Registry No.—I, 62076-97-5; III, 66-22-8; IV, 626-48-2; V, 608-34,4; VI, 615-77-0; urea, 57-13-6; methylurea, 598-50-5; thiourea, 62-56-6; propiolic acid, 471-25-0; tetrolic acid, 590-93-2.

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Synthesis of Hexahydroquino[8,7-*h*]quinolines. Cis and Trans Isomers of 3,9-Dimethyl-4b,5,6,10b,11,12-hexahydroquino[8,7-*h*]quinoline

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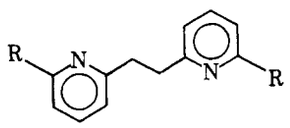
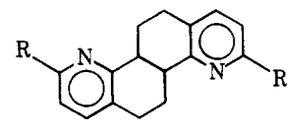
Received November 29, 1976

Preliminary findings suggestive of the biological importance of some 1,2-di(2-pyridyl)ethane derivatives (I) prompted a research program aimed at the synthesis of some steroidal



I

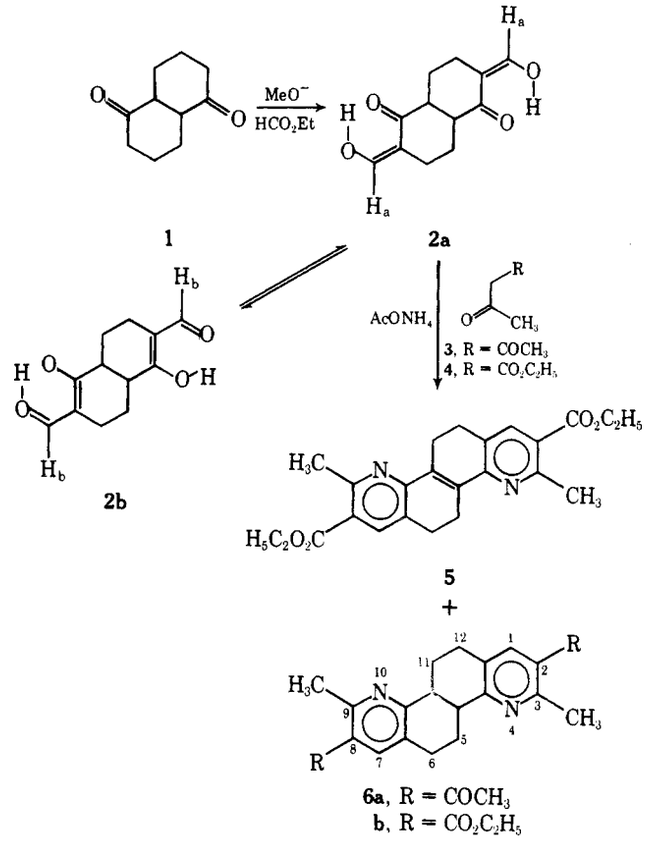


II

analogues which could be regarded as their rigid counterparts (II). The synthetic sequence leading to these type of medicinally interesting compounds started with pure *trans*-decalin-1,5-dione (1)[1] (Scheme I). Treatment of 1 with ethyl formate in pyridine utilizing sodium methoxide as catalyst afforded compound 2 in good yields. NMR spectral data of 2 seem to indicate that the compound exists as a mixture of rapidly equilibrating tautomers with an average signal for the H_a and H_b protons at δ 9.00. According to the formula proposed by Garbisch[2] for this type of equilibrium the mixture is 92% in favor of tautomer **2b.** In addition, a singlet at δ 14.5, accounting for two protons, underwent easy exchange with D_2O.

Heating 2 with either acetylacetone (3) or ethyl acetoacetate (4), without solvent and in the presence of ammonium acetate, afforded **6a** and **6b,** respectively, in fair yields. Along with **6b,**

