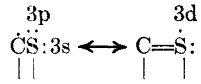
ated, the methyl triplet at τ 8.78 was partially converted to a doublet. Since the doublet peaks appeared between those of the triplet, the doublet to triplet intensity served as one estimate (32% exchange of α-hydrogens in 105 min at 95°). Careful examination of the methylene region showed the outer peaks decreased in intensity compared to the inner. By calculating the intensity expected for the inner region as three times the outer, and deducting this from the integrated absorbance of the inner, the difference may be assumed to be the contribution of hydrogen exchanged into DMSO. The value obtained, 30% exchange, is in excellent agreement with that estimated from the triplet region.

These results are in accord with other recent data indicating a greater ease of metalation[9] and of hydrogen exchange,[10] of hydrogen α to sulfur than α to phosphorus or silicon. These results are in accord with the hypothesis, advanced some years ago on the basis of the much greater stabilization of carbon radicals in vinyl copolymerization by sulfide than by silicon (or phosphide phosphorus),[11] that the enhanced capacity of sulfide to stabilize carbanion or free-radical carbon may be due to 3p–2p–π bonding with promotion of one or two 3p electrons on sulfide sulfur to nonbonding 3d orbitals. This opportunity is open to trivalent phosphorus to only a limited degree (by rehydridization of



$$\dot{\mathrm{C}}\overset{3p}{\ddot{\mathrm{S}}}{:}3s \longleftrightarrow \mathrm{C}{=}\overset{3d}{\dot{\mathrm{S}}}{:}$$

phosphorus from p^3 geometry to sp^2 geometry) and not at all to silicon or to sulfone sulfur or pentavalent phosphorus.

Experimental Section

Solutions of **dimsyl ion** (*ca.* 15%) were prepared by dissolving sodium hydride in deuterated DMSO.[7] About 0.4 ml was placed in a 5-mm-o.d. precision-bore nuclear magnetic resonance (nmr) tube. After addition of 10% by volume of reactant, the tubes were sealed and the nmr spectra were recorded. The tubes were then heated on a steam bath (95–100°) for various intervals and the spectra reexamined. **Tetramethylsilane** and **triethylamine** showed no nmr spectral changes even after 3 hr at 95°. The TMS was insoluble in DMSO; so the tube was shaken at frequent intervals.

Dimethyl Sulfide.—Before heating, the ratio of peak heights at τ 7.38 (DMSO) and 7.88 (DMS) was 1:45. After 15 min at 95°, it became 17:41, after 60 min, 23:11, corresponding to 29 and 66% exchange.

Diethyl Sulfide.—Before heating, the solution showed a quartet at τ 7.42 and a triplet at τ 8.78 (J = 6.6 cps). After heating to 95° for 105 min, the triplet area developed a doublet between the triplet peak τ 8.78 (J = 6.6 cps), each peak with a fine splitting (by α-^{2}H) of J' = 1.2 cps. The ratio of doublet area to triplet was 34.2:72.6 (32% exchange). From the relative integrated area under the outer and inner peaks of the quartet at τ 7.42, exchange at 15, 45, and 105 min corresponded to 14, 21, and 30% of the α-hydrogens, respectively.

When **TMS** was added to **potassium *t*-butoxide** (5%) in DMSO-d_6, gas was immediately released. The solution remaining in the nmr tube was sealed. The nmr showed singlets at τ = 7.38, 8.85, 9.85, and 10 ppm in the approximate ratio of 1:3:3:1. These may be assigned to DMSO, the *t*-butyl and trimethyl silyl groups of ***t*-butyl trimethyl ether** and to excess unreacted TMS, respectively. When this solution was heated to 95° for 75 min, a new singlet at τ 5.96 dominated the nmr spectra while those at τ 8.85, 9.85, and 10.0 were markedly decreased. This interesting observation awaits an explanation.

Benzyltrimethylsilane also reacted rapidly with potassium *t*-butoxide in DMSO, turning red; distillation of such a reaction mixture gave two products. ***t*-Butyl trimethylsilyl ether**, bp 100° [lit.[12] 101° (754 mm)], showed nmr singlets at τ 8.8 and 9.8 and infrared bands at 1000–1100 (ether), 1400 and 1360 (*t*-butyl), and 1410 cm^{-1} (trimethyl silyl). **Toluene** (bp 110°) was confirmed by ultraviolet and nmr spectra. After removal of the DMSO under reduced pressure, an unidentified thick oily reddish brown residue remained.

