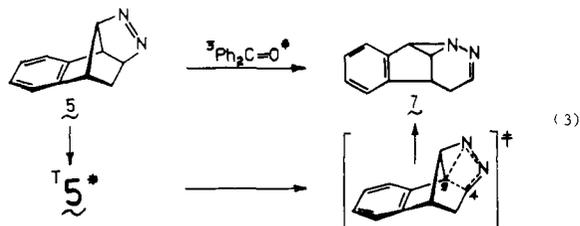


and C<sub>4</sub>-C<sub>5</sub>  $\sigma$  bonds are sufficiently weakened compared with the C<sub>1</sub>-N<sub>2</sub> and N<sub>3</sub>-C<sub>4</sub>  $\sigma$  bonds in this strained azoalkane that the retrocyclic process via  $5^{\ddagger}$  is preferred over N<sub>2</sub> extrusion to afford the expected diradical **4** (eq 1). Of course, instead of the concerted process via  $5^{\ddagger}$ , a stepwise mechanism involving first C<sub>1</sub>-C<sub>6</sub>  $\sigma$  bond rupture to yield a diradical is also likely. Whichever the mechanistic course, the thermal behavior of the azoalkane **6** is unusual; however, a few examples have been reported<sup>9</sup> in which azoalkanes transform into pyrazoles instead of expelling molecular nitrogen on heating.

In contrast to the thermolysis, direct photolysis of the azoalkane **5** in  $\sim 10^{-4}$  M pentane (Spectroquality) at 254 (quartz vessel) and 350 nm (Pyrex vessel) in a Rayonet reactor gave the expected tricycloalkene **2** (99.0  $\pm$  0.3% at 350 nm and 96.0  $\pm$  0.3% at 254 nm) and the bicycloalkadiene **1** (1.0  $\pm$  0.3% at 350 nm and 4.0  $\pm$  0.3% at 254 nm). Control experiments confirmed that under our photolysis conditions **1** is not transformed into **2**.<sup>10</sup> Consequently, the low yield of **1** suggests that the diradical **4**, formed on photoextrusion of N<sub>2</sub> from the singlet excited azoalkane **5**, efficiently cyclizes into **2** rather than rearranging into diradical **3** to give **1** (eq 1). Apparently, the diradical **4** represents an energy minimum on the singlet excited-state energy surface of the azoalkane.

The most surprising result was observed in the benzophenone-sensitized photolysis of azoalkane **5**, which was carried out in a Rayonet reactor, equipped with 300-nm lamps and employing solutions  $\sim 10^{-4}$  M **5** and  $\sim 10^{-3}$  M benzophenone in deaerated C<sub>6</sub>D<sub>6</sub>. Only 300-330-nm light was allowed to irradiate the sample by utilizing an appropriate K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>/K<sub>2</sub>CO<sub>3</sub> aqueous filter.<sup>4</sup> The only product that was detected by <sup>1</sup>H NMR was the novel diazavinylcyclopropane derivative **7**, mp 140 °C dec, C<sub>11</sub>H<sub>10</sub>N<sub>2</sub> elemental composition by combustion analysis, *m/e* 170. The following spectral data<sup>8</sup> confirm the structural assignment: <sup>1</sup>H NMR (CDCl<sub>3</sub>, Me<sub>4</sub>Si)  $\delta$  (ppm) 1.7-1.85 (2 H, H<sub>5</sub>, m), 3.3-3.8 (2 H, H<sub>1,6</sub>, m), 3.9 (1 H, H<sub>9</sub>, d, *J*<sub>19</sub> = 2.9 Hz), 6.7-7.2 (4 H, C<sub>6</sub>H<sub>4</sub>, m), 7.5 (1 H, H<sub>4</sub>, m); <sup>13</sup>C NMR (CDCl<sub>3</sub>, Me<sub>4</sub>Si)  $\delta$  (ppm) 27.24, 33.24, 46.96, 51.47, 123.01, 125.84, 127.30, 127.87, 137.27, 147.02, 156.99; IR (KBr)  $\nu$  (cm<sup>-1</sup>) 3050, 3030, 3025, 2955, 2921, 1600, 1480, 1460, 1442, 1345, 1330, 1310, 1230, 1200, 1160, 1070, 1005, 935, 920. This substance is thermally labile, leading to a complex product mixture, but the pyrazole **6** is not produced.