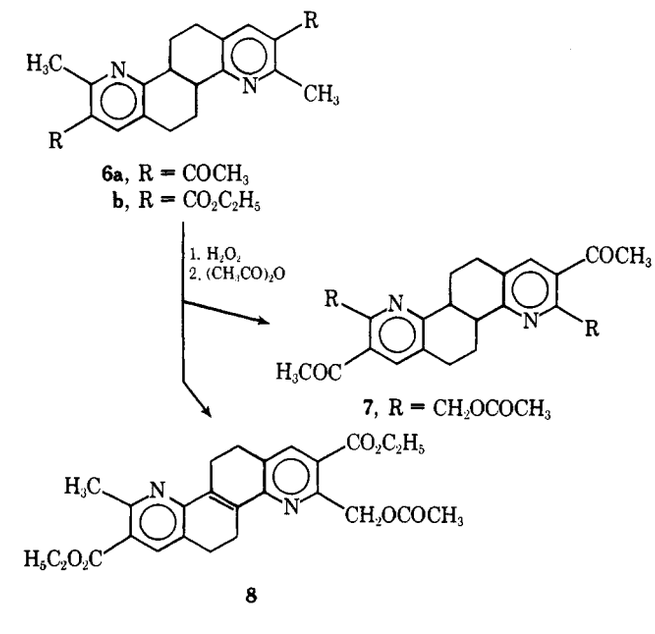
Scheme I



it was possible to isolate after chromatography a fluorescent material for which all available data indicated to have structure **5.** Structures of these compounds are in agreement with the appearance of singlets between δ 7.72 and 8.20, in the NMR spectra, which correspond to γ protons of a pyridine nucleus. This synthetic procedure is similar to the one employed by Breitmaier et al.[3] for the synthesis of cycloalkeno(*b*)pyridines from the corresponding α-(aminomethylene)cycloalkanones with either 3 or 4 in the presence of catalytic amounts of ammonium acetate.

An objective was to functionalize both α-methyl groups of the pyridine rings and later to eliminate the carbomethoxy group of **6b.** The functionalization step was successful when

Scheme II



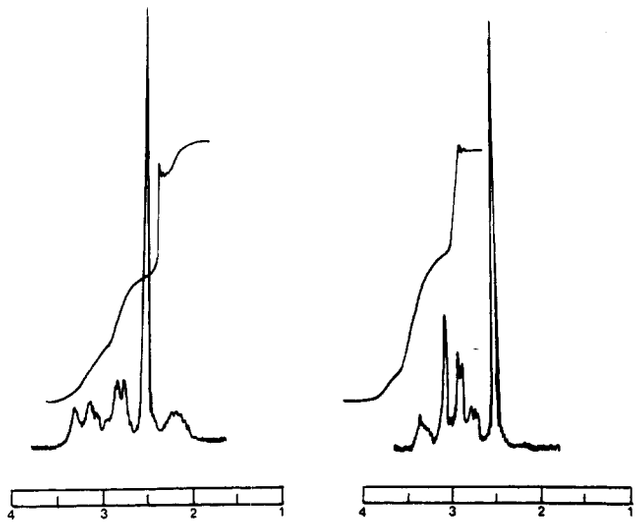
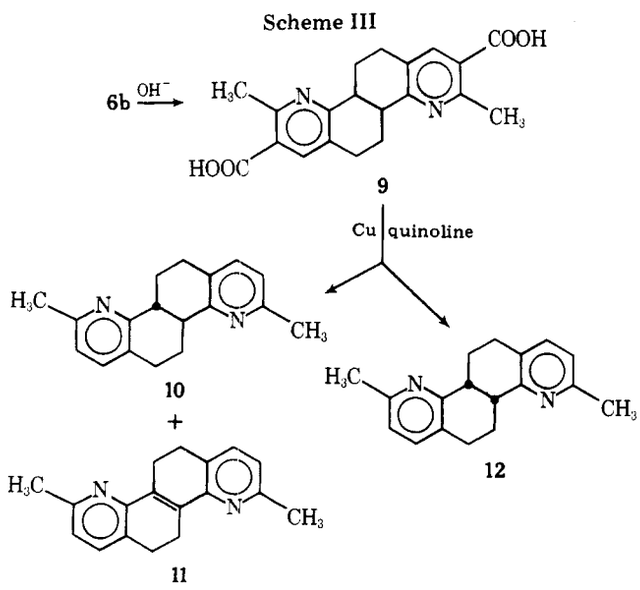


Figure 1. NMR spectra of cis and trans isomers **12** and **10**.

