the methoxypyrimidobenzothiazolium chloride IIb in 20 ml of methanol was refluxed for 3 hr. The excess solvent was removed *in vacuo*. The solid residue was treated with 50 ml of boiling acetonitrile and the mixture was filtered to separate 0.46 g of solid insoluble in the acetonirile. After the filtrate had stood for 2 days, 0.26 g (26%) of IVc were collected, mp >125° (slow dec).

An additional 0.4 g (36%) of IVc was obtained when the acetonitrile-insoluble solid was dissolved in methanol and ether was added carefully. The following assignment was made for the nmr spectrum (DMSO-d_6 solution): δ 7.2–7.72 (multiplet, aromatic H), 9.91 (broad, exchanges, NH_2), 4.81 (triplet, $\overset{+}{N}CH_2$), 3.97 (singlet, $-OCH_3$), 3.67 (singlet, $O{=}COCH_3$), and 2.91 [triplet, $-CH_2(C{=}O)O-$].

Anal. Calcd for $C_{12}H_{15}ClN_2O_3S$: C, 47.61; H, 4.99; N, 9.25. Found: C, 47.73; H, 5.08; N, 9.22.

Registry No.—IIa, 21140-01-2; IIb, 23230-61-7; III, 17326-07-7; IVa, 23230-63-9; IVb, 23230-64-0; IVc, 23230-65-1; IVd, 23230-66-2.

Acknowledgment.—We wish to thank Dr. K. Stevenson and Professor R. E. Lyle for helpful discussions and Dr. P. L. Levins for the spectral data.

Transformation Products of 2-(2-Imidazolin-2-yl)benzophenone

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Received September 8, 1969

2-(2-Imidazolin-2-yl)benzophenone, which has been shown to exist in two tautomeric forms (**1** and **2**),[2] was treated with *p*-toluenesulfonic acid in refluxing xylene to give the dehydrated compound **3** (Scheme I). It was found that **3** underwent a slow oxidation with air in refluxing ethanol using platinum on carbon as a catalyst to give the ketoimidazo compound **5**. This compound, on reduction with sodium borohydride, gave the imidazolylbenzhydrol **4**, which on dehydration gave the original imidazoisoindole **3**. The known reaction of dimethylsulfoxonium methylide with ketones to give epoxides *via* methylene transfer[3] prompted us to treat both compounds **1** and **5** with this reagent. The synthesis of other small heterocyclic ring systems by the use of this reagent has recently received some attention in the literature.[4] As anticipated, methylene transfer took place. The intermediates (such as A) were not isolated but cyclized in the reaction medium to give the observed products. Thus compound **1** gave the imidazoisoquinoline **6**. The corresponding ketone **5** gave the expected unsaturated product **9**. Further dehydration of **9** in boron trifluoride etherate in acetic acid gave the fully saturated derivative **8**. This compound was also obtained from compound **6**, first by dehydration with thionyl chloride to give the intermediate **7**, followed by dehydrogenation in refluxing tetralin with palladium on carbon as a catalyst. The structure of compound **7** was readily confirmed by an independent synthesis from isocoumarone (**10**) by treatment with ethylenediamine in the presence of *p*-toluenesulfonic acid. Similarly, compound **8** could be prepared by the catalytic dehydrogenation of **12**. This, in turn, was prepared in one of three ways. Treatment of either the dihydroisocoumarone **11** or 3-methyl-3-phenylphthalide (**13**) or its isomer **16** with ethylenediamine in the presence of *p*-toluenesulfonic acid all gave compound **12**.

Experimental Section[5]

5-Phenyl-5H-imidazo[2,1-*a*]isoindole (3). A. From Compound 1.—A mixture of 2.5 g (50 mmol) of 1[2], 0.5 g of *p*-toluenesulfonic acid, and 250 ml of *m*-xylene was heated under reflux for 1 hr in a 500-ml flask equipped with a Dean–Stark trap and condenser. Xylene was removed under reduced pressure, 40 ml of 0.1 *N* sodium hydroxide was added, and the mixture was extracted with methylene chloride. The extracts were washed with water, dried over anhydrous sodium sulfate, and evaporated to leave a pale pink solid. The solid was dissolved in 70 ml of hot ethyl acetate, treated with Norit, and filtered. The solution was concentrated to a volume of 40 ml, followed by the addition of 100 ml of petroleum ether and cooling. Filtration gave 8.9 g (76.7%) of **3** as a pale pink solid, mp 145–148° dec. Recrystallization twice from ethyl acetate–petroleum ether gave colorless prisms: mp 147–150° dec; uv max 224 mμ (inflection, ϵ 14,700), 280 (14,200), and 295 (inflection, 10,400); nmr ($CDCl_3$) δ 5.90 (singlet, 1 H) and multiplets centered at δ 7.20 (10 H) and 7.90 (1 H).

