mide. A 73% yield of phenyl disulfide was isolated from the mother liquor.

Acknowledgment. We acknowledge the assistance of Mr. Glen Bailey and Mrs. Edith Gong for infrared spectroscopic determinations and Mr. L. M. White and Miss Geraldine Secor for elemental analyses.

ALBANY 10, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND GEOLOGY, CLEMSON COLLEGE AND THE SCHOOL OF CHEMISTRY, GEORGIA INSTITUTE OF TECHNOLOGY]

The Furanoquinoline Alkaloids: Synthesis and Reactions of Some Related 4-Hydroxy-2-quinolones

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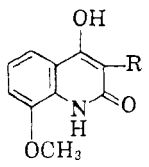
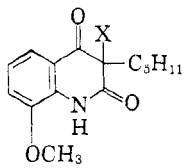
In the course of efforts directed at the total synthesis of some furanoquinoline alkaloids, 3-(3-methylbutyl)-4-hydroxy-8-methoxy-2-quinolone (Ib) was prepared. Ib with bromine gave 3-(3-methylbutyl)-3-bromo-8-methoxy-2,4(1H,3H)-quinolindione (IIa) which with base was reduced to Ib. In an effort to investigate the course of this reduction 1-methyl-3-benzyl-4-hydroxy-2-quinolone (VIII) was synthesized and brominated to give IX. This compound was also reduced when treated with base. The possible mechanism of these base catalyzed reductions is discussed.

In the course of efforts directed at the total synthesis of isopropylfuranoquinoline alkaloids, of the lunacrine[2] and balfourodine[3] groups, we attempted to prepare 3-(3-methyl-1-butenyl)-4-hydroxy-8-methoxy-2-quinoline (Ia). It was felt that this compound under appropriate conditions could be cyclized to a derivative of lunacrine. Al-





Ia. R = CH=CH—CH(CH$_3$)$_2$ IIa. X = Br
b. R = CH$_2$CH$_2$CH(CH$_3$)$_2$ b. X = OH

though we have been unable to effect the synthesis of Ia, the reactions of the expected precursors of Ia appear to be of sufficient interest to warrant their presentation.

It was proposed to bring about the synthesis of Ia *via* its saturated analog, 3-(3-methylbutyl)-4-hydroxy-8-methoxy-2-quinolone (Ib). Ib was prepared in good yield by the usual synthetic route for 3-alkyl-4-hydroxy-2-quinolones, through the interaction of an alkylmalonic ester and an aniline derivative in a high boiling solvent.[3,4] Diethyl isoamylmalonate[5] with *o*-anisidine in boiling phenyl ether afforded the desired hydroxyquinoline in good yield.

Treatment of Ib with either pyridinium bromide perbromide in acetic acid or *N*-bromosuccinimide in carbon tetrachloride gave a yellow bromo compound, $C_{15}H_{18}BrNO_3$. The infrared spectrum of the bromination product showed a split carbonyl band, with absorption at 5.86 μ and 6.01 μ, rather than the typical 4-hydroxyquinolone absorption exhibited by Ib. The ultraviolet spectrum of the yellow, bromo compound showed high intensity maxima at 235 and 240 mμ, instead of the complex spectrum of the parent compound. On the basis of the elemental analysis, and the rather drastic changes in spectral properties in the bromo compound, it was felt that the bromination product must be 3-(3-methylbutyl)-3-bromo-8-methoxy-2,4-(1H,3H) - quinolindione (IIa). Confirmation of this structure was obtained by the treatment of IIa with zinc–acetic acid, whereby the original 4-hydroxyquinolone was regenerated.

It was supposed that the reaction of IIa with base would afford the desired unsaturated quinolone derivative (Ia). When the bromoquinilindione (IIa) was treated with methanolic potassium hydroxide, the product in 60% yield was, however, the parent quinolone, 3 - (3 - methylbutyl) - 4 - hydroxy - 8-methoxy-2-quinolone. Attempted dehydrohalogenation of the bromo compound with collidine also effected reduction to the hydroxyquinolone. While there is some precedent for the reduction of α-halo ketones to the parent compound on treatment with collidine,[6] there seems to be no precedent for the reduction of an α-halo carbonyl compound by means of hydroxylic base.

