Addition of iodine to a mixture of isopropyl isonitrile and dimethyl sulfoxide also led to isocyanate, but the reaction was slower and some tar was produced. The use of chlorine was also successful. Phenylisonitrile also gave phenyl isocyanate with bromine and dimethyl sulfoxide.

Kornblum has observed oxidations of benzyl halides with dimethyl sulfoxide to yield carbonyl compounds.[7] The reaction of isonitrile dihalides with dimethyl sulfoxide has some analogies in the reaction of acid chlorides and acid anhydrides with dimethyl sulfoxide.[8,9]

Preliminary results with W. H. Krutzsch show that pyridine N-oxide also reacts with isonitriles in the presence of halogen (but not in their absence) to yield isocyanates. These results will be reported later in detail.

Experimental

Isopropylformamide.—This compound was prepared in 85% yield by refluxing 85.6 ml. of isopropylamine with 80.5 ml. of ethyl formate for 4 hr.[10] The product distilled at 198–199°.

Isopropylisonitrile.—The isonitrile was prepared from the formamide by the method of Casanova.[6] To a well stirred solution of 41 g. of *p*-toluenesulfonyl chloride in 100 ml. of distilled quinoline was added 18.4 g. of isopropylformamide at 75°. The system was maintained at 70 mm. and the isopropylisonitrile distilled to a receiver cooled in liquid nitrogen as it formed. The yield was 4.2 g. (30%), b.p. 88–89° (735 mm.),[11] on redistillation.

Substitution of benzenesulfonyl chloride for the *p*-toluenesulfonyl chloride specified by Casanova gave substantially lower yields.

Isopropyl Isocyanate.—A solution of 0.38 g. of isopropyl isocyanide (5.5 mmoles) and 0.70 g. of dimethyl sulfoxide (10 mmoles), which had been dried over and distilled from calcium hydride in 5 ml. of chloroform which had been dried over calcium hydride, was prepared; 0.034 g. of bromine (0.21 mmole of dry bromine in 0.2 ml. of chloroform) was added. The solution was refluxed for 24 hr. Infrared spectra were recorded prior to the addition of the bromine and periodically throughout the rest of the reflux time. Following completion of the reflux period, approximately 0.5 ml. of isopropylamine was added to the cooled reaction mixture. The crystals which formed were removed by filtration and recrystallized from ethanol to yield diisopropylurea, m.p. 190–191°. An authentic sample of isopropyl isocyanate was prepared from isopropyl iodide and silver cyanate; reaction of the isocyanate with isopropylamine gave an authentic sample of diisopropylurea,[12] m.p. and m.m.p. 190–191° with the preceding sample. The infrared spectra of the two samples were identical.

The gases from the reaction mixture were passed through a liquid nitrogen trap, and the material which collected was subjected to vapor phase chromatography (4-ft. silicone column operated at room temperature). Chloroform and a maximum of retention time identical with that of dimethyl sulfide appeared; infrared spectra of the isolated dimethyl sulfide and an authentic sample were identical. The yield of dimethyl sulfide appeared to be essentially equivalent (±10%) to the yield of isocyanate as judged by the area of the dimethyl sulfide v.p.c. maximum compared with calibrated isocyanate infrared determinations. The yield of isocyanate was approximately 80% from infrared measurements.

To 10 ml. of chloroform was added 1 ml. of isopropylisonitrile. Bromine was added until its color persisted in the solvent. The solvent was evaporated. The viscous liquid (isopropylimidocarbonyl dibromide)[3] which formed was washed with chloroform by decantation; then 10 ml. of chloroform and 1 ml. of dimethyl sulfoxide were added. After completion of the vigorous exothermic reaction, infrared spectra indicated that the isonitrile absorption were missing and had been replaced by the isocyanate maximum (yield, 82%). V.p.c. of the reaction mixture on a silicone column gave a fraction whose retention time and infrared spectrum were identical with those of an authentic sample of isopropyl isocyanate. Dimethyl sulfide was identified by v.p.c. Diisopropylurea,[12] m.p. 190–191°, was formed upon addition of isopropylamine.