Anal. Calcd for $C_{16}H_{12}N_2$: C, 82.73; H, 5.21; N, 12.06. Found: C, 82.82; H, 4.85; N, 12.03.

B. From Compound 4.—A solution of 0.5 g (2 mmol) of **4** and 0.1 g of *p*-toluenesulfonic acid in 50 ml of xylene was heated at reflux for 46 hr, using a Dean–Stark trap to collect the water formed. Solvent was removed under reduced pressure, 20 ml of 0.1 *N* sodium hydroxide was added, and the mixture was extracted with methylene chloride. The extracts were washed with water, dried over sodium sulfate, and evaporated to leave a yellow oil which crystallized upon scratching. The solid was dissolved in 25 ml of hot ethyl acetate, treated with Norit, filtered, and concentrated to a volume of 5 ml. Petroleum ether (5 ml) was added and the solution was cooled. Filtration gave 250 mg (53.9%) of **2** as colorless crystals, mp (and mixture melting point with a sample prepared as in A above) 146–148°.

2-(2-Imidazolyl)benzophenone (5).—A mixture of 11.6 g (50 mmol) of **3**, 5.0 g of a 10% platinum on carbon catalyst, and 300 ml of ethanol was heated at reflux, with a gentle stream of air bubbling through the mixture, for 16 hr. The mixture was filtered and the filtrate was evaporated under reduced pressure to leave a pale yellow solid. Recrystallization from ethyl acetate gave 8.2 g (66.1%) of **5**, mp 155–158° dec. Recrystallization gave the analytical sample as colorless prisms: mp 158–160° dec; uv max 251 mμ (ϵ 20,200) and 315 (2350); ir ($CHCl_3$) 1658 cm^{-1} (C=O).

Anal. Calcd for $C_{16}H_{12}N_2O$: C, 77.40; H, 4.87; N, 11.28. Found: C, 77.20; H, 4.85; N, 11.25.

2-(2-Imidazolyl)benzhydrol (4).—A solution of 4.96 g (20 mmol) of **5** and 1.89 g (50 mmol) of sodium borohydride in 75 ml of ethanol was heated under reflux for 2 hr. Ethanol was removed under reduced pressure and 50 ml of water was added. The mixture was extracted with methylene chloride and the extracts were washed with water, dried over sodium sulfate, and evaporated to leave a pale yellow oil. The oil was crystallized

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[1] To whom correspondence should be addressed.

[2] W. Metlesics, T. Anton, M. Chaykovsky, V. Toome, and L. H. Sternbach, *J. Org. Chem.*, **33**, 2874 (1968).

