groups appear at δ 1.23 (s) in the nmr spectrum (CCl₄), and the mass spectrum shows a molecular ion at m/e 202.

Allenes have been generated from β-lactone dimers of certain ketenes by high-temperature pyrolysis (150–650°).[12] However, there are no reports in the literature analogous to the facile hydrolytic decarboxylation reported here. Thus, the triethylamine-catalyzed conversion of **2** to **3** appears to be a new reaction. The ease with which this cleavage takes place may be a reflection of the stability of the proposed dicyanoallylcarbanionic intermediate **14**, and thus may be a general reaction for the asymmetrical dimers of cyanoketenes.[13]

Experimental Section

Reaction of *tert*-Butylcyanoketene (1) with 0.01 Equiv of Triethylamine. β-Lactone 2.—A solution of 13.3 mmol of *tert*-butylcyanoketene (1) was prepared by refluxing 2.0 g (6.67 mmol) of 2,5-diazido-3,6-di-*tert*-butyl-1,4-benzoquinone (8) in 20 ml of anhydrous benzene for 2 hr. The benzene solution was cooled to room temperature and 13 mg (0.13 mmol) of triethylamine was added. After 21 hr, an ir spectrum of the reaction solution showed no ketene absorption. The solvent was removed *in vacuo* at 0°, leaving a yellow solid which resisted further purification and recrystallization. It slowly decomposed upon heating and thus showed a broad melting range, 69–79°. However, all of the spectral data for this compound are in agreement with the β-lactone structure 2 *(vide supra)*.

3,5-Dicyano-2,2,6,6-tetramethyl-4-heptanone (9).—The ketone 9 was prepared in 45% yield by subjecting 0.8 g (3.3 mmol) of the β-lactone 2 to chromatography over silica gel. The same ketone could be prepared by allowing a small sample of 2 to stand exposed to the laboratory air for several days. Hexane recrystallization of the 0.35 g of white solid obtained from the silica gel chromatography gave an analytical sample of 9, mp 108–109°.

(12) J. C. Martin, U. S. Patent 3,131,234 (1964); *Chem. Abstr.*, **61**, 2969*f* (1964).

(13) The relaxation of possible steric interactions between the two *tert*-butyl substituents in going from the β-lactone to the allene may also be of major importance in this reaction.

Anal. Calcd for C₁₃H₂₀N₂O: C, 70.86; H, 9.15; N, 12.71. Found: C, 71.31; H, 8.89; N, 12.67.

Spectral data for 9 follow: ir (Nujol) 2260 (CN) and 1730 cm⁻¹ (C=O); nmr (CDCl₃) δ 1.19 (s, 18, (CH₃—C), 3.57 (s, 2, CH).

3,5-Dicyano-4-hydroxy-3-hydroxymethyl-2,2,6,6-tetramethylheptane (10).—To a solution of 0.5 g (2.2 mmol) of 2 in 25 ml of THF was added 0.18 g (4.8 mmol) of sodium borohydride. This mixture was stirred for 24 hr at room temperature. It was then diluted with water and extracted with dichloromethane. Removal of the solvent gave an oil which partially solidified upon addition of carbon tetrachloride. Filtration gave 50 mg (10% yield) of 10 as a white solid which was recrystallized from chloroform–hexane (1:1) to give the analytical sample, mp 226–227°.

Anal. Calcd for C₁₄H₂₄N₂O₂: C, 66.63; H, 9.59; N, 11.10. Found: C, 66.69; H, 9.55; N, 11.10.

Spectral data for compound 10 follow: ir (Nujol) 3350 (OH) and 2265 cm⁻¹ (CN); nmr (DMSO-d_6) δ 1.05 (s, 9), 1.15 (s, 9), 3.00 (s, 1), 3.67 (d, 2, J = 4 Hz), 4.18 (d, 1, J = 7 Hz), 5.35 (t, 1, J = 4 Hz), 5.77 (d, 1, J = 7 Hz).

