solid[10] which was dissolved in tetrahydrofuran at room temperature, cooled to −10°, and treated with ∼50% excess of 1:1 chlorotrimethylsilane–triethylamine.[11] Addition of pentane after stirring for 10 min, followed by addition of, and washing with, ice-cold saturated aqueous sodium bicarbonate, washing with brine, and drying gave the silyl enol ether 7 in 90% yield after distillation (Kugelrohr, 65° (0.7 mm)). The nmr spectrum showed a 3 H methyl singlet at δ(CDCl$_3$) 0.9 ppm and a 1 H doublet ($J \sim 1$ Hz) at 4.5 ppm.

Dropwise addition of the silyl ether 7 in *dry* glyme (4 ml/mmol) to 1.05 equiv of ethereal methyl lithium in glyme (4 ml/mmol) was followed by stirring at room temperature for 30 min, cooling to −78° under a stream of nitrogen, adding 1.2 equiv of the unsaturated ketone 4, R = CH$_3$,[12] in glyme, stirring for 10 min, and allowing to warm over 30 min. Work-up (saturated ammonium chloride solution), followed by refluxing with 5% sodium methoxide in methanol for 3 hr, gave (67% yield) the known tricyclic enone 8, mp 122°, identical with an authentic sample.[2]

Under the same conditions, the octalone 9[13] was transformed, via the trimethylsilyl enol ether (nmr: δ (CDCl$_3$) 0.94 (3 H, s), 4.7 (1 H, b s) from reductive trapping, into the tricyclic ketone 10, mp 141–142°:
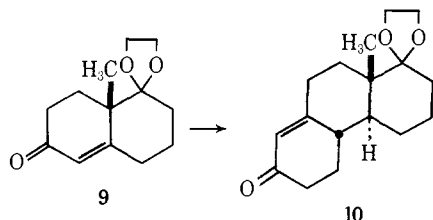
nmr δ 1.1 (3 H, s), 3.9 (4 H, s), 5.8 (1 H, b s). Acid hydrolysis converted 10 into the known corresponding dione, mp 122°.[14]

The use of the bis-annelating reagent 11 allows, as we have previously shown,[5] the addition of the equivalent of two rings at a time, thus leading to the type of tricyclic enone which we previously used[15] in the synthesis of (±)-progesterone. Under the conditions described for the conversion of 1 to 8, the silyl ether 13 (88% yield after Kugelrohr distillation at 75° (0.01 mm)) from the reductive trapping of 12[16] was reconverted to the lithium enolate 14 which was treated with

11, R = CH$_3$, and cyclized to give 15 (74% yield) mp 122°, identical with an authentic sample.[17]
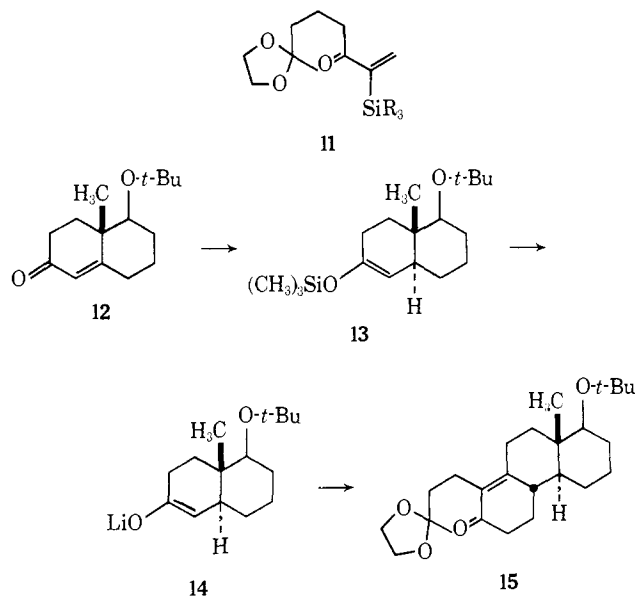
The stereo- and regiospecific transformation, via reductive methylation, of tricyclic enones, such as 15, to natural steroids has been described previously.[15]

It is clear that the growing usefulness of regiospecifically generated lithium enolates can now be extended to the Michael reaction, even with electrophilic olefins possessing exchangeable hydrogens.

