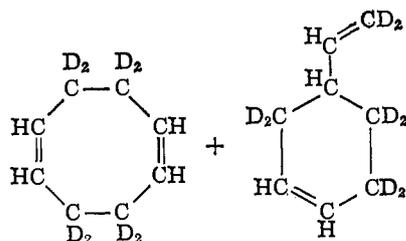
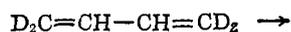


action with deuterium oxide gave C_2H_5D as a main gas product (confirmed by infrared and mass spectroscopy). Alcoholysis gave only ethane. The visible spectra of hydrolysis and alcoholysis products were identical with that of ferrous dipyriddy chloride.

The nickel complex has similar chemical properties with the iron complex, but the gaseous pyrolysis products contained a considerable amount of *n*-butane in addition to ethylene and ethane.

Oligomerization of butadiene was carried out at 50° in the presence of the catalytic amount of the dipyriddy complexes in benzene solution. Butadiene was converted with the iron complex in up to 95% yield to cycloocta-1,5-diene and 4-vinylcyclohexene in the ratio of 3:1. Ethylene was evolved, accompanied by ethane. Dimerization of butadiene-1,1,4,4- d_4 gave cyclooctadiene-3,3,4,4,7,7,8,8- d_8 and 4-vinyl- β,β - d_2 -cyclohexene-3,3,5,5,6,6- d_6 .



Cyclooligomerization of butadiene with the nickel complex gave cyclododecatriene in the yield of 30% with small amounts of cyclooctadiene and vinylcyclohexene. Acetylene was converted with the complexes to benzene and a black polymer with conjugated double bonds.

The detailed discussion of the mechanism of polymerization will be reported later.

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A Novel Photochemical Cycloaddition Reaction of Benzene

Sir:

Earlier reports on the photochemical addition reactions of benzene have invariably led to products in which the benzene has been found to add in its Kékulé structure.¹ We wish to report an instance in which the benzene molecule seems to have undergone addition in a Dewar structure. There is reason to believe that this reaction is by no means an isolated example and that the photochemical dimerization of benzene also follows a similar pathway.²

(1) H. J. F. Angus and D. Bryce-Smith, *J. Chem. Soc.*, 4791 (1960); G. O. Schenck and R. Steinmetz, *Tetrahedron Letters*, 21, 1 (1960).

(2) This is probably the origin of the yellow polymer that is the major product of the irradiation of liquid benzene at 2537 Å.

Photolysis of benzene solutions (20% by volume) of cyclobutene at 2537 Å. at room temperature gave a 50% yield (based on cyclobutene) of a product³ (b.p. 24° (1.5 mm.)) which could readily be separated by distillation at reduced pressure from the unreacted materials and any polymer that may be present. The material had an empirical formula of C_5H_6 (*Anal.*⁴ C, 90.98; H, 9.16. C_5H_6 requires C, 90.84; H, 9.16) and a molecular weight (mass spectrometry) of 132, so that it corresponded to a 1:1 adduct of benzene and cyclobutene. The n.m.r. spectrum⁵ showed two olefinic protons at τ 4.25 (singlet) and a complex absorption at τ 6.4-8.9 which accounted for all of the remaining protons. The absence of absorptions which could be attributed to cyclopropyl rings was noticeable in both the n.m.r. and infrared spectra. The compound absorbed exactly 1 mole of hydrogen when reduced with hydrogen gas at 10 cm. in the presence of Adams catalyst. The liquid product had the molecular formula $C_{10}H_{14}$ (*Anal.* Calcd. for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.54; H, 10.75. Molecular weight by mass spectrometry: 134; $n^{24}D$ 1.5051) and showed no absorption due to olefinic protons in its n.m.r. spectrum. Hydrogenation of the $C_{10}H_{12}$ product at 1 atm. in the presence of Adams catalyst led to the absorption of 2 moles of hydrogen to give a solid product (m.p. 71°), mol. wt. 136, which also showed no unsaturation in its n.m.r. spectrum.

It is obvious that both the 1:1 adduct and the $C_{10}H_{14}$ product must be tetracyclic and, further, should be made up of rings larger than three carbons. The thermal decomposition of the adduct in the vapor phase in a quartz cell in a degassed system proceeded rapidly at 200° and yielded benzene and butadiene, as identified by their ultraviolet spectra. Cyclobutene itself decomposes rapidly under identical conditions at ca. 150,⁶ while bicyclo[2.2.0]hexane (I) decomposes around 170,⁷ and bicyclo[2.1.1]hexane (II) decomposes at ca. 345.⁸ At 200°, it is unlikely that hydrogen migra-



tions and rearrangements of the carbon skeleton take place during pyrolysis. These results suggest that the structure of the adduct can be best represented by III,⁹ and it follows that the $C_{10}H_{14}$ product is probably IV.