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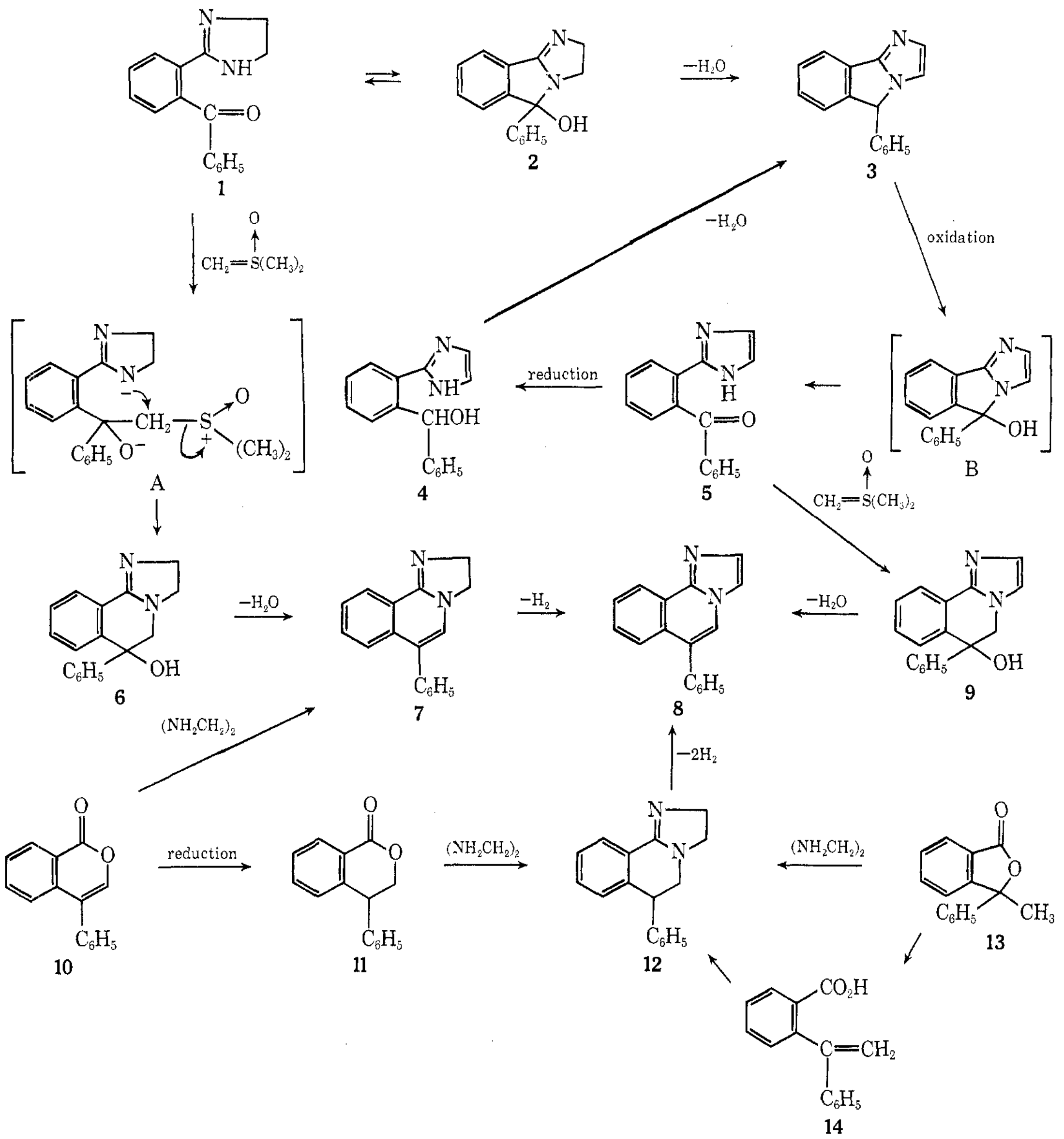
[4] See P. Bravo, G. Gaudiano, and A. Umani-Rochi, *Tetrahedron Lett.*, No. 9, 679 (1969), and references cited therein.

[5] All melting points were determined microscopically on a hot stage and are corrected. The uv spectra were determined in 2-propanol on a Cary Model 14 spectrophotometer, nmr spectra with a Varian A-60 instrument, and ir spectra on a Beckman IR-9 spectrophotometer. Petroleum ether refers to a fraction of bp 30–60°.

SCHEME I



from 20 ml of ethyl acetate. Filtration gave 4.0 g (80%) of the alcohol **4** as a white solid. Recrystallization from ethyl acetate gave colorless prisms, mp 155–156°, uv max 267 mμ (ε 11,400). The near-ir ($CHCl_3$) shows NH absorption at 1.47 μ (ε 0.8), and OH absorption at 1.43 μ (ε 0.18).

Anal. Calcd for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64; N, 11.19. Found: C, 76.77; H, 5.56; N, 11.23.

