Carbanion Photochemistry. 2. Kinetic Control of Product Formation in Reactions of Radicals with Carbanions

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Abstract: The interaction of resonance-stabilized carbanions with methyl radicals produced by the irradiation of the carbanions in dimethyl sulfoxide is governed by the pK_a of the carbanion conjugate acid to a greater extent than by the stability of the resulting radical anion. This kinetic effect is explained using energetic considerations based on the Hammond postulate and is further rationalized by a molecular orbital correlation diagram.

Our studies in carbanion photochemical mechanisms[1] have drawn us inexorably to an investigation of the interaction of radicals with anions, not only because of the significance of this process in carbanion photochemistry,[2] but also because of its involvement in the $S_{RN}1$ and related reactions.[3] The factors controlling the rate of reaction between radical and anion and the distribution of the resulting products have not been well studied. We have shown that the stability of the radical anion can have a decisive effect in determining product distribution. For instance, the $S_{RN}1$ photoarylation of trityl anion leads to predominant para arylation in contrast to the α arylation obtained through a radical–radical pathway.[4] We now report that radical anion stability is not the only factor affecting the rate of the reaction and, in fact, is a relatively minor contributor compared to the pK_a of the conjugate acid of the anion.

Results

Competitive Irradiation of Anions. The subjects of our work were triphenylmethyl anion (**1**), diphenylyldiphenylmethyl anion (**2**), and 1,1,3,3-tetraphenylpropenyl anion (**3**), all of which undergo photomethylation in dimethyl sulfoxide by a mechanism which we now know to be a modified $S_{RN}1$ process,[5] with the key step being the reaction of a methyl radical with the ground-state anion (see Scheme I). We were interested in the rate of reaction of the methyl radical with the anion.

Scheme I

$$\text{Ar}\ddot{\text{C}}\text{Ph}_2^- \xrightarrow[\text{Me}_2\text{SO}]{h\nu} \text{Ar}_3\dot{\text{C}}\text{Ph}_2 + \cdot\text{CH}_3 + \text{CH}_3\text{SO}^- \qquad (1)$$

1, Ar = Ph
2, Ar = C_6H_4Ph
3, Ar = $CH{=}CPh_2$

$$\cdot\text{CH}_3 + \text{Ar}\ddot{\text{C}}\text{Ph}_2^- \rightarrow \text{Ph}_2(\text{Ar})\text{CCH}_3^{-\cdot} \qquad (2)$$

$$\text{Ph}_2(\text{Ar})\text{CCH}_3^{-\cdot} + \text{Ar}\dot{\text{C}}\text{Ph}_2 \rightarrow \text{Ph}_2(\text{Ar})\text{CCH}_3 + \text{Ar}\ddot{\text{C}}\text{Ph}_2^- \qquad (3)$$

4, Ar = Ph
5, Ar = C_6H_4Ph
6, Ar = $CH{=}CPh_2$

However, such rates are difficult to obtain directly and we chose instead to obtain the relative rates from a competition experiment. We were aided by the fact that anions **1** and **2** have distinctively different chromophores, the bright red trityl anion having a λ_{max} in Me_2SO of 496 nm and the purple diphenylyldiphenylmethyl anion a λ_{max} of 600 nm (see Figure 1). Thus it was possible in principle to irradiate each anion independently in the presence of the other. If radical anion stability were the controlling factor in product formation, alkylation of the diphenylyl anion leading to the radical anion with the electron localized in the biphenyl moiety would predominate.

Two identical 50-mL solutions of 0.01 M total equimolar mixtures of anions **1** and **2** were prepared by treatment of the appropriate hydrocarbons with a twofold excess of potassium methylsulfinylmethide ("dimsyl"). At these concentrations, ion association and ion-pairing effects are known to be negligible.[6] One solution was irradiated at 546 nm, the other at 578 nm, using the appropriate solution filters and a Hanovia 450-W medium-pressure mercury lamp. Irradiation for 12 h and analysis of the products by gas chromatography using independently prepared products for standardization proved that the anion alkylated most readily was not the diphenylyl anion but rather the trityl anion (see Table I).