1,3-Di-*tert*-butyl-1,3-dicyanoallene (3). Method A.—To 10 ml of a benzene solution containing 6.7 mmol of the β-lactone 2 was added 50 mg (0.5 mmol) of triethylamine. An infrared spectrum taken immediately after addition of the amine showed the disappearance of all bands associated with the β-lactone. Thin layer chromatography showed only one spot. Removal of the solvent and purification of the resulting white solid by chromatography gave 0.923 g (68% yield) of the allene 3, mp 50.5–51.5°.

Anal. Calcd for C₁₃H₁₈N₂: C, 77.18; H, 8.97; N, 13.85. Found: C, 77.29; H, 8.90; N, 13.88.

Method B.—To a solution of 10.0 mmol of *tert*-butylcyanoketene (1) in 15 ml of benzene was added 30 mg (0.3 mmol) of triethylamine. An infrared spectrum taken immediately showed no ketene absorption. The solvent was removed *in vacuo* and the residue was purified by column chromatography over silica gel. There was collected 0.5 g (50% yield) of the allene 3 which was shown to be identical in all respects with that obtained by method A.

Method C.—A solution of 6.6 mmol of *tert*-butylcyanoketene (1) in 10 ml of benzene was cooled in an ice bath and anhydrous hydrogen chloride gas was passed through the solution for 30 min. A solution infrared spectrum showed the absence of ketene absorption and the presence of a carbonyl absorption corresponding to an acyl chloride at 1780 cm⁻¹. Nitrogen gas was then passed through the reaction solution in order to remove the excess hydrogen chloride. The resulting solution was stirred at 0° while adding, dropwise, 0.66 g (6.6 mmol) of triethylamine. The reaction mixture was then extracted with water and the benzene solution was separated and dried over anhydrous sodium sulfate. Removal of the solvent *in vacuo* gave 0.63 g (95% yield) of the allene 3.

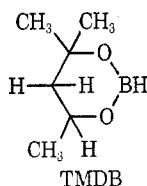### Relative Rates of Hydroboration of Several Olefins with 4,4,6-Trimethyl-1,3,2-dioxaborinane

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Recently we have demonstrated the utility of 4,4,6-trimethyl-1,3,2-dioxaborinane (TMDB) as a stable,

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TMDB

monomeric hydroborating agent.[2,3] It was found that TMDB could be added to olefins[2] and 1,2- and 1,3-dienes[3] at temperatures of 100–130° in 24–48 hr.

In this note we report the relative rates of hydroboration of several olefins with TMDB and compare the reactivity of TMDB with that of disiamylborane (DSB)[4] and 1,3,2-benzodioxaborole (BDB).[5] Table I

TABLE I
RELATIVE RATES OF HYDROBORATION UTILIZING TMDB

Olefin	$K_{rel}{}^a$ at 98 ± 0.1°
1-Octene	7.18
cis-2-Octene	1.19
trans-2-Octene	1.07
Cyclohexene	1.0

a See Experimental Section for the procedure and calculations involved in these studies.

shows the results when cyclohexene was allowed to compete with three other olefins separately for a deficiency of TMDB.

It is evident that the range of magnitudes of the relative rates is not large, since 1-octene is only 7.18 times more reactive than cyclohexene toward TMDB. In contrast to this result, 1-octene reacts 8400 times faster than cyclohexene toward DSB at 0°.[4] Also, cis-2-pentene was 161 times more reactive than cyclohexene (DSB) at 0°,[4] while cis-2-octene was only 1.19 times more reactive than cyclohexene (TMDB) at 98°. Interestingly enough, cis-2-pentene was 3.0 times more reactive than trans-2-pentene (DSB)[4] at 0°, while cis-2-octene was 1.1 times faster than trans-2-octene (TMDB) at 98°. It is quite obvious from these results that the effect of the oxygens on the boron–hydrogen bond moment is such that electron donation by oxygen 2p electrons to the vacant 2p orbital of boron makes the B–H bond moment of TMBD larger, and hence TMDB is less reactive in hydroboration. This effect raises the activation energy for hydroboration and makes any change in olefin structure (*i.e.*, 1-octene to 2-octene) with respect to the rate of reaction extremely small, as is observed. Although we have not done any quantitative relative rate measurements comparing TMDB with other stable dialkyloxy or diaryloxyboranes, we can qualitatively compare 1,3,2-benzodioxaborole (BDB),[5,6] a stable, benzene-substituted dioxaborane, with TMDB in their reactivity with several olefins. It is evident from Brown's data[5] that terminal olefins react reasonably well with BDB at 100° for 2 hr to give high yields (>95%) of adducts. Brown[5] also found that internal olefins such as cyclohexene and norbornene reacted well at 100° for 4 hr to also give >95% yields of hydroboration products. In contrast to this, TMDB reacts very slowly with 1-octene in diethyl