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(1) Department of Chemistry and Geology, Clemson College, Clemson, S. C.

(2) S. Goodwin and E. C. Horning, *J. Am. Chem. Soc.*, **81**, 1908 (1959).

(3) H. Rapoport and K. G. Holden, *J. Am. Chem. Soc.*, **81**, 3738 (1959).

(4) (a) R. G. Cooke and H. F. Haynes, *Aust. J. Chem.*, **7**, 273 (1954); (b) M. F. Grundon and N. J. McCorkindale, *J. Chem. Soc.*, 2177 (1957); (c) H. Rapoport and K. G. Holden, *J. Am. Chem. Soc.*, **82**, 4395 (1960).

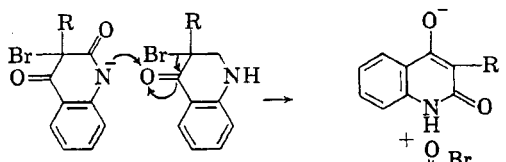
(5) A. C. Cope, C. M. Hoffman, C. Wycoff, and E. Hardenberg, *J. Am. Chem. Soc.*, **63**, 3454 (1941).

(6) G. Rosenkranz, O. Mancera, J. Gatica, and C. Djerassi, *J. Am. Chem. Soc.*, **72**, 4077 (1950).

The attempted dehydrohalogenation of IIa by means of silver nitrate in boiling ethanol gave no apparent reaction, and on more vigorous conditions, at reflux in diethylene glycol, a compound $C_{15}H_{19}NO_4$ was formed. The infrared and ultraviolet spectra were very similar to that of the parent bromo compound, and reduction with zinc–acetic acid gave 3 - (3 - methylbutyl) - 4 - hydroxy - 8 - methoxy-2-quinolone (Ib). On this basis, the product of the silver nitrate–diethylene glycol reaction must be 3 - (3 - methylbutyl) - 3 - hydroxy - 8 - methoxy - 2,4 (1H,3H)-quinolindione (IIb). Attempted dehydration of this compound under a number of conditions gave no identifiable products other than recovered starting material.

During the course of the reduction of the bromoquinolindione to the parent hydroxyquinoline with base it was observed that on the addition of base to an alcoholic solution of IIa the reaction mixture turned a deep red color, which faded to a pale yellow color on warming. Subsequent acidification gave the reduced product. It seemed possible that the initial step in the reduction was the abstraction of a proton from the nitrogen atom (III), followed by a nucleophilic attack of this anion upon the bromine atom giving an *N*-bromo compound and reduced material (IV).

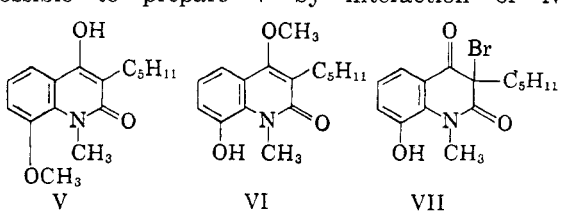
This *N*-bromo compound may then react with water or methanol to give IIa and the appropriate hypobromite.