(3) It was advantageous not to carry the reaction to completion, but terminate it when the solution turned intensely yellow, recover the unreacted cyclobutene and benzene, and irradiate the fresh solution.

(4) Microanalysis by Midwest Microlab, Inc., Indianapolis, Ind.

(5) The authors wish to thank Drs. E. B. Whipple and D. A. Arnold of the Union Carbide Research Institute, Tarrytown, N. Y., for the n.m.r. spectra. These spectra were obtained in carbon tetrachloride with $(CH_3)_4Si$ as internal reference.

(6) W. Cooper and W. D. Walters, *J. Am. Chem. Soc.*, **80**, 4220 (1958).

(7) C. Steel, R. Zand, P. Hurwitz, and S. G. Cohen, *ibid.*, **86**, 679 (1964).

(8) R. Srinivasan and A. A. Levi, **85**, 3363 (1963).

(9) The infrared spectrum of III as a pure liquid had a weak absorption at 1600 cm^{-1} which could be attributed to the double bond located in a cyclobutane ring. This absorption was absent in the infrared spectrum of IV. The olefinic protons in cyclobutene appear as a singlet at τ 4.05 (S. Borcic and J. D. Roberts, *ibid.*, **87**, 1054 (1965)).

Structure III can exist in one of four forms while IV can exist in three forms. The products that were isolated seem to be made up of one compound only in each case. It is interesting to note that the adduct III, as prepared, is yellow. Distillation at low pressure or passage through a gas chromatographic column did not decolorize the material. However, mild oxidation by air removed the yellow contaminant. The purified sample of III seems to have the same infrared spectrum as the yellow material (which analyzes exactly for $C_{10}H_{12}$). It is reasonable to suggest that the yellow color is due to a material possibly isomeric with III that is present in trace quantity.

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Direct Conversion of a Nucleoside to an Acid-Labile 5'-O-Alkoxyalkyl Derivative

Sir:

Direct, selective blocking of the 5'-(primary) hydroxyl of ribo- and deoxyribonucleosides is a frequently used synthetic procedure; it is presently achieved only by the classical formation of a triphenylmethyl ether.^{1,2} This communication reports that a ribonucleoside can also be converted predominantly to a 5'-monosubstituted derivative by reaction with an aliphatic ketal. Furthermore, the 5' substituent reported here is itself of potential value in syntheses of nucleosides and carbohydrates because of its lability under mildly acidic or even neutral conditions.³

2,2-Dimethoxypropane (10 ml.) was dissolved in a solution of uridine (0.25 g.) and di-*p*-nitrophenyl phosphate (0.01 g.) in *N,N*-dimethylacetamide (1.25 ml.). Portions neutralized with ammonia were chromatographed on paper in 2-propanol-water-ammonia (7:2:1) (solvent A) and 2-propanol-1% boric acid-ammonia (7:2:1) (solvent B; papers first steeped in 1% ammonium borate, blotted, and dried). Disappearance of uridine (R_f 0.38 and 0.10) was accompanied by the formation of a less hydrophilic, borate-complexing (*cis*- α -glycol-containing) component (R_f 0.56 and 0.33)⁴ which after 3 hr. comprised 75% of the ultraviolet light absorbing material; 5% unchanged uridine and a third component (R_f 0.76 in system B) were also present. The same mixture resulted when di-*p*-nitrophenyl phosphate was omitted and the reaction mixture was heated under reflux for 2 days. The major product reacted as a *cis*- α -glycol toward the periodate spray test.⁵ Tri-*n*-butylamine (25 μ l.) was added to the reaction conducted at 25° and volatiles were removed *in vacuo* (finally 0.5 mm., 40°). To a solution of the gum in chloroform (1 ml.) was added benzene (5 ml.), then

(1) A. M. Michelson, "The Chemistry of Nucleosides and Nucleotides," Academic Press Inc., New York, N. Y., 1963.

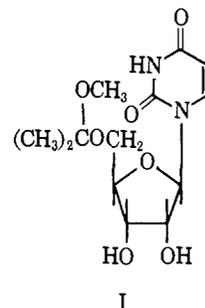
(2) H. G. Khorana, "Some Recent Developments in the Chemistry of Phosphate Esters of Biological Interest," John Wiley and Sons, Inc., New York, N. Y., 1961.

