

tartaric acid were dissolved in 100 ml of acetone; the solution was stored at 25° for 20 hr. The crystals were filtered and recrystallized twice from acetone to give 12 g (50% based on 0.032 mol present in 1) of **3a**: mp 184–185°; $[\alpha]_D -79.0^\circ$.

Anal. Calcd for $C_{23}H_{25}NO_3 \cdot C_{20}H_{15}O_8$ (749.78): C, 68.88; H, 5.78. Found: C, 68.63; H, 5.79.

Conversion of 7.5 g (0.01 mol) of **3a** by the procedure given for the preparation of **2b** afforded, after two crystallizations from acetonitrile, 3.8 g (86%) of **3b**: mp 122–124°; $[\alpha]_D -6.5^\circ$, $[\alpha]_{365} -20.9^\circ$; ORD and CD mirror images of **2b**.

Anal. Calcd for $C_{23}H_{25}NO_3 \cdot HBr$ (444.39): C, 62.17; H, 5.90. Found: C, 62.22; H, 5.55.

(-)-2-(S)-N-[2-(4-Benzoyloxyphenyl)-2-(3,4-dimethoxyphenyl)-ethyl] Formamide (**4**).—An aqueous solution of 7.3 g (16.4 mmol) of **3b** was rendered alkaline with sodium hydroxide and extracted with methylene chloride, and the extract evaporated. The residue was dissolved in 200 ml of methyl formate and heated at 60–65° under 20 atmospheres of nitrogen for 24 hr. The volatiles were evaporated and the residue dissolved in benzene and chromatographed over 45 g of silica gel. The benzene and benzene-ethyl acetate (80:20) eluates (700 mg) were discarded and the benzene-ethyl acetate (50:50) eluates were collected and evaporated to give 5.8 g (90%) of **4** as a colorless oil: bp 140° (0.02 mm); $n_D^{25} 1.5699$; uv max 226 m μ (ϵ 22,360), 278 (5010), 284 (4420) (sh); nmr (CDCl₃) δ 3.82 (s, 6, OCH₃), 5.00 (s, 2, OCH₂), 5.58 (b, 1, NH), 6.60–7.50 (m, 7, aromatic), 7.34 (s, 5, C₆H₅), and 8.05 (s, 1, CHO); ORD and CD spectra the same as given for **3b**, within experimental error.

Anal. Calcd for $C_{23}H_{25}NO_4$ (391.45): C, 73.63; H, 6.44. Found: C, 73.55; H, 6.54.

(-)-4-(S)-6,7-Dimethoxy-4-(4-hydroxyphenyl)-3,4-dihydroisoquinoline Hydrochloride (**5**).—A mixture of 16.4 g (42 mmol) of **4** and 18.6 ml of phosphorus oxychloride in 300 ml of acetonitrile was stirred and refluxed for 1 hr and evaporated under reduced pressure. The residue was suspended in 5% sodium hydroxide and extracted with ethyl acetate, and the extract evaporated. The residual oil (18 g) was dissolved in 150 ml of benzene, 150 ml of concentrated hydrochloric acid was added and the mixture was stirred vigorously at 25° for 15 hr and evaporated under reduced pressure. The residue was crystallized from a mixture of ethanol and ether to give 8.1 g (58%) of **5**·HCl: mp 221–222°; uv max 233 m μ (ϵ 19,350), 252 (15,000) (sh), 286 (5550), 310 (7400), and 363 (5150); nmr δ 3.80 (s, 3, OCH₃), 3.82 (s, 3, OCH₃), 4.06 (m, 2, CH₂), 4.48 (t, 1, J = 7 Hz, CH), 6.73, 6.90 (AA'BB', 4, aromatic), 6.87, 7.63 (2 s, 2, CH-7, 8), 9.08 (s, 1, CH=N), 9.55 (b, 1, OH or NH); $[\alpha]_D -139.5^\circ$; ORD (c 0.337, CH₃OH) $[\Phi]_{700} -309^\circ$, $[\Phi]_{589} -444^\circ$, $[\Phi]_{400} -495^\circ$ (pk), $[\Phi]_{350} -13,870^\circ$ (tr), $[\Phi]_{308} +8420^\circ$ (pk), $[\Phi]_{272} -3960^\circ$ (sh), $[\Phi]_{254} -17,330^\circ$ (tr), and $[\Phi]_{350} +24,760^\circ$ (pk); CD $[\theta]_{416} 0$, $[\theta]_{376} +6530$, $[\theta]_{356} 0$, $[\theta]_{329} -16,990$, $[\theta]_{302} 0$, $[\theta]_{292} +3920$, $[\theta]_{283} 0$, $[\theta]_{272} -2610$, $[\theta]_{266} -1310$, $[\theta]_{244} -42,470$, $[\theta]_{232} 0$, and $[\theta]_{228} +16,340$.