This novel photorearrangement of the azoalkane **5** into **7** is mechanistically rationalized in eq 3. Again, the triplet-sensi-



tized behavior of azoalkane **5** is unusual; however, a few examples have been reported<sup>11</sup> in which azoalkanes undergo related rearrangements rather than extruding molecular nitrogen on photolysis. As an analogy from hydrocarbon chemistry, we offer the photochemical conversion of norbornene into norcaradiene-2.<sup>12</sup> Similar to the mechanism in the hydrocarbon system, instead of the proposed concerted pathway, a suitable diradical mechanism can be envisaged, involving initial C<sub>4</sub>-C<sub>9</sub>  $\sigma$ -bond rupture in the triplet excited  $T^1S^*$ .

Each energization mode of azoalkane **5** has led to distinct products. Such divergent chemical behavior makes the tricyclic azoalkane **5** a unique case and underscores its novelty. Although these disconnected product channels of azoalkane **5** have severely limited the opportunities for elucidating the mechanistic details of the di- $\pi$ -methane rearrangement of

norbornadiene (**1**), the unprecedented observations reported herein provide new challenges for mechanistic investigation and synthetic utilization. For example, in view of the spin-state-specific behavior of azoalkane **5**, we intend to exploit it for single and triplet titration of chemienergized excited states.<sup>10</sup>

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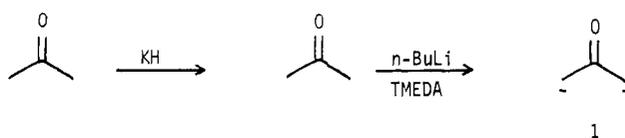
## $\alpha, \alpha'$ Dianions of Aliphatic Ketones and the 1,3,5 Trianion of 2,4-Pentanedione: Strongly Nucleophilic Carbonyl Synthons

Sir:

We report here the twofold ionization of unactivated ketones by treatment with strong bases to give highly nucleophilic  $\alpha, \alpha'$  dianions. Previous reports of  $\alpha, \alpha'$  dianions of unfunctionalized ketones have involved cases in which aromatic rings participated in delocalization of negative charge<sup>1-4</sup> or in which formation of the dianion created an aromatic ring.<sup>5</sup>

Potassioacetone, prepared from the ketone and excess KH (25 °C, 20 min) in ethyl ether,<sup>6</sup> was treated with equivalent amounts of *n*-butyllithium and tetramethylethylenediamine (0 °C, 5 min) to give the dianion salt as a yellow precipitate (Scheme I). Treatment of the dianion **1** with 1 equiv of methyl

### Scheme I



1

Table I

ketone dianion	electrophile	conditions <sup>a</sup>	product	yield, %
acetone	CH <sub>3</sub> I	Et <sub>2</sub> O, -78, 5	2-butanone	79 <sup>b</sup>
acetone	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	THF, -78, 10	4-phenyl-2-butanone	72
acetone (2 equiv)	C <sub>6</sub> H <sub>5</sub> COCH(Na)CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	THF, 0, 50	1-phenyl-1,3,5-hexanetrione	68
acetone (2 equiv)	C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	Et <sub>2</sub> O, -78, 1	2,4-hexanedione	58
3-pentanone	C <sub>6</sub> H <sub>5</sub> CHO	Et <sub>2</sub> O, -78, 2	1-hydroxy-2-methyl-1-phenyl-3-pentanone	92
cyclohexanone	CH <sub>3</sub> CHCH <sub>2</sub> O	Et <sub>2</sub> O, 0, 78	2-(2-hydroxypropyl)cyclohexanone	47
cyclohexanone	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	THF, -78, 10	2-benzylcyclohexanone	67

