Bromination of the nitroso halides. Ten grams of the dimer was suspended in 200 ml. of chloroform. To the nitroso chlorides, 8.88 g. of bromine in 20 ml. of chloroform was added slowly with stirring. To the nitroso bromides, 6.6 g. of bromine in 20 ml. of chloroform was added. The reaction was stirred for 1 hr. after the addition of bromine was complete, and then the solution was evacuated at the aspirator at room temperature with vigorous stirring. The solution became colorless and the product precipitated. The reactions were worked-up in exactly the manner described for the chlorination reactions. Pertinent data are given in Table I.

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On the Preparation of Codeinone

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The methods of Rapoport and Reist[2] and Highet and Wildman[3] for the preparation of codeinone, although the best yet devised for this ketone, require a lengthy preparation of either silver carbonate[2] or manganese dioxide.[3] From our experience, a modification of the original conditions of Rapoport eliminates the silver carbonate preparation and shortens the reaction time. We have found commercial silver carbonate in only 300 mole per cent excess to be as effective as the specially prepared reagent in 500 mole per cent excess. Although oxidation did not take place in boiling benzene, the reaction in refluxing toluene or xylene was complete within ten to fifteen minutes and yielded 80–85% of crude codeinone, m.p. 178–180°. The same yield was obtained with or without mechanical stirring.

Conditions also have been found for several Michael-type additions of nitrogen, carbon, and sulfur compounds to the conjugated carbonyl system of codeinone in benzene solution. In particular, adducts of piperidine, morpholine, nitromethane, and *N,N*-diethyldithiocarbamic acid were prepared. When these reactions were attempted in ethanol solution extensive darkening and decomposition were observed.

EXPERIMENTAL

Codeinone. To a solution of 10 g. (0.033 mole) of codeine in 150 ml. of toluene (reagent or technical grade) in a 500-ml., three necked flask fitted with a condenser was added 25 g. (0.091 mole) of commercial silver carbonate (Baker and Adamson). The olive-gray mixture was heated to reflux under a slow stream of nitrogen. After the color had changed to gray and then black (about 5 min.), reflux was continued for another 5 min. The insoluble mixture of silver and silver salts was removed by filtration and was washed with hot benzene. The combined organic solutions were concentrated with addition of petroleum ether (b.p. 69°) until crystallization began. Filtration gave 4.0 g., of codeinone m.p. 185°. A second crop of 4.2 g., m.p. 178–180°, brought the yield to 8.2 g. (82%), $\lambda_{\max}^{\mathrm{KBr}}$ 6.0 μ.

Piperidine adduct. Codeinone (4.0 g.) was heated to reflux for 1 hr. in 75 ml. of dry benzene containing 9 ml. of piperidine. The solvent was evaporated and the residue was recrystallized from 95% ethanol to give 2.6 g. of colorless rhombic crystals, m.p. 190–191° dec., $\lambda_{\max}^{\mathrm{KBr}}$ 5.85 μ.

Anal. Calcd. for $C_{23}H_{30}N_2O_3$: C, 72.22; H, 7.90; N, 7.32. Found: C, 72.08; H, 8.20; N, 7.87.

Morpholine adduct. Codeinone (2.0 g.) was heated to reflux for 2 hr. in 75 ml. of dry benzene containing 10 ml. of morpholine. The organic solution was washed twice with water and evaporated to dryness. Recrystallization from absolute ethanol gave colorless crystals, m.p. 208–210° dec., $\lambda_{\max}^{\mathrm{KBr}}$ 5.86 μ.

Anal. Calcd. for $C_{22}H_{28}N_2O_4$: C, 68.72; H, 7.34; N, 7.28 Found: C, 68.67; H, 7.26; N, 7.33.

Nitromethane adduct. Nitromethane (3 ml.) was added to a solution of 1 g. of sodium in 50 ml. of absolute ethanol. The excess solvent was decanted from the white precipitate which was then washed by decantation with absolute alcohol, dry ether, and finally dry benzene. A solution of 1.5 g. of codeinone in 50 ml. of dry benzene was added to the sodium salt. The mixture was heated to reflux for 2 hr. and filtered. The filtrate was evaporated and the residue recrystallized from benzene and then from ethanol to give 0.45 g. (25%) of white powder, m.p. 199–200°, $\lambda_{\max}^{\mathrm{KBr}}$ 5.83, 6.48, and 7.30 μ (NO_2).

Anal. Calcd. for $C_{19}H_{24}N_2O_5$: C, 63.33; H, 6.70; N, 7.71. Found: C, 63.51; H, 6.83; N, 7.74.

N,N-Diethyldithiocarbamic acid adduct. Triethylammonium *N,N*-diethyldithiocarbamate was prepared according to the procedure of Buess[4] from 1.9 ml. of triethylamine, 0.8 ml. of carbon disulfide, and 1.4 ml. of diethylamine. A solution of 2.0 g. of codeinone in 50 ml. of benzene was added to the reagent. A day later the solvent was removed at room temperature. The product, washed with water and dried, weighed 2.6 g. (86%). Recrystallization from a mixture of benzene and petroleum ether gave a white microcrystalline powder, m.p. 80–85° dec., which decomposed slowly on standing.

Anal. Calcd. for $C_{23}H_{30}N_2O_3S_2$: C, 61.85; H, 6.76; N, 6.29. Found: C, 60.78; H, 7.12, N, 6.27.

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