tried with **6a**, since its di-*N*-oxide when refluxed in acetic anhydride[4] rearranged in the expected manner to the desired diester **7**. However, in the case of **6b**, which was to be decarboxylated at a later stage, rearrangement of its di-*N*-oxide occurred in a different manner, affording compound **8** (Scheme II). A rearrangement of this type has been described in the literature for 1,2-di(6-methyl-2-pyridyl)ethane di-*N*-oxide.[4] Compound **8** was characterized by its NMR spectrum, which indicated that one α-methyl group had remained intact. The presence of a highly conjugated system was evidenced by the UV spectrum of **8**, which showed an intense absorption band at 364 nm similar to that of compound **5**. In addition, the compound in solution presented an intense fluorescence when observed under UV light. At the present time, we do not have a satisfactory explanation for the differences observed in the rearrangement of the di-*N*-oxides of **6a** and **6b**. In both cases, however, the yields are low and a great deal of tar is formed.

An alternative approach, which consisted of carrying out the decarboxylative step first, was attempted despite the possibility that a similar process that led to compound **8** would take place again at the functionalization step. Compound **6b** was hydrolyzed to the corresponding diacid (**9**) and, after several attempts to decarboxylate it, success was achieved by refluxing the compound in the presence of powdered copper in freshly distilled quinoline (Scheme III).

Scheme III



After workup, the material isolated showed a characteristic NMR AB pattern in the aromatic region, which suggested that decarboxylation had taken place. However, when the product was chromatographed on TLC it appeared to be a mixture of two components with two distinct R_f values. In addition, the spot with the larger R_f was highly fluorescent when observed under UV light, whereas the one with the smaller R_f was not. When the sample of crude decarboxylated product was column chromatographed, 0.5 g (15% yield) of the component with the larger R_f (first eluted) and 1.8 g (55% yield) of the component with the smaller R_f were separated. The first component, however, was found to be contaminated by the material responsible for the fluorescence. Several recrystallizations from ethyl acetate afforded a crystalline material, mp 215 °C, which was free from any fluorescence. The structure of the fluorescent contaminant was postulated to be the unsaturated compound **11** in view of the molecular ion peak at *m/e* 262 observed in the mass spectrum and the remarkable similitarity of its UV spectrum with that of compounds **5** and **8**. Both the purified material, mp 215 °C, and the last compound isolated from the column, mp 108 °C, showed similar IR, UV, and MS with characteristic molecular ion peaks at *m/e* 264. The NMR spectra, however, almost identical in the aromatic region, demonstrated substantial differences in the aliphatic region (Figure 1). Aside from the chemical shift of the singlet corresponding to both α-methyl groups at δ 2.5, only the compound with the smaller R_f value (mp 108 °C) presented broad resonance lines upfield relative to 2.5. All the evidence suggested the presence of cis and trans isomers of the decarboxylated product (**10** and **12**), but NMR data was not considered reliable enough to assign the corresponding structures.

Crystals of the higher melting isomer)mp 215 °C) obtained in lower yields and consequently thought to be from the cis isomer were found to be suitable for x-ray analysis. X-ray measurements[5] uniquely indicated space group $P2_{1/a}$, with a = 7.37 (1), b = 12.77 (1), c = 7.66 (1) Å, β = 100.5 (1)°. The observed density corresponds to two molecules in the unit cell and since this space group requires four asymmetric units, the compound must possess a center of symmetry. Since the cis structure does not have a center of symmetry, the higher melting isomer has to have the trans configuration.

In view of the fact that the trans isomer was obtained in lower yields it means that somewhere along the synthetic sequence from *trans*-**1** to the final decarboxylated mixture, the preferred stereochemistry was inverted to the most stable cis isomer. NMR spectral comparison between compound **2** and both *cis*- and *trans*-decalin-1,5-dione clearly established that compound **2** has the trans configuration. Furthermore, compound **2** was also obtained starting from pure *cis*-decalin-1,5-dione. In the following step, however, the stereochemistry of the isolated diester **6b** (85% yield) is likely to have been inverted to the cis configuration in view of the similarity observed for portions of the NMR spectra of both cis isomer **12** and diester **6b**, in the region corresponding to the decalin backbone protons. Diester **6b** was isolated chromatographically pure, and since reesterification of diacid **9**, obtained from the hydrolysis of pure **6b**, afforded a single product identical in all respect to its precursor, it means diacid **9** also has the cis configuration. After decarboxylation, the major product retained the preferred cis configuration and some smaller amount inverted to the trans configuration possibly by a mechanism involving removal of one of the acidic bridgehead protons during quinoline reflux.[6]

