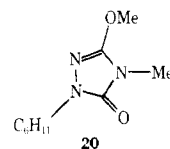


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Ionization and Fragmentation of Tri-*tert*-butylcarbinol. Evidence for a Transient *tert*-Butyl Carbanion in Me_2SO ?

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Received June 7, 1976

The title compound undergoes immediate fragmentation to di-*tert*-butyl ketone and isobutane when treated with the potassium salt of dimethyl sulfoxide in that solvent at 25 °C. The reaction is highly exothermic, the heat evolved corresponding closely to Schleyer's estimate of the strain energy. Tri-*tert*-butylcarbinol is unassociated in carbon tetrachloride under conditions where neopentyl alcohol and di-*tert*-butylcarbinol show strong intermolecular hydrogen bonding. The latter two alcohols are recovered quantitatively under the conditions where the title compound is cleaved completely. The evidence can be interpreted in terms of mechanisms which involve a *tert*-butyl radical or a *tert*-butyl carbanion. The latter seems much more likely.

In the course of a systematic investigation¹⁻⁵ of Brønsted acidity in dimethyl sulfoxide (Me_2SO), we observed a steady decrease in enthalpy of deprotonation (ΔH_D) for aliphatic alcohols as bulky groups were substituted on the α carbon. However, when the limiting member of the series, tri-*tert*-butylcarbinol, was deprotonated a highly exothermic release of heat was observed which far exceeded that expected from the trend of the less crowded members. An excellent correlation had been found previously between the $\text{p}K_a$'s of Brønsted acids in Me_2SO and their heats of deprotonation, ΔH_D .⁴ On that basis, the ΔH_D of -23.2 kcal/mol for tri-*tert*-butylcarbinol suggests that its $\text{p}K_a$ in Me_2SO should be about 22.5, or roughly equivalent to that of phenol. However, it was found that the alcohol did not dissolve in a dilute aqueous solution of sodium hydroxide. Examination of its acidity by Professor Bordwell's group at Northwestern University (using a Steiner-type indicator titration in Me_2SO) showed that the alcohol was not nearly as acidic as the heat of deprotonation suggested.

It was noted that easy fragmentation of the alcohol occurred in the pulsed ion cyclotron resonance spectrometer and that steric hindrance seemed to reduce the rate of the gas-phase proton transfer. Fragmentation in solution was also suggested by spectral evidence. A ^1H NMR spectrum of the deprotonation product showed a sharp singlet at 0.98 ppm, corresponding almost exactly to that of the starting alcohol. However, an infrared spectrum of the product solution showed a strong band in the carbonyl region at 1680 cm^{-1} suggesting the formation of di-*tert*-butyl ketone through a fragmentation

reaction similar to those reported by Cram,⁶ Zook,⁷ and Lomas⁸ in which either a *tert*-butyl carbanion or radical was ejected. Preliminary evidence supporting this possibility came when gas evolution was observed concurrently with deprotonation. Clearly, a careful recovery experiment was called for. The details of this investigation and strong evidence in favor of a facile base-catalyzed elimination of a *tert*-butyl carbanion will be described below.

Experimental Section

Synthesis. Tri-*tert*-butylcarbinol was prepared following the procedure of Bartlett and Lefferts.⁹ In our hands yields were low (ca. 40%) with some improvement to 60% by addition of tetramethylethylenediamine to activate the reaction of *tert*-butyllithium (Ventron). The product was freed of residual di-*tert*-butyl ketone by steam distillation then recrystallized repeatedly from an ethanol-ice water mixture and vacuum sublimed until it was homogeneous to gas chromatography on a 9-ft column of SF-96 on Chromosorb W. A constant, but not very sharp, melting point between 116 and 117 °C (lit.⁹ 117.5 °C) was achieved. The ^1H NMR spectrum in CHCl_3 at 250 MHz showed a single absorption at 0.98 ppm integrating for 27 protons and a small spike at 1.08 ppm, integrating for one proton, which disappeared in the presence of added D_2O .

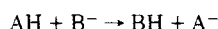
Di-*tert*-butylcarbinol was prepared by reduction of di-*tert*-butyl ketone in ether with LiAlH_4 . After solvent stripping, a white crystalline solid was left. The crystals were air dried and then dried over phosphorus pentoxide under vacuum. After several vacuum sublimations, the crystals gave a mp of 49–50 °C (lit.¹⁰ 50 °C). Analysis by GLC on a 9-ft column of SF-96 on Chromosorb W revealed only one peak. The ^1H NMR spectrum in CHCl_3 at 250 MHz showed a peak at 0.98 ppm integrating for 18 protons, a peak at 2.52 ppm for one

proton, and a single proton peak at 1.61 ppm which disappeared in the presence of D₂O.