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Conformational Analysis of Hydrocarbon Chains in Solution. Carbon Tetrachloride

Sir:

Very little is known about the conformational preferences of hydrocarbon chains longer than heptane and shorter than polyethylene, either in the gas phase[1] or in solution.[2] We present evidence which demonstrates the flexible nature and random orientation of hydrocarbon chains in carbon tetrachloride solution.

Our probe of chain conformation is a benzophenone substituted with a remotely attached hydrocarbon chain.[3] Conformations of the chain in which the chain

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(2) (a) G. W. Brady, C. Cohen-Addad, and E. F. X. Lyden, *J. Chem. Phys.*, **51**, 4039 (1969;) (b) G. W. Brady, *Accounts Chem. Res.*, **7**, 174 (1974); (c) K. Liu and R. Ullman, *J. Polym. Sci., Part A-2*, **6**, 451 (1968); (d) K. Liu, *ibid.*, **5**, 1209 (1967).

Table I. Quantum Yields, Rate Constants, and Lifetimes for 3 as a Function of Chain Length

| | Chain length | | | | | | | | | | |
---	1	3	9	10	11	12	14	16	18	20	22
τ^a	128	140	110	105	93	64	38.7	27.8	23.0	18.4	16.6
ϕ_t^b	0	0	0.02		0.043	0.063	0.12	0.12	0.12	0.13	0.17
ϕ_p^c	22.3	24.2	18.4	17.9	17.3	9.4	6.8	6.0	4.9	3.6	3.1
k_r^d	0	0	1.27	1.72	2.93	7.78	18.0	28.2	35.8	46.6	54.3
k_p^e	175	173	167	170	185	146	176	213	214	195	187

^{a} Measured phosphorescence lifetime in μsec. Estimated error $\pm 5\%$. ^{b} Quantum yield for disappearance of starting material. Estimated error $\pm 10\%$. ^{c} Quantum yield for phosphorescence ($\times 10^3$). ^{d} Rate constant for intramolecular phosphorescence quenching in 3, sec^{-1} ($\times 10^{-4}$). ^{e} Rate constant for phosphorescence, sec^{-1}.

achieves physical proximity to the ketone carbonyl oxygen give rise both to photochemistry and to phosphorescence quenching. Experiments were designed around the mechanism proposed in Scheme I below.

Scheme I
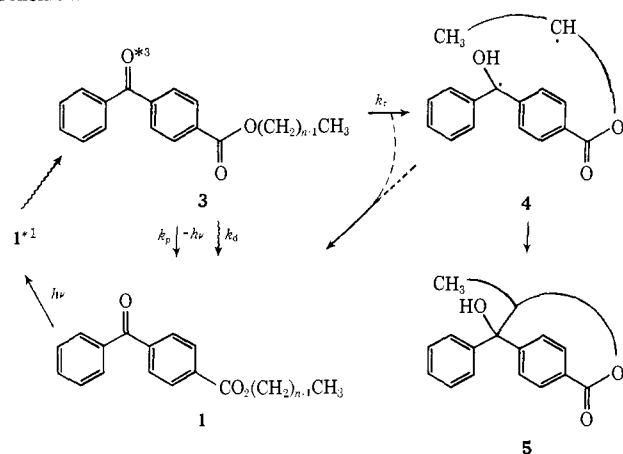
The products of the photoreaction have previously been described;[3f] we focused our attention on quantum yield and phosphorescence lifetime (τ) measurements. In order to suppress bimolecular reactions, solutions examined were approximately 1×10^{-3} M. Quantum yields for reaction (ϕ_r) were measured at 366 nm on an optical bench using the photochemical cross-section method of Johns[4,5] and ferrioxalate actinometry. Lifetimes were measured at 23° using single flashes from a Xenon Corp. air spark lamp in conjunction with an optical bench and a 1P28 phototube.[6] Oscilloscope traces were photographed. The decay curves were digitized and fitted logarithmically. Quantum yields for phosphorescence were obtained as described by

Saltiel.[8] The value $\phi_p = 1.5 \times 10^{-3}$ for benzophenone was taken as a standard.[8] Our benzophenone samples had lifetimes of 106 μsec in carbon tetrachloride.

