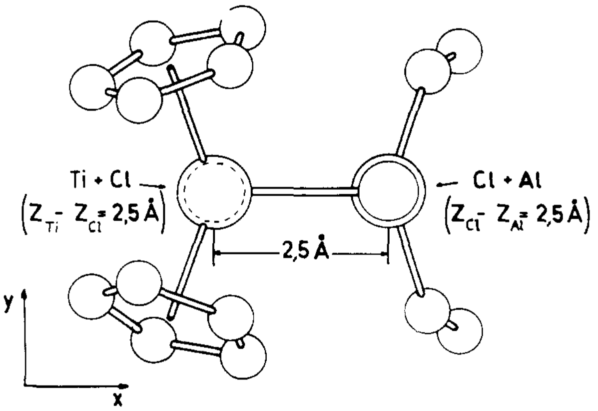

Fig. 3.—Model of the molecule corresponding to the Fourier projection.

complex are not parallel each other as in ferrocene. The orientation of these groups appears dependent on the type of the hybridization of the metal atom to which they are bonded. Further structural work for this and other similar compounds is going on in our laboratory.

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MILAN, ITALY IVANO W. BASSI

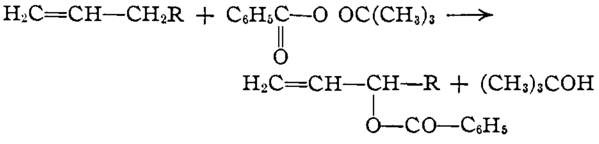
RECEIVED DECEMBER 26, 1957

THE REACTIONS OF *t*-BUTYL PERBENZOATE AND OLEFINS—A STEREOSPECIFIC REACTION[1]

Sir:

Although the reactions of benzoyl peroxide have been studied in great detail by various workers during the past several decades,[2] the chemistry of a related substance, *t*-butyl perbenzoate,[3] except for several kinetic studies,[4] has received little attention. In view of the low reactivity of the perbenzoate and of the difficulties in isolating well-defined products from its reaction mixtures this fact is not surprising.

It has now been found that *t*-butyl perbenzoate in the presence of a transition metal salt catalyst (such as a cuprous halide, cupric 2-ethylhexoate or cobaltous 2-ethylhexoate), reacts with various olefins to give the corresponding allylic benzoates.



$$H_2C{=}CH{-}CH_2R + C_6H_5\underset{\underset{O}{\|}}{C}{-}O\ OC(CH_3)_3 \longrightarrow H_2C{=}CH{-}\underset{\underset{O-CO-C_6H_5}{|}}{CH}{-}R + (CH_3)_3COH$$

Generally, olefins undergo radical reactions to give mixtures of isomeric allylic compounds[5]; but *t*-butyl perbenzoate under similar conditions gives only one allylic benzoate. It appears, therefore, that this reagent reacts stereospecifically, and can thus in certain instances be utilized to advantage for preparative purposes.

The reaction of *t*-butyl perbenzoate and cyclohexene in the presence of cuprous bromide at 80° gives a 70% yield of cyclohex-1-en-3-yl benzoate. *Anal.* Calcd. for $C_{13}H_{14}O_2$: C, 77.40; H, 6.96. Found: C, 77.35; H, 6.71. Similarly, 1-octene gives oct-1-en-3-yl benzoate. *Anal.* Calcd. for $C_{15}H_{20}O_2$: C, 78.00; H, 8.63. Found: C, 78.25; H, 8.99. No isomeric oct-2-en-1-yl benzoate can be detected by examination of the infrared spectra of all fractions from repeated distillations of this material. Under the same conditions, 1-hexene gives only hex-1-en-3-yl benzoate. *Anal.* Calcd. for $C_{13}H_{16}O_2$: C, 76.60; H, 7.85. Found: C, 76.87; H, 8.17.

On the other hand, the reaction of cyclohexene and benzoyl peroxide under comparable experimental conditions gives a mixture of the saturated cyclohexyl and the unsaturated cyclohexenyl benzoates in a ratio of about 35 to 65. *Anal.* Calcd. for $C_{13}H_{14}O_2/C_{13}H_{16}O_2$ = 65/35: C, 76.84; H, 7.50. Found: C, 77.13; H, 7.70; ozonolysis, 66% unsaturation. The reaction of benzoyl peroxide and 1-octene under these conditions gives, among other products, a mixture of allylic benzoates which was analyzed by determining its infrared spectrum.[6]

The mechanism and applications of this reaction are now being investigated; results will be reported at a later date.

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[1] This investigation is supported by a grant from the Office of Naval Research.

