benzene filtrate. One recrystallization from absolute ethanol gave the analytical sample, m.p. 132–133.5°.

Anal. Calcd. for $C_{12}H_3F_9N_2$: C, 41.63; H, 0.87; F, 49.4; N, 8.09. Found: C, 41.81; H, 0.98; F, 49.2; N, 8.13.

The F^{19} n.m.r. spectrum in acetone exhibited multiplets at 61.8, 64.8, 76.2, 79.0, and 85.6 p.p.m. Two unidentified, weak fluorine environments (80.7 and 82.3 p.p.m.) appeared similar to the absorption at 79.0 p.p.m. which was assigned to the fluorine *ortho* to the hydrazino function. These may have arisen due to formation of the hydrazone in acetone solution.

F^{19} Nuclear Magnetic Resonance Data.—The F^{19} spectra were run on a Varian V-4300-2 D.P. spectrometer at 40.0 Mc./sec. Chemical shifts are reported in p.p.m. from trifluoroacetic acid.

Acknowledgment.—The authors wish to thank J. V. Pustinger, Jr., of the Monsanto Research Corporation for the determination and interpretation of the n.m.r. spectra reported in this work. The source of perfluorinated starting materials was the Imperial Smelting Company Ltd., Avonmouth, England.

The Action of Acetic Anhydride on Osazones and Hydrazones

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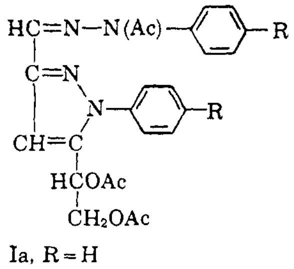
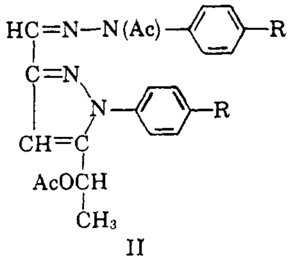
Like the phenyl derivatives, the *p*-bromophenylosazones obtained from D-galactose, L-rhamnose, and D-xylose, when refluxed with acetic anhydride, yielded dianhydro-*p*-bromophenylosazone acetates Ib, IIb, and IIIb, respectively. The phenylosazone from D-glucose yielded an acetylated monoanhydrophenylosazone (IV) in addition to the acetylated dianhydrophenylosazone Ia reported earlier. Compound IV on hydrolysis yielded 3,6-anhydro-D-*ribo*-hexose phenylosazone (V) from which it could also be prepared. D-Galactose phenylhydrazone and penta-*O*-acetyl-*aldehydo*-D-galactose phenylhydrazone yielded, on boiling with acetic anhydride, *N*-acetylpenta-*O*-acetyl-*aldehydo*-D-galactose phenylhydrazone (VI).

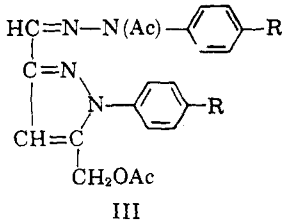
It has been shown[2] that monosaccharide phenylosazones, when refluxed with acetic anhydride, yield colorless dianhydrophenylosazone acetates having pyrazole rings. Thus, hexoses of the D-series yielded Ia and 6-deoxy-L-hexoses IIa; and pentoses, whether D or L, yielded the optically inactive IIIa. We have now extended this reaction to the *p*-bromophenylosazones and obtained the corresponding acetylated dianhydro-*p*-bromophenylosazones. Thus D-*lyxo*-hexose *p*-bromophenylosazone (from D-galactose) yielded 5-(D-*glycero*-1,2-diacetoxyethyl)-1-(*p*-bromophenyl)-3-formylpyrazole *N*-acetyl-*p*-bromophenylhydrazone (Ib), and 6-deoxy-L-*arabino*-hexose *p*-bromophenylosazone (from L-rhamnose) yielded 5-(L-*glycero*-1-acetoxyethyl)-1-(*p*-bromophenyl)-3-formylpyrazole *N*-acetyl-*p*-bromophenylhydrazone (IIb). Similarly, D-*threo*-pentose *p*-bromophenylosazone (from D-xylose) yielded 5-acetoxymethyl-1-(*p*-bromophenyl)-3-formylpyrazole *N*-acetyl-*p*-bromophenylhydrazone (IIIb). This, like the previously investigated phenyl derivative, was hydrolyzed and treated with *p*-nitrophenylhydrazine to yield by *trans*-hydrazonation 1-(*p*-bromophenyl)-3-formyl-5-(hydroxymethyl)-pyrazole *p*-nitrophenylhydrazone.



