[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF ARTHRITIS AND METABOLIC DISEASES, NATIONAL INSTITUTES OF HEALTH, PUBLIC HEALTH SERVICE, U. S. DEPARTMENT OF HEALTH, EDUCATION AND WELFARE]

Ribofuranose Derivatives from 3,5-Di-*O*-benzoyl-D-ribosyl Chloride. II. Further Reactions of 5-*O*-Benzoyl-1,2,3-*O*-benzylidyne-α-D-ribose*

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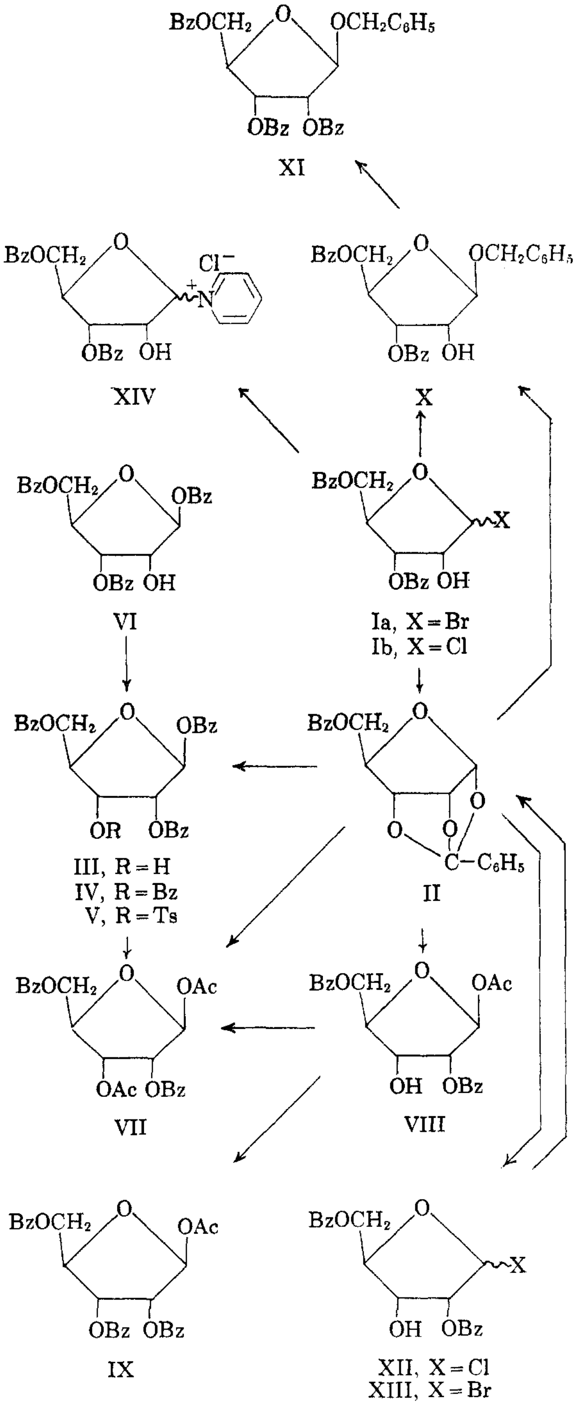
The behavior of 5-*O*-benzoyl-1,2,3-*O*-benzylidyne-α-D-ribose (II) with benzoic acid, acetic acid, acetic anhydride, benzyl alcohol, and hydrogen chloride is described.

In the preceding paper[1] we have described how treatment of 3,5-di-*O*-benzoyl-D-ribosyl chloride[2] (Ib) in benzene solution with mercuric acetate results in dehydrohalogenation with the formation of the somewhat unusual structure 5-*O*-benzoyl-1,2,-3-*O*-benzylidyne-α-D-ribose (II). In the course of investigations designed to throw light on this structure we observed that the orthobenzoate cage in 5-*O*-methylsulfonyl-1,2,3,-*O*-benzylidyne-α-D-ribose was readily cleaved by benzoic acid at room temperature to give a di-*O*-benzoyl-5-*O*-methylsulfonyl-D-ribose. We wish now to report cleavage of the orthobenzoate cage in II by a variety of reagents.

