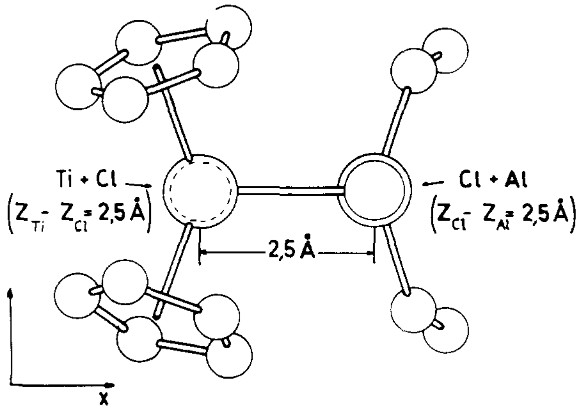

Fig. 3.—Model of the molecule corresponding to the Fourier projection.

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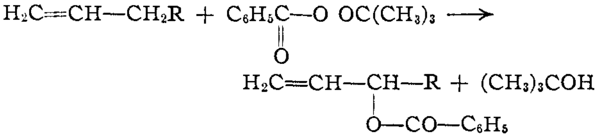
THE REACTIONS OF *t*-BUTYL PERBENZOATE AND OLEFINS—A STEREOSPECIFIC REACTION[1]

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.



$$H_2C{=}CH{-}CH_2R + C_6H_5C({=}O){-}O\,OC(CH_3)_3 \longrightarrow H_2C{=}CH{-}CH(O{-}CO{-}C_6H_5){-}R + (CH_3)_3COH$$

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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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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[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.

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