Anal. Calcd for $C_{17}H_{17}NO_3 \cdot HCl$ (319.79): C, 63.85; H, 5.67. Found: C, 64.06; H, 5.85.

(-)-4-(S)-7-Hydroxy-4-(4-hydroxyphenyl)-6-methoxy-3,4-dihydroisoquinoline (**6**).—A solution of 11.0 g (34.5 mmol) of **5** in 300 ml of 48% hydrobromic acid was stirred at 100° for 6 hr and evaporated under reduced pressure. The residue was dissolved in water, neutralized with sodium bicarbonate, and extracted with ethyl acetate (four 125-ml portions). The extracts were evaporated and crystallized from a mixture of ethanol and ether to give 7.4 g (80%) of **6**: mp 207–208°; uv max 233 m μ (ϵ 30,700), 280 (8400), and 318 (5000); nmr δ 3.65 (s, 3, OCH₃-6), 6.45, 6.82 (s, 2, CH-5,8), 6.60, 6.86 (AA'BB', 4, CH-2',3',5',6'), 8.12 (b, 1, CH-1), and 9.03 (b, 2, OH); $[\alpha]_D -222.4^\circ$, ORD (c 0.507, 0.1 N HCl in CH₃OH) $[\Phi]_{700} -334^\circ$, $[\Phi]_{589} -468^\circ$, $[\Phi]_{408} +2390^\circ$ (pk), $[\Phi]_{344} -10,620^\circ$ (tr), $[\Phi]_{305} +10,360^\circ$ (pk), $[\Phi]_{254} -10,090^\circ$ (tr), and $[\Phi]_{230} +35,060^\circ$ (pk); CD $[\theta]_{430} 0$, $[\theta]_{280} +5260$, $[\theta]_{260} 0$, $[\theta]_{328} -16,480$, $[\theta]_{302} 0$, $[\theta]_{290} +2450$, $[\theta] -2800$ (sh), $[\theta]_{244} -30,140$, $[\theta]_{231} 0$, and $[\theta]_{225} +4210$.

Anal. Calcd for $C_{16}H_{16}NO_3$ (269.29): C, 71.36; H, 5.61. Found: C, 71.22; H, 5.79.

(-)-4-(S)-7-Hydroxy-4-(4-hydroxyphenyl)-6-methoxy-2-methyl-3,4-dihydroisoquinolinium Iodide (**7**).—A solution of 5.0 g (18.5 mmol) of **6** and 26 ml of methyl iodide in 300 ml of methanol was stored at 25° for 24 hr and evaporated. The residue was crystallized from a mixture of methanol and ether to give 5.3 g (69%) of **7**: mp 242–243°; uv max 215 m μ (ϵ 29,100), 251 (20,600), 280 (5900), 312 (10,000), and 370 (7300); nmr δ 3.63 (s, 3, +NCH₃), 3.79 (s, 3, OCH₃), 4.08 (m, 2, CH₂), 4.53 (t, 1, J

