sorption with the carbon–deuterium absorption). A strong carbon–carbon triple bond stretch was observed at 1982 cm^{-1} in the Raman with a corresponding weak absorption at 1980 cm^{-1} in the infrared.

(*Z*)-3,3-Dimethylbutene-*1*-d_1 (*Z*-1) was prepared in 85% yield from 3,3-dimethylbutyne-*1*-d_1 by the procedure of Brown and Gupta:[21] ir (neat) 2270, 802, 727 cm^{-1}; NMR (neat) δ 5.80 (m, 1, J_{H-H} = 12.0, J_{H-D} = 2.8 Hz), 4.73 (slightly broadened doublet, 1, J_{H-H} = 12.0 Hz), 1.03 (s, 9).

(*E*)-3,3-Dimethylbutene-*1*-d_1 (*E*-1) was prepared in 85% yield by hydroboration of 3,3-dimethylbutyne with 1,3,2-benzodioxaborole followed by deuterolysis of the intermediate at vinylborane with acetic acid-d_1 as has been previously described:[21] ir (neat) 2270, 980, 838 cm^{-1}; NMR (neat) δ 5.76 (m, 1, J_{H-H} = 18.0, J_{H-D} = 1.8 Hz), 4.78 (slightly broadened doublet, 1, J_{H-H} = 18 Hz), 1.01 (s, 9).

***threo*-3,3-Dimethylbutan-1-ol-*1,2*-d_2 (*threo*-2)** was prepared from *Z*-1 following the general procedure of Lane.[22] To a solution of 1.3 ml (10 mmol, 0.85 g) of *Z*-1 in 10 ml of THF in a three-necked, 100-ml, round-bottomed flask equipped with magnetic stirring bar, reflux condensor, and pressure equalized addition funnel was added 3.5 ml of a 0.95 M THF solution of deuterioborane–methyl sulfide at 0 °C dropwise with stirring. This reaction mixture was stirred for 1 h at 0 °C and 3 h at room temperature. Then 0.5 ml of absolute methanol was added by syringe and the reaction mixture cooled to 0 °C. The intermediate alkylborane was then oxidized by addition of 1.1 ml of 3 N aqueous sodium hydroxide followed by addition of 1.2 ml of a 30% hydrogen peroxide solution. After refluxing for 1 h, the reaction mixture was worked up by pouring it into a mixture of 40 ml of ice water and 20 ml of ether. The aqueous phase was separated and washed four times with 25-ml portions of ether. The combined ethereal phase was then washed twice with 10-ml portions of sodium thiosulfate. To ensure complete recovery of all the partially water soluble alcohol, these thiosulfate washes were in turn extracted with four 10-ml portions of ether. The combined ethereal phases were then dried (Na_2SO_4) and the ether was removed by fractional distillation. The resulting yellow oil was purified by a short-path distillation and isolated in 84% yield: bp 140–145 °C (lit.[7] bp 140–145 °C); ir (CS_2) 3350, 1294, 1128, 1075, 1045, 991, and 940 cm^{-1}; deuterium-decoupled NMR ($CDCl_3$) δ 3.65 (d, 1, J = 5.6 Hz), 3.47 (s, 1), 1.49 (d, 1, J = 5.6 Hz), 0.93 (s, 9).

***erythro*-3,3-Dimethylbutan-1-ol-*1,2*-d_2 (*erythro*-2)** was prepared from *E*-1 according to the procedure described for *threo*-**2**. The product alcohol was isolated in 85% yield by distillation: bp 140–145 °C (lit.[7] bp 140–145 °C); ir (CS_2) 3350, 1300, 1120, 1100, 1045, 1000, and 933 cm^{-1}; deuterium- decoupled NMR ($CDCl_3$) δ 3.65 (d, 1, J = 10.2 Hz), 3.52 (s, 1), 1.48 (d, 1, J = 10.2 Hz), 0.94 (s, 9). The infrared spectra for *erythro*- and *threo*-**2** mainly differ in the 1000–1125-cm^{-1} region, *threo*-**2** having a strong peak at 1075 cm^{-1} which is only present as a shoulder in *erythro*-**2**.

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Registry No.—*Z*-1, 6833-43-8; *E*-1, 57002-05-8; *threo*-**2**, 52291-61-9; *erythro*-**2**, 23930-47-4; 3,3-dimethylbutyne, 917-92-0; 3,3-dimethylbutyne-*1*-d_1, 6833-44-9.