6-Hydroxy-6-phenyl-2,3,5,6-tetrahydroimidazo[2,1-*a*]isoquinoline (6).—Sodium hydride (12.0 g of 60% oil dispersion, 0.30 mol) was placed in a 1-l., three-necked flask and swirled with 50 ml of petroleum ether. The petroleum ether was decanted, 250 ml of dry dimethyl sulfoxide [distilled from calcium hydride, bp 64° (4 mm)] was added and the system was placed under nitrogen. With stirring, 68 g (0.31 mol) of trimethyloxosulfonium iodide[3] was added, in portions over a period of 20 min, through a piece of Gooch tubing connected to the flask. After the mixture had been stirred for 1 hr, 25.0 g (0.1 mol) of **1** was added, as the solid, over a period of 5 min. The reaction mixture was then heated at 100° for 30 min, cooled, and poured into 1 l. of ice–water. Filtering gave 21.2 g (80.4%) of **6** as a tan solid which was recrystallized from methanol–chloroform (Norit) to give colorless prisms: mp 264–266° dec; uv max 237 mμ (ε 13,300), 282 (3620), and 302 (inflection, 2600); ir ($CHCl_3$) 1618 cm^{-1} (sharp, strong).

Anal. Calcd for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60. Found: C, 77.10; H, 6.06; N, 10.85.

6-Phenyl-2,3-dihydroimidazo[2,1-*a*]isoquinoline (7). A. From Compound 6.—A suspension of 10.6 g (0.04 mol) of **6** in 105 ml of pyridine was stirred and cooled while 24 g (14.5 ml, 0.2 mole) of thionyl chloride was added at 25–30°. When the addition was completed, stirring was continued at room temperature for a total of 1.5 hr. The orange solution was poured into 1.6 l. of ice–water with stirring, basified with 50% sodium hydroxide solution, and diluted to 2 l. with water to give a yellow solid. After 30 min, the solid was collected by filtration and dried partially on the funnel. The damp solid was dissolved in chloroform which was dried over sodium sulfate and evaporated to give 7.3 g (74%) of **7** as a pale yellow solid, mp 155–159°. Recrystallization from benzene–hexane solution (Norit) gave pure **7** as pale yellow needles: mp 160–161° dec; uv max 207 mμ (ε 42,300), 267 (10,750), 272 (15,300), and 340 (9500); ir ($CHCl_3$) 1640 cm^{-1} (strong).

Anal. Calcd for $C_{17}H_{14}N_2$: C, 82.90; H, 5.73; N, 11.37. Found: C, 38.24; H, 5.94; N, 11.42.

B. From Compound 10.—A mixture of 11.1 g (0.05 mol) of **10**[6] and 58 g (0.25 mol) of ethylenediamine *p*-toluenesulfonate was stirred in an open flask at 190–200° for 6 hr. After cooling, the pale yellow, hard mass was covered with 200 ml of hot water, broken up with a spatula, and stirred for 30 min. The pale yellow solid was collected by filtration, air dried partially on the funnel, and dissolved in 200 ml of chloroform. The chloroform solution was washed twice with 75-ml portions of 1 *N* sodium

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[6] F. Daro and P. Condorelli, *Boll. Sedute Accad. Gioenia Sci. Nat. Catania*, **6**, 606 (1960); *Chem. Abstr.*, **58**, 9010 (1963).

hydroxide solution and once with water. After having been dried over sodium sulfate, the solution was evaporated *in vacuo* to give 12.3 g (100%) of pale yellow solid, mp 150–160°. Recrystallization from benzene gave **7** as pale yellow needles, mp (and mmp with a sample prepared by method A), 160–161°.

6-Phenylimidazo[2,1-*a*]isoquinoline (8). A. From Compound 9.—A solution of 850 mg (3.24 mmol) of **9** and 0.5 ml of boron trifluoride etherate in 10 ml of acetic acid was heated under reflux for 5 hr and poured into 30 ml of water which was then basified with 50% aqueous sodium hydroxide. The mixture was extracted with chloroform and the extracts were combined, washed with water, dried over sodium sulfate, and evaporated to yield 700 mg (88.5%) of **8** as a white solid. Recrystallization from benzene–hexane gave the pure product as colorless needles: mp 152–153.5°; uv max 250 mμ (inflection, ε 41,700), 257 (52,800), 287 (inflection, 9000), and 324 (1400); nmr ($CDCl_3$) δ 7.47 (center of 10 H multiplet), 7.74 (1 H, singlet), and 8.67 (1 H, multiplet).