= 8 Hz, CH), 6.72, 6.99 (AA'BB', 4, aromatic), 6.75, 7.28 (2s, 2, CH-5,8), 9.15 (s, 1, CH=N), and 9.50 (b, 2, 2 OH), $[\alpha]_D -88.9^\circ$; ORD (c 0.746, CH₃OH) $[\Phi]_{700} -304^\circ$, $[\Phi]_{589} -430^\circ$, $[\Phi]_{410} +1100^\circ$ (pk), $[\Phi]_{348} -11,020^\circ$ (tr), $[\Phi]_{308} +7440^\circ$ (pk), $[\Phi]_{270} -5510^\circ$ (sh), $[\Phi]_{259} -23,140^\circ$ (tr), and $[\Phi]_{230} +7710^\circ$ (pk); CD $[\theta]_{430} 0$, $[\theta]_{380} +5450$, $[\theta]_{256} 0$, $[\theta]_{330} -13,820$, $[\theta]_{306} 0$, $[\theta]_{296} +3270$, $[\theta]_{288} 0$, $[\theta]_{270} -6540$ (sh), $[\theta]_{246} -32,020$, $[\theta]_{234} 0$, and $[\theta]_{230} +14,540$.

Anal. Calcd for $C_{17}H_{18}INO_3$ (411.24): C, 49.65; H, 4.41. Found: C, 49.64; H, 4.48.

(-)-4-(S)-7-Hydroxy-4-(4-hydroxyphenyl)-6-methoxy-2-methyl-1,2,3,4-tetrahydroisoquinoline (**8**).—To a stirred solution of 4.11 g (10 mmol) of **7** in 300 ml of methanol was added 6 g of sodium borohydride over 1 hr. After stirring for 3 hr, the reaction mixture was evaporated and the residue dissolved in water, acidified with 6 N hydrochloric acid, neutralized with sodium bicarbonate, and extracted with ethyl acetate. The organic extract was evaporated and the residue crystallized from ether to afford 2.3 g (81%) of **8**: mp 216–217°; uv max 225 m μ (ϵ 16,400) (sh), 282 (4800), and 293 (3000) (sh); nmr δ 2.27 (s, 3, NCH₃), 3.42 (s, 2, CH₂-1), 3.54 (s, 3, OCH₃), 3.97 (t, 1, J = 6 Hz, CH-4), 6.28, 6.51 (2 s, 2, CH-5,8), 6.67, 6.97, (AA'BB', 4, aromatic), and 8.97 (b, 2, OH); mass spectrum *m/e* (rel intensity) 285 (29), 242 (100), 241 (87), 227 (25), 225 (65), 211 (55), 210 (37), 199 (12), 197 (14), 182 (17), 181 (32), 169 (13), 165 (15), 153 (18), 152 (19); compound **8** was identical in thin layer chromatographic behavior with natural cherylline⁸ in the following solvent systems, acetonitrile-concentrated ammonium hydroxide (90:10), chloroform-methanol (70:30), chloroform-methanol-diethylamine (92:3:5), methanol-acetic acid (1:1); $[\alpha]_D -71.9^\circ$ [lit.¹ $[\alpha]_{25}^{25} -69^\circ$ (c 0.2, CH₃OH)]; ORD (c 0.249, CH₃OH) $[\Phi]_{700} -131^\circ$, $[\Phi]_{589} -189^\circ$, $[\Phi]_{295} -12,150^\circ$ (tr), $[\Phi]_{278} +16,040^\circ$ (pk), $[\Phi]_{258} +2520^\circ$ (tr), $[\Phi]_{242} +9170^\circ$ (pk), and $[\Phi]_{229} -13,750^\circ$ (tr); CD $[\Phi]_{308} 0$, $[\Phi]_{290} -17,570$, $[\theta]_{280} 0$, $[\theta]_{275} +3860$, $[\theta]_{255} +640$, $[\theta]_{240} +12,860$, $[\theta]_{235} 0$, and $[\theta]_{225} -22,290$; identical within experimental error, in ORD and CD with natural cherylline.¹

Anal. Calcd for $C_{17}H_{19}NO_3$ (285.33): C, 71.56; H, 6.71. Found: C, 71.27; H, 6.66.

(+)-4-(R)-7-Hydroxy-4-(4-hydroxyphenyl)-6-methoxy-2-methyl-1,2,3,4-tetrahydroisoquinoline (Unnatural Cherylline, Antipode of **8**).—This was obtained from **2b** by the methods described for the conversion of **3b** into **8** via the dextrorotatory antipodes of **4**, **5**, **6**, and **7**: mp 214–215° (from ether); identical in tlc, uv, and nmr with **8**; ORD and CD mirror images of **8**.