To determine if this result was unique to the two anions used, we investigated the competition between triphenylmethyl anion and the tetraphenylallyl anion **3**. In the latter case radical anion intermediates would place the extra electron in a diphenylvinyl moiety, which should be even more favorable than a diphenylyl moiety. Unfortunately, the similarity between the absorption spectra of the two anions precluded unequivocal irradiation of one species in the presence of the other. Our approach to decoupling the photochemical electron transfer step from the radical anion forming step was to irradiate the pure anion simultaneously with a mixture. Using an optical arrangement similar to the merry-go-round, and a solution filter to pass both 546- and 578-nm wavelengths, we irradiated 5-mL solutions of 0.01 M tetraphenylallyl anion **3** prepared as above and 0.01 M tetraphenylallyl anion in the presence of 0.01 M triphenylmethyl anion. Again, both anions were methylated, and the results are listed in Table II. Significantly, more tetraphenylbutene **6** was produced in the presence of triphenylmethyl anion than in its absence despite the fact that the triphenylmethyl anion was competing for light absorption! We attribute this unexpected result to the fact that allyl anion **3** captures methyl radical more efficiently than it undergoes photochemical electron transfer, although energy transfer from trityl anion may account for part of this phenomenon. In any event, we see that, despite the greater light capture by tetraphenylallyl anion and the greater stability of the product radical anion, the major product is still triphenylethane **4**. Thus some energetic constraint other than radical anion stability must be operative, which we may determine by examining the thermodynamics of the reaction.

Discussion

Thermodynamics of Radical Anion Formation. The thermodynamics for the process radical + anion → radical anion cannot be obtained directly. Instead we must obtain the relative energies for the process by using a thermochemical cycle (see

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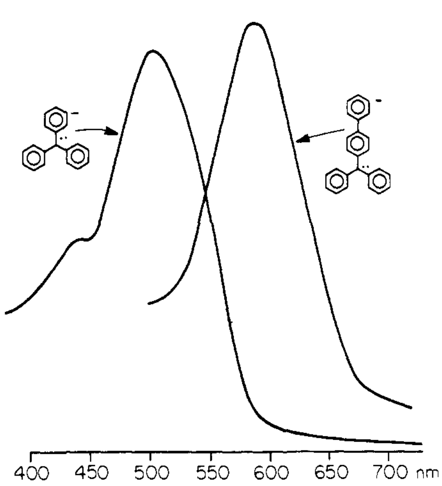
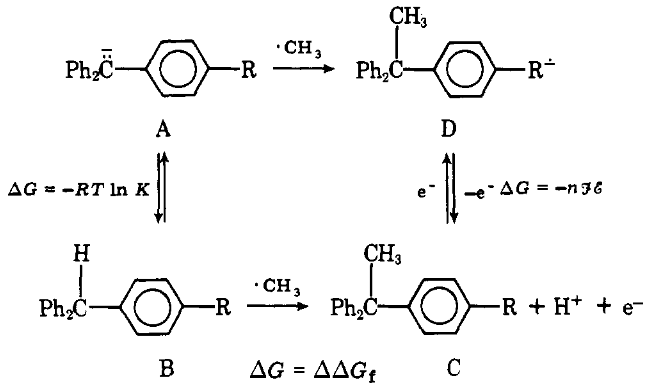


Figure 1. Relative absorbances.

Scheme II



Scheme II). This technique has been used to estimate pK_as of various hydrocarbons,[7] and we employ it here to estimate the energetics of the triphenylmethyl/diphenylyldiphenylmethyl system. We wish to estimate the free energy ΔG for the process A → D, which we cannot obtain directly. The energy for the process A → B is given by $-RT \ln K$, i.e., $-2.3RT\text{p}K_a$, while that for C → D is given by the reduction potential (vs. H^+/H_2)[8] of the neutral C. Finally, the free energy of the process B → C is given by the free energy of the hydrogen ion (0),[8] plus the increment in free energy of formation for the homologation R-H → $R\text{-}CH_3$ (2 kcal)[9] less the free energy of formation of methyl radical (34.6 kcal).[10] Using the values 30.6 and 29.4 for the pK_as of triphenylmethane and diphenylyldiphenylmethane,[6] respectively, and the values 2.89 and 1.99 V as the half-wave reduction potentials of benzene and biphenyl,[11] respectively, we obtained the estimated free energies for the overall process listed in Table III. We see that the overall reaction is exothermic, as we might predict, but that the reaction of the biphenyl system is more exothermic by 19 kcal. How then do we account for the formation of the less stable product? Although the $\Delta G_{C\to D}$ term favors the biphenyl product, the $\Delta G_{A\to B}$ term favors reaction of the more basic anion. That is, the energy gain upon methylation is analogous to the energy gain upon protonation of structurally similar anions. The exoergicity of the reaction implies that the transition state is more accurately represented by the reactants, according to Hammond's postulate. Although a smaller overall contributor to the free energy of the reaction, the pK_a effect plays a dominant role in the activation energy of the reaction.[12]