ether to give a 28% isolated yield of adduct after heating for 3 days at 100° (sealed tube) and similarly with cyclohexene at higher temperatures (2 days at 100° and 1 day at 210°) to give a 57% yield of adduct.[2] In a comparion using a bicyclic olefin [norbornadiene (TMDB) *vs.* norbornene (BDB)] we found that TMDB adds to norbornadiene in 16% yield (92% exo, 8% endo) after heating for 50 hr at 130°, while Brown[5] can add BDB to norbornene at 100° for 4 hr in >95% yield. These results point up the fact that in BDB, where oxygen is bonded to a benzene ring, a dramatic increase in hydroboration rates is observed, since the oxygen 2p electrons can resonate into the benzene ring, thus making the B–H bond moment much weaker and hence more reactive. Steric factors must also enter into this rate decrease for TMDB, since its reactivity with the more reactive norbornadiene (as compared to norbornene in addition reactions) was inordinately slow as compared to cyclohexene. This apparent steric factor in TMDB does not seem important with BDB, as evidenced from the latter's reactivity.

Although TMDB reacts more slowly with olefins as compared to DSB or BDB, its stability and that of its adducts allow one to isolate the hydroboration product for direct identification.[2,3]

Experimental Section

Procedure for Determining the Relative Rates of Hydroboration for TMDB with Several Olefins.—The method entails the use of an internal standard along with the two olefins, which compete for a deficiency of TMDB. The internal standard and the calibration curves are used to determine the concentration of the olefins after a given time. Thus a typical competitive experiment was run as follows.

In an ampoule was accurately weighed 1.7953 g (0.016 mol) of 1-octene, 1.3142 g (0.016 mol) of cyclohexene, 2.0520 g (0.016 mol) of nonane (internal standard), and 1.0157 g (0.008 mol) of TMDB.[3] The gas–liquid chromatography (glc) was done on a 20 ft × 0.375 in. silicone nitrile column at 50° (50 ml/min) with a sample of 6 μl. The ampoule was sealed and placed in a constant-temperature bath at 98 ± 0.1° for 78 hr. The ampoule was removed and the contents were analyzed again by glc using the above described conditions. The ratio of areas of each olefin to the area of the internal standard (nonane) was then measured by the height times half-width method. This ratio was then found on a calibration curve of known concentration *vs.* area. The ratio of concentration of olefin to internal standard was found and a simple calculation gave the concentration of the olefin after a certain period of time.

The calculation for K_{rel} was carried out using the following equation.

$$K_{rel} = \frac{k_1}{k_2} = \frac{\log\left[\dfrac{\text{concn initial (octene)}}{\text{concn final}}\right]}{\log\left[\dfrac{\text{concn initial (cyclohexene)}}{\text{concn final}}\right]}$$

Reaction of TMDB with Norbornadiene.—In an ampoule was placed 8.0 g (0.084 mol) of norbornadiene, 5.4 g (0.042 mol) of TMDB, and 2 ml of anhydrous ether. The ampoule was sealed and then heated at 130° for 50 hr. Distillation gave 1.5 g (16%), bp 64–67° (0.15 mm), of product. Analysis by glc on a 5 ft × 0.25 in. silicone nitrile column at 100° (40 ml/min) gave two peaks, the first being the endo isomer (8%) and the second the exo isomer (92%) with the same retention times as those of authentic samples.[7]

Registry No.—TMDB, 23894-82-8; 1-octene, 111-66-0; cis-2-octene, 7642-04-8; trans-2-octene, 13389-42-9; cyclohexene, 110-83-8; norbornadiene, 121-46-0.

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(3) R. H. Fish, *ibid.*, **90**, 4435 (1968).
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(7) W. G. Woods and I. S. Bengelsdorf, *J. Org. Chem.*, **31**, 2769 (1966).