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Conformational Isomerism in *o*-Tolyldi-*tert*-butylcarbinol

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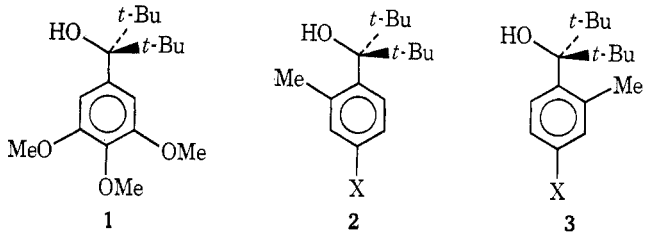
Barriers to rotation about sp^2–sp^3 and sp^3–sp^3 carbon to carbon bonds have been measured mainly by the NMR method[1] for a wide variety of compounds. Among the highest observed for nonbridged structures is the free energy of activation (18.7–21.4 kcal/mol) for rotation of the phenyl ring in 3,4,5-trimethoxyphenyldi-*tert*-butylcarbinol (1).[1c,2]

Our interest in the reactivity of congested tertiary carbinols and their derivatives[3] led us to synthesize *o*-tolyldi-*tert*-alkylcarbinols by condensation of *o*-tolyllithium with di-*tert*-alkyl ketones. GLC analysis of the crude product from the reaction with di-*tert*-butyl ketone revealed the presence of two components, denoted **2a** and **3a**, in the ratio 14:86,



1 2 3

a, X = H; b, X = OMe

whereas after distillation the product was exclusively **2a.** The unstable isomer, **3a** could, however, be isolated by chromatography on alumina in pentane and was found to differ significantly from **2a** in the ir absorption of the hydroxyl group and in the NMR of the aromatic and hydroxyl protons. A more dramatic difference in behavior was found when the dehydration rates were determined: **3a** reacts approximately 10 000 times faster than **2a.**

It is clear that **2a** and **3a** are conformational isomers, "atropisomers".[4] On the basis of kinetic[5] and spectral similarities it can be affirmed that isomer **2a** is of the same type as **2b** whose structure has been determined crystallographically.[7] In this molecule the distance between the carbon of the *o*-methyl group and the hydroxyl oxygen is very small (2.66 Å), this oxygen lying in a plane at 11.6° to the ring plane. Isomer **3a** therefore can only have a structure in which the *o*-methyl group is in the vicinity of the *tert*-butyl groups. The spectral data, as well as the relative amounts of **2a** and **3a** obtained in the synthesis and their relative dehydration rates, are consistent with this assignment. Thus, condensation of the aryllithium with di-*tert*-butyl ketone leads to the lithium

alkoxide ion pair. The preponderance of the less stable alcohol isomer can reasonably be attributed then to the steric requirements of the lithium ion and its solvation shell. In the same way, protonation of the hydroxyl group, the first step of the dehydration reaction, must in **2a** be hindered by the proximity of the *o*-methyl to such an extent that this step has a very small equilibrium constant or may even be rate determining.[8] This feature is absent in **3a** whose reactivity may be further enhanced by relief of steric strain between the *o*-methyl and *tert*-butyl groups in the normally rate-determining heterolytic bond cleavage step.[9]

Rate constants for the conversion of **3a** into **2a** in dodecane indicate that the activation enthalpy is 25.9 kcal/mol, that is, over 11 kcal/mol greater than that for rotation about the phenyl to sp^3 carbon bond of **1** in nonane.[2] This value is unusually high for rotation involving an sp^3 carbon; to date comparable values have only been reported for 9-arylfluorenes[10] and triarylmethanes.[11]

Experimental Section

Gas Chromatography. GLC was performed on a 25-cm column of 10% SE-30 on Chromosorb 80/100 at 120 °C with an inlet pressure of 1 atm. By this means the extent of **3a** → **2a** isomerization is limited to 5%; the data have been corrected appropriately.

Synthesis of *o*-Tolyldi-*tert*-butylcarbinol. Di-*tert*-butyl ketone was added to an equimolar quantity of *o*-tolyllithium in ether at ambient temperature (20 °C) under argon. After 1 h the reaction mixture was poured onto ice, washed with water, and dried over Na_2SO_4 before evaporation of the solvent at reduced pressure. GLC analysis of the crude reaction product revealed two compounds, **2a** and **3a**, in the ratio 14:86 and having retention times of 90 and 120 s, respectively. Distillation of this mixture gave **2a** in good yield [69%, bp 116 °C (2mm), mp 35 °C]. The unstable isomer **3a** was readily separated from the **2a**–**3a** mixture by chromatography on a column of alumina (Brockmann activity II–III) in pentane.

Alcohol **2a** has ir (CCl_4) 3644 cm^{-1} (free hydroxyl); NMR (Me_2SO) singlet (δ 1.11), 18 H of *tert*-butyl; singlet (δ 3.84), 1 H of hydroxyl; singlet (δ 2.60), 3 H of methyl; multiplet (δ 6.95), 3 aromatic H; multiplet (δ 7.42), 1 aromatic H.

Anal. Calcd for $C_{16}H_{26}O$: C, 81.99; H, 11.18. Found: C, 81.78; H, 10.96.

