lamp[7] with a Pyrex filter in a quartz immersion well, with stirring by a stream of nitrogen. Photolysis was complete in 1 hr. After evaporation of the dioxane, the residue was dissolved in water and washed with chloroform. The product contained a small amount of a colored water-soluble impurity and was further purified by preparative tlc in silica gel, using $CHCl_3$-MeOH-HOAc (90:30:5). It was precipitated from methanol with ether in nearly quantitative yield, mp 195-200°,[8] $[\alpha]^{27}D$ +18.3 (*c* 1, EtOH).

To confirm further that no racemization occurred in any of the reactions, we esterified N^{α}-Boc-N^{im}-(ONB)-His with CH_2N_2, removed the ONB group by irradiation, and separated the reaction products by preparative tlc. An almost quantitative yield of N^{α}-Boc-L-histidine methyl ester was obtained, mp 124-125.5° (EtOAc-petroleum ether). The ORD spectrum of this sample was identical with that of an authentic sample synthesized from histidine methyl ester hydrochloride, with $[\alpha]_{290}$ −50.7.

Work is in progress on the synthesis of peptides using this protecting group.

Acknowledgment. This work was supported by grants from the National Science Foundation and from Eli Lilly and Company. We thank Dr. Robert Archer, Dr. Bruce H. Frank, and Mr. Allen Pekar of the Lilly Research Laboratories for the use of the equipment needed in the photolysis experiments and for the ORD data.

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(5) N^{α}-Boc-N^{im}-ONB-His, Calcd for $C_{18}H_{22}O_6N_2 \cdot H_2O$: C, 52.93; H, 5.92; N, 13.72. Found: C, 52.98; H, 5.68; N, 13.75, $[\alpha]D^{27}$ +12.9 (*c* 2, MeOH). Satisfactory nmr and ir spectra were obtained.

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Received August 22, 1974

5-Thiomethylpentane-2,3-dione. A Unique Natural Product from the Striped Hyena

Sir:

Ruzicka's isolation of civetone and muskone in 1926[1] opened the area of mammalian scent materials.[2] Only recently have compounds of further chemical interest[3] been identified. We now report the isolation of 5-thiomethylpentane-2,3-dione from the anal scent gland of the striped hyena (*Hyaena hyaena*), the first α-diketone thioether from a natural source.

Analysis (gc-mass spectral) of a chloroform extract of waxy material deposited by either sex[4] indicated two volatile components, representing 2% of the total material. The more volatile of these, mol wt 146, appeared to contain sulfur. In addition to the parent, P + 1, and P + 2, large peaks were observed at *m/e* 118, 103, 90, 75, 61, and 43. The second less volatile compound exhibited *m/e* 224 and did not contain sulfur. Material of mol wt 146 was collected by vacuum distillation of crude, waxy material at 55° (2 mm) into cold traps, followed by preparative glc, giving a light yellow odoriferous oil[5] which exhibited the following pmr spectrum: δ 2.03, s, 3 H; 2.30, s, 3 H; 2.63, t, 2 H, J = 5.5 Hz; 2.95, t, 2 H, J = 5.5 Hz. The two methylene groups are adjacent, indicated by their coupling, and the presence of only ten protons shows that other groups must be present to achieve a mol wt of 146. The ir spectrum confirmed this, showing a single carbonyl absorption at 5.82 μ. Further confirmation was achieved by preparation of a dimethoxime[6] which exhibited *m/e* 204, 173, 157, 142, 127, 126, 125, 95, and 61 and a substituted quinoxaline[7] which indicates that the two carbonyl groups are adjacent to each other in the original molecule: *m/e* 218, 203, 190, 171, 143, 108, 76, and 61.[8] On the basis of these derivatives, and the pmr and ir spectra, the structure of the 146 material is $CH_3COCOCH_2CH_2SCH_3$ (I).

Synthesis of I was achieved from biacetyl, sodium hydride, and chloromethyl methyl sulfide as well as by mixing equimolar amounts of biacetyl, formaldehyde, methanethiol, and a catalytic amount of diethylamine[9] at 0° followed by distillation at 70°. The residue of this distillation was distilled, bp 72° (3 mm), giving 30% of I; as bissemicarbazone, mp 234.0-234.5° dec, mmp 234.0-235.0° dec. *Anal.* Bissemicarbazone, $C_8H_{16}N_6O_2S$, calcd: C, 36.90; H, 6.19; N, 32.29; S, 12.31. Found: C, 37.08; H, 5.98; N, 32.59; S, 12.31. The mass spectrum, retention times, and ir and pmr spectra of synthetic I purified by preparative glc[5] were identical with those of the natural material.

Although n-butyl mercaptan and dicrotyl sulfide have been identified as odorous components of skunk[10] and di- and trisulfides have been found in ponerine ants,[11] this thioether containing an α-dicarbonyl represents a unique natural product. The nature of the mol wt 224 compound, its relationship to I, and scent-marking behavior are under investigation.