III

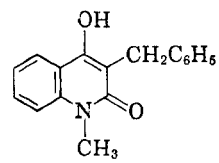
IV

In order to test this hypothesis it was desired to prepare an *N*-alkyl analog of the bromo compound (IIa.) If the reaction sequence III→IV correctly represents the course of the reduction, then base treatment of 1-methyl-3-(3-methylbutyl)-4-hydroxy-2-quinolone (V) should proceed to give the *N*-methyl derivative of Ia. It was indeed possible to prepare V by interaction of *N*-methyl-*o*-anisidine and isoamyl malonic ester; however, the yield of this reaction was only 10%. An alternate approach seemed to be through the reaction of dimethyl sulfate with 3-(3-methylbutyl) - 4 - hydroxy - 8 - methoxy - 2 - quinolidione (Ib), followed by cleavage of the 4-methyl ether with hydrogen bromide.[4a] This reaction gave, in addition to recovered starting material and a small quantity of the *N*-methyl derivative, a compound $C_{16}H_{21}NO_3$. This compound was isomeric with 1 - methyl - 3 - (3 - methylbutyl) - 4 - hydroxy-8-methoxy-2-quinolone, and also contained one methoxyl group. On this basis this material must be 1 - methyl - 3 - (3 - methylbutyl) - 4 - methoxy-8-hydroxy-2-quinolone (VI). Treatment of a small quantity of solid but impure methylation product (see Experimental) with pyridinium bromide perbromide gave in addition to IIa, a minute quantity of an isomeric yellow bromo compound. The only structure consistent with these data is that of 1-methyl-3-(methylbutyl)-3-bromo-8-hydroxy-2,-4(1H,3H)-quinolindione (VII).[8]

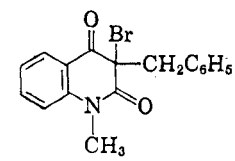


V VI VII

In view of the difficulties at arriving at workable quantities of the desired *N*-methyl derivative, a model compound, 1-methyl-3-benzyl-4-hydroxy-2-quinolone (VIII) was prepared from diethyl benzylmalonate and *N*-methylaniline.



VIII



IX

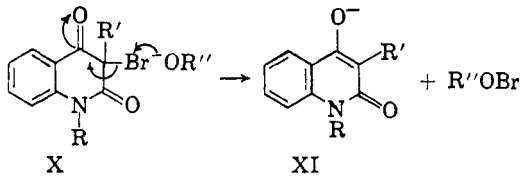
Treatment of the *N*-methylbenzyl compound with pyridinium bromide perbromide gave the expected yellow bromo compound (IX), the structure of which was confirmed by its reduction to the parent hydroxy quinolone by zinc–acetic acid. Treatment of 1-methyl-3-benzyl-3-bromo-2,4(1H,-3H) - quinolindione (IX) with base effected reduction to 1-methyl-3-benzyl-4-hydroxy-2-quinolone (VIII). Although this reaction followed the same course as the corresponding reaction in the nonmethylated series, the red color which was formed on base treatment of IIa was not evident in the base treatment of IX. While this does not necessarily indicate that the debrominations in the two series proceed by a different mechanism, this possibility cannot be excluded.

There remain two probable reaction paths for this unusual debromination reaction. The first is the possible direct interaction of the bromo compound with solvent, in a manner analogous to the reaction of *N*-bromosuccinimide with hydroxylic solvents,[9] or alcohols[10] in neutral solution to give

(7) H. Gilman, D. Esmay, and R. K. Ingham, *J. Am. Chem. Soc.*, **73**, 470 (1951) have observed the debromination of 2,8-dibromodibenzofuran by means of sodium hydroxide in boiling triethylene glycol; however, the mechanism of this reaction remains somewhat unclear.

(8) Whether this compound is derived from VI under the acid conditions of the bromination, or from the unisolated 1-methyl-3-(3-methylbutyl-4,8-dihydroxy-2-quinolone) is not known.

hypobromites or other oxidized products. The second probable course of this reaction is a nucleophilic attack of hydroxide, or alkoxide upon the bromine atom (X) to give the reduced product and the appropriate hypobromite (XI).[11]



X XI

While it is not possible to state clearly which of the above reaction paths is that followed in these debrominations, there is some evidence favoring the nucleophilic attack of hydroxide on the bromine atom. The *N*-methylbromo compound (IX) is recovered unchanged after being heated in boiling methanol for six hours, while in basic methanol, 45% yield of debrominated compound is obtained in two hours. This evidence is indicative of a base-catalyzed reaction and is most consistent with the path X to XI.

Although there appear to be very few, if any, authentic examples of the nucleophilic attack of hydroxylic base upon halogen atoms, there exists a class of bromo compounds which reacts with polar solvents to give reduced products, namely the compounds related to 2,4,4,6-tetrabromo-2,5-cyclohexadienone.[12]

It has been found that 2,4,4,6-tetrabromo-2,5-cyclohexadienone reacts with water to give two products,[13] and with ethanol to give a mixture of phenols, and the odor of acetaldehyde.[14] No mechanisms for these reactions have been suggested, and they may be similar to that of the debromination of 3-alkyl-3-bromo-2,4(1H,3H)-quinolindiones.