When 5-*O*-benzoyl-1,2,3-*O*-benzylidyne-α-D-ribose (II) was treated in benzene solution with benzoic acid the orthoester grouping was cleaved and a tri-*O*-benzoyl-D-ribose isolated in crystalline form.[3] This ester differed in its physical properties from the anomeric 1,3,5-tri-*O*-benzoyl-D-riboses[1] and other previously known D-ribose tribenzoates. It did not exhibit mutarotation and, on cautious benzoylation, gave β-D-ribofuranose tetrabenzoate (IV). Methylation with Purdie's reagents, followed by debenzoylation, led to a sirup which appeared, on paper partition chromatography, to be a mixture of 2- and 3-*O*-methyl-D-riboses. Although migration of benzoyl groups had obviously occurred during methylation the evidence thus far obtained indicated the substance to be 1,2,5-tri-*O*-benzoyl-β-D-ribose (III). Further evidence tending to favor this structure was obtained as follows. Heating 1,3,5-tri-*O*-benzoyl-β-D-ribose (VI) readily converts it into the new ester. Indeed this conversion can be demonstrated by heating at 135° a potassium bromide plate containing VI whereupon the characteristic infrared spectrum of VI is replaced by that of III. On steric grounds, migration of a benzoyl



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* This paper is a contribution in honor of Lyndon F. Small, former Editor of the Journal.

[1] R. K. Ness and H. G. Fletcher, Jr., *J. Org. Chem.*, **22**, 1465 (1957).

[2] R. K. Ness and H. G. Fletcher, Jr., *J. Am. Chem. Soc.*, **78**, 4710 (1956).

[3] This substance was actually first encountered by us in a mixture resulting from the action of mercuric benzoate on Ib. There it was accompanied by II and, indeed, may have been a secondary product derived from II.

from C_3 to C_2 appears more likely than from C_5 to C_2 and we therefore regard III as the most probable structure for the new D-ribofuranose tribenzoate. It may be noted that the attack on the orthobenzoate cage in II by benzoic acid presumably results first in cleavage of the C1 oxygen linkage with inversion at C1, the potential benzoyl group of II becoming a normal benzoyl at C2 without further inversion.

The behaviour of 5-*O*-benzoyl-1,2,3-*O*-benzylidyne-α-D-ribose (II) with acetic acid was next investigated. Here, a rapid reaction was observed at room temperature in an inert solvent system and an *O*-acetyl-di-*O*-benzoyl-D-ribose isolated in good yield. Benzoylation of this substance to the known 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribose[4] (IX) demonstrated the position of the acetyl group. Acetylation afforded a di-*O*-acetyl-di-*O*-benzoyl-β-D-ribose. The same, fully acylated ribose could also be obtained from 1,2,5-tri-*O*-benzoyl-β-D-ribose (III) through acetylation followed by replacement of the benzoyl group at C1 through the action of acetic anhydride and boron trifluoride.[1] Since this new ester was not identical with the known 1,2-di-*O*-acetyl-3,5-di-*O*-benzoyl-β-D-ribose,[5] the hydroxyl group in the initial product must be at C3 or C5. On mechanistic and steric grounds the latter isomer seems highly unlikely since it would require migration of the benzoyl at C5 in II to C3 or C2.[6] Formula VIII is, therefore, assigned to the product obtained from the orthoester through the action of acetic acid.

Warm acetic anhydride converted the orthoester II into a mixture from which 1,2-di-*O*-acetyl-3,5-di-*O*-benzoyl-β-D-ribose was isolated in 6.8% yield and 1,3-di-*O*-acetyl-2,5-di-*O*-benzoyl-β-D-ribose (VII) isolated in 41% yield.

Benzyl alcohol was found to cleave the orthoester II at an elevated temperature to give a crystalline benzyl D-riboside dibenzoate; the same product was obtained much more rapidly at room temperature when boron trifluoride was used as a catalyst. Further benzoylation converted the dibenzoate into the known benzyl β-D-ribofuranoside tribenzoate[4] (XI). Since the dibenzoate could readily be synthesized from 3,5-di-*O*-benzoyl-D-ribosyl chloride (Ib) we are inclined to assign structure X to it, with the benzoyl group derived from the orthobenzoate cage attached to C3 rather than C2 as in III, VII, and VIII.