Quantum yields and lifetimes are presented in Table I. Rate constants are obtained as follows: $1/\tau_n = k_p + k_d + k_r$. The phosphorence rate constant is a property only of the chromophore. The constant k_d is a sum of chain length independent unimolecular rate constants for processes that contribute to radiationless decay. These include solvent quenching, internal conversion, and solvent impurities. For chains too short to reach the ketone carbonyl (e.g., $n = 1$) $1/\tau_1 = k_p + k_d$. This defines the working equation (1).

$$\frac{1}{\tau_n} - \frac{1}{\tau_1} = k_{r,n} \qquad (1)$$

Phosphoresence quantum yields decrease with chain length in a parallel fashion to the decrease in phosphoresence lifetimes. From the definition ($\phi_{p,n} = k_{p,n}\tau_n$), $k_{p,n}$ may be calculated. The table shows that the rate constant for phosphorescence is independent of chain length and has an average value of $k_p = 182 \pm 13$ sec^{-1}.

The radiationless decay constant k_d is calculated to be 7600 sec^{-1} for $n = 1$ and 7000 sec^{-1} for $n = 3$. These are the same within experimental error. The constant k_d is, therefore, a property only of the chromophore and the solvent.

While k_r in Scheme I may very well be the rate constant for hydrogen abstraction, it is, phenomenologically, the rate constant for intramolecular collisional quenching of emission by the chain. These rate constants, $k_{r,n}$, contain all the information about the conformation of the chain.[9] These first-order rate constants are proportional to the probability that the triplet C=O and a CH$_2$ group will collide with the proper geometry for quenching. If we assume unactivated CH$_2$ groups to be equally reactive,[10] and if the i'th CH$_2$ in an n carbon chain has a probability, $P_{i,n}$, of achieving a reactive geometry, then eq 2 holds (k has units of sec^{-1}).

$$k_{r,n} = k\sum_{i}^{n-1} P_{i,n} \qquad (2)$$

In other words, $\sum P_{i,n}$ expresses the probability that any CH$_2$ group in the chain will occupy the reactive volume

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(5) All samples were degassed by five freeze–pump–thaw cycles at less than 1×10^{-5} Torr. Quantum yields were obtained by observing disappearance of starting material using a Cary 16 spectrophotometer and matched 1.000-cm uv cells. Quantum yields were independent of irradiation time up to 20% conversion.

(6) Carbon tetrachloride was purified by Schuster's method,[7] and all experiments were carried out with a single 2-l. batch of purified solvent. Approximately 5–10% reproducibility could be obtained on a day-to-day basis. Better results were obtained for samples simultaneously prepared and degassed. Sample purity was indicated by less than 10% variation in τ and ϕ_r over a concentration range of 5×10^{-4} to 2×10^{-3} M.

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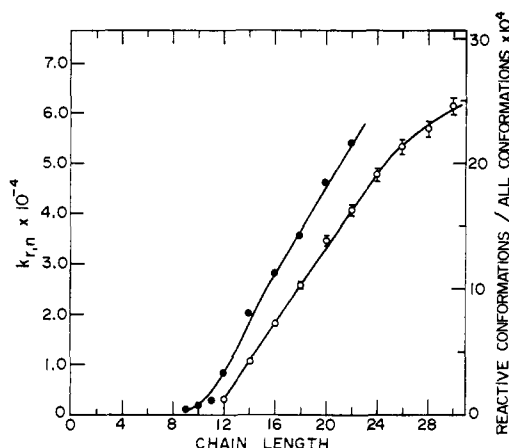
Figure 1. Measured rate constants $k_{r,n}$ (●) for intramolecular hydrogen abstraction in **3** and fraction of reactive conformations (○), both plotted against chain length. The latter quantities are obtained from lattice-based Monte Carlo calculations (ref 11). The reactive sites are taken to be the two lattice sites adjacent to the ketone oxygen in **3** coplanar with the rings. These represent the space occupied by the nonbonding orbitals on this oxygen in **1**. Error bars represent one standard deviation.