Although there appear to be no reported cases of a nucleophilic attack of hydroxide ion upon a bromine atom, there are a number of related reductions of vicinal dibromides with very strong bases. Reductions of this type include the debromination of stilbene dibromide,[15] cinnamic acid dibromide,[16] and *trans* - 9,10 - dibromotetrahydro - *exo* - dicyclopentadiene with sodium amide.[17]

EXPERIMENTAL[18]

3-(3-Methylbutyl)-4-hydroxy-8-methoxy-2-quinolone. A mixture of 17 g. of diethyl isoamylmalonate and 4.5 g. of *o*-anisidine was heated 1 hr. under reflux in 30 ml. of phenyl ether. After the product precipitated on cooling, the reaction mixture was diluted with hexane, and the crystals were collected. Recrystallization from aqueous acetic acid gave 5.89 g. (55%) of white crystals, m.p. 233–235°. Recrystallization from ethyl acetate gave the analytical sample, m.p. 235–236°. λ_{max} 236 mμ, log ε 4.89; 238, log ε 4.89; log ε 4.11; 3.05 log ε 4.06.

Anal. Calcd. for $C_{15}H_{19}NO_3$: C, 68.86; H, 7.32; N, 5.35. Found: C, 68.95; H, 7.37; N, 5.38.

3-(3-Methylbutyl)-3-bromo-8-methoxy-2,4(1H,3H)-quinolidione. (a) To a solution of 2.4 g. of 3-(3-methylbutyl)-4-hydroxy-8-methoxy-2-quinolone in 150 ml. of acetic acetic acid was added 3.4 g. of pyridinium bromide perbromide. The red solution was allowed to stand overnight at room temperature, poured into 300 ml. of water, the precipitated product was collected and washed well with water. Recrystallization from cyclohexane gave 2.59 g. (87%) of golden yellow crystals, m.p. 110–114°. The analytical sample was recrystallized from cyclohexane to give lustrous yellow crystals, m.p. 116–117°; λ_{max}: 235 mμ, log ε 4.52; 240, log ε 4.49.

Anal. Calcd. for $C_{15}H_{18}BrNO_3$: C, 52.95; H, 5.33; Br, 23.49; N, 4.12. Found, C, 53.14; H, 5.46; Br, 23.70; N, 4.06.

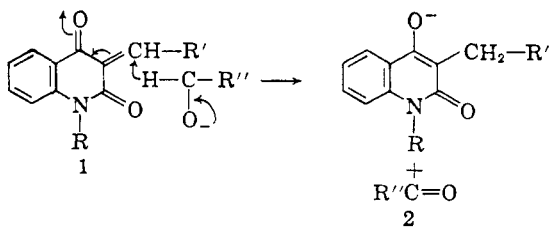
(b) A suspension of 0.50 g. of hydroxyquinolone and 0.23 g. of *N*-bromosuccinimide in 30 ml. of carbon tetrachloride was heated under reflux 24 hr. The reaction mixture was filtered hot, and concentrated to dryness, affording a yellow oil which slowly crystallized. Recrystallization from cyclohexane gave 0.2 g. (31%) of yellow crystals, m.p. and mixed m.p. 113–115°.

Base treatment of 3-(3-methylbutyl)-3-bromo-8-methoxy-2,4-(1H,3H)-quinolindione. (a) To a solution of 2.0 g. of potassium hydroxide in 50 ml. of methanol was added 1.8 g. of bromoquinolindione. The yellow solution immediately turned blood red, which faded to pale yellow in a few minutes. The reaction mixture was heated 2 hr. under reflux, cooled, diluted with water, and acidified with 10% hydrochloric acid. The resulting white crystals were collected, washed with water, and recrystallized from aqueous acetic acid to give 0.89 g. (60%) of 3-(3-methylbutyl)-4-hydroxy-8-methoxy-2-quinolone, m.p. and mixed m.p. 233–235°.