When the orthobenzoate II was treated with hydrogen chloride, a crystalline halide was obtained; hydrogen bromide gave an amorphous product. These two substances may be represented by XII and XIII; the chloride was found to revert to II when treated in benzene solution with silver benzoate, otherwise these halides were not further investigated. However, the bromide as formed is more levorotatory ($[\alpha]^{20}_{D}$ *ca.* −71° in CH_2Cl_2) than the chloride ($[\alpha]^{20}_{D}$ *ca.* −29° in CH_2Cl_2), suggesting that these halides are β-anomers.

Finally, the halide Ib has been found to give a crystalline quaternary salt with pyridine; the position of the benzoyl groups (possibly XIV) and the anomeric configuration of this substance remain to be investigated.

EXPERIMENTAL[7]

1,2,5-Tri-O-benzoyl-β-D-ribose (III). (*a*) *From 5-O-benzoyl-1,2,3-O-benzylidyne-α-D-ribose* (II). A solution of 1.026 g. of 5-*O*-benzoyl-1,2,3-*O*-benzylidyne-α-D-ribose[1] and 2.5 g. of benzoic acid in 20 ml. of dry benzene was warmed at 40° for 6.5 hr. The reaction mixture was diluted with 10 ml. of pentane and 1.34 g. of material removed by filtration. Washed well with methanol and dried, this product (957 mg., 69%) melted at 184–185° (4°/min.). After two recrystallizations, one from acetone-pentane and another from ethanol, the melting point was essentially unchanged although some variation in melting point was observed depending on the rate of heating. The pure compound showed in chloroform (*c* 2.42) a rotation of $[\alpha]^{20}_{D}$ −20.5°.

Anal. Calcd. for $C_{26}H_{22}O_8$: C, 67.52; H, 4.79. Found: C, 67.61; H, 5.07.

(*b*) *From 1,3,5-tri-O-benzoyl-β-D-ribose* (VI). A crude preparation of 1,3,5-tri-*O*-benzoyl-D-ribose (93.4 mg.)[1] which melted at 134°, resolidified and finally melted again at 167°, showed $[\alpha]^{20}_{D}$ +1.4° in chloroform (*c* 0.93). The solid was heated in a 140° bath for 4 min., during which time it sintered and resolidified. The total reaction mixture then showed $[\alpha]^{20}_{D}$ −11.5° in chloroform solution; from ether solution it yielded 43.3 mg. (46%) of slightly impure 1,2,5-tri-*O*-benzoyl-β-D-ribose, m.p. 178–180° and $[\alpha]^{20}_{D}$ −19.8° (*c* 1.23). The infrared absorption spectrum (potassium bromide plate) showed it to be identical with the product prepared as described in (a) above.

The thermal transformation of the 1,3,5-isomer to the 1,2,5-isomer could be demonstrated readily through infrared measurements. When a potassium bromide plate containing pure 1,3,5-tri-*O*-benzoyl-β-D-ribose was heated at 110° for 50 min. and then 200 min. at 135° the IR absorption spectrum was found to have changed completely from that of the 1,3,5-isomer to that of the 1,2,5-isomer.

β-D-Ribofuranose tetrabenzoate (IV) *from 1,2,5-tri-O-benzoyl-β-D-ribose* (III). 1,2,5-Tri-*O*-benzoyl-β-D-ribose (15.1 mg.) was benzoylated with a cold mixture of benzoyl chloride (0.03 ml.) and pyridine (1 ml.) in the normal fashion. The addition of water afforded 16.7 mg. (89%) of crystalline product melting at 120–121° either alone or in admixture with authentic β-D-ribofuranose tetrabenzoate (m.p. 121–122°).[4]

1,2,5-Tri-O-benzoyl-3-O-p-tolylsulfonyl-β-D-ribose (V). 1,2,5-Tri-*O*-benzoyl-β-D-ribose (104.5 mg.) was added to a solution of 54 mg. of tosyl chloride in 1.0 ml. of dry pyridine

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[4] R. K. Ness, H. W. Diehl, and H. G. Fletcher, Jr., *J. Am. Chem. Soc.*, **76**, 763 (1954).