Scale models confirm that the cis configuration appears to be less strained and more flexible than the trans configuration for these type of compounds. In addition, as inferred from Figure 2, it is likely the NMR signals observed upfield from δ 2.5 for the cis isomer might correspond to those decalin

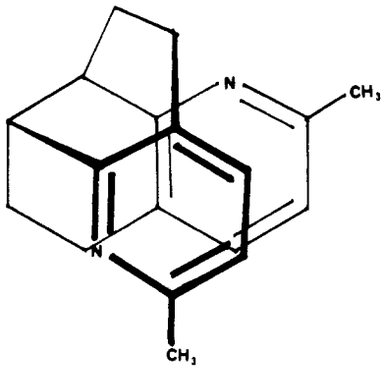


Figure 2. Puckered conformation of the cis isomer (12).

backbone protons situated above the shielding cone of the aromatic pyridines, a situation that is never encountered in the more rigid trans configuration.

Finally, when the functionalization step in the cis isomer (12) was carried out through its corresponding di-*N*-oxide, the reaction underwent extensive decomposition and no pure product could be isolated.

Experimental Section

General. All chemical reagents are commercially available. They were purchased either from E. Merck or Aldrich Chemical Co. Melting points were determined by means of an Electrothermal capillary melting point apparatus, and they are uncorrected. A Perkin-Elmer Model 727 infrared spectrophotometer was employed for IR spectra, using either Nujol mulls or chloroform solutions. A Varian Associates Model EM-360 analytical NMR spectrometer was used for NMR spectra of deuteriochloroform solutions with internal tetramethylsilane (δ 0.00 ppm) at ambient temperatures. Ultraviolet spectra were recorded on a Beckman Model 25 spectrophotometer, utilizing 1-cm path cells. Mass spectra were obtained in a Hitachi Perkin-Elmer RMU-6H instrument at 70 eV. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn.

***trans*-Decalin-1,5-dione (1).** This compound was prepared according to the procedure of Johnson et al., mp 162–164 °C [lit.[1] mp 164–166 °C].

***trans*-2,6-Bis(hydroxymethylene)decalin-1,5-dione (2).** A mixture of 1.66 g (10 mmol) of **1**, 2.16 g (40 mmol) of $NaOCH_3$, 9.2 mL (130 mmol) of ethyl formate, and 70 mL of dry pyridine was stirred under nitrogen at room temperature for 21 h. After the mixture was adjusted to a pH between 5 and 6 with the aid of 51 mL of AcOH and 471 mL of water, it was extracted with benzene several times. The benzene layers were thoroughly washed with water and then were extracted with 2% KOH solution. The basic extracts were washed with ether and then after reacidification with AcOH they were thoroughly extracted again with benzene. The benzene extracts were dried (Na_2SO_4) and then were reduced to dryness to give 2 g (90%) of crude **2**. Recrystallization from acetone afforded **2** as a fine yellow powder, mp 155–157 °C: IR (Nujol) 1640 and 1570 cm^{-1}; NMR ($CDCl_3$) δ 2.3 (br m, 10), 9.00 (s, 2), and 14.50 (s, 2); mass spectrum *m/e* 222 ($M^{+}\cdot$).

Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.69; H, 6.38.

***cis*-Diethyl 3,9-Dimethyl-4b,5,6,10b,11,12-hexahydroquino[8,7-*h*]quinoline-2,8-dicarboxylate (6b).** A mixture of 2 g (9 mmol) of **2** and 3.10 g of ethyl acetoacetate (**4**) was heated for 18 h at 125 °C in the presence of 2.78 g of ammonium acetate. The solid formed was taken up in $CHCl_3$ and extracted with 25% HCl. The acid extracts were washed with ether and, after basification with 25% NaOH, the yellow precipitate formed was extracted with $CHCl_3$, dried (Na_2SO_4), and reduced to dryness to give 3.12 g (85%) of crude product. After column chromatography by means of SiO_2 and chloroform, and following recrystallization from ethyl acetate, 1.28 g (35%) of pure **6b** was obtained as colorless crystals, mp 201–202 °C: IR ($CHCl_3$) 1720 and 1600 cm^{-1}; NMR ($CDCl_3$) δ 1.38 (t, 6), 2.25 (br m, 4), 2.70 (s, 6), 3.10 (br m, 6), 4.40 (q, 4), and 7.97 (s, 2); mass spectrum *m/e* 408 ($M^{+}\cdot$).