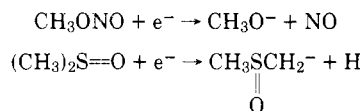
For comparison, di-*tert*-butyl ketone (Chemical Samples Co.) showed a single absorption at 0.98 ppm. Except for peak heights at equivalent concentrations, this spectrum was identical with that of tri-*tert*-butylcarbinol whose hydroxyl proton has been exchanged with D₂O.

Neopentyl alcohol (Aldrich Chemical Co.) was recrystallized from petroleum ether and vacuum sublimed to a constant melting point, 54.6–55.6 °C (lit.¹¹ 53 °C). ¹H NMR spectra in CDCl₃ at 60 MHz showed peaks at 0.98, 3.2, and 3.9 ppm integrating respectively for nine, two, and one protons, the latter absorption being removable upon treatment with D₂O.

Spectra. The pulsed ion cyclotron resonance (ICR) spectrometer designed and constructed at the University of California, Irvine, was utilized for the determination of the gas-phase acidities of neopentyl alcohol, di-*tert*-butylcarbinol, and tri-*tert*-butylcarbinol.² The instrument is essentially a mass spectrometer which is capable of trapping gaseous ions efficiently for times up to several seconds.¹² The relative acidity of the Brønsted acids AH and BH can be determined by measuring equilibrium constants for reactions such as



The pulsed ICR spectrometer can measure the equilibrium abundance of the two anions A[−] and B[−], and an ionization gauge calibrated by a capacitance manometer was used to measure the partial pressures of AH and BH in the system. Experiments were performed at very low pressures in the range from 10^{−6} to 10^{−4} Torr. Under these conditions the anions A[−] and B[−] exist as free gaseous ions. Both positive ion and negative ion mass spectra can be obtained by this technique. Positive ion spectra were taken at short delay times for each of the alcohols, and in all cases the positive ion ICR spectra were found to resemble closely the conventional electron impact mass spectra. This serves as a check for the purity of the samples as admitted into the spectrometer. Negative ions were generated by dissociative electron capture on methyl nitrite or Me₂SO



Since the strongest base of the alkoxide series in the gas phase is CH₃O[−] it was most generally useful as a deprotonating reagent for the other aliphatic alcohols.

Proton magnetic resonance spectra were recorded on either a Varian A-60D, a Hitachi-Perkin Elmer R-20, or the HF-250 MHz instrument at Mellon Institute. Reproductions of the spectra of the three alcohols discussed here, before and after recovery experiments, are presented in ref 13. Chemical shifts are referred to an external tetramethylsilane standard. Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrometer or a Beckman IR4 spectrometer. Mass spectra were recorded on an Associated Electrical Industries MS-9 spectrometer.

Recovery Experiments. Upon finding that tri-*tert*-butylcarbinol underwent a rapid exothermic reaction in K⁺Me₂SYL[−] solutions, careful quantitative recovery experiments were initiated with di-*tert*-butylcarbinol and neopentyl alcohol as controls. The K⁺Me₂SYL[−] base concentrations were usually 0.1 M; however, the base concentration was varied from 0.05 to 1.0 M for tri-*tert*-butylcarbinol with the same results. The apparatus and procedure followed were essentially the same for all three recovery experiments except that the tri-*tert*-butylcarbinol experiment was repeated on a vacuum line. A 150-mL round-bottom flask equipped with a gas inlet tube, O-ring-adapted joint, and a ground glass joint was connected to a mineral oil bubbler and purged continuously with argon. Forty milliliters of pure Me₂SO were measured from the storage bottle. A 20-mL hypodermic syringe was used to withdraw 10 mL of the 1.0 M K⁺Me₂SYL[−] stock solution for delivery into the flask. Purified carbinol was added to a solids addition bulb which was fitted onto the ground glass joint. A balloon was stretched over the mouth of the O-ring joint and was bound tightly. The basic solution was stirred continuously with a magnetic spin bar. The flask and balloon were filled several times with argon, which was expelled through the bubbler. The solids addition bulb was rotated slowly so that alcohol addition was complete after 20 to 25 min. Neither the solution nor balloon showed any evidence of gas evolution in the case of neopentyl or di-*tert*-butylcarbinol.