(3) Acid-labile (substituted trityl) blocking groups for nucleoside 5'-hydroxyls are, for example, required for some syntheses of polynucleotides [Y. Lapidot and H. G. Khorana, *J. Am. Chem. Soc.*, **85**, 3852 (1963); G. Weimann, H. Schaller, and H. G. Khorana, *ibid.*, **85**, 3835 (1963)].

(4) 2',3'-O-Isopropylideneuridine, which cannot form a borate complex, had R_f values of 0.59 and 0.66 in systems A and B, respectively.

(5) J. A. Cifonelli and F. Smith, *Anal. Chem.*, **26**, 1132 (1954).

cyclohexane (25 ml.), and the suspension was shaken for 1 hr. The precipitated gum was reprecipitated from chloroform as above,⁶ and its solution in solvent A (0.3 ml.) was applied to a column (2.7 \times 32 cm.) of cellulose powder⁷ in solvent A. Elution with this solvent (4.5-ml. fractions collected) effected extensive separation of the major product (fractions 25-30) from uridine (29-33). Removal of solvent *in vacuo* from fractions 25-28, and addition of benzene (9 ml.) to a solution of the residue in chloroform (2 ml.), gave white needles, 163 mg. (46%), chromatographically homogeneous in systems A and B. Addition of benzene (19 ml.) to its solution in dioxane (2 ml.) gave needles (122 mg.), m.p. 96-103° dec. *Anal.*⁸ Calcd. for $C_{13}H_{20}N_2O_7 \cdot 0.5C_6H_6$: C, 54.08; H, 6.52; N, 7.89. Found: C, 54.19; H, 6.80; N, 8.03. At pH 7.25 ϵ_{max} was 10,100 (261 $m\mu$) and 9600 (204 $m\mu$), ϵ_{min} 2250 (231 $m\mu$); at pH 12, ϵ_{max} was 7700 (261 $m\mu$), ϵ_{min} 5600 (242 $m\mu$). These absorption characteristics are indistinguishable from those of uridine,⁹ indicating the absence of substitution on the uracil moiety. Elemental analysis shows that the product is not a symmetrical ketal containing two uridine residues, and it is therefore concluded to be 5'-O-1''-methoxyisopropyluridine (I).



Hydrolysis of I gave a single ultraviolet-absorbing product with the R_f of uridine in solvents A, B, and 2-propanol-water (7:3; run on diethylaminoethylcellulose). The half-life of I (0.01 *M*) was 1 min. at 25° in 0.1 *M* acetate buffer, pH 4.7, and 5 min. at 100° in 0.05 *M* phosphate buffer, pH 7.2 (25°).

Other 1-alkoxyalkyl groups, namely, alkoxyethyl¹⁰ (from chloromethyl alkyl ethers) and tetrahydropyranyl¹¹ and ethoxyethyl¹² (from α,β -unsaturated ethers), have been used to protect carbohydrate¹⁰ and nucleoside^{12,13} hydroxyls, although the feasibility of selectively blocking primary hydroxyls is not known. The selectivity¹⁴ of 2,2-dimethoxypropane in the present

(6) The benzene-cyclohexane contained the by-product(s) (R_f 0.76, system B), tributylammonium di-*p*-nitrophenyl phosphate and traces of the major product.

(7) Whatman CC31; first freed of fine particles in water.

(8) By A. Bernhardt, Mülheim, Germany.

(9) J. J. Fox and D. Shugar, *Biochim. Biophys. Acta*, **9**, 369 (1952); D. Voet, W. B. Gratzner, R. A. Cox, and P. Doty, *Biopolymers*, **1**, 193 (1963).

(10) G. R. Ames, H. M. Blackmore, and T. A. King, *J. Appl. Chem. (London)*, **14**, 503 (1964).

(11) G. F. Woods and D. N. Kramer, *J. Am. Chem. Soc.*, **69**, 2246 (1947).

(12) S. Chladek and J. Smrt, *Chem. Ind. (London)*, 1719 (1964).

(13) M. Smith, D. H. Rammner, I. H. Goldberg, and H. G. Khorana, *J. Am. Chem. Soc.*, **84**, 430 (1962).

(14) Limited reaction did occur at the 2' and 3' positions: treatment of the by-product of the reaction with 0.01 *N* HCl for 5 min., 25°, gave equal amounts of uridine and 2',3'-O-isopropylideneuridine. Reaction of equimolar proportions of 2,2-dimethoxypropane and uridine in *N,N*-dimethylformamide catalyzed by relatively high concentrations of hydrogen ion gives a high yield of 2',3'-O-isopropylideneuridine [S. Chladek and J. Smrt, *Collection Czech. Chem. Commun.*, **28**, 1301 (1963)].