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 mμ (ε 780) whereas the dienone shows a band at 342 mμ (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 compounds are amine hydrofluorides formed by defluorination of the dienone.

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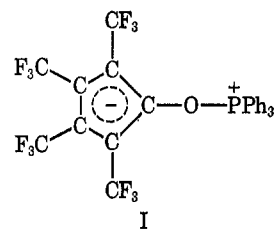
Experimental Section

Infrared spectra were recorded on a Grubb–Parson's spectromaster. 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(trifluoromethyl)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) φ −11.4 (m), −12.2 (m); uv (CH_2Cl_2) 307 mμ (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.



I

Registry No.—I, 25396-73-0.

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Preparation and Photolysis of 3-Azido-3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose[1]

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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-aldehydo 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.
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The substrate was 3-azido-3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose, obtained in 40% yield from 1,2:5,6-di-*O*-isopropylidene-3-*O*-(*p*-tolysulfonyl)-α-D-glucofuranose by nucleophilic displacement with sodium azide in hexamethylphosphoramide.[3] Synthesis of this azide was recently reported by this laboratory[4] using dimethylformamide as the solvent for the tolysulfonyloxy displacement. The disadvantage of the method was the 15 days required for disappearance of the starting material. In hexamethylphosphoramide, however, the reaction time is reduced to 18 hr. After extracting the products from the reaction mixture, silica gel column chromatography separates the azide from an olefinic by-product, 3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-*erythro*-hex-3-enofuranose.

When a benzene solution of the azide is exposed to ultraviolet radiation for 18 hr, the starting material completely disappears, as indicated by the absence of azide absorption at 2150 cm^{-1}. The syrup obtained after concentration of the reaction mixture is refluxed with aqueous ether to convert the photoproduct, presumably the imine, to the ketone hydrate, isolated in 34% yield. The hydrate is a crystalline compound,[5] whereas the ketone, 1,2:5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuran-3-ulose, is a syrup.

An authentic sample of the ketone was prepared according to the method of Sowa and Thomas,[6] by oxidation of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose with methyl sulfoxide in the presence of acetic anhydride. This ketone on conversion to the hydrate was identical with the photoproduct derivative.

Experimental Section

Irradiations with unfiltered ultraviolet light were conducted using a Hanovia 200-W low-pressure mercury lamp (654A36) inserted into a water cooled quartz immersion well. Melting points were measured on a Fisher-Johns apparatus and are corrected. Infrared spectra were obtained with a Perkin-Elmer Model 337 spectrophotometer.

3-Azido-3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose.—To a solution of 1,2:5,6-di-*O*-isopropylidene-3-*O*-(*p*-tolysulfonyl)-α-D-glucofuranose (4.14 g, 0.01 mol) in 50 ml of hexamethylphosphoramide heated to 120° is added, with stirring, sodium azide (5.2 g, 0.08 mol). After 18 hr the reaction mixture is cooled to 25° and transferred with the aid of 25 ml of water to a Friedrich liquid–liquid extractor and extracted with 250 ml of hexane. After 12 hr, the hexane extract is washed 4 times with 250-ml portions of water to remove the small remaining quantity of hexamethylphosphoramide. The hexane extract is dried over anhydrous sodium sulfate and filtered. The filtrate is concentrated to a syrup and chromatographed over a silica gel column (4 × 65 cm) using benzene–ethyl acetate (20:1 v/v) as eluent. Only two carbohydrate components are present in the reaction mixture and in the column eluate as determined by thin layer chromatography using benzene–ethyl acetate (6:1 v/v) as irrigant. The column fractions containing the faster moving olefin component are combined and concentrated to a syrup, whereupon the residue spontaneously crystallized (0.75 g, 31%). It is recrystallized from hexane to give 3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-*erythro*-hex-3-enofuranose, mp 51° (lit.[7] mp 51°). The ir spectrum in Nujol shows a strong olefinic band at 1650 cm^{-1}. The slower moving azide fractions from the column are then collected and concentrated to a syrup. This is dissolved in 10 ml of hexane and left at 0° for 24 hr, whereupon 3-azido-3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose crystallizes as long needles: mp 38–39°; $[\alpha]^{25}D$ +72° (*c* 1.0, chloroform); yield 1.14 g (40%).

Photolysis of 3-azido-3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose.—The above azide (4.85 g) in 1 l. of benzene was irradiated 18 hr after which the solution was concentrated and refluxed with aqueous ether (50 ml). After concentrating to dryness, the syrup was applied to a silica gel column and eluted with chloroform–acetone (15:1 v/v). Progress was followed by tlc and the fraction containing the ketone hydrate crystallized from ether–hexane: mp 113–114°; $[\alpha]^{25}D$ +45° (*c* 1.0, chloroform); yield 1.6 g (34%). R_f and ir values and mixture melting point were identical with those of an authentic sample. Elemental analysis agreed with calculated values.

Registry No.—3-Azido-3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranonse, 21870-78-0.

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Synthesis of N-Carbobenzoxyamino Acid and Peptide Pentafluorophenyl Esters as Intermediates in Peptide Synthesis

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Recently we have shown that peptide bond formation, by use of active esters in the presence of triethylamine under conditions where oxazolones are not known to form, led to racemization *via* α-hydrogen abstraction.[1] Kinetic studies demonstrated the superiority of the pentafluorophenyl ester in the synthesis of peptides, where racemization by α-hydrogen abstraction can occur. N-Carbobenzoxy-S-benzyl-L-cysteine active esters were studied as to their relative rates of racemization and coupling, and it was found that the pentafluorophenyl ester could be coupled in better than 90% yield in 5 min with virtually no racemization.[2] Previous work had shown that there is no racemization when N-carbobenzoxyglycyl-L-phenylalanine pentafluorophenyl ester is coupled with glycine ethyl ester in the Anderson test.[3] The high reactivity of the pentafluorophenyl esters[2] indicates that these compounds can be used in the synthesis of peptide active esters in a variation of the mixed anhydride procedure. Thus a N-protected amino acid pentafluorophenyl ester can be coupled with a slowly reacting amino acid active ester, such as *p*-nitrophenyl ester, to yield N-protected dipeptide active ester.[2b] This variation of the "backing-off procedure"[4] can be helpful in preparing optically pure intermediates for high-molecular-weight sequential polypeptides. Peptide pentafluorophenyl esters can be prepared either by the "pentafluorophenol complex"[5] or through the mixed anhydride procedure;[6]

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