(9) C. O. Guss and R. Rosenthal, *J. Am. Chem. Soc.*, 77, 2549 (1955).

(10) (a) M. Z. Barahat and G. M. Mousa, *J. Pharm. Pharmacol.*, 4, 155 (1952), *Chem. Abstr.*, 46, 7998 (1952); (b) L. F. Fieser and S. Rajagopalan, *J. Am. Chem. Soc.*, 71, 3935 (1949).

(11) A third possible mechanism is a dehydrohalogenation to an *ortho*-quinoid structure (1), which may then be reduced by alkoxide to give an aldehyde or ketone, and the debrominated compound (2):



1 2

Although this mechanism appears to be quite unprecedented, and might be considered to be rather unlikely, it cannot be excluded on the basis of the current data.

(12) We would like to thank Dr. Erling Grovenstein, Jr., for pointing out the possible analogy between our compounds, and the cyclohexadienone derivatives.

(13) L. G. Cannell, *J. Am. Chem. Soc.*, 79, 2927 (1957).

(14) W. M. Lauer, *J. Am. Chem. Soc.*, 48, 449 (1926).

(15) T. H. Vaughn, R. R. Vogt, and J. A. Nieuwland, *J. Am. Chem. Soc.*, 56, 2120 (1934).

(16) R. V. Paulson and W. S. MacGregor, *J. Am. Chem. Soc.*, 73, 679 (1951).

(17) P. Wilder and O. T. Youngblood, *J. Am. Chem. Soc.*, 78, 3795 (1956). We would like to thank Dr. Wilder for calling our attention to the debrominations by strong base.

(18) Melting points were determined on a Fisher-Johns melting point apparatus, and are uncorrected. Infrared spectra were carried out in chloroform solution, or as Nujol mulls on a Perkin-Elmer Model 137 spectrophotometer. Ultraviolet spectra were determined in 95% ethanol on a Beckmann Model DK-1 recording spectrophotometer. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

(b) A suspension of 0.2 g. of the bromo compound in 7 ml. of collidine was heated under reflux for 2 hr. The deep brown solution was cooled, diluted with water, and made basic with 10 ml. of 10% potassium hydroxide. The aqueous layer was washed with three portions of ether, then acidified with 10% hydrochloric acid. The precipitated solid was collected and recrystallized from aqueous acetic acid to give 0.05 g. (36%) of hydroxyquinolone, m.p. and mixed m.p. 230–232°.

Reduction of 3-(3-methylbutyl)-3-bromo-8-methoxy-2,4(1H,3H)-quinolindione. To a solution of 0.2 g. of the bromoquinolindione in 10 ml. of acetic acid was added 0.3 g. of zinc dust, and the mixture heated 0.5 hr. under reflux. The colorless solution was decanted into water, the precipitated solid was collected and recrystallized from aqueous acetic acid to give 0.11 g. (78%) of hydroxyquinolone, m.p. and mixed m.p. 233–234°.

(b) To a boiling solution of 0.3 g. of 3-(3-methylbutyl)-3-bromo-8-methoxy-2,4(1H,3H)-quinolindione in 15 ml. of isopropyl alcohol was added 0.2 g. of sodium borohydride, and the solution heated under reflux 3 hr. The colorless solution was poured into water, acidified with 10% hydrochloric acid, and the precipitated solid collected. Recrystallization from aqueous acetic acid afforded 0.17 g. (81%) of 3-(3-methylbutyl)-4-hydroxy-8-methoxy-2-quinolone, m.p. and mixed m.p. 232–234°.

3-(3-Methylbutyl)-3-hydroxy-8-methoxy-2,4(1H,3H)-quinolindione. To a solution of 0.78 g. of bromo compound in 40 ml. of diethylene glycol was added 0.49 g. of silver nitrate dissolved in the minimum amount of water, and the solution heated for 5 hr. under reflux. After cooling the reaction mixture was diluted with water, and extracted with three portions of methylene chloride. The extracts were combined, washed well with water, 5% sodium hydroxide, and 10% hydrochloric acid, dried, and the solvent removed at reduced pressure to give a pale brown oil. The oil crystallized on trituration with cyclohexane–ethyl acetate, and on recrystallization from the same solvent pair gave 0.13 g. of gummy crystals, m.p. 86–90°. Repeated recrystallization from cyclohexane-ethyl acetate gave pale yellow crystals, m.p. 93–95°. λ_{max} 235 mμ, log ε 4.58.