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Acidities of Carbon Acids. IV.[1] Kinetic *vs.* Equilibrium Acidities as Measures of Carbanion Stabilities. The Relative Effects of Phenylthio, Diphenylphosphino, and Phenyl Groups

Sir:

It has become common practice to use rates of deuterium exchange, or the like, to obtain evidence concerning such important questions as the effects of aromaticity,[2] antiaromaticity,[3] homoaromaticity,[4] heteroatom substitution,[5] and s character,[6] on relative carbanion stabilities. It has been clear for some time, however, that interpretation of the kinetic data is made difficult by the existence of factors such as internal return and ion pairing. If internal return is present, as is often the case, the rate-limiting step is not the rate of carbanion formation but rather the rate of exchange of solvent molecules at the carbanion site.[7] If ion pairing occurs, as is true for most of the solvents used for such studies (Et_2O, THF, CHA, NH_3, *t*-BuOH, MeOH, etc.), relative rates may vary markedly, depending on the nature of the cation, the anion, and the solvent. For example, Shatenshtein and Gvozdeva found the ratio of exchange rates, $k^{\varphi SCH_3}/k^{\varphi CH_3}$, to vary from 10^4 to 40 to 0.2 in changing from KNH_2–NH_3 to $NaCH_2SOCH_3$–DMSO to *t*-BuOK–DMSO.[8,9]

To add to these difficulties there is evidence that the Brønsted α coefficient, which relates kinetic to equilibrium acidities, is not readily predictable and may sometimes be anomalous.[12] The existence of Brønsted α coefficients greater than one and less than zero[12] shows that, even when internal return and ion pairing effects are absent, kinetic acidities may misrepresent carbanion stabilities. A coefficient larger than one means that the kinetic acidity has overestimated carbanion stability, as judged by equilibrium acidities. On the other hand, comparisons of kinetic acidities often leads one to underestimate carbanion stabilities. For example, nitromethane is deprotonated by HO^- in water at a rate only *ca.* 100 times that for acetone,[13] whereas the difference in their equilibrium constants is *ca* 10^{10} in water,[14] and $10^{9.7}$ in DMSO.[1] In addition, when substituents are introduced near the acidic site, polar, steric, and/or conjugative effects may affect kinetic acidities in such a way as to indicate an order of carbanion stability the *inverse* of that actually present. The effect of Me substitution on deprotonation rates in the series CH_3NO_2, $MeCH_2NO_2$, and Me_2CHNO_2 is an example where kinetic acidities predict the wrong order of anion stabilities, as judged by equilibrium acidities (negative Bronsted α).[12] We now present what appears to be a similar example from the effects of α-heteroatom substitution.

The relative rates of exchange of phenyl methyl sulfide, dimethylphenylphosphine, and toluene with potassium amide in liquid ammonia have been reported to be: $C_6H_5SC\mathit{H}_3$ (10^4) > $C_6H_5P(C\mathit{H}_3)_2$ (2) > $C_6H_5C\mathit{H}_3$ (1.0).[5] From these results it would appear that the relative order of effectiveness of groups in stabilizing carbanions is $C_6H_5S \gg C_6H_5P > C_6H_5$. The relative effects of the $(C_6H_5)_2P$, C_6H_5S, and C_6H_5 groups have now been assessed by measuring equilibrium acidities in DMSO with methyl phenyl sulfone as the parent acid. The p*K*'s of $GCH_2SO_2C_6H_5$ with G = H, C_6H_5S, $(C_6H_5)_2P$, and C_6H_5 were found to be 29.0_5, 20.3, 20.2, and 23.4, respectively.[16,17] Assuming that the effect on acidity is primarily one of carbanion stabilization,[1] the effects range from 5.9 to 9.1 powers of ten,[18] corresponding to *ca.* 8.0–12.5 kcal/mol at 25°.

It is noteworthy that the effect of the phenyl group on carbanion stability observed is larger (Δ pK = 5.6) than any reported previously in solution,[19] and that the effect of the phenylthio group is even larger.[21] The effect of the diphenylphosphino group appears to be slightly larger than that for the phenylthio group, judging from acidities in the G_2CH_2 series; thus, p*K*'s for G = $(C_6H_5)_2P$, C_6H_5S, C_6H_5 were found to be 29.9, 30.8, and 32.3,[22] respectively. It appears, then, that the C_6H_5P group, instead of being much less effective at carbanion stabilization than the C_6H_5S group, as kinetic acidities suggest, may be slightly more effective. It follows from these results that, although kinetic acidities often give a rough guide to carbanion stabilities, conclusions regarding relative carbanion stabilities derived from kinetic measurements must be regarded as tentative, at best.[23]

Acknowledgment. We are grateful to the National Science Foundation (GP-29539X) for support of this investigation.

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