Acknowledgment.—The work reported herein was conducted under the Undergraduate Research Participation Program of the National Science Foundation; this support is gratefully acknowledged.

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[7] N. Kornblum, J. W. Powers, G. J. Anderson, W. J. Jones, H. O. Carson, O. Levand, and W. M. Weaver, *J. Am. Chem. Soc.*, **79**, 6562 (1957); I. M. Hunsberger and J. M. Tien, *Chem. Ind.* (London), 88 (1959).

[8] L. Horner and P. Kaiser, *Ann.*, **626**, 19 (1959); H. W. Kircher, *Anal. Chem.*, **30**, 1540 (1958).

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[10] J. Moffat, M. Newton, and G. Papenheimer, *J. Org. Chem.*, **27**, 4058 (1962).

[11] I. Ugi and R. Meyr, *Ber.*, **93**, 237 (1960).

[12] A. W. Hoffman, *ibid.*, **15**, 756 (1882).

Analysis of the Structure of Dehydro-D-glucosazone by Nuclear Magnetic Resonance and by Comparison of Its Optical Isomers

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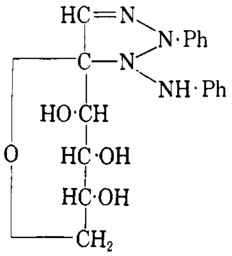
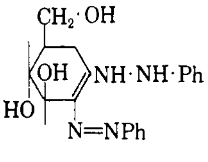
Mester and Moczar[1] found structure II for dehydro-D-glucosazone rather than structure I previously proposed by Diels and co-workers.[2]



I



II

The gross structure (II) has now been confirmed by application of nuclear magnetic resonance spectroscopy. However, the n.m.r. evidence requires the D-*ribo* rather than the D-*arabino* configuration for II, a conclusion supported by chemical evidence reported herein. The n.m.r. spectrum of tri-*O*-acetyl-dehydro-D-glucosazone was determined at 60 Mc.p.s. in deuterated chloroform and the spectrum is shown in Fig. 1. The presence of three *O*-acetyl groups, five hydrogens attached to the sugar carbon chain, two hydrogens on nitrogen, and two phenyl groups was indicated by integration. The sharp doublet at 6.2 p.p.m. and well shifted chemically from other signals requires the presence of a hydrogen coupled with one only neighboring hydrogen. The spacing for this signal, 3 c.p.s., is found in the quartet of intensity one centered at 5.3 p.p.m. The position of the latter signal is characteristic of hydrogens on secondary carbons in carbohydrate structures which are

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[1] L. Mester and E. Moczar, *Chem. Ind.* (London), 554 (1962).

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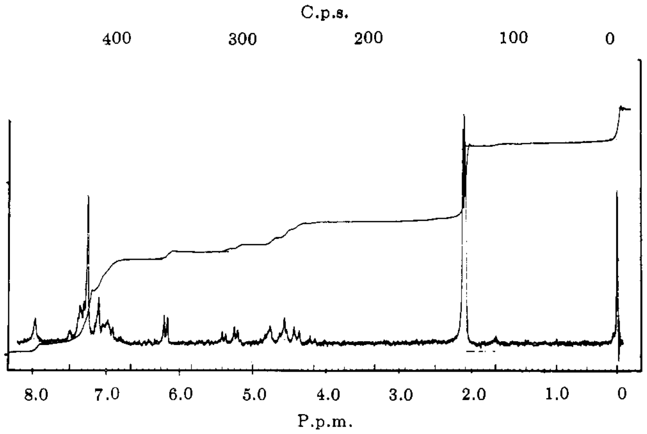
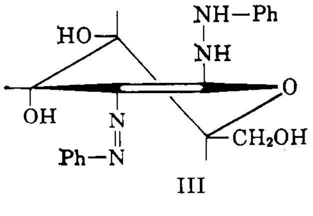


Fig. 1.—The nuclear magnetic resonance spectrum of tri-*O*-acetyldehydro-D-glucosazone.

bonded to an acetoxy group.[3,4] The latter signal can be assigned, therefore, to the 4-hydrogen and the broad spacing of 10 c.p.s. found in the quartet requires the hydrogen to be axially oriented and coupled with two hydrogens, one of which is axial in orientation and must be the 5-hydrogen. The other hydrogen must be quasi-equatorially oriented in view of the small coupling. This hydrogen must give rise to the doublet at 6.2 p.p.m. and must be located at the 3-position because of its chemical shift. Its position at 0.9 p.p.m. to lower field can be assigned to the decreased diamagnetic shielding of equatorial over axial hydrogens[5] together with paramagnetic deshielding arising from the neighboring double bond.