Anal. Calcd. for $C_{16}H_{19}NO_4$: C, 64.96; H, 6.91; N, 5.05. Found: C, 64.88; H, 7.01; N, 4.86.

Reduction of 3-(3-methylbutyl)-3-hydroxy-8-methoxy-2,4-(1H,3H)quinolindione. To a solution of 0.1 g. hydroxyquinolindione (m.p. 86–90°) in 5 ml. of acetic acid was added 0.2 g. zinc dust, and the mixture heated under reflux 1 hr. The colorless solution was cooled, poured into water, and the solid collected. Recrystallization from aqueous acetic acid gave 0.05 g. of 3-(3-methylbutyl)-4-hydroxy-8-methoxy-2-quinolone, m.p. and mixed m.p. 232–234°.

1-Methyl-3-(3-methylbutyl)-4-hydroxy-8-methoxy-2-quinolone. A mixture of 0.43 g. of *N*-methyl-*o*-anisidine[19] and 1.5 g. of isoamyl malonic ester was heated under reflux in 3 ml. of phenyl ether for 3 hr. The dark brown reaction mixture was cooled, diluted with hexane, and extracted twice with 5% sodium hydroxide. The aqueous layer was washed with methylene chloride, warmed to drive off excess methylene chloride, and acidified with acetic acid to give 0.08 g. (9.7%) of white powder, m.p. 115–119°. Repeated recrystallization from aqueous acetic acid gave white crystals, m.p. 126–128°.

Anal. Calcd. for $C_{16}H_{21}NO_3$: C, 69.79; H, 7.69; N, 5.10. Found: C, 70.18; H, 7.55; N, 5.23.

Reaction of 3-(3-methylbutyl)-4-hydroxy-8-methoxy-2-quinolone with dimethyl sulfate. To a solution of 4.36 g. of the quinolone in 75 ml. of 20% sodium hydroxide was added 20 ml. of dimethyl sulfate. The reaction mixture was heated under reflux 3 hr., with 4-ml. portions of dimethyl sulfate, and 6-ml. portions of base being added at 30-min. intervals. After cooling, the mixture was diluted to about 300 ml. with water, and extracted with two portions of methylene chloride. The organic extracts were washed with water, dried, and the solvent was removed at the water pump to give 4.0 g. of yellow oil. This material was suspended in 150 ml. of 30% hydrobromic acid, and heated under reflux 3 hr. The solution was cooled, diluted with water, and the liquid decanted from the precipitated gum. The residue was dissolved in 5% sodium hydroxide, washed with methylene chloride, filtered, and then acidified with acetic acid to give a white solid. The precipitated material was dissolved in methylene chloride, dried, and the solvent removed at reduced pressure, leaving a white powder. This residue was triturated with ethyl acetate, and the insoluble material collected, giving 0.47 g. of recovered 3-(3-methylbutyl)-4-hydroxy-8-methoxy-2-quinolone, m.p. and mixed m.p. 231–233°. The ethyl acetate solution was concentrated to a small volume, diluted with cyclohexane, and cooled, affording 0.73 g. of white solid, m.p. 118–126°. A solution of 0.6 g. of this material in a small volume of anhydrous ether was chromatographed on 18 g. of neutral alumina, Brockmann activity III. Elution with dry ether gave 0.07 g. of 1-methyl-3-(3-methylbutyl)-4-hydroxy-8-methoxy-2-quinolone, m.p. and mixed m.p. 124–125°. Further elution with chloroform gave 0.19 g. of 1-methyl-3-(3-methylbutyl)-4-methoxy-8-hydroxy-2-quinolone, which formed crystals from cyclohexane, m.p. 110–111°. Recrystallization from the same solvent gave the analytical sample m.p. 112–113°.