With sodium methoxide in DMF, benzyltrimethylsilane gave a red reaction mixture. It was stripped under aspirator pressure and the volatile material was redistilled at atmospheric pressure to give **methyl trimethylsilyl ether**, bp 55–57° (lit.[12] 55.5°).

Diethyl sulfide reacted with potassium *t*-butoxide in DMSO-d_6 on heating to 95° for 2 hr. Some of the methylene protons shifted downfield by 3 cps and some of the methyl protons unfield by 3 cps, without change of the splitting pattern. This is *not* due to hydrogen exchange, but its cause has not been established.

Registry No.—Dimethyl sulfoxide, 67-68-5; *t*-butyl trimethylsilyl ether, 13058-24-7; toluene, 108-88-3; methyl trimethylsilyl ether, 1825-61-2.

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Enolization of Ketones. IV.[1] The Rate and Orientation of Base-Catalyzed Deuteration of Some Methyl Ketones

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According to the currently accepted mechanism, both base-catalyzed halogenation and deuteration of ketones proceed *via* the same rate-determining step, the formation of the enolate anion (or enol). This means that the orientation and the reaction rates for the two reactions would be identical or nearly identical.[2–6]

In a series of papers, one of us has studied the orientation of base-catalyzed halogenation and deuteration of 2-butanone.[7–13] Evidence was found that two different base-catalyzed halogenations exist for this ketone and, unexpectedly, in neither of these is the orientation of halogenation the same as the orientation of deutera-

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tion.[11] This lead to the hypothesis that different mechanisms operate for halogenation and deuteration. Halogenations performed in D_2O and experiments where hypobromous acid was used as the halogenating agent gave indication that base-catalyzed halogenation and deuteration of ketones are not competetive reactions. It was suggested that nonenolic mechanisms operate in the halogenations.[12,13]

If such is the case, it is evident that the enolization of ketones is favorably studied by reactions other than halogenations, which has been very often used before,[2–6] *e.g.*, racemization and deuteration.

The deuteration of 2-butanone has also been studied by Warkentin and Tee[14,15] and by Bothner-By and Sun.[16] Warkentin and Tee reported that different bases gave different values for the orientation of the deuteration, *e.g.*, sodium acetate, sodium *p*-nitrophenoxide, and sodium deuterioxide.[14,15] However, this is in disagreement with the results of an independent investigation.[9] This discrepancy is discussed in a separate paper and it was suggested to be due to the extrapolation technique used by Warkentin and Tee and the incorrect omission of a term arising from solvent catalysis.[10] Bothner-By and Sun, who also used sodium acetate as base in their deuterations, reported values for the orientation of substitution in perfect harmony with those reported in ref 9 for acetate and some other inorganic bases.[16]

Warkentin and Tee have discussed the influence of an alkyl group on the rate of enolization[14,15] and, contrary to what is reported previously by House and Kramar for strong bases in organic solvents,[17] they found that in aqueous solvents a methyl group accelerated the rate of enolization. In our opinion, it is difficult to draw any general conclusions from the study of a single ketone.

In the present investigation we have studied the base-catalyzed deuteration of a number of methyl ketones other than 2-butanone using nmr technique. The observed and calculated rate constants were obtained as described before [18–21] and our results are summarized in Table I. In addition to the rate constants, we have calculated the K_D values, which are a measure of the orientation of the deuterations. K_D is defined as 3-deuteration/1-deuteration (k_{CH_2}/k_{CH_3} or k_{CH}/k_{CH_3}).

TABLE I

PSEUDO-FIRST-ORDER RATE CONSTANTS (40°)[a]

Ketone[d]	Amt,[b] ml	$k_1 \times 10^5$, sec^{-1} CH$_3$	CH$_2$	CH	K_D
Acetone	0.20	10.9[c]	...	...	...
2-Butanone	0.20	4.9	3.0	...	0.61
2-Pentanone	0.20	4.5	1.3	...	0.29
2-Hexanone	0.15	4.6	1.2	...	0.23
2-Heptanone	0.10	5.1	1.6	...	0.32
3-Methyl-2-butanone	0.15	4.9	...	$<10^{-2}$	$<10^{-2}$
3-Methyl-2-pentanone	0.15	4.0	...	$<10^{-2}$	$<10^{-2}$
3-Ethyl-2-pentanone	0.10	3.8	...	$<10^{-2}$	$<10^{-2}$
Pinacolone	0.15	3.0	...	...	...
4,4-Dimethyl-2-pentanone	0.10	0.55	0.03	...	0.06