about the ketone oxygen in **3**. Since the methyl group is unreactive in **3**,[3f] one sums over $n - 1$ carbons only.

To demonstrate that the hydrocarbon chains in **1** are randomly oriented and flexible within the stricture of tetrahedral bond angles, one must calculate $\Sigma P_{i,n}$ as a function of n for such a flexible chain. We have presented[11] a lattice-based Monte Carlo method for estimating hydrocarbon chain conformations in molecules such as **1**. This method takes rigorous account of the volume excluded by the chain and the benzophenone. By choosing certain lattice sites as reactive (e.g., those adjacent to the reactive C=O in **3**), one may estimate the total number of reactive conformations, $m_{r,n}$, for a chain n carbons long. One can also estimate the total number of conformations, $m_{t,n}$, available on a diamond lattice to a chain of length n. The ratio of (reactive conformations/all conformations) for an n carbon chain equals $\Sigma P_{i,n}$ for a flexible hydrocarbon chain.

$$\sum_i^{n-1} P_{i,n} = \frac{m_{r,n}}{m_{t,n}} \tag{3}$$

While the details of the calculations, and of modeling molecules like **1** in a tetrahedral lattice, have been presented before,[11] it is important that we emphasize certain weaknesses and artifacts inherent in these calculations. Lattice-based calculations assume equal bond lengths for C–O, C–C, and C–H; consequently, C–H bond lengths are exaggerated. Hard sphere potentials underestimate CH–HC nonbonding interactions and seem to exaggerate steric interactions of CH_2 groups with the faces of the aromatic rings. The first two tend to off-set one another. The net effect, however, is to exaggerate somewhat the length of the shortest chain which can achieve a reactive conformation. This artifact has been described in some detail.[12] A more troublesome detail is that we are unable in these calculations to distinguish gauche from trans

rotamers in the chain. This has the effect of biasing the $(m_{r,n}/m_{t,n})$ ratios we calculate in favor of more highly coiled conformations of the chain. The extent to which this perturbs the calculated curve in Figure 1 is unknown.

Figure 1 presents both the experimentally determined dependence of $k_{r,n}$ on chain length and the ratio of (reactive conformations/all conformations) estimated from the Monte Carlo calculations. The horizontal shift between the two curves is consistent with the limitations of the lattice model discussed above. Choosing the reactive distance at twice the O–H bond length in **4** shifts the calculated curve so that 11 carbon chains become reactive. Expanding the reactive volume has no effect on the curve shape.

The agreement between the experimental results and the calculated reactive fraction of chain conformations for a randomly oriented flexible chain is excellent. The agreement is at the limit of what one might expect for the theoretical model at its current level of sophistication.

While rigorous conclusions cannot be drawn until quantitative calculations show that our data are inconsistent with alternative models, it seems unlikely that hairpin conformations[2c,d] or micellar aggregation with extended chains[2a,b] are favored in dilute carbon tetrachloride solution. It is possible that a small, unfavorable solvent-chain enthalpy acts to cause gauche and trans rotamers in the chain to become isoenergetic. The chains, however, appear to be highly flexible; within the framework of tetrahedral bond angles, they assume all possible orientations.

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Effect of Crown Ether on the Conformational Equilibrium of Sodium Acetylacetonate

Sir:

The structures of enolate anions derived from β-dicarbonyl compounds have long been a topic of interest.[1–11] Dynamic nuclear magnetic resonance

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