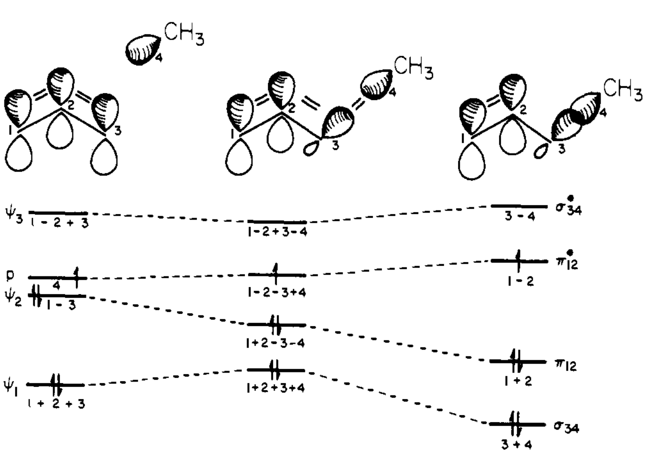


Figure 2. Correlation diagram.

Table I. Results of Competition Experiment between **1** and **2**

	expt 1	expt 2
irradiation wavelength	546[a]	578[a]
starting materials		
mmol trityl anion (**1**)	0.257	0.275
mmol biphenylyl anion (**2**)	0.175	0.196
products		
mmol triphenylethane (**4**)	0.157	0.174
mmol *p*-tolyldiphenylethane[b]	0.046	0.060
mmol 4-diphenylyldiphenylethane (**5**)	0.035	0.034
ratio **1** products/**2** products	85:15	87:13

[a] Serial filter solutions were used. The first cell contained 0.2 M $KCrO_4 \cdot 6H_2O$ in a pH 10 solution. The second cell contained either 0.50 M $NiSO_4$ in water (500 nm) or 0.43 M $CoSO_4 \cdot 6H_2O$ in water (600 nm); absorption spectra of the filter solutions were taken before and after the irradiations to ensure that no degradation in the solutions had occurred. [b] This is the "unidentified product" of ref 1.

Table II. Results of Competition Experiment between **1** and **3**[a]

	expt 1	expt 2
starting materials		
mmol trityl anion (**1**)		0.0593
mmol allyl anion (**3**)	0.0451	0.0417
products		
mmol triphenylmethane		0.0128
mmol tetraphenylpropene	0.0349	0.0220
mmol triphenylethane (**4**)		0.0302
mmol *p*-tolyldiphenylethane		0.0061
mmol tetraphenylbutene (**6**)	0.0025	0.0064
ratio **1** products/**3** products		85:15

[a] A pH 10 buffered solution of 0.2 M $K_2CrO_4 \cdot 6H_2O$ was used to filter out all light below 450 nm.

Table III[a]

anion	$\Delta G_{A\to B}$	$\Delta G_{B\to C}$	$\Delta G_{C\to D}$	$\Delta G_{A\to D}$
triphenylmethyl	−41.7	−32.6	66.7	−7.6
biphenylyldiphenylmethyl	−40.1	−32.6	45.9	−26.8

[a] Values in kcal.

Molecular Orbital Considerations. The analysis of the kinetic effect in controlling reactivity can be illustrated more dramatically by using a correlation diagram for a model system, the interaction of a methyl radical with an allyl anion. Using the technique of "MO following"[13] we construct the orbitals of the half-reacted product analogously to those for butadiene and add the Hückel orbitals for the starting allyl anion and methyl radical as well as the final σ and π orbitals (see Figure 2). The one modification to this one-electron treatment is placement of the methyl orbital at slightly higher energy than the allyl nonbonding MO, reflecting the greater electron affinity of allyl radical.[14] The significant feature of the correlation diagram is that it is the half-occupied methyl orbital which eventually becomes the π^* orbital of the product. Thus any perturbation of the orbital system to lower the energy of the

π^* orbital, i.e., to make the radical anion more stable relative to the neutral, cannot be perceived until the reaction is very close to product. For an early transition state this effect will be minimal. It is instructive to consider the correlation diagram with the odd electron removed, i.e., an empty orbital reacting with an anion. This diagram corresponds to the protonation of an anion, and the maximum on this energy surface corresponds to the kinetic pK_a (or pK_b), which for hydrocarbons closely approximates the true pK_a. Thus for reaction of a radical with resonance-stabilized carbanions, the kinetics of the reaction are controlled not by the half-occupied orbital but by the subjacent orbitals!