Anal. Calcd. for $C_{15}H_{18}NO_2$ (OCH_3): C, 69.79; H, 7.69; N, 5.10; OCH_3, 11.27. Found: C, 69.66; H, 7.52; N, 5.10; OCH_3, 11.10.

Treatment of 0.32 g. of the crude material, m.p. 118–126°, in 10 ml. of acetic acid with 0.42 g. of pyridinium bromide perbromide for 12 hr., followed by dilution with water, and collection of the precipitate gave a yellow-orange powder. Recrystallization from hexane afforded 0.21 g. of a mixture of pale yellow and yellow crystals, m.p. 75–82°. The crystals were separated mechanically and recrystallized from hexane to give bright yellow crystals of 3-(3-methylbutyl)-3-bromo-8-methoxy-2,4(1H,3H)quinolindione, m.p. and mixed m.p. 113–114°, and paler yellow crystals of 1-methyl-3-(3-methylbutyl)-3-bromo-8-hydroxy-2,4(1H,3H)quinolindione, m.p. 97–98°.

Anal. Calcd. for $C_{16}H_{18}BrNO_3$: C, 52.95; H, 5.33. Found: C, 53.15; H, 5.45.

1-Methyl-3-benzyl-4-hydroxy-2-quinolone. A solution of 9.3 g. of diethyl benzylmalonate and 2.0 g. of *N*-methylaniline in 15 ml. of phenyl ether was heated 1.5 hr. under reflux. On cooling, a white solid precipitated, the reaction mixture was diluted with hexane, and the product collected to give 5.7 g. of pale brown powder, m.p. 165–205°. The powder was suspended in hot 10% sodium hydroxide and the solution filtered to remove insoluble material. On acidification with acetic acid the clear yellow solution gave 2.20 g. (43%) of white solid, m.p. 217–219°. Recrystallization from aqueous acetic acid gave the analytical sample as white crystals, m.p. 219–220°; λ_{max}: 278 mμ, log ε 4.06; 287, log ε 4.06; 318, log ε 3.99; 330 (sh), log ε 3.87.

Anal. Calcd. for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 77.31; H, 5.69; N, 5.48.

1-Methyl-3-benzyl-3-bromo-2,4(1H,3H)quinolindione. To a solution of 1.2 g. of the benzylhydroxyquinolone in 60 ml. of acetic acid was added 1.6 g. of pyridinium bromide perbromide. The reaction was allowed to stand overnight, poured into water, and the yellow precipitate collected. Recrystallization from cyclohexane gave 1.25 g. (80%) of bromo compound, m.p. 155–157°. Recrystallization from cyclohexane gave the analytical sample, m.p. 157–158°; λ_{max}: 243 mμ, log ε 4.59; 248, log ε, 4.58.

Anal. Calcd. for $C_{17}H_{14}BrNO_3$: C, 59.32; H, 4.10; N, 4.07. Found: C, 59.36; H, 4.00; N, 3.98.

Reduction of 1-methyl-3-benzyl-3-bromo-2,4(1H,3H)quinolindione. To a solution of 0.1 g. of the bromo compound in 6 ml. of acetic acid was added 0.2 g. of zinc dust, and the reaction mixture was heated 40 min. under reflux. The acetic

(19) M. Clerc-Bory and C. Mentzer, *Bull. Soc. Chim.*, 814 (1953).

acid solution was decanted from the residual zinc, concentrated to a small volume, and cooled, giving 0.05 g. (69%) of benzylhydroxyquinolone, m.p. and mixed m.p. 218–219°.