Anal. Calcd for $C_{17}H_{19}NO_3$ (285.33): C, 71.56; H, 6.71. Found: C, 71.63; H, 6.76.

Registry No.—**2a**, 25528-07-8; **2b**, 25528-08-9; **3a**, 25528-09-0; **3b**, 25515-38-2; **4**, 25641-45-6; **5**, 25515-39-3; **6**, 25515-40-6; **7**, 25515-41-7; (-)-(S)-**8**, 23367-61-5; (+)-(R)-**8**, 25515-34-8.

Acknowledgment.—We are indebted to our Physical Chemistry Department, under the direction of Dr. P. Bommer, for the analytical and spectral data. We are particularly grateful to Dr. V. Toome for the ORD and CD determinations and to Mr. J. O'Brien for technical assistance.

A New Ylide from

Tetrakis(trifluoromethyl)cyclopentadienone and Triphenylphosphine

D. M. ROUNDHILL AND G. WILKINSON

Chemistry Department, Washington State University, Pullman, Washington 99163, and Inorganic Chemistry Laboratories, Imperial College, London S.W.7., U. K.

Received February 26, 1970

The reaction between hexafluorobut-2-yne and chlorobis(carbonyl)rhodium dimer gives good yields of tetrakis(trifluoromethyl)cyclopentadienone.¹ When

(1) R. S. Dickson and G. Wilkinson, *J. Chem. Soc.*, 2699 (1964).

solutions containing this dienone and triphenylphosphine are mixed at room temperature, the yellow color of the dienone is immediately discharged and from the reaction a compound of stoichiometry $C_{27}H_{15}F_{12}OP$ is obtained in excellent yield. The product of the reaction is considered to be a new ylide, tetrakis(trifluoromethyl)cyclopentadienonetriphenylphosphorane (I), on the basis of the following spectral data.

Tetrakis(trifluoromethyl)cyclopentadienone shows bands in the infrared at 1684 (C=C stretch) and 1718, 1761 cm^{-1} (C=O stretch),¹ but this new compound shows only two bands at 1502 and 1582 cm^{-1} , which can be assigned to the aromatic double bonds, the keto bands being no longer present. In addition, the spectrum shows a strong band at 1107 cm^{-1} which is expected for the structure shown because of the presence of a quaternary triphenylphosphonium group.²

The ^{19}F nmr spectrum of the compound at 56.4 MHz shows two resonances of equal area separated by 43.7 Hz, but at 94.1 MHz these are now separated by 79 Hz. The peaks are therefore two separate resonances centered at -11.4 and -12.2 ppm and correspond closely to the reported nmr spectrum of tetrakis(trifluoromethyl)cyclopentadienone itself which shows two resonances at -7.9 and -10.1 ppm.¹ This similarity of the spectra shows that the triphenylphosphine must have combined with the dienone through the oxygen atom since addition to carbon in a Michael manner would give a compound with four nonequivalent CF_3 groups. Each of the peaks is too complex for good resolution but ^{19}F - ^{19}F homonuclear spin decoupling on each of the resonances causes them to collapse to singlets showing that the splitting is due entirely to ^{19}F - ^{19}F coupling with the ^{31}P - ^{19}F coupling being immeasurably small. This evidence strongly supports the structure proposed since the nmr should show two resonances for equivalent pairs of CF_3 groups, and it would also show a small ^{19}F - ^{31}P coupling, because the P atom is as far away from the fluorines as possible. The uv spectrum of the ylide is also markedly different from the initial dienone. This new compound shows an absorption at 307 $m\mu$ (ϵ 780) whereas the dienone shows a band at 342 $m\mu$ (ϵ 360).

This reaction differs from that found between hexafluoroacetone and triphenylphosphine; in this case with hexafluoroacetone two molecules of the ketone add to one molecule of the phosphine to give a 5-membered ring phospholane compound.³ The ylide is favored in the reaction with tetrakis(trifluoromethyl)cyclopentadienone because of two features: transfer of an electron pair into the ring causes the formation of the aromatic cyclopentadienide ring; and the electron transfer is further favored by the electron-withdrawing CF_3 groups substituent on the cyclopentadienone.

