1.4547), and 10.5 g. (50%) of starting material was recovered. The product formed a benzamide derivative melting at 148–149.5° when crude, and at 150–150.5° after recrystallization from 95% ethanol (reported[6] m.p. for the benzamide, 151°). Its phenylthiourea derivative melted at 150–151° (reported[7] m.p. for phenylthiourea 145°).

*Anal.* Calcd. for $C_{14}H_{20}N_2S$ (phenylthiourea): C, 67.73; H, 8.13. Found: C, 67.76; H, 8.42.

*m-Toluidine.* A 41% conversion (9 g.) into *cis*-3-methylcyclohexylamine was obtained (b.p. 149–150°, $n_D^{20}$ 1.4512) and 7 g. (33%) of starting material was recovered. The product formed a benzamide derivative melting at 126–127° (reported[8] m.p. 124.5-125.8°) and a phenylthiourea melting at 139–140° (reported[7,9] m.p. 105–106°).

*Anal.* Calcd. for $C_{14}H_{20}N_2S$ (phenylthiourea derivative): C, 67.73; H, 8.13; N, 11.20. Found: C, 67.80; H, 8.40; N, 11.23.

*p-Toluidine.*[1] A 49% conversion (11 g.) into *trans*-4-methylcyclohexylamine was obtained ($n_D^{20}$ 1.4509),[1] and 3 g. (14%) of starting material was recovered.

*Alkylbenzenes* (Table I). The alkylbenzene reductions were carried out in the usual fashion with 500–600 ml. of methylamine, 0.34 mole of aromatic and either 4 or 6 equivalents of lithium. In the cases where 4 equivalents of metal were used, the reaction was allowed to proceed for approximately 3 hr. With six equivalents the reaction time was about 6 hr.

*Alkylcyclohexenes* (Table II). The alkylcyclohexenes were reduced in approximately 300 ml. of methylamine using 0.2 mole of olefin and two equivalents of lithium.

*N,N-Dimethylaniline.* (*a*) (*4-Equivalents of lithium*). The reduction of 41.2 g. (0.34 mole) of *N,N*-dimethylaniline by 10.2 g. (1.45 g. atoms) of lithium in 500 ml. of methylamine was carried out in the usual manner. After 2 hr. the solution was colorless, and the solvent was then allowed to evaporate. Five hundred ml. of water was added and then 10% hydrochloric acid until the aqueous layer was acidic. This aqueous layer was then extracted thoroughly with ether and the ether solution dried over anhydrous sodium sulfate (extract No. 1). The acidic solution remaining was made basic with solid sodium hydroxide, and the basic solution was then extracted with ether. This extract (extract No. 2) was also dried over anhydrous sodium sulfate. Subsequent distillation of extract No. 1 through a Todd column, gave 13.2 g. (40%) of cyclohexanone (b.p. 154–155°; $n_D^{21}$ 1.4490). Distillation of extract No. 2 gave 13.7 g. of material boiling at 162–164° ($n_D^{22}$ 1.4673). An infrared spectrum of this cut showed an olefin band at 6 microns. Subsequent analysis of this material by gas chromatography (carbowax "1500" on firebrick packing) showed it to contain approximately 5% *N,N*-dimethylcyclohexylamine, 33% 3-dimethylaminocyclohexene and 62% 4-dimethylaminocyclohexene.

(*b*) *Excess lithium.* The reduction was repeated with 41.2 g. of *N,N*-dimethylaniline (0.34 mole) and 16.8 g. (2.4 g. atoms) of lithium in 500 ml. of methylamine. The reaction time was 7 hr., after which the product was worked up as described above. Distillation of extract No. 1 gave 11.7 g. (35%) of cyclohexanone (b.p. 154–155°, $n_D^{21}$ 1.4492). Distillation of extract No. 2 gave 11.5 g. (27%) of cyclohexyldimethylamine (b.p. 159–161°, $n_D^{22}$ 1.4540). A gas phase chromatogram showed the latter to be only slightly contaminated with 3- and 4-dimethylaminocyclohexenes.

*N-Methylaniline* (*excess lithium*). The product from the reduction of 36.4 g. (0.34 mole) of *N*-methylaniline with 16.8 g. (2.4 g. atom) of lithium in 500 ml. of methylamine for 7 hr. was worked up as described above. Distillation of extract No. 1 gave 1 g. of residue whose infrared spectrum showed no carbonyl band. Distillation of extract No. 2 gave 6.1 g. (16%) of *N*-methylcyclohexylamine (b.p. 148–150°, $n_D^{24}$ 1.4562) and 22.7 g. (62%) of recovered *N*-methylaniline (b.p. 195–196°, $n_D^{24}$ 1.5685). A gas phase chromatogram and an infrared spectrum of the *N*-methylcyclohexylamine showed it to be slightly contaminated with cyclohexanone.

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## Substituted 12-Aminobenz[*a*]acridines

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The activity of a number of substituted 7-aminobenz[*c*]acridines against *E. histolytica in vitro* and in intestinal amaebiasis in rats has been reported by Elslager and co-workers[1,2] and by Short and co-workers.[3] The present communication deals with the preparation of a number of substituted 12-aminobenz[*a*]acridines for trials against *E. histolytica*.