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[3] N. A. Milas and D. M. Surgenor, THIS JOURNAL, **68**, 642 (1946).

[4] A. T. Blomquist, A. F. Ferris and I. A. Berstein, *ibid.*, **73**, 3408, 3412, 5546 (1951).

[5] M. S. Kharasch, R. Malec and N. C. Yang, *J. Org. Chem.*, **22**, 1443 (1957); M. S. Kharasch, P. L. Pauson and W. Nudenberg, *J. Org. Chem.*, **18**, 322 (1953); L. Bateman and J. I. Cunneen, *J. Chem. Soc.*, 941 (1950).

[6] M. S. Kharasch and A. Fono, *J. Org. Chem.*, in press.

[7] Deceased, manuscript prepared by G. S.

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RECEIVED NOVEMBER 14, 1957

BRANCHED-CHAIN HIGHER SUGARS[1,2]

Sir:

Formation of normal ketohexoses by aldol condensation of glycerose has been known since 1890.[3] The production of a branched-chain hexose by condensation of 2,3-*O*-isopropylidene-glycerose was reported in 1930.[4] Treatment of higher sugars with alkali yields a variety of rearrangement and degradation products,[5] but except for a normal-chain dodecitol, described as a product of "reductive coupling" and isolated from an electrolyzed sugar–alkali mixture,[6] no products of self-condensation with more than 6 carbons have been reported. It has now been found that aldoses, substituted to preclude ketose and 2,3-enediol formation, undergo aldol condensation to form (in reasonably good yield) branched-chain aldoses having twice the number of carbon atoms. By selec-

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[1] This work was sponsored by the Division of Research, Atomic Energy Commission.

[2] Presented before the Division of Carbohydrate Chemistry at the 132nd Meeting of the American Chemical Society at New York, N. Y., September 11, 1957.

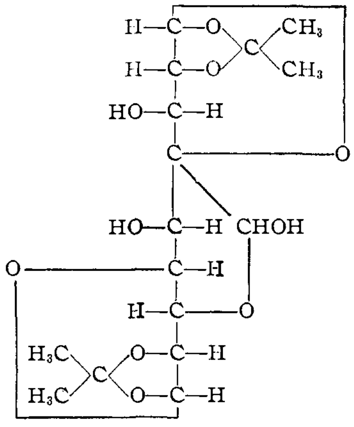
[3] E. Fischer, *Ber.*, **23**, 2114 (1890).

[4] H. O. L. Fischer and E. Baer, *ibid.*, **63**, 1749 (1930).

[5] J. U. Nef, *Ann.*, **357**, 294 (1907); **376**, 1 (1910); **403**, 204 (1913).

[6] M. L. Wolfrom, W. W. Binkley, C. C. Spencer and B. W. Lew, THIS JOURNAL, **73**, 3357 (1951).

tion of suitable raw materials, branched-chain sugars containing from 8 to 14 carbon atoms may be prepared. A variety of sugar derivatives having from 4 to 7 carbon atoms is being investigated. The results are illustrated with 5-aldo-1,2-*O*-isopropylidene-D-*xylo*-pentofuranose[7,8] (6 g. in 500 ml. of lime water), which gave a product, I, in 30% yield after 20 hr. at room temperature; compound I gradually decomposes above 235°; $[\alpha]^{24}\text{D} + 55.6°$ (*c* 1, water) at equilibrium; calculated molecular weight is 376 and a value of 374 was found in formamide. *Anal.* Calcd. for $C_{16}H_{24}O_{10}$: C, 51.1; H, 6.4. Found: C, 50.8; H, 6.5.


I

Structure I has been assigned to the product from the following: one mole of I reacted with only one mole of alkaline iodine; but after acid hydrolysis the resulting monobasic acid dialdehyde reacted with two more moles of hypoiodite per mole. Thus I is a branched-chain trialdehyde. I shows no carbonyl absorption in the infrared. On acetylation, only three acetyl groups are introduced. On reduction with sodium borohydride, followed by acetylation, four hydroxyl groups are substituted. I therefore has two free hydroxyl groups and a third in a hemiacetal ring. Mild acid readily removes one isopropylidene group from I. Partial oxidation of this product with periodate, followed by hydrolysis and separation of D-glucuronic acid, establishes the branching point to be at carbon atom 4 and, furthermore, establishes the configurations of carbon atoms 5 to 8. In forming I by an aldol condensation, no change in configuration of carbon atoms 1 to 3 of the starting material seems probable; hence those of carbon atoms 1 to 3 and 7 to 9 of the product are known. No evidence is yet available for assigning the configuration at carbon atom 4. A systematic name for the decose derivative is 9-aldo-4-*C*-formyl-1,2:8,9-di-*O*-isopropylidene-L-*xylo*-L-*altro*-(or L-*xylo*-L-*ido*)-nono-1,4:6,-9-difurano-4(1′),7-pyranose. This work will be described in detail in a forthcoming publication.