Anal. Calcd for $C_{24}H_{28}N_2O_4$: C, 70.56; H, 6.91; N, 6.86. Found: C, 70.75; H, 6.88; N, 6.90.

Diethyl 3,9-Dimethyl-5,6,11,12-tetrahydroquino[8,7-*h*]quinoline-2,8-dicarboxylate (5). From the chromatography column of the previous reaction, a yellow powder contained in the first fractions was isolated. Recrystallization from acetone afforded 0.05 g (1.4%) of **5** as yellow crystals, mp 229–229.5 °C: IR (Nujol) 1720 and 1600 cm^{-1}; NMR ($CDCl_3$) δ 1.40 (t, 6), 2.90 (s, 6), 3.2 (s, 8), 4.50 (q, 4), and 8.20 (s, 2); mass spectrum *m/e* 406 ($M^{+}\cdot$).

Anal. Calcd for $C_{24}H_{26}N_2O_4$: C, 70.91; H, 6.45; N, 6.89. Found: C, 70.86; H, 6.50; N, 6.81.

***cis*-2,8-Diacetyl-3,9-dimethyl-4b,5,6,10b,11,12-hexahydroquino[8,7-*h*]quinoline (6a).** This compound, obtained under the same experimental conditions as for **6b**, afforded after recrystallization from CH_3CN pure **6a**, mp 251–253 °C: IR ($CHCl_3$) 1690 and 1600 cm^{-1}; NMR ($CDCl_3$) δ 2.20 (br m, 4), 2.65 (s, 6), 2.75 (s, 6), 3.00 (br m, 6), and 7.72 (s, 2); mass spectrum *m/e* 348 ($M^{+}\cdot$).

Anal. Calcd for $C_{22}H_{24}N_2O_2$: C, 75.83; H, 6.94; N, 8.04. Found: C, 76.01; H, 6.86; N, 8.19.

***cis*-2,8-Diacetyl-3,9-bis(acetoxymethyl)-4b,5,6,10b,11,12-hexahydroquino[8,7-*h*]quinoline (7).** After isolation of 1.53 g (4 mmol) of the crude *N*-oxide of **6a**, which was prepared according to general literature procedures,[4] it was heated at 100 °C for 6 h with 8 mL of acetic anhydride. The mixture was cooled and the solid which formed was filtered and washed with water. The solid was recrystallized from CH_3CN to afford 0.45 g (37%) of pure **7**, mp 239–240 °C: IR (Nujol) 1740, 1680, 1600, and 1240 cm^{-1}; NMR ($CDCl_3$) δ 2.20 (br m, 4), 2.25 (s, 6), 2.60 (s, 6), 3.00 (br m, 6), 5.50 (s, 4), and 7.70 (s, 2); mass spectrum *m/e* 464 ($M^{+}\cdot$).

Anal. Calcd for $C_{26}H_{28}N_2O_6$: C, 67.22; H, 6.08; N, 6.03. Found: C, 67.03; H, 5.98; N, 6.05.

Diethyl 3-Acetoxymethyl-9-methyl-5,6,11,12-tetrahydroquino[8,7-*h*]quinoline-2,8-dicarboxylate (8). A similar procedure as for **7** was followed starting with 2.2 g (5.4 mmol) of **6b**. The corresponding di-*N*-oxide rearranged in acetic anhydride and, after reduction to dryness, the semisolid residue obtained was treated with charcoal in bng acetone. Following filtration, cooling gave a yellow powder. It was collected and chromatographed by use of SiO_2 and benzene–ethyl acetate (2:1). The first fraction collected was recrystallized from ethyl acetate to afford 0.4 g (16%) of **8** as fine yellow crystals, mp 154–156 °G IR (Nujol) 1750, 1720, 1600, and 1260 cm^{-1}; NMR ($CDCl_3$) δ 1.40 (t, 6), 2.20 (s, 3), 2.80 (s, 3), 3.00 (br s, 8), 4.4 (q, 4), 5.65 (s, 2), 8.00 (s, 1), and 8.10 (s, 1); mass spectrum *m/e* 464 ($M^{+}\cdot$).