The acridine derivatives were obtained by the interaction of 0.005 mole of 12-chlorobenz[*a*]-acridine, prepared from *N*-(2-naphthyl)anthranilic acid according to Bachman and Picha,[4] with a slight excess of the appropriate amine in phenol at 120 for a period of 2 hr. in the presence of powdered sodium carbonate to neutralize the liberated hydrochloric acid. The reaction mixture was poured into an excess of an aqueous solution of potassium hydroxide and the sticky precipitate, on solidification, was filtered off and dried after washing with water. The dry solid was dissolved in ether and the ether extract was treated with hydrogen chloride gas to precipitate the hydrochloride, or with a solution of salicylic acid in ether to precipitate and salicylate. The salt was purified by crystal-

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TABLE I

SUBSTITUTED 12-AMINOBENZ[*a*]ACRIDINES

| No. | Base | Salt | Crystallizing Solvent | M.p.[a] of Salt | Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found |
|---|---|---|---|---|---|---|---|---|
| 1 | 12-*p*-Chloroanilinobenz[*a*]acridine | HCl | Methanol | 265 | 70.58 | 70.96 | 4.10 | 3.98 |
| 2 | 12-*p*-Iodoanilinobenz[*a*]acridine | $C_7H_6O_3$[b] | Benzene-ethanol | 212 | 61.64 | 61.99 | 3.60 | 3.22 |
| 3 | 12-Anilinobenz[*a*]acridine | 3 $C_7H_6O_3$ | Benzene | 220 | 71.93 | 71.72 | 4.63 | 4.86 |
| 4 | 12-*p*-Toluidinobenz[*a*]acridine | 2 $C_7H_6O_3$ | 50% Ethanol | 210 | 74.75 | 75.03 | 4.92 | 5.23 |
| 5 | 12-*m*-Chloroanilinobenz[*a*]acridine | $C_7H_6O_3$, $2H_2O$[c] | Chloroform | 190 | 68.12 | 68.00 | 4.72 | 4.48 |
| 6 | 12-*m*-Iodoanilinobenz[*a*]acridine | $C_7H_6O_3$ | Ethanol | 185 | 61.64 | 61.85 | 3.60 | 3.30 |
| 7 | 12-*m*-Toluidinobenz[*a*]acridine | 1.5 $C_7H_6O_3$ | Benzene | 195 | 76.53 | 76.90 | 4.99 | 4.97 |
| 8 | 12-*p*-Anisidinobenz[*a*]acridine | 1.5$C_7H_6O_3$ | Ethanol | 207 | 74.33 | 74.45 | 4.85 | 4.80 |

[a] All melting points are uncorrected. [b] $C_7H_6O_3$ = salicylic acid. [c] $H_2O$, calcd., 6.81%; found, 6.72%.

lization from a suitable solvent. The data are recorded in Table I.

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## Derivatives of Sulfenic Acids. XXXIII. 2,4-Dinitrophenyl Selenium Trichloride[1]

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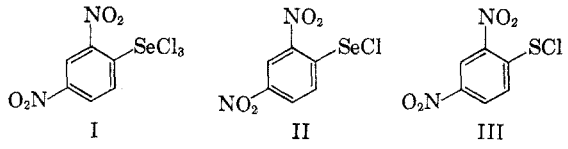
The recent papers of Jenny and co-workers[2] on various selenenyl derivatives prompt us to report a study, carried out some time ago, concerning 2,4-dinitrophenyl selenium trichloride (I).




I II III

Our purpose was to prepare 2,4-dinitrobenzeneselenenyl chloride (II) for comparison with the well known sulfur analog,[3] 2,4-dinitrobenzenesulfenyl chloride (III). While numerous selenenyl halides have been reported, including 2,4-dinitrobenzeneselenenyl bromide[4] and 2-nitrobenzeneselenenyl chloride,[5] II has not been described previously.

The synthesis of III is generally carried out by the catalytic chlorinolysis of bis(2,4-dinitrophenyl) disulfide.[6] This procedure, using chlorine gas, did not permit the convenient chlorinolysis of the very insoluble bis(2,4-dinitrophenyl) diselenide. In the course of the work, however, a superior method for cleaving bis(2,4-dinitrophenyl) disulfide was devised, involving the use of sulfuryl chloride and pyridine. This procedure was succesful in the chlorinolysis of the corresponding diselenide, but the product obtained was not the selenenyl chloride (II), but the trichloride (I). The use of sulfuryl chloride as reagent for chlorinolyses of disulfides and diselenides has been previously reported by Behaghel and Seibert.[4a]

Since selenocyanates are known to undergo brominolysis to selenenyl bromides,[7] the direct chlorinolysis of 2,4-dinitrophenyl selenocyanate was attempted. The reaction proceeded smoothly, the product again being the selenium trichloride (I). Further study established that the trichloride is in equilibrium with the monochloride (Equation 1);

$$\underset{\text{I}}{ArSeCl_3} \rightleftharpoons \underset{\text{II}}{ArSeCl} + Cl_2 \qquad (Ar = 2,4\text{-dinitrophenyl}) \quad (1)$$

and that pure I can be prepared by using excess sulfuryl chloride in the chlorinolysis of the selenocyanate or bis(2,4-dinitrophenyl) diselenide; and II results by heating I in an evacuated atmosphere. The reverse reaction was demonstrated by converting the monochloride (II) to trichloride, by reaction of the former with excess chlorine. Such reversible relations of the trichloride and monochloride derivatives have been noted previously, both in the selenium[8] and the sulfur series.[9]

2,4-Dinitrophenyl selenium trichloride (I) is an excellently crystalline solid, which may be stored for long periods without change. As expected, however, I decomposes on heating and does not exhibit a sharp melting point. The bright yellow crystals begin to turn orange at 70°; at 80–85°, chlorine is evolved and at 100°, the whole mass turns to an

(1) The research reported in this document was made possible, in part, through support extended by the Office of Scientific Research, Air-Research and Development Command, under Contract No. AF-49-638-330.

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