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RECEIVED NOVEMBER 29, 1957

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[7] K. Iwadare, *Bull. Chem. Soc. Japan*, **16**, 40 (1941).

[8] R. Schaffer and H. S. Isbell, THIS JOURNAL, **79**, 3864 (1957), have characterized the crystalline product as a dimer, bis-(5-aldo-1,2-*O*-isopropylidene-D-*xylo*-pentofuranose)-3,5′:5′,5-cyclic acetal.

TERNARY OXIDES OF TETRAVALENT MOLYBDENUM

Sir:

In two recent publications[1,2] in THIS JOURNAL McCarroll, Katz and Ward present the results of work on the characterization and the crystal structure of ternary oxides of tetravalent molybdenum of the type $A_2Mo_3O_8$ ($A = Mg^{+2}, Zn^{+2}, Co^{+2}$, etc.). In the second of these publications[2] the authors state that "no ternary oxides of tetravalent molybdenum were known until Scholder, Klemm and Brixner[3,4] reported the preparation of the compounds $BaMoO_3$, $SrMoO_3$, $CaMoO_3$ and $MgMoO_3$." As the formulation of this statement is rather categorical, it should be pointed out that it is not entirely correct.

Seventy years ago Muthmann[5] in a paper on lower molybdenum oxides made a special section[6] devoted to "Verbindungen des Molybdändioxyds mit Basen" in which he describes the preparation, properties and composition of two compounds of exactly the type discussed by McCarroll, *et al.*, *viz.*, $Zn_2Mo_3O_8$ and $Mg_2Mo_3O_8$. Muthmann's paper is cited by Gmelin.[7]

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[1] W. H. McCarroll, R. Ward and L. Katz, THIS JOURNAL, **78**, 2910 (1956).

[2] W. H. McCarroll, L. Katz and R. Ward, *ibid.*, **79**, 5410 (1957).

[3] R. Scholder and W. Klemm, *Angew. Chem.*, **66**, 467 (1954).

[4] R. Scholder and L. Brixner, *Z. Naturforsch.*, **10b**, 178 (1955).

[5] W. Muthmann, *Ann. Chem. Liebigs*, **238**, 108 (1887).

[6] Ref. 5, pp. 134–137.

[7] "Gmelins Handbuch der anorganischen Chemie," System-Nr. 53: Molybdän, 8 Aufl., Verlag Chemie G. m. b. H., Berlin, 1935, pp. 288 and 298.

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RECEIVED DECEMBER 2, 1957

THE MECHANISM OF FORMATE ACTIVATION[1]

Sir:

The formation of N^{10}-formyltetrahydrofolic acid[2] ($f^{10}FH_4$) from formate, ATP and FH_4 according to equation 1 was first observed with pigeon liver preparations,[3,4] and later encountered during a study of formiminoglycine degradation by extracts of *Clostridium cylindrosporum*.[5] The mechanism of

$$HCOOH + ATP + FH_4 \longrightarrow f^{10}FH_4 + ADP + P_i \quad (1)$$

this reaction has now been investigated with an enzyme, the formate activating enzyme (also

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[1] This investigation was supported by the Atomic Energy Commission (contract No. AT(45-1)-173), the Institutional Grant to the University of Washington by the American Cancer Society, the Life Insurance Medical Research Fund and the United States Public Health Service (Grant No. CY-3310).

[2] The following abbreviations will be used: FH_4, 5,6,7,8-tetrahydrofolic acid; $f^{10}FH_4$, N^{10}-formyltetrahydrofolic acid; f^{5-10} FH_4, N^5,N^{10}-methenyltetrahydrofolic acid; FH_4-P, a phosphorylated derivative of tetrahydrofolic acid (position of the phosphate group not specified); DPN and DPNH, oxidized and reduced diphosphopyridine nucleotide; ATP and ADP, adenosine tri- and di-phosphates; Pi, inorganic phosphate; TRIS, tris-(hydroxymethyl)-aminomethane.

[3] G. R. Greenberg, *Federation Proc.*, **13**, 745 (1954).

[4] G. R. Greenberg, L. Jaenicke and M. Silverman, *Biochim. et. Biophys. Acta*, **17**, 589 (1955).

[5] J. C. Rabinowitz and W. E. Pricer, Jr., THIS JOURNAL, **78**, 4176 (1956).