Anal. Calcd for $C_{26}H_{28}N_2O_6$: C, 67.22; H, 6.08; N, 6.03. Found: C, 67.09; H, 6.02; N, 5.92.

Hydrolysis and Decarboxylation of 6b. A mixture of 5.1 g (12.5 mmol) of **6b**, 110 mL of ethanol, 110 mL of water, and 1.46 g of KOH was refluxed for 2 h. Once the alcohol was removed by distillation, the aqueous solution was treated with 10% HCl until a pH of 3 was reached. After cooling overnight in the refrigerator a fine solid was formed which was filtered and dried, affording 4.3 g of the crude diacid (**9**). A mixture of 2.33 g of the diacid, 9.8 g of powdered copper, and 400 mL of freshly distilled quinoline was refluxed for 4 h, whereupon a vigorous evolution of CO_2 took place. After distilling off the quinoline, the residue was taken up in $CHCl_3$, filtered, and reduced to dryness. The remaining dark semisolid (still contaminated with some quinoline) was chromatographed by means of 200 g of SiO_2 with ethyl acetate as eluent. The first product collected was the trans isomer (**10**), which afforded 0.5 g (15%) of a material still contaminated by a fluorescent compound. Several recrystallizations from ethyl acetate afforded a crystalline material free from any fluorescence, mp 215–217 °C: IR (Nujol) 1600 and 1580 cm^{-1}; NMR ($CDCl_3$) δ 2.5 (s, 6), 2.95 (m, 10), 6.90 (d, 2, J = 4 Hz), and 7.32 (d, 2, J = 4 Hz); mass spectrum *m/e* (rel intensity) 264 (100) (parent), 263 (88), 249 (16), 158 (20), 146 (12), 144 (22), 133 (12), 132 (28), and 131 (28).

Anal. Calcd for $C_{18}H_{20}N_2$: C, 81.77; 7.63; N, 10.60. Found: C, 81.63 H, 7.56; N, 10.42.

After collecting some quinoline as a second fraction, the cis isomer (**12**) began to elute from the column, affording 1.8 g (55%) of pure product which was recrystallized as white needles from ethyl acetate, mp 106–108 °C: IR (Nujol) 1600 and 1580 cm^{-1}; NMR ($CDCl_3$) δ 2.25 (br m, 2), 2.50 (s, 6), 3.15 (br m, 8), 6.95 (d, 2, J = 4 Hz), and 7.40 (d, 2, J = 4 Hz); mass spectrum *m/e* (rel intensity) 264 (100) (parent), 263 (60), 249 (16), 158 (8), 146 (62), 144 (38), 133 (24), 132 (34), and 131 (34).

Anal. Calcd for $C_{18}H_{20}N_2$: C, 81.77; H, 7.63; N, 10.60. Found: C, 81.60; H, 7.81; N, 10.42.

Acknowledgment. The authors wish to thank Dr. Víctor M. Márquez, Sr., for his encouragement during this study and Dr. Tatsuhiko Nakano and Professor Joseph H. Burchalter for their very helpful discussions throughout the course of this work.

Registry No.—1, 42245-85-2; **2a**, 62016-00-6; **2b**, 62016-12-0; **3**, 123-54-6; **4**, 141-97-9; **5**, 62016-01-7; **6a**, 62016-02-8; **6a** di-*N*-oxide, 62016-03-9; **6b**, 62016-04-0; **6b** di-*N*-oxide, 62016-05-1; **7**, 62016-06-2; **8**, 62016-07-3; **9**, 62016-08-4; **10**, 62016-09-5; **11**, 62016-10-8; **12**, 62016-11-9.

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(5) J. V. Silverton and O. W. Adams, private communication, Laboratory of Chemistry, NHLBI, NIH, Bethesda, Md., 20014.
(6) One of the referees suggested that the acidity of these protons may be greatly enhanced by complexation of the nitrogen atoms with carboxyl protons or copper ions.