The multiplet from 4.60 to 5.32 p.p.m. corresponds to three hydrogen atoms and can be assigned to the hydrogen of C-5 and to the two hydrogens of C-6. Similar splitting in this region was observed in the case of the acetylated sugar osazones themselves[6] and are characteristic of a *C*-methylene group which holds an acetate function.[3-5] Signals at this position were not present in the spectrum of di-*O*-acetyl-dehydro-L-rhamnosazone. A doublet centered around 1.44 p.p.s., typical for a methyl group, was present.

The group of lines centered around 2.10 p.p.m. can be assigned to the three acetate methyl groups. Finally there are two peaks at 7.97 and at 12.50 p.p.m. which seem to correspond to the two N-H bonds. Therefore, structure III is assigned to dehydro-D-glucose phenylosazone. This is the same structure which we found for

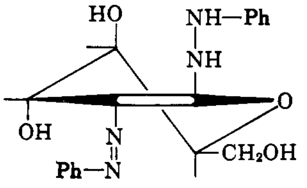


III

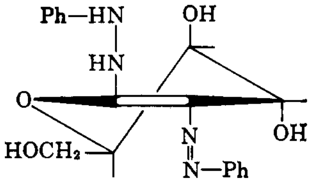
dehydro-D-glucosazone on the basis of chemical investigations,[1] except that the hydroxyl group of C-3 is *not* stabilized in the equatorial position corresponding to the original D-glucose configuration, but it is turned to the axial position (D-allose configuration). This transposition is certainly due to the encumbrance of this hydroxyl in the equatorial position with the *vicinal* azo group, and is brought about through the action of the alkaline medium during the dehydrogenation.

We found another proof of this transposition. In the D-series of hexoses four dehydroosazones (derived from D-glucose, D-galactose, D-allose, and D-gulose) may be expected, if *no* transposition occurs. If in the cases of D-glucose and D-galactose the C-3 hydroxyl undergoes a transposition to the axial position as expected, D-glucose should give the same dehydroosazone as D-allose, while D-galactose should give the same as D-gulose. Furthermore dehydro-D-glucosazone and dehydro-L-allosazone, on the one hand, and dehydro D-galactosazone and dehydro-L-gulosazone, on the other hand, must be optical antipodes (enantiomers)

The experimental data are in accord with this expectation. We found that dehydro-D-glucosazone [m.p. 202–203°, $[\alpha]^{24}\text{D}$ +346° (*c* 0.5, 1:1 pyridine–ethanol)] is identical with dehydro-D-allosazone [m.p. 203°, no depression with dehydro-D-glucosazone, identical infrared spectra, and optical rotatory power], while dehydro-D-galactosazone [m.p. 212°, $[\alpha]^{24}\text{D}$ +300° (*c* 1, 1:1 pyridine–ethanol] and dehydro-L-gulosazone [m.p-212–213°, identical infrared spectra, but $[\alpha]^{24}\text{D}$ −298°] are enantiomers.



Dehydro-D-galactose phenylosazone $[\alpha]_D$ + 300°



Dehydro-L-gulose phenylosazone $[\alpha]_D$ − 298°

This is a direct proof of the transposition of the C-3 hydroxyl in dehydro-D-glucosazone to the axial position, as was found by n.m.r.

Experimental

Dehydro-D-glucosazone was prepared by air oxidation of D-glucose phenylosazone in pyridine–water solution containing potassium hydroxide, by the method of Diels and co-workers[2] m.p. 203–204°, $[\alpha]^{24}\text{D}$ +346° (*c* 0.5, 1:1 pyridine–ethanol).