[5] R. K. Ness and H. G. Fletcher, Jr., *J. Am. Chem. Soc.*, **76**, 1663 (1954).

[6] Normally *O* to *O* migrations of acyl groups proceed from secondary to primary positions; the reverse migration has been observed under forcing conditions. See: R. C. Hockett, H. G. Fletcher, Jr., E. L. Sheffield, and R. M. Goepp, Jr., *J. Am. Chem. Soc.*, **68**, 927 (1946); R. C. Hockett, H. G. Fletcher, Jr., E. L. Sheffield, R. M. Goepp, Jr., and S. Soltzberg, *J. Am. Chem. Soc.*, **68**, 930 (1946). However, P. E. Verkade and O. E. van Lohuizen [*Koninkl. Ned. Akad. Wetenschap., Proc. Ser. B.*, **56**, 324 (1953)] have found that the equilibrium mixture obtained from monoglycerides under acid conditions contains a small but aperciable quantity of the β-monoglyceride.

[7] Melting points are corrected.

which had previously been cooled to 0°. One minute later the reaction mixture was allowed to warm to room temperature. After 25 min., 2 drops of water was added; crystallization was spontaneous. Several milliliters more water was added and the product removed: 132 mg., m.p. 158–175°. Recrystallization from 22 ml. of absolute alcohol gave 111 mg. (80%) of pure material as fine needles melting at 169–170° (in bath at 165°, 4°/min., rapid darkening just above m.p.). A second recrystallization failed to change this value. In chloroform (*c* 1.02) the pure substance showed $[\alpha]^{20}_{D}$ −4.1°.

Anal. Calcd. for $C_{33}H_{28}O_{10}S$: C, 64.27; H, 4.58. Found: C, 64.47; H, 4.81.

*1-O-Acetyl-2,5-di-O-benzoyl-β-*D*-ribose* (VIII) *from 5-O-benzoyl-1,2,3-O-benzylidyne-α-*D*-ribose* (II). 5-*O*-Benzoyl-1,2,3-*O*-benzylidyne-α-D-ribose (103 mg.), dissolved in 2.0 ml. of methylene chloride, was treated with 2.0 ml. of glacial acetic acid. Within 3 min. the rotation of the solution was constant, and after 8 min. toluene was added and solvent then removed *in vacuo.* Toluene and ether were successively evaporated from the sirup. From ether-pentane the product (94.6 mg., 78%) crystallized as dense clumps of fine needles melting at 99–100°. Two recrystallizations from ether-pentane gave pure 1-*O*-acetyl-2,5-di-*O*-benzoyl-β-D-ribose melting at 101–103° and showing $[\alpha]^{20}_{D}$ −25.0° in chloroform (*c* 2.9).

Anal. Calcd. for $C_{21}H_{20}O_8$: C, 62.99; H, 5.04. Found: C, 62.93; H, 5.07.

Benzoylation of 43.9 mg. of the above-described product with benzoyl chloride in pyridine afforded 47.0 mg. (85%) of crystalline material melting at 129–131° either alone or in admixture with authentic 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribose (IX).[4]

*1,3-Di-O-acetyl-2,5-di-O-benzoyl-β-*D*-ribose* (VII). (a) *From 5-O-benzoyl-1,2,3-O-benzylidyne-α-*D*-ribose* (II). A solution of 215.7 mg. of 5-*O*-benzoyl-1,2,3-*O*-benzylidyne-α-D-ribose in 4 ml. of acetic anhydride was heated at 105° for 6 hr. and then poured into ice water. The gummy mass which formed after several hours was dissolved in 1 ml. of absolute alcohol. Seeding with 1,2-di-*O*-acetyl-3,5-di-*O*-benzoyl-β-D-ribose[5] gave 19.2 mg. (6.8%) of this ester in crude form, m.p. 115–124°. Two recrystallizations of this crop yielded a pure product which did not depress the melting point of authentic 1,2-di-*O*-acetyl-3,5-di-*O*-benzoyl-β-D-ribose. The main filtrate, on standing, crystallized; a little pentane was added and 91.1 mg. of practically pure 1,3-di-*O*-acetyl-2,5-di-*O*-benzoyl-β-D-ribose, m.p. 109–110°, obtained. A second crop of less pure material raised the yield to 115 mg. (41%). Recrystallization of the purer fraction from ethanol and from ethanol-pentane gave platelets, m.p. 111–112°, $[\alpha]^{20}_{D}$ +23.4° in chloroform (*c* 1.7).