Ia, R = H
b, R = Br



II



III

D-*arabino*-Hexose phenylosazone, when refluxed with acetic anhydride, yielded in addition to 5-(D-*glycero*-1,-2-diacetoxyethyl)-3-formyl-1-phenylpyrazole *N*-acetylphenylhydrazone (Ia) reported earlier,[2] a yellow product which proved to be *N*-acetyl-4,5-di-*O*-acetyl-3,6-anhydro-D-*ribo*-hexose phenylosazone (IV). The structure of this compound was determined from combustion analysis and from *O*-acetyl[3] and total acetyl[4] determinations. The infrared spectrum of IV revealed both *N*- and *O*-acetyl groups at 1675 and 1725 cm.$^{-1}$, respectively, as well as the C=N group at 1600 cm.$^{-1}$. Deacetylation with either methanolic ammonia or methanolic *n*-butylamine yielded a monoanhydrophenylosazone which no longer possessed the amide or ester bands. This compound consumed one mole of periodate and was identical with Diels' monoanhydrophenylosazone[5] (V), obtained by refluxing D-*arabino*-hexose phenylosazone with methanolic sulfuric acid. Furthermore, acetylation of Diels' compound with boiling acetic anhydride afforded our initial *N*-acetyl-di-*O*-acetylanhydrophenylosazone (IV). Identity in both cases was established by mixture melting points and by comparison of infrared spectra. Since Diels' monoanhydrophenylosazone has been shown[6] to be 3,6-anhydro-D-*ribo*-hexose phenylosazone (V) formed by a Walden inversion on C-3, it was concluded that our product was the *N*-acetyl-4,5-di-*O*-acetyl-3,6-anhydro-D-*ribo*-hexose phenylosazone (IV). The position of the *N*-acetyl group on the C-1 hydrazone has not been confirmed, but was allotted by analogy to I, II, and III.

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(1) Visiting Fellow at The Ohio State University until July, 1964.

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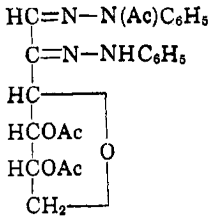
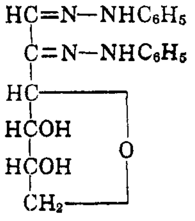
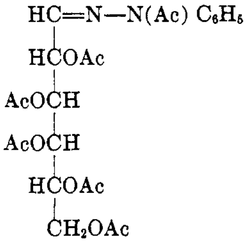
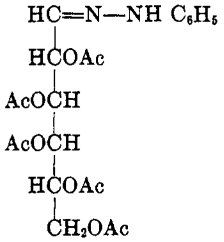

IV


V

Acetylation of D-galactose phenylhydrazone with boiling acetic anhydride afforded a new hexaacetyl derivative VI which showed both *N*- and *O*-acetyl groups at 1700 and 1750 cm.$^{-1}$, respectively, and a C=N group at 1630 cm.$^{-1}$. Estimation of *O*-acetyl and total acetyl agreed with those calculated for a *N*-acetylpenta-*O*-acetylhexose phenylhydrazone. Hydrolysis with methanolic ammonia followed by treatment with phenylhydrazine yielded D-*lyxo*-hexose phenylosazone. Furthermore, acetylation of the known penta-*O*-acetyl-*aldehydo*-D-galactose phenylhydrazone[7] (VII) with boiling acetic anhydride afforded our product, which was therefore identified as *N*-acetyl penta-*O*-acetyl-*aldehydo*-D-galactose phenylhydrazone (VI).

The structures of the compounds described in this paper have been confirmed by study of their proton magnetic resonance spectra to be published later.


VI


VII

From the above it seems that osazones and acyclic sugar hydrazones when acetylated with pyridine and acetic anhydride yield *O*-acetates,[4,7,8] whereas the more vigorous reaction with boiling acetic anhydride can lead to acetylation on both nitrogen and oxygen.

Experimental[9]

5-(D-*glycero*-1,2-Diacetoxylethyl)-1-(*p*-bromophenyl)-3-formylpyrazole *N*-Acetyl-*p*-bromophenylhydrazone (Ib).—D-*lyxo*-Hexose *p*-bromophenylosazone (20 g., from D-galactose) was refluxed for 1 hr. with acetic anhydride (100 ml.). The clear solution was poured onto crushed ice (500 g.) and left overnight. The aqueous solution was decanted and the residual oil was washed repeatedly with water; after several days it solidified and was crystallized from dilute ethanol as colorless needles soluble in ethanol, chloroform, and ether, and insoluble in water, m.p. 120°.

