EXPERIMENTAL

The ^{13}C NMR spectra of 20% solutions of the compounds in $CDCl_3$ containing cyclohexane (as the internal standard) were obtained at room temperature with a WH-90 spectrometer with an operating frequency of 22.63 MHz. The spectra were recorded under pulse conditions with a pulse duration of 5 μsec. The error in the shift on the δ scale from tetramethylsilane (in the case of a computer memory of 4-kilobytes and a scanning range of 6000 Hz) was ± 0.1 ppm.

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BENZO[g]ISOQUINOLINIUM BENZOYLMETHYLIDS

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Stable benzo[g]isoquinolinium methylids were obtained from N-phenacylbenzo[g]isoquinolinium bromides and two of its benzene ring-substituted analogs. The first of these quaternary salts was converted to benzo[g]isoquinolinium dibenzoylmethylid. 3-Benzoyl-1,2-dicarbomethoxynaphth[2,3-g]indolizine was obtained from the same salt with dimethyl acetylenedicarboxylate (via a 1,3-dipolar cycloaddition reaction).

Having at our disposal a relatively simple method for the synthesis of benzo[g]isoquinolines [1], the chemistry of which has thus far been studied to only a limited extent, we attempted to ascertain the possibility of the synthesis of benzo[g]isoquinolinium benzoylmethylids from them.

In the present research we used the previously synthesized benzo[g]isoquinoline (I), as well as 8-methyl- and 7,8-dimethylbenzo[g]isoquinolines (II, III) [2]. Benzo[g]isoquinolines I and III were converted to quaternary salts, viz., 2-phenacyl- and 7,8-dimethyl-2-phenacylbenzo[g]isoquinolinium bromides (IV, V), in quantitative yields by reaction with bromoacetophenone. The ylids of these nitrogen-containing heterocyclic systems, viz., benzo[g]isoquinolinium benzoylmethylid (VI) and 7,8-dimethylbenzo[g]isoquinolinium benzoylmethylid (VIII), were obtained by treatment of these salts with a solution of potassium carbonate. 8-Methylbenzo[g]isoquinolinium methylid (VII) was similarly obtained without isolation of the corresponding quaternary salt. Benzo[g]isoquinolinium dibenzoylmethylid (IX) was obtained via the Schotten—Baumann reaction by benzoylation of quaternary salt IV.

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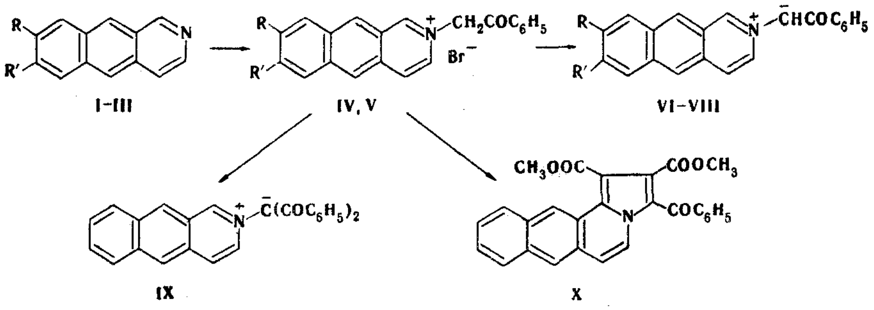

I IV, VI R=R'=H; II, VII R=H, R'=CH_3; III, V, VIII R=R'=CH_3

3-Benzoyl-1,2-dicarbomethoxynaphth[2,3-g]indolizine (X), which was obtained as high-melting yellow-orange crystals, was synthesized via 1,3-dipolar cycloaddition from quaternary salt IV (it is converted to ylid VI by treatment with triethylamine) and dimethyl acetylenedicarboxylate. The disappearance of the α-H signal (δ 9.08 ppm, s, 1H in starting I) and the presence of a doublet signal (J = 8.5 Hz) of the α' proton at 8.48 ppm (δ 8.40 ppm, d, J = 8.0 Hz in starting I) constitute evidence for angular fusion of the indolizine fragment with the naphthalene fragment in X.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The UV spectra of solutions of the compounds in chloroform were recorded with a Hitachi EPS-3T spectrophotometer. The PMR spectra were obtained with a Bruker WP-80CW spectrometer. The mass spectra were obtained with MKh-1303 and MS-30 spectrometers.