<sup>a</sup> Solvent, temperature (°C), time (minutes). <sup>b</sup> Isolated as the 2,4-dinitrophenylhydrazone.

iodide (-78 °C, 5 min) gave 2-butanone which was isolated in 79% yield as the 2,4-dinitrophenylhydrazone (see Table I). GLC of the crude alkylation mixture before derivatization showed the product to be uncontaminated by 3-pentanone or 3-methyl-2-butanone which might have arisen by dialkylation reactions. A similar alkylation with benzyl chloride (-78 °C, 10 min) gave 4-phenyl-2-butanone in 72% yield. In contrast to the unusually high reactivity of the dianion of acetone, the monoanion required 12 h at 20 °C to yield 55% benzylation product. Dialkylation is not a significant side reaction in the alkylations of the dianion, even when excess alkylating agent is employed, because the monoanion resulting from the first alkylation reaction is much less reactive than the dianion. We believe the reactive intermediate involved in these alkylations is the 1,3 dianion rather than the 1,1 dianion.<sup>7</sup>

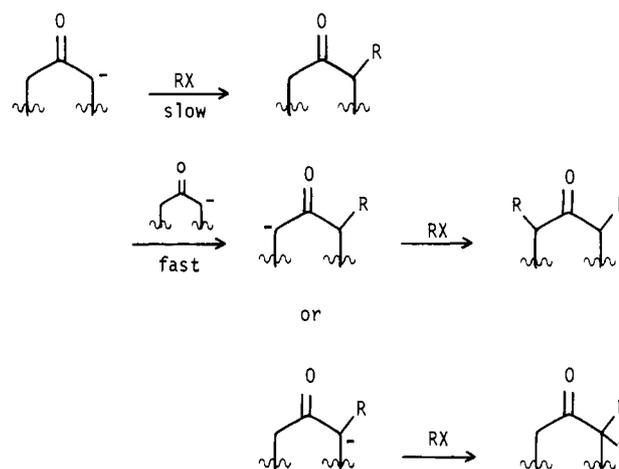
A further demonstration of the strong nucleophilicity of dianion **1** is its acylation by the sodium salt of methyl benzoylacetate to give 1-phenyl-1,3,5-hexanetrione in 68% yield (Table I). The condensation was carried out in tetrahydrofuran at 0 °C; because of the basicity of the dianion, it was necessary to add the acylating agent immediately after formation of the dianion to minimize decomposition of the solvent. The reaction is particularly noteworthy because of the low electrophilicity of the acylating agent. In a previous study<sup>8</sup> of acylations by ionized β-keto esters, no reaction between the monoanion of a ketone and the monoanion of a β-keto ester could be detected, even when substantially more vigorous reaction conditions were employed. The condensation of ethyl propionate with the dianion was complete after 2 min at -78 °C using ether as the solvent giving propionylacetone in 58% yield. By comparison, Hauser and co-workers treated monosodioacetone with ethyl propionate for 2 h in refluxing ether to obtain the same product in 60% yield.<sup>9</sup>

The ability of aliphatic ketones to form dianions appears to be fairly general; cyclohexanone and 3-pentanone have been converted into their dianions (**2** and **3**) by the above procedure. Reactions with the dianions are facile; examples are given in Table I.