Friedel–Crafts Type Preparation of Triphenylphosphine[1a]

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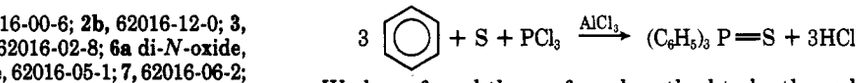
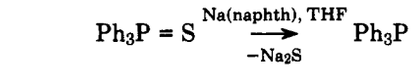
Triarylphosphines, of which triphenylphosphine is the most widely employed member, are generally prepared through organometallic precursors, such as the reaction of phenylmagnesium halides or phenyllithium with phosphorus trihalides.[2]

We now wish to describe a convenient, simple Friedel–Crafts type preparation of triphenylphosphine. The reaction of phosphorus trichloride with benzene under Friedel–Crafts conditions has been widely studied, but only phenyldichlorophosphine and diphenylchlorophosphine have been obtained as products, and under no conditions could the reaction be directed to yield triphenylphosphine (probably owing to an unfavorable disproportionation equilibrium).[3] Phosphorus oxychloride also fails to give triphenylphosphine oxide. Phosphorus sulfochloride ($PSCl_3$), on the other hand, yields triphenylphosphine sulfide upon reaction with benzene and excess aluminum chloride.[4] As triphenylphosphine sulfide offers the possibility of being desulfurized (reduced) to give triphenylphosphine this reaction path offered a good possibility to the simplified Friedel–Crafts type preparation of triphenylphosphine without recourse to organometallic reagents.

We have now found a greatly simplified method to prepare triphenylphosphine sulfide in 71% yield directly from benzene by reacting it with sulfur, phosphorus trichloride, and aluminum chloride. Various methods can be applied for the desulfurization of triphenylphosphine sulfide.[5-7]



We have found the preferred method to be the reduction with sodium naphthanide,[7] giving 89% yield, although desulfurization with iron filings (80%) is also convenient. The reaction with Raney nickel,[6] however, gave considerably lower (15%) yields.



Experimental Section

Preparation of Triphenylphosphine. Into a 500-mL round-bottom flask fitted with a reflux condenser and drying tube under nitrogen purge were added $AlCl_3$ (64 g, 0.48 mol), PCl_3 (16.55 g, 0.12 mol), S (3.85 g, 0.12 mol), and excess benzene (150 mL), to serve both as a reactant and solvent. The solution was stirred magnetically while being heated to reflux for a period of 8 h. Thereafter, to the cooled solution 125 mL of ice water was added. The organic layers were separated and the water layer extracted three times with benzene. The combined benzene solution was dried over Na_2SO_4, and after evaporating solvent left a yellow solid. Recrystallization from acetone–water yielded 25 g (71%) of pure triphenylphosphine sulfide, $Ph_3P{=}S$, mp 158–160 °C. Desulfurization of triphenylphosphine sulfide can be carried out by method A or B.

A. With Sodium Naphthanide.[7] To a 50-mL flask fitted with a reflux condenser and nitrogen purge were charged 25 mL of THF, 6.1 g of naphthalene (0.05 mol), and 1.1 g of Na (0.05 mol). To the deep green solution was added slowly with stirring 4.6 g of triphenylphosphine (0.02 mol). After the addition was complete, the solution was refluxed for 4 h. The cooled solution was quenched with water. Steam distillation followed by extraction with ether and recrystallization from ethanol gave 3.69 (89%) of pure triphenylphosphine, mp 79–81 °C.

B. With Iron Filings.[4] To a 250-mL round-bottom flask fitted with reflux condenser and thermometer and under nitrogen purge were added 25 g of triphenylphosphine sulfide (0.1 mol) and 0.1 g of Fe filings (0.15 mol). The reaction mixture was heated to 370 °C for 2 h. After cooling the crude product was dissolved in ethanol and filtered, and after evaporation of solvent recrystallized from fresh ethanol to give 18.0 g (8) of triphenylphosphine, mp 79–81 °C.

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Registry No.—Triphenylphosphine, 603-35-0; benzene, 71-43-2; PCl_3, 7719-12-2; triphenylphosphine sulfide, 3878-45-3; sulfur, 7704-34-9.

References and Notes

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