Anal. Calcd. for $C_{23}H_{22}O_9$: C, 62.44; H, 5.01. Found: C, 62.41; H, 5.01.

(*b*) *From 1-O-acetyl-2,5-di-O-benzoyl-β-*D*-ribose* (VIII). 1-*O*-Acetyl-2,5-di-*O*-benzoyl-β-D-ribose (29 mg.) was acetylated with acetic anhydride and pyridine in the usual manner to yield 14.2 mg. (44%) of 1,3-di-*O*-acetyl-2,5-di-*O*-benzoyl-β-D-ribose melting at 110–111°, $[\alpha]^{20}_{D}$ +23° in chloroform (*c* 1.0). Mixture with the product obtained in (a) above failed to depress this melting point.

(*c*) *From 1,2,5-tri-O-benzoyl-β-*D*-ribose* (III). 1,2,5-Tri-*O*-benzoyl-β-D-ribose (103.3 mg.) was acetylated with 2.0 ml. of a 2:1 mixture of pyridine-acetic anhydride at −5°. After 17 hrs. at −5°, the mixture was treated with 0.6 ml. of water and cooled in an ice bath for 35 min. Methylene chloride was added and the organic layer washed successively with water, 3*N* sulfuric acid, and saturated aqueous sodium bicarbonate. Moisture was removed with magnesium sulfate and the solution concentrated *in vacuo* to give 129.6 mg. of sirup which was treated with 4.0 ml. of a mixture made from 20 ml. of acetic anhydride and 1 ml. of 7*M* boron trifluoride in ether. After 13 min. ice was added and the mixture stirred at 0° for 2 hr. Methylene chloride was then added and the organic layer washed successively with water and aqueous sodium bicarbonate. After drying with sodium sulfate and removing the solvent *in vacuo* a residue was obtained; crystallization from ether-pentane afforded 49.8 mg. (50%) of crystalline product, m.p. 109–111°, $[\alpha]^{20}_{D}$ +26° (*c* 2.2, chloroform). When mixed with 1,3-di-*O*-acetyl-2,5-di-*O*-benzoyl-β-D-ribose, prepared from 5-*O*-benzoyl-1,2,3-*O*-benzylidyne-α-D-ribose, as described above, it melted at 109–111°.

*Benzyl 3,5-di-O-benzoyl-β-*D*-riboside* (X). (*a*) *From 3,5-di-O-benzoyl-*D*-ribosyl bromide (Ia).* Benzyl alcohol (2 ml.) was added to 1.05 g. of 3,5-di-*O*-benzoyl-D-ribosyl bromide (m.p. 105–107°). Thirty seconds later silver oxide was added. A slight spontaneous warming of the reaction mixture was noticed and therefore the reaction flask was immediately cooled in an ice bath. Eight minutes later the silver compounds were removed by filtration and washed with methylene chloride. The filtrate was concentrated at 90° (0.03 mm.) and the residue extracted with warm cyclohexane. On cooling the extract deposited 0.06 g. of needles melting at 132–135°. The gum left after the extraction was dissolved in 15 ml. of ether to give 0.11 g. of needles (m.p. 133–136°). The filtrate after concentration and dilution with ethanol-pentane yielded an additional 0.15 g. of crystalline material. These three fractions were combined and recrystallized from ether (methylene chloride used to dissolve fractions being displaced by ether on the steam bath as evaporation occurred). A second recrystallization from ether gave 0.26 g. (23%) of pure material melting at 140–141°. A third recrystallization from 1:1 ethanol-ether did not change this value. The product showed $[\alpha]^{20}_{D}$ −49.2° (*c* 2.10 in chloroform).

