 37 (1943); H. T. Openshaw and R. Robinson, *J. Chem. Soc.*, 941 (1937).

in 50 ml. of benzene was added to the hot mixture and refluxing was continued for 18.5 hours. At this point a hydrolyzed sample of the reaction mixture was no longer alkaline to phenolphthalein and gave only a slight purple color with ferric chloride. Ether and dilute hydrochloric acid were added and the ethereal extract was washed with sodium bicarbonate and dried. Distillation gave 3.77 g. (32.2%) of the keto nitrile, b.p. 182–185.5° at 22 mm. A redistilled sample gave a negative ferric test and crystallized from petroleum ether (b.p. 20–40°) in colorless needles, m.p. 42–42.5°.

The semicarbazone was recrystallized from aqueous methanol; m.p. 203.5–204°.

Anal. Calcd. for $C_{11}H_{16}O_3N_4$: C, 52.4; H, 6.4; N, 22.2. Found: C, 52.4, 52.3; H, 6.5, 6.5; N, 22.6, 22.4.

DEPARTMENT OF CHEMISTRY
SMITH COLLEGE
NORTHAMPTON, MASS.
MILTON D. SOFFER
ROBERTA A. STEWART

RECEIVED JULY 10, 1952

Some Aldehydic Hydrazones of Triaminoguanidine

As potential coupling components in the formation of triformazans the derivatives listed in Table I were prepared. The general method was by refluxing for 10 to 15 minutes equimolar quantities of triaminoguanidine nitrate, dissolved in water, and the carbonyl component, dissolved in ethanol. Those derivatives which formed oils under these conditions were isolated as picrates. The hydrazones were crystallized from water or ethanol or mixtures of the two solvents, and occasionally from pyridine, which solvent usually removed the nitric acid and formed the free base of the hydrazone. Terephthalaldehyde and hydratropic aldehyde reacted anomalously.

TABLE I[1,2]

TRIAMINOGUANYLHYDRAZONES $(R_1CH{=}N{-}NH)_2{-}C{=}N{-}N{=}CH{-}R_1{\cdot}HNO_3$

Carbonyl compound	Empirical formula of hydrazone	M.p., °C.	Yield,[b] %	Nitrogen analyses, % Calcd.	Found
Acrolein	$C_{10}H_{19}N_7O_5$[c,m]	Not below 360°[d]	60	30.9	31.4
4-Chlorobenzaldehyde	$C_{22}H_{20}Cl_3N_7O_4$[a,l]	159	95	17.7	17.9
Cinnamaldehyde	$C_{28}H_{29}N_7O_4$[a,l]	147	85	18.6	18.5
2,4-Dihydroxybenzaldehyde	$C_{22}H_{30}N_6O_{11}$[e,l]	218[d]	69	15.1	14.5
2,3-Dimethoxybenzaldehyde	$C_{28}H_{33}N_7O_9$[l]	153	98	16.0	15.4
4-Dimethylaminobenzaldehyde	$C_{28}H_{38}N_{10}O_4$[a,l]	200	96	24.2	24.2
2,4-Dinitrobenzaldehyde	$C_{22}H_{15}N_{13}O_{16}$[p]	249	36	26.0	25.7
Formaldehyde	$C_{10}H_{15}N_9O_9$[f,l]	157	81	31.1	31.5
Furfural	$C_{16}H_{16}N_6O_4$[a,g,l]	82	90	23.8[r]	24.5
2-Hydroxybenzaldehyde	$C_{22}H_{21}N_7O_6$[l]	145	90	20.5	20.2
4-Hydroxy-3-methoxybenzaldehyde	$C_{25}H_{26}N_6O_6$[g,k]	220	96	16.6	16.6
4-Isopropylbenzaldehyde	$C_{31}H_{39}N_7O_3$[h,l]	147	90	17.6	18.2
4-Methoxybenzaldehyde	$C_{25}H_{29}N_7O_7$[a,l]	148	81	18.2	18.5
2-Nitrobenzaldehyde	$C_{22}H_{21}N_9O_8$[i,g,k]	201	97	23.5	23.4
3-Nitrobenzaldehyde	$C_{22}H_{19}N_9O_7$[a,g,k]	232	84	24.2[q]	23.6
Piperonal	$C_{25}H_{22}N_6O_7$[a,g,k]	223	93	16.2	15.8
Δ-3-Tetrahydrobenzaldehyde	$C_{28}H_{35}N_9O_7$[j,l]	185	91[j]	20.6	20.7
2-Thiophene aldehyde	$C_{16}H_{15}N_7S_3O_3$[l]	153	98	21.0	21.4

[a] Analysis corresponds to a monohydrate. [b] These yields include working up of all mother liquors, etc. [c] Analysis corresponds to a dihydrate. [d] Substance fuses at *ca.* 120° in its water of crystallization, resolidifies and then behaves as described. [e] Full analysis corresponds to hydrazone (free base) pentahydrate. Thus, calcd.: C, 47.4; H, 5.4. Found: C, 47.5; H, 5.0. Picrate (m.p. 205°) calcd. for $C_{23}H_{23}O_{13}N_9$: N, 18.1; found: N, 17.8. [f] Isolated as picrate. [g] Isolated as free base. [h] Picrate, m.p. 199°. *Anal.* Calcd. for $C_{37}H_{41}N_9O_7$: N, 17.9. Found: N, 17.8. [i] Analysis corresponds to dihydrate. [j] Yield is for crude material. Analysis is for picrate, for which substance m.p. 185°; calcd.: C, 55.2; H, 5.7. Found: C, 55.3; H, 5.7. [k] Recrystallized from pyridine. [l] Recrystallized from aqueous ethanol. [m] Recrystallized from water. [p] Insoluble in most organic solvents. [q] Calcd.: C, 50.7; H, 3.6. Found: C, 50.6; H, 3.4. [r] Calcd.: C, 54.4; H, 3.7. Found: C, 54.0; H, 4.3.

DEPT. OF CHEMISTRY
UNIVERSITY COLLEGE
CORK, IRELAND
F. L. SCOTT
M. CASHMAN
J. REILLY

RECEIVED MAY 20, 1952

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(1) All m.ps. are uncorrected.

(2) Analyses by Drs. Weiler and Strauss, Oxford.