Anal. Calcd. for $C_{24}H_{22}Br_2N_4O_5$: C, 47.6; H, 3.7; N, 9.3. Found: C, 48.1; H, 4.1; N, 9.7.

5-(L-*glycero*-1-Acetoxyethyl)-1-(*p*-bromophenyl)-3-formylpyrazole *N*-Acetyl-*p*-bromophenylhydrazone (IIb).—6-Deoxy-L-*arabino*-hexose *p*-bromophenylosazone (5 g. from L-rhamnose) was refluxed with acetic anhydride (25 ml.) for 1 hr. and then poured onto ice (100 g.). The crystals that separated overnight were collected and crystallized from dilute ethanol as needles, m.p. 170°.

Anal. Calcd. for $C_{22}H_{20}Br_2N_4O_3$: C, 48.2; H, 3.7; N, 10.2. Found: C, 48.1; H, 3.9; N, 10.1.

5-(Acetoxymethyl)-1-(*p*-bromophenyl)-3-formylpyrazole *N*-Acetyl-*p*-bromophenylhydrazone (IIIb).—D-*threo*-Pentose *p*-bromophenylosazone (5 g. from D-xylose) was refluxed with acetic anhydride (25 ml.) for 1 hr., then poured onto crushed ice. The product crystallized from dilute ethanol as needles, m.p. 176°.

Anal. Calcd. for $C_{21}H_{18}Br_2N_4O_3$: C, 47.2; H, 3.4; N, 10.5. Found: C, 47.2; H, 3.7; N, 10.2.

1-(*p*-Bromophenyl)-3-formyl-5-(hydroxymethyl)pyrazole *p*-Nitrophenylhydrazone.—5-(Acetoxymethyl)-1-(*p*-bromophenyl)-3-formylpyrazole *N*-acetyl-*p*-bromophenylhydrazone (IIIb, 0.5 g.) was hydrolyzed with 20% ethanolic ammonia (50 ml.) overnight at room temperature. The product was evaporated to dryness, dissolved in ethanol (10 ml.), and treated with *p*-nitrophenylhydrazine (0.2 g.) in hot ethanol (10 ml.) and acetic acid (1 ml.). The mixture was refluxed for 1 hr. and, on cooling, orange needles which were separated recrystallized from ethanol–water, m.p. 234°.

Anal. Calcd. for $C_{17}H_{14}BrN_5O_3 \cdot H_2O$: C, 47.0; H, 3.7; N, 16.2. Found: C, 46.9; H, 4.0; N, 16.8.

***N*-Acetyl-4,5-di-*O*-acetyl-3,6-anhydro-D-*ribo*-hexose Phenylosazone (IV). A. From D-*arabino*-Hexose Phenylosazone.**—D-*arabino*-Hexose phenylosazone (20 g.) was refluxed with acetic anhydride (100 ml.) for 30 min. and then poured onto 1 kg. of crushed ice. After 3 days the product solidified yielding two types of crystals: colorless ethanol-soluble needles of Ia which were washed away with cold ethanol, and yellow, insoluble, prismatic needles which were filtered and recrystallized from hot ethanol, m.p. 172–173°, $[\alpha]^{21}D$ $-108°$ (*c* 2.9, chloroform).

Anal. Calcd. for $C_{24}H_{26}N_4O_6$: C, 61.8; H, 5.6; N, 12.0; O, 20.6; total CH_3CO, 29.8; CH_3CO (OAc), 18.4. Found: C, 61.3; H, 5.9; N, 12.2; O, 20.7; total CH_3CO, 27.5; CH_3CO (OAc), 17.9.

B. From Diels' Anhydrophenylosazone (V).—Diels' anhydrophenylosazone (2 g.) prepared from D-*arabino*-hexose phenylosazone and methanolic sulfuric acid[5] was refluxed with acetic anhydride (50 ml.) for 2 hr. and then poured onto crushed ice (500 g.). After 24 hr. the crystals that separated were filtered, washed with water and ethanol, and crystallized from ethanol, m.p. and m.m.p. 172–173°.

Anal. Found: C, 61.8; H, 5.9; N, 12.0.