Conclusions

The relative role of pK_a and radical anion stability in determining the outcome of radical anion combination reactions has important consequences for understanding reactivities in $S_{RN}1$ and related reactions. In general, where regioselecitivity in $S_{RN}1$ reactions is attributed to radical anion stability, consideration of the pK_a of the conjugate acid would lead to the same prediction. To our knowledge this work is the first in which the two effects act in opposite direction and allow clear distinction between the two. The relative purity of products, absence of dimers, and lack of other products associated with radical–radical reactions provide a further contrast. The high exothermicity of radical–radical reactions generally results in no activation energy and diffusion-controlled reactions. Reactions of radicals with anions, although sufficiently exothermic to be kinetically controlled, are accompanied by activation energies and are more discriminate in reactivity. In the limit, if the anionic reactant is sufficiently nonbasic, other reactions may compete. We believe that this explains the failure of certain stabilized carbanions such as enolates of 1,3-dicarbonyl compounds to undergo the $S_{RN}1$ arylation.[3e]

Experimental Section

Melting points were taken on a hot-stage apparatus and are uncorrected. Nuclear magnetic resonance spectra were obtained on a Varian T-60 spectrometer.

Manipulations. Apparatus and nonvolatile materials were degassed repeatedly by evacuating to less than 0.1 Torr and purging with argon dried and deoxygenated with an Ace-Burlitch inert atmosphere system. Liquids were transferred by reaching through the bore of a 4-mm three-way stopcock with the needle of a degassed syringe or with a double-tipped stainless steel needle. A stream of argon through the side opening of the stopcock protected the liquid from air.

Photochemical Equipment. Irradiations were carried out with a Hanovia 450-W lamp in a Pyrex immersion well equipped with an ellipsoidal reflector which focused the light on a cylindrical 3 × 20 cm reaction vessel. Light filtration was provided by a cylindrical container surrounding the immersion well and containing 0.1 M K_2CrO_4 in a pH 10 buffered medium. This filter solution effectively excluded all light below 450 nm. Additional filtration, if necessary (see below), was provided by an additional cylindrical container surrounding the reaction flask.

Analyses. Gas chromatographic analysis was performed on a Varian 3700 gas chromatograph using a 3-m column of 2% OV-101 on Chromosorb G. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Materials. Dimethyl sulfoxide was purified as described by Bordwell[6] and stored over molecular sieves. Solutions of potassium methylsulfinylmethide ("dimsyl") were prepared by syringing 20 mL of 20–25% potassium hydride in an argon-filled serum-capped 50-mL centrifuge tube, adding 20 mL of dry pentane, and successively shaking, centrifuging, removing, and readding pentane onto the potassium hydride. After the third centrifugation, the pentane and dissolved oil were removed by syringe, the entire apparatus pumped dry, and the weight of potassium hydride remaining measured by difference. A 25-mL portion of dimethyl sulfoxide was added through a Teflon tube under a positive pressure of nitrogen, and, after the frothing had subsided, the remaining hydrogen was removed under vacuum. The concentrated solution was transferred under argon to a Schlenk tube equipped with an automatic buret and diluted to 200 mL with additional dimethyl sulfoxide. The solution was titrated with potassium hydrogen phthalate using phenolphthalein as indicator. A typical solution had a total base concentration of 0.2 M. Solutions prepared in this manner were stored without noticeable decomposition for 2 weeks, provided that light was excluded.