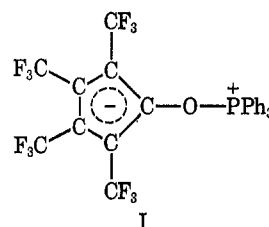
A similar adduct has been obtained with the same dienone and 1,2-bis(diphenylphosphino)ethane except then the stoichiometry now shows that two molecules of dienone have added to each molecule of the diphosphine. The dienone does not react with triphenylarsine or triphenylstilbine, but it has been reported to give colorless compounds with amines.¹ Further investigation of this reaction has shown that these com-

pounds are amine hydrofluorides formed by defluorination of the dienone.

Experimental Section

Infrared spectra were recorded on a Grubb-Parson's spectrometer. Nuclear magnetic resonance spectra were obtained on Varian V-4311 and HA-100 spectrometers operating at 56.4 and 94.1 MHz, respectively, and chemical shifts are given relative to benzotrifluoride as internal reference. Ultraviolet spectra were recorded on a Perkin-Elmer 350 spectrometer. Mass spectra were recorded on a MS9 spectrometer. Microanalyses were performed by A. Bernhardt, Mülheim, Ruhr, and molecular weights were obtained by Mechrolab osmometer operating at 36°.

Tetrakis(trifluoromethyl)cyclopentadienonetriphenylphosphorane (I).—When a yellow solution of tetrakis(trifluoro-



methyl)cyclopentadienone (0.12 g, 1 mol) in CH_2Cl_2 was added to a solution of triphenylphosphine (0.15 g, 1.7 mol) in the same solvent, the color was immediately discharged. The solution was boiled and MeOH was added dropwise until colorless crystals formed. The compound was recrystallized from CH_2Cl_2 -MeOH in a similar way to give 0.17 g (80%) of the required product: mp 219–224°; ir (Nujol mull) 1582, 1502, 1276, 1211, 1107, 1043, 934, 752, 699 cm^{-1} ; nmr (CH_2Cl_2) δ -11.4 (m), -12.2 (m); uv (CH_2Cl_2) 307 $m\mu$ (ϵ 780). *Anal.* Calcd for $C_{27}H_{15}F_{12}OP$: C, 52.6; F, 37.1; mol wt, 614.06687. Found: C, 52.2; F, 36.8; mol wt, 619 ($CHCl_3$ osmometer), 614.0668 (mass spectrograph). The compound is soluble in $CHCl_3$ but insoluble in MeOH.

Registry No.—I, 25396-73-0.

Acknowledgment.—We wish to thank Dr. A. M. Aguiar of Tulane University for helpful discussions.

Preparation and Photolysis of 3-Azido-3-deoxy-1,2,5,6-di-O-isopropylidene- α -D-allofuranose¹

ROY L. WHISTLER AND LANDIS W. DONER

Department of Biochemistry, Purdue University,
Lafayette, Indiana 47907

Received January 5, 1970

The photochemistry of organic azides has been of interest in the last several years. One application has been made to carbohydrates in that methyl 2,3,4-tri-O-acetyl-6-azido-6-deoxy- α -D-glucopyranoside has been photolyzed and hydrolyzed to yield the 6-aldehyde derivative.² We have found that the introduction of carbonyl functions into secondary positions of sugars may be accomplished by photolysis of the appropriate secondary azide to the corresponding imino derivative which is readily converted to the ketone.

(1) This work was supported by the Corn Refiners Association Inc., Journal Paper No. 3938 of the Purdue Agricultural Experiment Station, Lafayette, Ind. 47907.

(2) D. Horton, A. E. Luetzow, and J. C. Wease, *Carbohydr. Res.*, **8**, 366 (1968).

(2) F. S. Ramirez and S. Levy, *J. Amer. Chem. Soc.*, **79**, 67 (1957).

(3) R. F. Stockel, *Tetrahedron Lett.*, 2833 (1966).