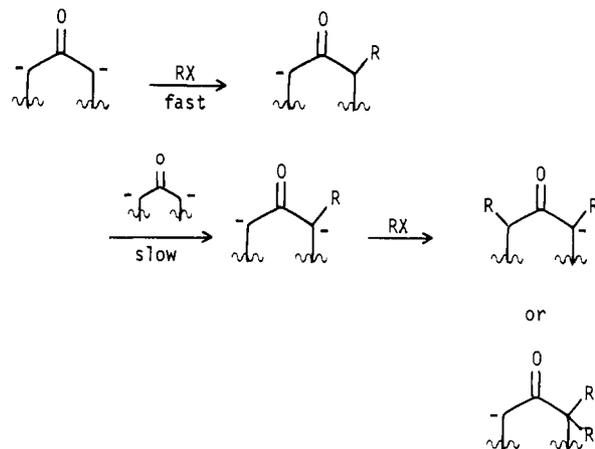


Alkylations of the monoanions of ketones are complicated by formation of di- and trialkylation products in instances where proton transfer between the alkylation product and the enolate anion competes with the alkylation reaction, since the resulting enolate anion can also undergo alkylation (Scheme II).<sup>10</sup> Alkylations of the dianion of ketones (Scheme III) circumvent this problem because the rate of the alkylation reaction is *elevated* by the high charge density of the dianion. At the same time proton transfer is *suppressed* by the negative charge that remains on the alkylation product. The practical value of keto dianions in synthesis may be limited mainly to

Scheme II

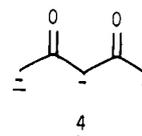


Scheme III



symmetrical ketones; mixtures of products have been obtained from alkylation of 2-butanone and other unsymmetrical ketones.<sup>11</sup>

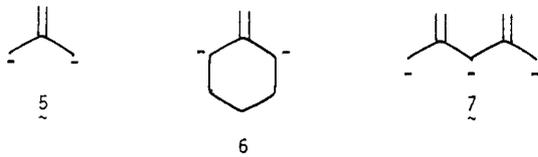
We have employed a similar technique to convert 2,4-pentanedione into its 1,3,5 trianion (**4**). The monoanion of the



diketone, prepared in cyclohexane (NaH, 20 °C, 30 min), was combined with 2 equiv of tetramethylethylenediamine and treated with 2 equiv of *sec*-butyllithium (slow addition, 0 °C). The mixture was stirred for 24 h at 20 °C to obtain the trianion. Treatment with 1 equiv of benzyl chloride for 5 min at 0 °C gave 62% 1-benylation product, 1-phenyl-3,5-hexanedione. Neither 1,3- nor 1,5-dialkylation was observed. The corresponding alkylation of the dianion of 2,4-pentanedione was <5% complete under these conditions. Dialkylation of the

trianion was achieved by treatment with 2 equiv of benzyl chloride for 4 h at 20 °C. The sole dialkylation product (64% yield) was 1,7-diphenyl-3,5-heptanedione arising from 1,5-dialkylation. Dialkylation of the trianion with methyl iodide (2 equiv, 20 °C, 1.5 h) gave 3,5-heptanedione in 59% yield. It can be concluded that the trianion of 2,4-pentanedione is substantially more nucleophilic than the dianion, although the dianion itself is a strong nucleophile.

The new anions described herein bear a formal relationship to the dianions of 2-methylpropene (**5**) and methylenecyclohexane (**6**) and the trianion of 2,4-dimethyl-1,3-pentadiene (**7**) which have been prepared from the hydrocarbons<sup>12-14</sup> by



treatment with strong bases. Y-Delocalized systems, such as these anions, may possess aromatic stabilization.<sup>14,15</sup>

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## On the Prediction of Angles in Tetrahedral Complexes and Pseudotetrahedral Complexes with Stereoactive Lone Pairs

Sirs:

In a recent paper Schmiedekamp et al.<sup>1</sup> showed that it is possible to remove some of the apparent inconsistencies found when the VSEPR model is used to make numerical predictions of the angles in tetrahedral molecules if, rather than considering the interbond angles, one considers the space occupied by bonding and nonbonding (lone pair) electrons. Using ab initio electron density calculations they propose a method for determining the centroid of the lone pair which allows them

to determine the angles between bonds and lone pairs, or between two lone pairs, in addition to the angles between bonds. They then use the triple-angle average  $\langle\theta\rangle$  (average of the three angles formed by a bond or a lone pair) as a measure of the angular space occupied by the bonding or lone-pair electrons. When this is done, the triple-angle averages fall into natural groups according to bond type and geometry; for example, single S-H and S-F bonds have  $\langle\theta\rangle \sim 103^\circ$  and double S-O bonds and S-(lone-pair) orbitals have  $\langle\theta\rangle \sim 114^\circ$ . They conclude that the angular space required by a particular bond depends on the central atom and whether the bond is a double or single bond, with lone pairs occupying the same angular space as a double bond.