Alcohol **3a** was obtained as a slightly impure oil with ir (CCl_4) 3613 and 3650 cm^{-1} (π-bonded[12] and free hydroxyl); NMR (Me_2SO) singlet (δ 1.13), 18 H of *tert*-butyl; singlet (δ 4.35), 1 H of hydroxyl; singlet (δ 2.62), 3 H of methyl; multiplet (δ 7.00), 3 aromatic H; multiplet (δ 8.01), 1 aromatic H.

Synthesis of *p*-Methoxy-*o*-tolyldi-*tert*-butylcarbinol. Addition of the aryllithium to di-*tert*-butyl ketone gave, after the usual workup, a product mixture which yielded pure **2b** upon standing for 4–5 weeks (4%, mp 96 °C). No attempt was made to isolate **3b.**

Anal. Calcd for $C_{17}H_{28}O_2$: C, 77.22; H, 10.67. Found: C, 77.01; H, 10.63.

Alcohol **2b** has ir (CCl_4) 3643 cm^{-1} (free hydroxyl); NMR (Me_2SO) singlet (δ 1.09), 18 H of *tert*-butyl; singlet (δ 2.61), 3 H of methyl; singlet (δ 3.72), 3 H of methoxyl; singlet (δ 3.78), 1 H of hydroxyl; multiplet (δ 6.53), 2 aromatic H; multiplet (δ 7.38), 1 aromatic H.

Isomerization Kinetics. A thermostated solution of **3a** (0.02 M) and an internal standard, octadecane (0.01 M) in dodecane was sampled at convenient intervals and the reaction mixture analyzed by GLC as described above. First-order rate constants (±1–5%) were determined from the relative peak areas of **3a** and octadecane: 80 °C, 1.26×10^{-5}; 95 °C, 5.64×10^{-5}; 112 °C, 2.75×10^{-4}; 130 °C, 1.26×10^{-3} s^{-1}, whence $\Delta H^{\pm} = 25.9 \pm 0.4$ kcal/mol and $\Delta S^{\pm} = -8.2 \pm 0.9$ eu.

Dehydration Kinetics. Owing to the low solubility of octadecane a modification of the above method was employed. Samples (200 μl) of a solution of the alcohol (0.02 M) in H_2SO_4–acetic acid at 25 °C were quenched in 20% Na_2CO_3 solution (5 ml). After addition of 20 μl of a 0.1 M solution of octadecane in benzene the mixture was extracted with pentane (500 μl). Dehydration rates constants were as follows: **2a** (10% v/v H_2SO_4 in anhydrous acetic acid), 1.53×10^{-5}; **2b** (10% H_2SO_4), 3.02×10^{-4}; **3a** (2% H_2SO_4), 2.74×10^{-3} s^{-1}. For comparison *p*-tolyldi-*tert*-butylcarbinol has rate constants of 4.24×10^{-3} and 6.31×10^{-5} s^{-1} in 10% and 2% H_2SO_4, respectively. We estimate then that the **3a**:**2a** rate ratio is at least 10^4.

Registry No.—**2a**, 59434-44-5; **2b**, 59434-45-6; di-*tert*-butyl ketone, 815-24-7; *o*-tolyllithium, 6699-93-0.

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A Convenient Two-Step Synthesis of 2,6-Di-*tert*-butyl-4-methylpyridine, a Sterically Hindered Nonnucleophilic Base

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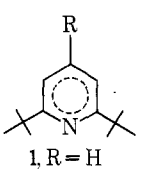
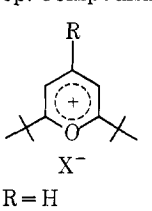
It is well known that pyridine rings containing the 2,6-di-*tert*-butyl functionality enable such bases to distinguish between Bronsted (protonic) and Lewis acids owing to steric crowding in the region of the nitrogen atom.[1a] In connection with some aspects of our work on vinyl triflate chemistry we had need of relatively large amounts of such a nonnucleophilic base. However, the usual synthesis of 2,6-di-*tert*-butylpyridine (**1**) from pyridine and *tert*-butyllithium requires anhydrous conditions, gives low yields, and results in a mixture of isomers that requires tedious separation.[1b] Hence, we decided to look for improved ways of preparing this or similar sterically hindered pyridine bases and wish to report the results in this note.

Pyridines substituted in the 2,6 positions are easily synthesized from the corresponding pyrylium salts[2] in nearly quantitative yields, i.e., conversion of **3** should yield **1**. Although pyrylium salt **3** is difficult to obtain, pyrylium salts substituted with an additional methyl group in the 4 position, **4**, are readily available in a single step. Compound **4** may then



1, R = H
2, R = CH_3



3, R = H
4, R = CH_3
5, R = CH_3; X = OTf