Triphenylmethane was obtained from Aldrich Chemical Co. and was either used as received or recrystallized from methanol. 1,1,3,3-Tetraphenylpropene was prepared by the method of Garbisch[15] and had mp 125–126 °C (lit.[15] mp 125–126 °C). Diphenylyldiphenylmethane was obtained by the method of Bordwell.[6]

1-(4-Tolyl)-1,1-diphenylethane. To 0.674 g (2.61 mmol) of (4-tolyl)diphenylmethane in 10 mL of Me_2SO was added 15 mL (5.52 mmol) of 0.368 M potassium dimsyl. The red solution was allowed to equilibrate for 30 min; then 0.40 mL (6.42 mmol) of methyl iodide was added. Water (30 mL) was added and the solution extracted three times with ether. The extracts were dried and concentrated, leaving a slowly crystallizing oil. The crystals were recrystallized from hexane to yield 0.464 g (1.71 mmol, 65%) of colorless prisms, mp 66–68 °C. The spectral data: NMR ($CDCl_3$) δ 2.15 (s, 3 H, Ar_3CCH_3), 2.29 (s, 3 H, $ArCH_3$), 7.00 (s, 4 H, C_6H_4), 6.89–7.32 (m, 10 H, aromatic). Anal. ($C_{21}H_{20}$) C, H.

1,1,1-Triphenylethane. To 1.04 g (4.28 mmol) of triphenylmethane in 10 mL of Me_2SO was added 13 mL (4.78 mmol) of potassium dimsyl. The red solution was allowed to equilibrate for 30 min; then 0.311 mL (5.0 mmol) of methyl iodide was added dropwise. The red color disappeared after ca. 90% of the methyl iodide was added. A few drops of water were added and the solution was allowed to stand. After 7 days, long needles had formed. These were removed by filtration to yield 0.747 g (2.90 mmol, 68%) of crystals, mp 90–92 °C (lit.[16] mp 90–92.5 °C). Additional less pure product was obtained by adding 10 mL of water to the filtrate and allowing the cloudy mixture to stand for several days more. The spectral data: NMR ($CDCl_3$) δ 2.17 (s, 3 H, CH_3), 7.00–7.38 (m, 15 H, aromatic).

1,1,3,3-Tetraphenyl-1-butene. Evans' procedure[17] was used with slight modification. To 15 mL of freshly distilled benzene were added 2.00 g of 1,1-diphenylethylene (Aldrich Chemical Co.) and 0.25 mL of stannic chloride. The blue-green mixture was stirred for 4 days, decomposed with 10 mL of water, and ether extracted. Recrystallizations of the organic residue in methanol yielded 1.56 g (78%) of 1,1,3,3-tetraphenyl-1-butene as colorless prisms, mp 112–115 °C (lit.[17] mp 111–113 °C). The spectral data: NMR ($CDCl_3$) δ 1.44 (s, 3 H), 6.85 (s, 1 H), 7.25 (br s, 20 H); MS *m/e* (rel intensity) 360 (100), 345 (16), 283 (14), 282 (29); IR ($CHCl_3$) 2980, 1590, 1485, 1440, 1020, 685, 590 cm^{-1}.

Preparative Photolysis of Triphenylmethylpotassium. To 1.601 g (6.50 mmol) of triphenylmethane in 15 mL of dimethyl sulfoxide contained in the reaction vessel was added 35 mL (7.0 mmol) of 0.20 M potassium dimsyl. The degassed solution was irradiated without a solution filter until the red color disappeared (ca. 3 h). The solution was added to 200 mL of water and ether extracted. Silica gel chromatography of the residue after concentration yielded 0.954 g of a white solid. Recrystallization from methanol yielded 0.852 g (3.30 mmol, 50%) of colorless prisms. The melting point (90.0–92.5 °C) and spectral data were identical with those of 1,1,1-triphenylethane.[16] The mother liquor and remaining hydrocarbon fractions from the chromatography column were combined. Preparative high-pressure liquid chromatography and preparative gas chromatography failed to separate the residue, which proved by analytical gas chromatography, analytical high-pressure liquid chromatography, and NMR comparison to be a mixture of 1,1,1-triphenylethane and 1-(4-tolyl)-1,1-diphenylethane.

Preparative Photolysis of 1,1,3,3-Tetraphenyl-1-propen-3-ylpotassium. A solution of 0.875 g (2.52 mmol) of 1,1,3,3-tetraphenylpropene in 35 mL of dimethyl sulfoxide was placed in the photolysis vessel, thoroughly degassed under vacuum, and purged with dry argon. A 15-mL portion (3.0 mmol) of 0.20 M potassium dimsyl was added by syringe, the resulting deep red solution vacuum degassed for several minutes, and argon reintroduced. The solution was irradiated for 12 h, excess base decomposed by adding 10 mL of water, the solvent removed in vacuo, and the residue taken up in an ether–water mixture. Separation of the organic fraction followed by drying and concentrating in vacuo gave a brown residue. Silica gel chromatography (2% ether–hexane) yielded 0.7212 g (2.01 mmol, 80%) of 1,1,3,3-tetraphenyl-1-butene, mp 105–109 °C. Recrystallization from methanol yielded colorless prisms, mp 111.5–113.5 °C (lit.[17] mp 111–113 °C).