[a] We assume the rate constants to be accurate within ±12%. [b] Each run consisted of ketone, 0.5 ml of catalyst, and 0.8 ml of dioxane. [c] This value was obtained by multiplying k_{CH_3}(obsd) by a factor of 6 and dividing by a factor of 2. [d] Registry numbers are given in consecutive order: 67-64-1, 78-93-3, 107-87-9, 591-78-6; 110-43-0; 536-80-4, 565-61-7, 6137-03-7, 75-97-8, 590-50-1.

Examining the rates for methyl deuteration in Table I, acetone was found to be the most reactive of the ketones. The values for all the other unbranched methyl ketones were about half of that of acetone ($4.5–5.1 \times 10^{-5}$ sec^{-1}), while the values for the branched ketones were lower and in the case of 4,4-dimethyl-2-pentanone about 20 times lower than acetone. The reason for this large decrease is still unclear. In the case of acid-catalyzed reactions, which we have recently studied,[18] the rate of methyl deuterations was in general larger for the branched ketones than for the unbranched ketones and the highest rate was observed for 4,4-dimethyl-2-pentanone.

From an examination of Table I, it is evident that in all cases the deuteration of a methylene or a methine group is slower than that of a methyl group. In the case of 2-butanone this effect is small, but for the more highly branched ketones the effect is very pronounced (a factor of 100 or more). The same effect was also observed for acid-catalyzed enolization.[18] This decrease in rate can be caused by steric factors, by the inductive effect of an alkyl group, or both.

Experimental Section

Nmr measurements were carried out on a Varian A-60 spectrometer. The experimental procedure has been previously described.[18] The base catalyst was prepared by diluting 0.564 g of anhydrous sodium carbonate to 25 ml with deuterium oxide (<99.7%). Measurements were performed in homogeneous systems in duplicate.

The pseudo-first-order rate constants were calculated on a Control Data 3600 computer using a linear least-squares program designed to accept the integral values from the nmr spectra. The resulting rate constants have been corrected for the apparent changes in base concentration resulting from changes in the volume of ketone used to meet solubility requirements.

Deuteration was generally followed for somewhat less than one half-life during which time the plots were linear. Acetone was followed through 73% deuteration. Deviation from linearity was considerable after one half-life.

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(19) Rates and rate constants can be defined in two ways. Either they are the *total* rates, which means that they are on a per *group* basis, or they are on a per *hydrogen* basis. In recent papers dealing with deuterations of ketones,[9,14–18] both ways are used. As this is confusing, it seems necessary that a careful discussion should be made of the various definitions of terms and conventions in use. The following abbreviations are used: k_{hal}(obsd) = observed rate constants for halogenations; k_D(obsd) = observed rate constants (by nmr) for deuterations; $k^{group} = k^{total}$ = rate constants on a per group basis; $k^{hydrogen}$ = rate constants on a per hydrogen basis. Accordingly, $k_{CHn}{}^{total} = k_{CHn}{}^{group} = nk_n{}^{hydrogen}$. In most reactions, *i.e.*, halogenations of ketones, the observed rates are the total rates, *i.e.*, per group basis (k_{hal}(obsd) = k^{group}). One exception is the rates for deuterations obtained by nmr technique, which are on a per hydrogen basis (k_D(obsd) = $k^{hydrogen}$). In the present series of papers,[9,18] we wanted to compare a quotient of deuteration rates (K_D) with a quotient of halogenation rates (K_{Br}).[11–13] Therefore we have calculated and given the total rates for deuteration,[9] *i.e.*, per group basis: $k_{CH_3}{}^{group} = 3k_{CH_3}{}^{hydrogen} = 3k_D$(obsd); $k_{CH_2}{}^{group} = 2k_{CH_2}{}^{hydrogen} = 2k_D$(obsd). The same method has also been used by Bothner-By and Sun[16] and by Wiberg and Nigh.[20] On the other hand, values given by Warkentin and Tee[14,15] and by Hine, *et al.*,[21] are on a per hydrogen basis.

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