Tri-*O*-acetyldehydro-D-glucosazone was obtained by acetylation of the former compound by a mixture of pyridine–acetic anhydride,[2] m.p. 173°. The n.m.r. spectrum was determined at 60 Mc. in deuterated chloroform with tetramethylsilane as an internal reference standard on a Varian Associates spectrometer, Palo Alto, California.

Dehydro-D-galactosazone was prepared by air oxidation of D-galactose phenylosazone in methanolic potassium hydroxide solution following the method of Diels and co-workers,[2] m.p. 212°, $[\alpha]^{24}\text{D}$ +300° (*c* 1, 1:1 pyridine–ethanol).

Dehydro-L-gulosazone was prepared from L-gulose phenylosazone in the same way, m.p. 212–214°, $[\alpha]^{24}\text{D}$ −298° (*c* 1, 1:1 pyridine–ethanol).

Anal. Calcd. for $C_{18}H_{20}O_4N_4$: C, 60.67; H, 5.62; N, 15.73. Found: C, 60.29; H, 5.52; N, 15.10.

Dehydro-D-allosazone was obtained by air oxidation of D-allose phenylosazone in methanolic potassium hydroxide solution in the same manner as the previous products, m.p. 203–204°, no depression with dehydro-D-glucosazone, identical infrared spectra, $[\alpha]^{24}\text{D}$ +346° (*c* 0.5, 1:1 pyridine–ethanol).

Dehydro-L-rhamnosazone was prepared from L-rhamnose phenylosazone by air oxidation in methanolic potassium hy-

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(3) R. U. Lemieux, R. K. Kullnig, H. J. Bernstein, and W. G. Schneider, *J. Am. Chem. Soc.*, **79**, 1005 (1957).

(4) M. L. Wolfrom, A. Thompson, and D. R. Lineback, *J. Org. Chem.*, **27**, 2563 (1962).

(5) R. U. Lemieux, R. K. Kullnig, H. J. Bernstein, and W. G. Schneider, *J. Am. Chem. Soc.*, **80**, 6098 (1958).

(6) L. Mester, E. Moczar, and J. Parello, unpublished results.

droxide solution. It was recrystallized from acetonitryl–acetone (1:2), m.p. 223°, $[\alpha]^{24}D$ −180° (c 0.5, 1:1 pyridine–ethanol).

Anal. Calcd. for $C_{18}H_{20}O_3N_4$: C, 63.51; H, 5.92; O, 14.11; N, 16.49. Found: C, 63.55; H, 5.88; O, 14.31; N, 16.71.

Di-*O*-acetyldehydro-L-rhamnosazone was obtained by acetylation of the former compound by a mixture of pyridine–acetic anhydride at 20°. It was recrystallized from ethanol, m.p. 180–181°.

Anal. Calcd. for $C_{22}H_{24}O_5N_4$: C, 62.25; H, 5.70; N, 13.20. Found: C, 62.64; H, 5.74; N, 13.29.

Acknowledgment.—We would like to express our appreciation to Professor M.-M. Janot (Paris) and Professor R. U. Lemieux (Alberta, Canada) for their suggestions, to Mr. J. Parello for the interpretation of the n.m.r. spectra, and to Mrs. M. Mester and Mrs. L. Allais for their assistance.

Addition of Acetaldehyde to Fluoroethylenes[1]

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Free-radical addition of aliphatic aldehydes to fluorinated olefins has been shown to yield ketones derived from addition of an acyl radical to the terminal carbon of the double bond.[2,3] It also has been shown that fluoroaldehydes add to fluoroolefins to give fluorooxetanes rather than carbonyl compounds.[4] In the present work it has been shown that under certain circumstances both types of products can be produced simultaneously.