Anal. Calcd. for $C_{26}H_{24}O_7$: C, 69.63; H, 5.39. Found: C, 69.50; H, 5.56.

Benzoylation of the benzyl riboside dibenzoate (21 mg.) in the usual manner afforded 22 mg. of a crude product melting at 63–84°. After one recrystallization from ethanol-hexane and one from ethanol, the melting point of the tribenzoate was 86–88°. When mixed with authentic benzyl β-D-ribofuranoside tribenzoate[4] there was no depression of the melting point. The rotation of the tribenzoate in chloroform was $[\alpha]^{20}_{D}$ +15° (*c* 0.58); pure benzyl β-D-ribofuranoside tribenzoate had earlier been found[4] to show $[\alpha]^{20}_{D}$ +14.9° in chloroform.

(*b*) *From 5-O-benzoyl-1,2,3-O-benzylidyne-α-*D*-ribose* (II). A solution of 220.4 mg. of 5-*O*-benzoyl-1,2,3-*O*-benzylidyne-α-D-ribose in 5 ml. of freshly distilled benzyl alcohol was heated at 140° for 1.5 hr. The mixture was then concentrated *in vacuo* (0.25 mm. and 120° bath) to a sirup which, dissolved in ether-pentane, afforded 96 mg. (33%) of a crystalline product melting at 133–140°. One recrystallization from ethanol and another from ether gave benzyl β-D-ribofuranoside dibenzoate melting at 141–142°; a mixed melting point with the product obtained in (a) above was undepressed. The same transformation could be accomplished catalytically in somewhat higher yield as follows. A suspension of 319.1 mg. of 5-*O*-benzoyl-1,2,3-*O*-benzylidyne-α-D-ribose in 2 ml. of freshly distilled benzyl alcohol was treated with 0.03 ml. of 7*M* boron trifluoride in ether. Within 7 min. solution was complete and 7 min. later *ca.* 3 ml. of ether and *ca.* 10 ml. of pentane were added. The crystalline product (229.8 mg., 55%) which formed melted at 130–136°; successive recrystallizations from carbon tetrachloride, 1:1 ethanol-pentane and ethanol afforded clusters of heavy needles melting at 139–141°, $[\alpha]^{20}_{D}$ −48.6° in chloroform (*c* 1.4). A mixed melting point with the product obtained in (a) above was undepressed.

*2,5-Di-O-benzoyl-*D*-ribosyl chloride* (XII). 5-*O*-Benzoyl-1,2,3-*O*-benzylidyne-α-D-ribose (0.5033 g.) was dissolved in 3.15 ml. (1.00 mole-equivalent) of 0.472*M* hydrogen chloride-methylene chloride. After 75 seconds, 9.5 ml. of pentane was added and crystallization occurred rapidly. Two minutes later, 5.5 ml. more of pentane was added. The product was separated by filtration after cooling to −5°: 0.5099 g. (91%), m.p. (with dec.) 127–128° (in bath at 120°, 10°/min.). One recrystallization from ether-pentane gave the pure halide melting (with dec.) at 128–129° (in bath at 120°, 10°/min.) and exhibiting in methylene chloride (dried over Drierite) (c 0.39) $[\alpha]^{20}_{\mathrm{D}}$ −29° (5 min.) → ±0° (97 min.) and in absolute chloroform (c 1.79) −20° (4 min.) → +42° (65 hr.).

Anal. Calcd. for $C_{19}H_{17}O_6Cl$: C, 60.56; H, 4.55; Cl, 9.41. Found: C, 60.44; H, 4.42; Cl, 9.34.

*5-O-Benzoyl-1,2,3-O-benzylidyne-α-*D*-ribose* (II) *from 2,5-di-O-benzoyl-*D*-ribosl chloride* (XII). Crystalline 2,5-di-O-benzoyl-D-ribosyl chloride (42.3 mg.) was added to a rapidly stirred suspension of 114 mg. of silver benzoate in dry benzene. Ten minutes later the insoluble salts were removed by filtration and washed with methylene chloride. The filtrate and washings were combined and concentrated to a crystalline mass. From 1:1 acetone-ether, crystallization occurred after which an equal volume of pentane was added. The crystalline product was recrystallized from methylene chloride-pentane: 20.7 mg. (55%), m.p. 180–182°, $[\alpha]^{20}_{\mathrm{D}}$ +44° (c 1.00, chloroform). When mixed with authentic 5-O-benzoyl-1,2,3-O-benzylidyne-α-D-ribose,[1] the melting point was not depressed.