2-Phenacyl- and 7,8-Dimethyl-2-phenacylbenzo[g]isoquinolinium Bromides (IV, V). A mixture of 3.3 g (18.5 mmole) of benzo[g]isoquinoline I and 3.8 g (19 mmole) of bromoacetophenone in 30 ml of acetonitrile was refluxed for 2 h, after which the solvent was removed, and the residue was triturated in absolute ether to give 5.6 g (80%) of salt IV with mp 222-224°C (from ethanol). IR spectrum: 1703 cm^{-1} (CO). PMR spectrum [CF_3COOH, tetramethylsilane (TMS)], δ: 9.27 (s, 1H, 1-H), 8.47 (s, 1H, 10-H), 8.00 (s, 2H, 5-H), and 5.94 ppm (s, 2H, NCH_2). Found %: Br 20.8; N 3.6. $C_{21}H_{16}BrNO$. Calculated %: Br 21.2; N 3.7. Similarly, the reaction of 1 g (5 mmole) of III and 1.2 g (6 mmole) of bromoacetophenone gave 1.8 g (92%) of quaternary salt V with mp 166-168°C (from ethanol). IR spectrum: 1695 cm^{-1} (CO). UV spectrum, λ_{max} (log ε): 288 (5.02), 380 (3.76), 360 (3.90), 382 (4.22), and 460 nm (3.72). PMR spectrum (CF_3COOH, TMS), δ: 9.21 (s, 1H, 1-H), 8.83 (s, 1H, 10-H), 8.47 (s, 1H, 5-H), and 6.89 ppm (s, 2H, NCH_2). Found %: Br 19.8; N 3.1. $C_{23}H_{20}BrNO$. Calculated %: Br 20.0; N 3.4.

Benzo[g]isoquinolinium Benzoylmethylid (VI) and 7,8-Dimethyl- (VIII) and 8-Methylbenzo[g]isoquinolinium Benzoylmethylid (VII). A) A 15-ml sample of a solution of potassium carbonate and 20 ml of water (in 10-ml portions) were added successively with vigorous stirring to a solution of 1.34 g (3.4 mmole) of salt IV in 20 ml of acetonitrile, and the resulting orange precipitate was washed with 5 ml of water and dried to constant weight in a vacuum desiccator over P_2O_5 to give 0.63 g (62%) of ylid VI with mp 212-214°C. IR spectrum: 1675 and 1625 cm^{-1} (CO). UV spectrum, λ_{max}, nm (log ε): 258 (4.62) and 290 sh (4.10). PMR spectrum (CF_3COOH^a, CF_3COOD^b, hexamethyldisiloxane), δ: 9.12 (s, 1H, 1-H), 8.52 (s, 1H, 10-H), 8.20 (s, 1H, 5-H), 5.94 (s, 2H, $NCH_2{}^a$), and 5.94 ppm (s, 1H, $NCHD^b$). Found %: N 5.1; M^+ 297. $C_{21}H_{15}NO$. Calculated %: N 4.7; M 297. Similarly, the reaction of 1.5 g (3.7 mmole) of quaternary salt V gave 0.7 g (58%) of ylid VIII with mp 176-178°C. IR spectrum: 1690, 1630, and 1610 cm^{-1} (CO). UV spectrum, λ_{max}, nm (log ε): 258 (4.72), 290 sh (4.16), 396 (3.44), 430 (3.16), and 466 sh (3.06). PMR spectrum (CF_3COOH, TMS), δ: 9.50 (s, 1H, 1-H), 8.94 (s, 1H, 10-H), 8.60 (s, 1H, 5-H), 6.41 (s, 2H, NCH_2), and 2.60 ppm (s, 6H, 7,8-CH_3. Found %: N 4.1. $C_{23}H_{29}NO$. Calculated %: N 4.3.

B. A 2-g (5 mmole) sample of II was refluxed with 1.2 g (6 mmole) of bromoacetophenone in 25 ml of acetonitrile for 4 h, after which the mixture was cooled, and a solution of 1.6 g of potassium carbonate in 20 ml of water was added to the dark-cherry-red solution. The resulting precipitate was washed successively with water and ether and dried to constant weight to give 1.8 g (73%) of ylid VII with mp 247-248°C. IR spectrum: 1685 and 1635 cm^{-1} (CO). UV spectrum, λ_{max}, nm (log ε): 257 (4.70) and 320 sh (4.00). PMR spectrum (CF_3COOH, TMS), δ: 9.54 (s, 1H, 1-H), 8.94 (s, 1H, 10-H), 8.68 (s, 1H, 5-H), 6.34 (s, 2H, NCH_2), and 2.62 ppm (s, 3H, 8-CH_3). Found %: N 4.7; M^+ 311. $C_{22}H_{17}NO$. Calculated %: N 4.5; M 311.