Murray-Rust, Dunitz, and Bürgi<sup>2</sup> have also used the triple-angle average to study distortions found in many tetrahedral groupings of atoms in the solid state. By converting the bond lengths into Pauling-like bond numbers or bond valences,<sup>3</sup> they remove the effects of atomic size and bring all the tetrahedral groups to the same scale. They find that in all the cases studied the bond lengths (expressed in terms of bond valences,  $S$ ) are related to the triple angle average  $\langle\theta\rangle$  by

$$S/V = 2.25 \cos^2\langle\theta\rangle \quad (1)$$

where  $V$  is the valence of the central atom.

They conclude that the angles required by various ligands in tetrahedral groups are independent of the nature of the atoms forming the group and depend only on the deviations of bond valences from the average.

In an earlier paper<sup>4</sup> I have shown that, by fitting two limiting geometries, the regular tetrahedron ( $S/V = 1/4$ ,  $\langle\theta\rangle = 109.5^\circ$ ) and the planar triangle where one ligand has been removed to infinity ( $S_1/V = 1/3$ ,  $S_2/V = 0$ ,  $\langle\theta_{11}\rangle = 120^\circ$ ,  $\langle\theta_{12}\rangle = 90^\circ$ ), one can derive a relationship for predicting individual bond angles ( $\theta$ ) using the average bond valence  $\langle S \rangle$  of the two bonds defining the angle. A quadratic expression (eq 2) is the simplest relation that gives correctly the three angles found in the above two limiting geometries:

$$\theta = 109.5 + 180(\langle S \rangle/V - 1/4) - 652(\langle S \rangle/V - 1/4)^2 \quad (2)$$

This equation works well for predicting the angles in phosphates, sulfates,<sup>5</sup> and perchlorates<sup>6</sup> and can be used in reverse as an alternative method of assigning bond valences. It also works with lone-pair  $S(\text{IV})$  complexes ( $\text{SO}_3^{2-}$ ,  $\text{Me}_2\text{SO}$ ) provided that the sulfur is treated as hexavalent and the lone pair is regarded as a double-bonded ligand ( $S = 2.0$ ).<sup>7</sup>

This latter observation supports the conclusion of Schmiedekamp et al.<sup>1</sup> that the angular requirements of a lone pair are similar to those of a double-bonded oxygen and suggest that, at least for the present purposes, lone pairs can be treated as ions like oxygen having a formal charge of  $-2$  but lacking a nucleus and core electrons. Such a view is in agreement with the findings of Galy, Meunier, Andersson, and Åström<sup>8</sup> that in crystals the lone pair occupies a volume comparable to an O or an F atom.

By considering the lone pair as a dibasic ligand, the neutral molecules discussed by Schmiedekamp et al.<sup>1</sup> can all be written in the form  $A(\text{VI})X_2Y_2$  or  $A(\text{V})XY_3$  where  $A$  is the hexa- or pentavalent central atom (S, O, P, or N),  $X$  is oxygen or a lone pair, and  $Y$  is F or H. The triple-angle averages for  $X$  and  $Y$  can be calculated from their valences ( $S_1$ ) using eq 3 which has been derived by averaging eq 2 over the appropriate three angles recognizing that the sum of all four bond valences is equal to  $V$ :

$$\langle\theta\rangle = 109.5 + 60(S_1/V - 1/4) - 217.3[(S/V)^2]_4 - 1/16] \quad (3)$$

Here  $[(S/V)^2]_4$  is the value of  $(S/V)^2$  averaged over all four bonds. Equation 3 gives the following values for  $\langle\theta\rangle$  (the values