*N-[3,5-Di-O-benzoyl-*D*-ribosyl]pyridinium chloride* (XIV). Dry pyridine (0.5 ml.) was added to 500 mg. of crystalline 3,5-di-O-benzoyl-D-ribosyl chloride. The temperature of the mixture rose slightly and within 10 min. crystallization began. Another ml. of pyridine was added and the reaction mixture was warmed on the steam bath for 1 hr. Methylene chloride (8 ml.) was added to the cooled mixture and the crystalline product, 350 mg. (58%), removed: m.p. 164–166°. Recrystallization from ethanol gave clear prisms, m.p. 171–177° (in bath at 160°, 12°/min.), $[\alpha]^{20}_{\mathrm{D}}$ −64.1° in water (c 1.21).

Anal. Calcd. for $C_{24}H_{22}O_6NCl$: C, 63.23; H, 4.87; N, 3.07. Found: C, 63.19; H, 4.95; N, 3.09.

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BETHESDA 14, MD.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Formation of Naphthalenes from Indenes. IV.[1] The Effect of Substitution at the Ethylenic Double Bond*

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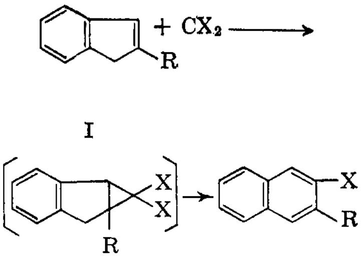
The yields of 2-halonaphthalenes obtained from eight substituted indenes, in which the substituent has been varied from electron withdrawing to electron donating, indicate that the addition of dihalocarbene to the indene double bond is inhibited by the groups chlorine, bromine, carbethoxy, or phenyl. When the substituent is electron-donating, such as methyl, isopropyl, or ethoxy, the yields of naphthalenes are comparable to those obtained with unsubstituted indene. These data support the view that the two electrons in the dihalocarbene are paired, and that carbenes seek centers of high electron density.

The use of 2-substituted indenes in reactions with haloform and potassium *t*-butoxide results in the formation of 2,3-disubstituted naphthalenes.

2-Chloro-, bromo-, and fluoronaphthalene, and 1-methyl-2-bromonaphthalene have recently been prepared[1,4] by a new method, which involves the reaction of indene, or 3-methylindene, with the appropriate haloform and potassium *t*-butoxide. An investigation of the reaction of eight other monosubstituted indenes with haloform and potassium *t*-butoxide has now been made in order to further define the scope of this synthesis, and to gain additional information concerning the general reaction of carbenes with olefins.

Optimum conditions for the synthesis of 2-halonaphthalenes[1,4] by this method involve the use of excess indene as solvent. In this study a standard procedure was employed using benzene as solvent. The yields of naphthalenes were not optimum (37% compared to 67% for 2-chloronaphthalene); however, the use of this procedure permitted: a direct comparison to be made of the reactivity of the various substituted indenes, the use of indenes which are solid at the reaction temperature, and the use of relatively small amounts of indenes. The indenes studied contained substituents which varied from



I

II III

a. R = CH_3, X = Cl
b. R = OC_2H_5, X = Br
c. R = Cl, X = Cl
d. R = Br, X = Cl
e. R = $CO_2C_2H_5$, X = C

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* This paper is a contribution in honor of Lyndon F. Small, former Editor of the Journal.

(1) Preceding paper. W. E. Parham and R. R. Twelves, *J. Org. Chem.*, **22**, 730 (1957).

(2) This work was supported in part by a grant (NSF-G2163) from the National Science Foundation.

(3) Visking Corporation Fellow (1954–1955).

(4) W. E. Parham, H. E. Reiff, and P. Swartzentruber, *J. Am. Chem. Soc.*, **78**, 1437 (1956).