Anal. Calcd for $C_{17}H_{12}N_2$: C, 83.58; H, 4.95; N, 11.47. Found: C, 83.39; H, 4.95; N, 11.39.

B. From Compound 7.—A mixture of 24.6 g (0.1 mol) of **7** and 5 g of 25% palladium on carbon in 200 ml of tetraline was stirred under reflux for 2 hr. After cooling, the mixture was diluted with 150 ml of chloroform and filtered. The pale yellow filtrate was treated with 80 ml of 2.4 *N* methanolic hydrogen chloride solution and extracted into water (five 100-ml portions). The aqueous extracts were combined, basified with 2 *N* sodium hydroxide solution, and extracted with chloroform (three 100-ml portions). The light purple chloroform extract was dried over sodium sulfate and evaporated to give an oil which solidified on cooling to give a tan solid. Recrystallization from benzene–hexane (charcoal) gave 10.9 g (45%) of **8** as colorless needles, mp and mmp 150–151°.

C. From Compound 12.—A mixture of 2.5 g (0.01 mol) of **12** and 0.5 g of 25% palladium on carbon in 10 ml of tetralin was stirred at reflux for 5 hr. The warm mixture was filtered and the catalyst was rinsed with tetralin. The filtrate was diluted with petroleum ether until cloudy and cooled in an ice bath with occasional scratching. Tan crystals were collected after 15 min and air dried to yield 1.3 g (54%) of **8**, mp 142–147°. Recrystallization from benzene gave **8** as colorless needles, mp (and mixture melting point with a sample as prepared in A above) 152–153.5°.

6-Hydroxy-6-phenyl-5,6-dihydroimidazo[2,1-*a*]isoquinoline (9).—Sodium hydride (6.0 g of a 60% oil dispersion, 0.15 mol) was placed in a 1-l., three-necked flask and swirled with 50 ml of petroleum ether. The petroleum ether was decanted, 250 ml of dry dimethyl sulfoxide [distilled from calcium hydride, bp 64° (4 mm)] was added, and the system was placed under nitrogen. With stirring, 36.8 g (0.16 mol) of trimethyloxosulfonium iodide was added, in portions over a period of 15 min, through a piece of Gooch tubing connected to the flask. After the solution had been stirred for 45 min, 12.2 g (0.0492 mol) of **5** was added over a period of 5 min. Stirring was continued for 2 hr at room temperature and then at 70–80° for 1 hr. The reaction mixture was poured into 1 l. of ice-water which was then extracted with chloroform. The extracts were combined, washed with water, dried over sodium sulfate, and evaporated to leave a yellow, semisolid mass. Trituration with 40 ml of ethyl acetate, cooling, and filtering gave 2.8 g (21.7%) of white crystals, which were recrystallized from ethanol to give **9** as colorless prisms, mp 231–233° dec. The mother liquors were shown, by thin layer chromatography to consist mainly of starting material with several impurities: uv max 286 mμ (ε 14,840) and 300 (inflection, 10,000); nmr (CD_3COOD) δ 4.72 (2 H, quartet), 7.18 (10 H, multiplet), and 8.18 (1 H, multiplet).

Anal. Calcd for $C_{17}H_{14}N_2O$: C, 77.84; H, 5.38; N, 10.68. Found: C, 77.60; H, 5.47; N, 10.45.

6-Phenyl-2,3,5,6-tetrahydroimidazo[2,1-*a*]isoquinoline (12). A. From 3-Phenyl-3-methylphthalide (12).[7]—A mixture of 11.2 g (0.05 mol) of **13** and 58 g (0.25 mol) of ethylenediamine *p*-toluenesulfonate was heated in an oil bath at 190–200° with stirring for 20 hr. The melt was cooled, stirred with warm water, and extracted with 100 ml of chloroform. The chloroform extract was washed twice with 50-ml portions of 1 *N* hydrochloric acid, dried over sodium sulfate, and evaporated to dryness. The resulting orange oil was warmed with 50 ml of benzene with occasional scratching to give the toluenesulfonic acid salt of **12** as white crystals, mp 170–175°. The crude salt was dissolved in chloroform. The chloroform solution was washed twice with 50-ml portions of 1 *N* sodium hydroxide solution and once with water. After having been dried over sodium sulfate, the chloroform solution was evaporated to give 7.3 g (59%) of **12** as nearly colorless crystals. Recrystallization from benzene–hexane solution (Norite) gave colorless crystals: mp 133–134°; uv max 273 mμ (ε 13,800) and 280 (4100); ir ($CHCl_3$) 1615 cm^{-1} (strong).