Addition of tri-*tert*-butylcarbinol, however, caused a gas to be evolved which was captured in the balloon. After quenching the solution with ice, neutralizing with 0.1 N HCl, extracting with ether, and

drying the ethereal solution over potassium carbonate, GLC analysis revealed that no tri-*tert*-butylcarbinol was recovered and that a new compound had been formed. Infrared analysis identified this product as di-*tert*-butyl ketone. Analysis on a 10-ft column of 3% SE-30 and on a 10-ft column of 3% OV-17 positively confirmed this identification by spiking with authentic material. No trace of di-*tert*-butylcarbinol was seen on the GLC recording and this was confirmed by spiking with a bona fide sample. In contrast, complete recovery of pure neopentyl alcohol and di-*tert*-butylcarbinol was achieved through the same work-up from treatment of these compounds with K⁺Me₂SYL[−].

In a replica experiment the same reaction vessel was assembled and connected to the vacuum line via the O-ring joint. The system was evacuated several times and then isolated from the pump. The solid alcohol was added slowly and the gas was collected in a gas buret. When all the sample was dissolved and gas evolution was complete, a liquid nitrogen cold trap was used to condense the gas in a storage flask fitted with a vacuum stopcock. The line was reopened to the pump to remove all noncondensable impurities. The storage flask and the reaction flask were closed and removed from the vacuum line. This sample of gas was identified positively as isobutane by comparison with a sample from Union Carbide. A separate experiment performed with K⁺Me₂SYL[−]-*d*₅ in Me₂SO-*d*₆ (99.5%, Norrell Chemical Co.) gave identical results except for a parent peak at *m/e* 59 and several fragmentation patterns shifted by one mass unit.

Mass spectra were run at 15, 20, 75 eV for the collected gas and at 20 and 70 eV for authentic samples of isobutane and isobutene under the same conditions. These experiments showed clearly that the product gas was isobutane which did not contain a detectable amount of the olefin.

Results

Gas-Phase Reactions. Reaction of CH₃O[−] with ethanol, 2-propanol, *tert*-butyl alcohol, neopentanol, and di-*tert*-butylcarbinol in the pulsed ICR spectrometer gave exclusively the corresponding M-1 alkoxide ions. However, tri-*tert*-butylcarbinol under the same conditions fragmented to give negative ions at *m/e* 199, 141, and 127 with relative abundances 9, 100, and 14%, respectively. Even when a weaker base such as CH₃SOCH₂[−] was used, fragmentation to give the same peaks was still observed. The small peak at *m/e* 199 is probably the conjugate base of tri-*tert*-butylcarbinol. We can only speculate on the structures of the two ions of lower mass.

Association Studies. The unusually crowded structure of tri-*tert*-butylcarbinol implies that its alkoxide ion would receive less stabilization by solvation or ion pairing than would those from less hindered alcohols. It should also be less associated through hydrogen bonding than other alcohols. An IR concentration study of the hydroxyl band (~2.72 μm) shows it to be unusually sharp. It does not broaden or shift when the concentration is varied from 2.5 to 10% carbinol in carbon tetrachloride. In sharp contrast, neopentyl alcohol exhibits two bands in the O–H stretching region due to a hydrogen-bonded and a nonhydrogen-bonded stretching frequency. The nonhydrogen-bonded stretching frequency is superimposable upon the hydroxyl band of tri-*tert*-butylcarbinol.

Although tri-*tert*-butylcarbinol does not self-associate, it can act as a hydrogen-bond donor to the solvent. In Me₂SO, the hydroxyl stretching frequency is lowered and the band is broadened.

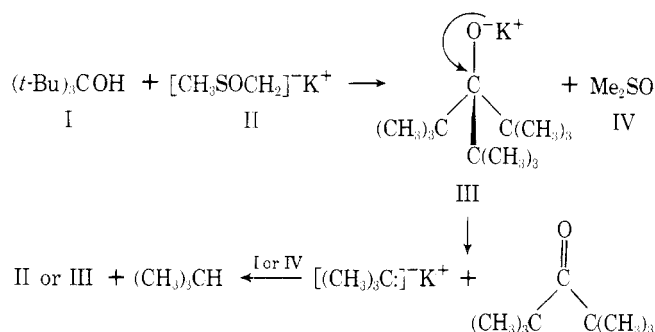
In further contrast to neopentyl and other alcohols studied, a thermometric titration of tri-*tert*-butylcarbinol into carbon tetrachloride shows no detectable heat of dilution.