Ultraviolet irradiation in the gas phase of mixtures of acetaldehyde and a fluorinated ethylene resulted in complex mixtures from which the ketone derived from addition of an acetyl radical to the CF_2 group of the olefin and the oxetane derived from cycloaddition of the aldehyde to the olefin were isolated by vapor–liquid partition chromatography (v.l.p.c.). Four olefins, tetrafluoroethylene, chlorotrifluoroethylene, bromotrifluoroethylene, and 1,1-dichloro-2,2-difluoroethylene, were studied. The major product in each case, as expected, was the ketone. The physical properties of the three new ketones isolated in this study are listed in Table I. 1,1-Dichloro-2,2-difluorobutanone-3, which has been described previously,[3] also is listed because some of the physical properties measured have not been reported. The yield of ketone is affected by reaction conditions (see Experimental) in approximately the way that would be expected assuming a free-radical mechanism as suggested by earlier workers.[2,3,5]

It is worth noting that, although both acetaldehyde and the olefin were present in substantial amount[6] in the final reaction mixture, increasing the time of irradiation actually decreased the yield. We attribute this to decomposition of the ketone under the influence of ultraviolet light.

The orientation of the addition was established by means of the n.m.r. spectra of the addition products. The data presented in Table II clearly excludes 2-halo-1,1,2-trifluorobutanone-3 as the structure of the ketone from either chlorotrifluoroethylene or bromotrifluoroethylene. The 2-halo structure would require CH chemical shifts more like that of 1,1,2,2-tetrafluorobutanone-3. The CF_2 shifts would be closer to that of the terminal CF_2 group in the tetrafluoro compound. The splittings of the CH, CF, and CF_2 groups would all be different from those observed, and the CH–CF and CH–CF_2 coupling constants would be smaller and greater, respectively, by about a factor of ten. Similar arguments exclude 1,1-difluoro-2,2-dichlorobutanone-3 as the structure of the ketone from 1,1-dichloro-2,2-difluoroethylene. These results support the conclusion of Muramatsu and Inukai[3] that the acyl radical attacks the CF_2 group.

In addition to the ketone, from tetrafluoroethylene and 1,1-dichloro-2,2-difluoroethylene, a second 1:1 adduct was isolated; and from chlorotrifluoroethylene, two more 1:1 adducts were obtained. Oxetane structures were assigned on the basis of infrared and n.m.r. spectra. In each case the infrared spectrum showed total absence of carbonyl absorption. Bands attributable to symmetric and asymmetric deformation of the methyl group were present. The proton n.m.r. spectra showed two resonances in the ratio of 3:1.

Only one oxetane is possible from tetrafluoroethylene, namely 2H-2-methyltetrafluorooxetane. Its F^{19} n.m.r. spectrum showed two approximately equal resonances both of which exhibited a typical weak-strong-strong-weak (AB) pattern (see Table III). The high-field pattern showed doublet fine structure indicating proximity to a single spin-one-half nucleus (the single proton). The pronounced shift of the other CF_2 resonance to lower field indicates that that CF_2 group is adjacent to an oxygen.[4]

Two oxetanes are possible from 1,1-dichloro-2,2-difluoroethylene. Only one was obtained, and it was assigned the structure 2H-3,3-dichloro-4,4-difluoro-2-methyloxetane on the basis of the very low-field position of the CF_2 resonance.

From chlorotrifluoroethylene four oxetanes (two *cis–trans* pairs) are possible; only two were isolated. The striking similarity in their infrared spectra suggested that they were a *cis–trans* pair. The low-field position of the CF_2 resonance in the n.m.r. spectra of both compounds supported this assignment and indicated that they were isomers of 2H-3-chloro-2-methyltrifluorooxetane. The n.m.r. spectrum of the lower boiling isomer was too complex for complete analysis, but the large CH–CF coupling constant and the apparent lack of coupling between the CH_3 and CF groups in the higher boiling isomer indicated that the latter was the *cis* (with respect to the CH_3 and Cl groups) isomer. Harris and Coffman[4] also assigned the *cis* configuration to the higher boiling isomer of the four fluorooxetanes for which they isolated *cis* and *trans* isomers.

The mass spectra of the four oxetanes were consistent with the assigned structures. The primary cracking

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[1] This work was performed under the auspices of the U. S. Atomic Energy Commission.

[2] J. D. LaZerte and R. J. Koshar, *J. Am. Chem. Soc.*, **77**, 910 (1955).

[3] H. Muramatsu and K. Inukai, *J. Org. Chem.*, **27**, 1572 (1962).

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[6] Each was in the order of 20–30%.