Anal. Calcd for $C_{17}H_{16}N_2$: C, 82.23; H, 6.50; N, 11.28. Found: C, 82.55; H, 6.68; N, 11.28.

B. From *o*-(δ-Methylenebenzyl)benzoic acid (14).[8]—A mixture of 4.5 g (0.02 mol) of **14** and 23.2 g (0.1 mol) of ethylenediamine *p*-toluenesulfonate was heated with stirring in an oil bath at 190–200° for 20 hr. The melt was cooled, dissolved in 75 ml of warm water, and extracted with 100 ml of chloroform. The chloroform extract was washed twice with 50-ml portions of 1 *N* hydrochloric acid, dried over sodium sulfate, and evaporated to dryness to give an orange oil. The oil was warmed with 30 ml of benzene with occasional scratching to give the toluenesulfonic acid salt of **12** as tan crystals, mp 170–175°. The salt was converted into the base as above to give 3 g (60%) of **12**, mp and mmp 133–134°.

C. From 3,4-Dihydro-4-phenylisocoumarin (11).—A mixture of 1.7 g (0.008 mol) of **11** and 9.3 g (0.04 mol) of ethylenediamine *p*-toluenesulfonate was stirred at 190–200° for 6 hr and cooled to give a pale yellow solid. The mass was covered with 50 ml of warm water and broken up with a spatula. The mixture was extracted with chloroform. The chloroform extract was washed twice with 1 *N* hydrochloric acid, dried over sodium sulfate, and evaporated to dryness to give an orange oil. The oil was warmed with 10 ml of benzene with scratching to give the toluenesulfonic acid salt of **12** as nearly colorless crystals, mp 175–178°. The salt was converted into the base as for A above to give 1 g (53%) of **12** as pale yellow crystals. Recrystallization from benzene–hexane solution (charcoal) gave colorless crystals, mp and mmp 133–134°.

3,4-Dihydro-4-phenylisocoumarin (11).—To a suspension of 3.3 g (0.09 mol) of sodium borohydride in 150 ml of ethanol was added in portions 7.2 g (0.03 mol) of *o*-(α-formylbenzoyl)benzoic acid, which was prepared from 4-phenylisocoumarin by the method of Berti.[8] The mixture became hot and hydrogen was evolved. When the exothermic reaction had abated, the mixture was stirred and refluxed for 3 hr. The turbid, white solution was evaporated under reduced pressure to give a gummy, white solid. This solid was stirred with 300 ml of water, acidified with 6 *N* hydrochloric acid, and extracted with chloroform. After having been dried over sodium sulfate, the chloroform extract was evaporated under reduced pressure to give a colorless oil. The oil was stirred with aqueous sodium bicarbonate solution until it became viscous. The sodium bicarbonate solution was decanted and the gum was stirred with cold water until it solidified. The yield of waxy, white solid after air drying was 6.1 g (91%). Crystallization from hexane (40 ml/g) gave 3,4-dihydro-4-phenylisocoumarin (**11**) as white prisms: mp 58–60°; uv max 232 mμ (ε 11,100), and 282 (1800); ir ($CHCl_3$) 1725 cm^{-1} (strong).

Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.33; H, 5.39. Found: C, 80.35; H, 5.51.

Registry No.—**3**, 23293-85-8; **4**, 23293-86-9; **5**, 23293-87-0; **6**, 23293-88-1; **7**, 23293-89-2; **8**, 23293-90-5; **9**, 23293-91-6; **11**, 23293-92-7; **12**, 23293-93-8.

Acknowledgment.—We are indebted to the following members of the Physical Chemistry Department under the direction of Dr. P. Bommer: Dr. Toome for the uv spectra, Dr. T. Williams for nmr spectra, Mr. S. Traiman for ir spectra, and Dr. F. Scheidl for the microanalyses. We also wish to thank Professor G. Büchi for helpful discussions.

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