Benzo[g]isoquinolinium Dibenzoylmethylid (IX). A 1.2-ml (8 mmole) sample of benzoyl chloride and 3 ml (20 mmole) of triethylamine were added successively to a solution of 2.5 g (6.6 mmole) of quaternary salt IV in 30 ml of chloroform, and the mixture was stirred for 1 h. The solvent was removed, and the residue was dissolved in ethanol and precipitated by the addition of absolute ether to give 2.05 g (70%) of dibenzoylmethylid IX as a red-brown powder with mp 172-174°C. IR spectrum: 1503 cm^{-1} (CO). UV spectrum, λ_{max}, nm (log ε): 256 (4.68), 340 (3.88), 396 (3.48), 436 sh (3.42), and 500 nm (3.20). PMR spectrum ($CDCl_3$, TMS), δ: 9.50 (s, 1H, 1-H), 8.75 (s, 1H, 10-H), and 8.37 ppm (s, 1H, 5-H). Found %: N 3.3; M^+ 401. $C_{28}H_{19}NO_2$. Calculated %: N 3.5; M 401.

3-Benzoyl-1,2-dicarbomethoxynaphth[2,3-g]indolizine (X). A 1.64-g (14 mmole) sample of dimethylacetylenedicarboxylate and 1.7 g (17 mmole) of triethylamine were added to a solution of 2.2 g (6 mmole) of salt IV in 35 ml of chloroform, and the mixture was refluxed for 8 h. It was then cooled and washed with water. The chloroform solution was dried with magnesium sulfate, and the chloroform was removed by distillation. The residue was chromatographed with a column (H = 50 cm, d = 2.5 cm, activity II aluminum oxide, elution with ether) to give 0.4 g (15%) of X in the form of golden crystals with mp 198-199°C (from ethanol). UV spectrum, λ_{max} (log ε): 260 (4.90), 300 (5.00), 330 (4.60), 385 (4.48), and 405 nm (4.44). PMR spectrum ($CDCl_3$, TMS), δ: 9.30 (s, 1H, 11-H), 8.48 (d, 1H, 4-H), 8.07 (s, 1H, 6-H), 7.10 (d, 1H, 5-H), and 4.00 and 3.23 ppm (s, 3H each, $COOCH_3$). Found %: C 74.3; H 4.6; N 3.2; M^+ 437. $C_{27}H_{19}NO_5$. Calculated %: C 74.1; H 4.3; N 3.2; M 437.

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PREPARATION AND SOME PROPERTIES OF 2H-IMIDAZOLE 1,3-DIOXIDES, DERIVATIVES OF ALICYCLIC 1,2-DIOXIMES

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The corresponding 2H-imidazole 1,3-dioxides were obtained by the reaction of cyclohexanedione and cycloheptadione 1,2-dioximes with acetone, cyclopentanone, and methyl ethyl ketone. The reactions of these compounds with hydroxylamine hydrochloride, $NaBH_4$, a Grignard reagent, and acetic anhydride in the presence of H_2SO_4 were studied in the case of 2,2-dimethyl-4,5,6,7-tetrahydro-2H-benzimidazole 1,3-dioxide. Bromination of the latter and 2,2-dimethylcyclohepta-2H-imidazole 1,3-dioxide with N-bromosuccinimide gave the corresponding dibromo derivatives, the bromine atoms in which are replaced by acetoxy and hydroxy groups. 4,7-Dihydroxy-2,2-dimethyl-4,5,6,7-tetrahydro-2H-benzimidazole 1,3-dioxide, which was obtained by oxidation with MnO_2, was converted to a quinone, viz., 2,2-dimethyl-4,7-dioxo-4,7-dihydro-2H-benzimidazole 1,3-dioxide.

2H-Imidazole N,N'-dioxides are presently difficult-to-obtain compounds to which very little study has been devoted; only a few examples of their synthesis are known [2, 3]. At the same time, 2H-benzimidazole 1,3-dioxides are rather well known and have unusual reactivities [4]. The aim of the present research was to synthesize and study the properties of

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