Reaction of 1-methyl-3-benzyl-3-bromo-2,4(1H,3H)quinolindione with base. To a solution of 0.5 g. of potassium hydroxide in 12 ml. of methanol was added 0.2 g. of 1-methyl-3-benzyl-3-bromo-2,4(1H,3H)quinolindione, and the reaction heated 2 hr. at reflux. The clear yellow solution was cooled, diluted with water, extracted with methylene chloride, and the aqueous layer acidified with acetic acid to give a white solid. Recrystallization from aqueous acetic acid gave 0.07 g. (45%) of 1-methyl-3-benzyl-4-hydroxy-2-quinolone, m.p. and mixed m.p. 216–218°. After 6 hr. in refluxing aqueous methanol, the bromo compound was recovered unchanged.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Preparation of 1,1,1-Trichloro-3-nitro-2-alkenes[1]

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The condensation of chloral with nitro paraffins has been found to take place in the vapor phase at 360° in the presence of a magnesium sulfate-amine catalyst. Formaldehyde has also been found to condense satisfactorily with nitro paraffins under similar conditions but not a variety of other carbonyl compounds. In both cases the corresponding nitro alcohols are formed as well as the expected nitro olefins.

Nitro olefins with the general structure $CCl_3CH{=}CRNO_2$ were desired for other studies contemplated in this laboratory. A logical approach to these compounds appeared to lie in the condensation of chloral with nitro paraffins according to reactions (1) and (2). The first of these reactions has been reported

$$CCl_3CHO + RCH_2NO_2 \longrightarrow CCl_3CHOHCHRNO_2 \quad (1)$$

$$CCl_3CHOHCHRNO_2 \longrightarrow CCl_3CH{=}CRNO_2 + H_2O \quad (2)$$

for R=H by Chattaway and Witherington[3] and for $R=CH_3$ by Chattaway, Dewitt, and Parkes.[4] These reactions were carried out by condensing chloral with the corresponding nitro paraffins in the liquid phase using sodium sulfite or potassium carbonate as catalysts. The second reaction was studied for R=H by Irving and Fuller[5] who treated this trichloronitro alcohol with phosphorus pentoxide at elevated temperatures.

It occurred to us that chloral might be caused to condense with nitro paraffins directly, and nitro olefins obtained in one step, by operating in the vapor phase over a suitable catalyst. A search of the literature revealed a patent by Hasche[6] claiming a similar vapor phase condensation between nitro paraffins and formaldehyde using a variety of inorganic acids and salts as catalysts. Unfortunately the patent discloses no data on yields or purity of the products. Accordingly, it was decided to re-examine this method as a preliminary step in achieving the desired syntheses.

Studies with formaldehyde and nitropropane indicated that the catalysts recommended by Hasche give only traces of 2-nitro-1-butene. Hence, a number of other substances were tested, and it was found that a combination of magnesium sulfate and amines was considerably more effective than any other catalyst. Neither the magnesium sulfate nor the amines alone gave more than a few per cent of nitro olefins while together they gave up to 40% conversion. Next an attempt was made to determine the type of amine which worked best. It was found that ammonia and primary amines were ineffective, secondary amines were moderately effective, and low molecular weight tertiary amines (C_3 to C_6) were best.

The condensation conversions are highly dependent upon the concentration of amine catalyst in the reaction mixture and on the temperature of the reaction zone. The effective range of concentration found for triethylamine was 0.10 to 1.00 mole per cent with optimum results being obtained at about 0.23 mole per cent. Similarly the effective range of temperature in the reactor was 200° to 390° with optimum conversions being obtained at about 290–350°.

In all of the above runs 2-nitro-1-butanol was also formed. The principal factor affecting the nitro alcohol–nitro olefin ratio was the amine concentration with higher concentrations of amine favoring higher ratios of alcohol. Optimum conversions (*ca.* 45%) to 2-nitro-1-butanol were obtained with 2.0–4.0 mole per cent of triethylamine.

Application of the above information to the synthesis of nitro olefins from other primary nitro paraffins than 1-nitropropane showed that 1-nitrobutane gave similar conversions while nitroethane gave much poorer conversions to nitro

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(3) F. Chattaway and D. Witherington, *J. Chem. Soc.*, 1178 (1935).

(4) F. Chattaway, J. Dewitt, and G. Parkes, *J. Chem. Soc.*, 1294 (1936).

(5) H. Irving and H. Fuller, *J. Chem. Soc.*, 1989 (1948).

(6) R. L. Hasche, U. S. Pat. 2,298,375 (Oct. 13, 1938).