Hydrolysis of *N*-Acetyl-4,5-di-*O*-acetyl-3,6-anhydro-D-*ribo*-hexose Phenylosazone.—Substance IV (1 g.) was either shaken overnight at room temperature with 50 ml. of methanol nearly saturated with ammonia or refluxed for 1 hr. with 50 ml. of methanol and 1 ml. of *n*-butylamine. The clear reaction product was evaporated to dryness in a vacuum desiccator, dissolved in hot ethanol, and crystallized by the addition of hot water to incipient turbidity. 3,6-Anhydro-D-*ribo*-hexose phenylosazone ("Diels'" anhydrophenylosazone, V) was obtained in the form of yellow needles, m.p. 175°, undepressed on admixture with an authentic specimen and with an infrared spectrum identical with that of the latter.

Anal. Calcd. for $C_{18}H_{20}N_4O_3$: C, 63.5; H, 5.9; N, 16.5. Found: C, 63.7; H, 6.2; N, 16.5.

***N*-Acetylpenta-*O*-acetyl-*aldehydo*-D-galactose Phenylhydrazone (VI). A. From D-Galactose Phenylhydrazone.**—D-Galactose phenylhydrazone (10 g.) was refluxed with acetic anhydride (150 ml.) for 1 hr. and the solution was then poured onto 1 kg. of crushed ice and left overnight. The clear solution was then extracted with ether and the latter washed with an aqueous solution of sodium hydrogen carbonate and dried. The residue obtained after ether removal was dissolved in 10 ml. of cold ethanol and crystallized by the addition of water (50 ml.). *N*-Acetylpenta-*O*-acetyl-*aldehydo*-D-galactose phenylhydrazone crystallized in shining prisms, m.p. 135°, $[\alpha]^{21}D$ $+37°$ (*c* 1, chloroform).

Anal. Calcd. for $C_{24}H_{30}N_2O_{11}$: C, 55.3; H, 5.8; N, 5.4; total CH_3CO, 49.4; CH_3CO (OAc), 41.2. Found: C, 55.0; H, 5.7; N, 5.7; total CH_3CO 49.3; CH_3CO (OAc), 43.2.

B. From Penta-*O*-acetyl-*aldehydo*-D-galactose (VII).—The pentaacetate[7] (1 g.) was refluxed with acetic anhydride (25 ml.) for 30 min. and the solution was then poured on 200 g. of crushed ice and left overnight. The water-soluble portion was extracted with ether, washed with aqueous sodium hydrogen carbonate, and dried. The residue obtained on solvent removal was crystallized as above, m.p. 135° undepressed on admixture with the above material. Both products had identical infrared spectra.

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[7] M. L. Wolfrom and C. C. Christman, *J. Am. Chem. Soc.*, **53**, 3913 (1931).

[8] A. Gerecs, *Tetrahedron*, **19**, 1455 (1963); M. L. Wolfrom, G. Fraenkel, D. R. Lineback, and F. Komitsky, *J. Org. Chem.*, **29**, 457 (1964).

[9] Melting points are uncorrected; infrared spectra were measured with a Perkin-Elmer Infracord spectrophotometer. Microanalytical determinations were made by W. N. Rond, The Ohio State University, and A. Bernhardt, Max Plank Institut, Mülheim, Germany.

Deacetylation of VI and Conversion to D-*lyxo*-Hexose Phenylosazone.—*N*-Acetyl-penta-*O*-acetyl-*aldehydo*-D-galactose phenylhydrazone (1 g.) was treated with 50 ml. of methanol nearly saturated with ammonia and left overnight at room temperature, then evaporated to dryness in a vacuum desiccator. The residue was dissolved in water (20 ml.) and heated with phenylhydrazine (0.5 g.) and acetic acid (0.5 ml.) on the water bath for 1 hr. On cooling, D-*lyxo*-hexose phenylosazone separated in its characteristic crystalline shape and was identified by mixture melting point and comparative infrared spectra.

Acknowledgment.—H. El Khadem is indebted to the Educational and Cultural Exchange Program of the United States State Department for a Fulbright Grant to visit The Ohio State University where part of this work was carried out, to Professor M. L. Wolfrom for his valued advice and counsel, and to The Ohio State University for the laboratory facilities provided.