The spectral data were identical with those of authentic 1,1,3,3-tetraphenyl-1-butene.

Preparative Photolysis of (4-Diphenylyl)diphenylmethylpotassium. A solution of 1.23 g (3.84 mmol) of diphenylyldiphenylmethane in 30 mL of dimethyl sulfoxide was treated with 20 mL (4.00 mmol) of 0.20 M dimsyl potassium and the solution degassed in the manner previously described. The solution was irradiated for 96 h, i.e., until the purple color had been replaced by a light brown, the reaction quenched with 2 mL of water, and the solvent removed in vacuo. The extracted from ether washing of the residue was washed three times with water, dried, and concentrated. Recrystallization from methanol yielded light yellow crystals (1.02 g, 3.12 g, 82%). Recrystallization from hexane yielded 0.88 g of colorless prisms, mp 92-93 °C. The spectral data: NMR ($CDCl_3$) δ 2.21 (s, 3 H, CH_3), 6.9-7.6 (m, 19 H, aromatic); IR ($CDCl_3$) 3060, 3052, 2990, 1601, 1500, 1491, 1450, 1030, 1012, 762, 733, 698 cm^{-1}. Anal. ($C_{26}H_{22}$) C, H.

Competitive Irradiation Experiments. Solutions of mixtures of the anions were prepared analogously to those for preparative photolysis of individual anions, using a 50% excess of base over the amount required to quantitatively deprotonate the hydrocarbons. For the diphenylyldiphenylmethyl/triphenylmethyl experiments, additional filter solutions were used as described in Table I, and irradiations were carried out in 50-mL vessels for 12 h. For the tetraphenylallyl/triphenylmethyl experiments, the irradiations were carried out in 5-mL irradiation tubes, irradiations were carried out for 2 h, and identical tubes were arranged so as to ensure virtually identical light absorption throughout the irradiation. Analyses of the mixtures were performed by gas chromatography using independently prepared products to calibrate the chromatograph. The amounts of starting materials used and products formed are listed in the appropriate tables.

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A Novel Cycloaromatization Reaction. Regiocontrolled Synthesis of Substituted Methyl Salicylates[1]

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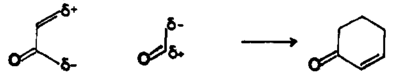
Abstract: A new method of constructing six-membered rings, involving the condensation of two three-carbon units, one with two nucleophilic sites and the other containing two electrophilic sites, is reported. The regiochemistry of the reaction is controlled by the differential reactivities of these sites. 1,3-Bis(trimethylsiloxy)-1-methoxybuta-1,3-diene (**1**) constitutes the three-carbon fragment with two nucleophilic sites. Condensation of **1** with various equivalents of β-dicarbonyl compounds and titanium tetrachloride gave substituted methyl salicylates. The regiochemistry is controlled by the order of reactivity of the electrophilic sites, which is conjugate position of enone > ketone > monothioacetal, acetal.

The two common methods of construction of six-membered rings (Diels–Alder and Robinson annelation) consist of the union of two framents, one with two carbon atoms and the other with four carbons. Regiochemistry in these reactions is essentially controlled by the direction of polarization within each fragment as represented schematically in eq 1 for the Robinson annelation. In this paper we describe a new method of constructing six-membered rings, involving the condensation of two three-carbon units, one with two nucleophilic sites and the other containing two electrophilic sites. Furthermore, the regiochemistry of the reaction is controlled by the differential reactivities of these sites, as in eq 2.



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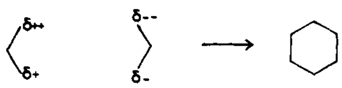

(2)

Recently we reported in a preliminary communication[2] on the use of 1,3-bis(trimethylsiloxy)-1-methoxybuta-1,3-diene (**1**) as the equivalent of methyl acetoacetate dianion. It is evident from the reactions of **1** with a number of electrophiles that the nucleophilic site at C-4 is more reactive than that at C-2.[2] Compound **1** can therefore constitute one of the three-carbon

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