Discussion

The evidence presented in the foregoing sections may be summarized as follows: (a) In the gas phase, tri-*tert*-butylcarbinol is the most acidic of the aliphatic alcohols we have studied. Its behavior follows the systematic trend established by its less branched homologues. However, it is kinetically unstable and shows a strong tendency to fragment. (b) Reaction of tri-*tert*-butylcarbinol with dimsylate anion in Me₂SO is anomalously exothermic. This is not due to its abnormally high acidity, as shown by its failure to dissolve in aqueous

sodium hydroxide and its failure to titrate with $K^+Me_2SYL^-$ in Me_2SO in the predicted pK_a range. (c) Recovery experiments, which retrieved neopentyl alcohol and di-*tert*-butylcarbinol quantitatively after deprotonation in Me_2SO , show that tri-*tert*-butylcarbinol is converted completely and instantly to di-*tert*-butyl ketone and isobutane.

We propose that this reaction occurs through the expulsion of a *tert*-butyl carbanion in accordance with the following mechanistic scheme:



This mechanism is entirely analogous to the retro-Grignard addition proposed by Zook⁷ for the cleavage of di-*tert*-butylneopentylcarbinol with sodium hydride in ether. Cram⁶ likewise observed cleavage of some heavily substituted tertiary alcohols in the course of his classic investigations of electrophilic aliphatic substitution. The striking feature in the present case is the instantaneous expulsion of a completely aliphatic moiety under relatively moderate conditions in a strongly basic solution. Zook's cleavage required reaction times of 1 to 6 h at 200 to 400 °C. Cram's leaving groups carried resonance stabilizing aromatic or cyano groups.

Schleyer¹⁴ has calculated the strain energy for tri-*tert*-butylmethane as 40.4 kcal/mol and that for 1,1-di-*tert*-butyléthane is 15.0 kcal/mol. The heat of reaction of tri-*tert*-butylcarbinol with $K^+Me_2SYL^-$, -23.2 kcal/mol, is close to the difference (-25 kcal/mol) in strain energy for these compounds and is probably the driving force for the reaction.

We can produce no iron-clad evidence against a radical cleavage pathway^{8,15} through *tert*-butyl radical or di-*tert*-butylketyl. Tri-*tert*-butylmethyl radical and di-*tert*-butylmethyl radical are remarkably stable because of steric hindrance against dimerization.¹⁶ One might reasonably presume

that di-*tert*-butylketyl would also be fairly long lived for the same reason. However, the lack of coupling products⁶ in our product mixture and the initiation of the reaction by strong base make a radical pathway seem much less likely than the carbanion mechanism.¹⁷ In view of the high rate of the reaction and the high melting point of Me_2SO , CIDNP or ESR experiments to test for *tert*-butyl radicals at low temperatures would be difficult, but not impossible.^{18,19}

Acknowledgments. We are glad to acknowledge support of this work by NSF Grant GP-6550-X.

Registry No.—Tri-*tert*-butylcarbinol, 41902-42-5; di-*tert*-butylcarbinol, 14609-79-1; neopentyl alcohol, 75-84-3; dimethyl sulfoxide, 67-68-5.

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- The editor has pointed out that the absence of isobutene in the gaseous product argues against radical disproportionation of *tert*-butyl radicals. Correspondingly, the absence of di-*tert*-butylcarbinol in the worked-up solution argues against formation and disproportionation of an intermediate ketyl.
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Periselectivity in the [4 + 2] and [6 + 4] Cycloadditions of Diphenylnitrilimine to Tropone

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Received July 19, 1977

The cycloaddition of diphenylnitrilimine, generated from the dehydrochlorination of α -chlorobenzylidene phenylhydrazine, to tropone gives a [6 + 4] adduct in 4% yield, a 2:1 adduct (4%) of unknown structure, and three partially aromatized [4 + 2] adducts in 54, 5, and 5% yield. Attempted photochemical decarbonylation of the [6 + 4] adduct gave only a mixture of rearranged products, while pyrolysis of the [6 + 4] adduct resulted in a [1,5]sigmatropic shift and formation of one of the partially aromatic [4 + 2] adducts. The periselectivity observed here is similar to that of nitrile oxide, but differs substantially from that observed with other dipoles and with dienes. Electronic origins of these differences are discussed.

Introduction

In 1970, we reported the first examples of [6 + 4] cycloadditions of 1,3-dipoles across the termini of trienes.^{2,3} The [6

+ 4] cycloaddition of diphenylnitrilimine to tropone² and the [6 + 4] cycloaddition of diazomethane to dimethylfulvene³ were prototypes of a general method for the synthesis of new heterocyclic systems. However, in the interim, remarkably few