Infrared Spectra and Synthesis of Some Polyphenyls

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Phillips Petroleum Company, Bartlesville, Oklahoma

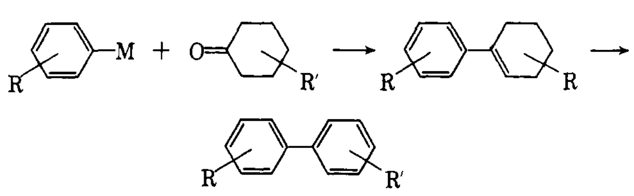
Received August 16, 1963

A general method of preparing polyphenyls by the addition of an aryl Grignard or an aryllithium to a substituted cyclic ketone followed by dehydration and aromatization was used to synthesize five polyphenyls heretofore unreported. These newly prepared polyphenyls are 3-bromo-*m*-terphenyl, 2,3′-di-(3-xenyl)biphenyl, 2,4-di(3-xenyl)biphenyl, 2,4-di(4-xenyl)biphenyl, and 3,5-diphenyl-4′-(3-xenyl)biphenyl. In addition, ten known polyphenyls were prepared, some by new routes. Infrared spectral correlations were developed which apply to *meta*- and *para*-type linkages in polyphenyls. These correlations are useful in indicating (a) the presence of single or consecutive *meta*- or *para*- and 1,3,5-substituted benzene rings in large polyphenyl molecules, and (b) the type of substitution present in the terminal groups of polyphenyls.

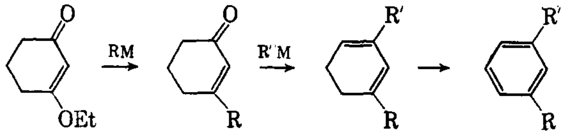
During a recent program under an Atomic Energy Commission Contract,[1] the need arose to prepare certain selected polyphenyls, particularly quaterphenyls and hexaphenyls. This was done for the most part by extending the methods of Woods and Scotti.[2] An examination of the infrared spectra of polyphenyls which are described in the literature and those obtained during the present study revealed certain characteristic shifts of assigned absorption bands in the 11.0- to 15.0-μ region. These band shifts were dependent upon the number and type of linkages involved.

Discussion

Syntheses.—The best general method found for the unambiguous synthesis of polyphenyls was that of the addition of an aryl Grignard or an aryllithium to an aryl cyclic ketone followed by dehydration and aromatization according to the following general scheme.

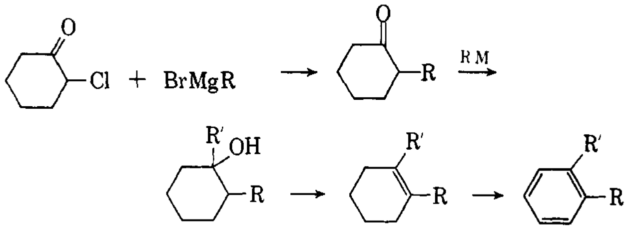


The introduction of internal *meta* linkages was accomplished by the method of Woods and Tucker,[3] whereby the monoethyl ether of dihydroresorcinol was treated (twice) with an aryl Grignard or an aryllithium followed by aromatization.



The compound 3-bromo-*m*-terphenyl was prepared by this method. 3-Ethoxycyclohex-2-en-1-one was added to 3-bromophenylmagnesium bromide, and the resulting 3-(3-bromophenyl)cyclohex-2-en-1-one added to phenylmagnesium bromide to give 3-bromodihydro-*m*-terphenyl. This was aromatized with bromine in chloroform to the desired 3-bromo-*m*-terphenyl.

The introduction of *ortho* linkages in positions other than terminal was brought about by the use of 2-chlorocyclohexanone.[2] An aryl Grignard was added to 2-chlorocyclohexanone, whereby rearrangement occurred giving the intermediate 2-aryl substituted cyclohexanone. This product was added to another aryl Grignard or aryllithium followed by hydrolysis, dehydration, and aromatization to the desired polyphenyl.



The Grignards of 3-xenyl bromide and 4-xenyl bromide were added to 2-chlorocyclohexanone to give the compounds 2-(3-xenyl)cyclohexane and 2-(4-xenyl)-cyclohexanone.[2] The butyllithium interchange products of 3-bromo-*m*-terphenyl and 4-bromo-*m*-terphenyl[4] were added to 2-(3-xenyl)cyclohexanone which after dehydration and aromatization gave, respectively, 2,3′-di(3-xenyl)biphenyl and 2,4′-di(4-xenyl)biphenyl. Lithio-*p*-terphenyl[5] was treated with 2-(4-xenyl)cyclohexanone in a similar manner to give 2,4′-di(4-xenyl)-biphenyl. Preparative details are given here only when the compounds were not found in the literature

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