Table I[a]

reaction	ΔH°, kcal/mol, at 25 °C		
	NP,Na	BZO,Na	BZO,K
A(THF) + I⁻,M⁺(THF) → A⁻·,M⁺(THF) + $\frac{1}{2}$I₂(THF)	+59.1 ± 1.4	+51.2 ± 1.2	+49.3 ± 0.7
$\frac{1}{2}$I₂(THF) + M(s) → I⁻,M⁺(THF)	−75.3 ± 0.3[b]	−75.3 ± 0.3	−85.2 ± 0.3
A(s) → A(THF)	+2.7 ± 0.1[c]	+2.1 ± 0.1	+2.1 ± 0.1
A(s) + M(s) → A⁻·,M⁺(THF)	−13.5 ± 1.8	−22.01 ± 1.6	−33.8 ± 0.8
A(g) → A(s)	−17.4[d]	−22.7	−22.7
A⁻·(g) → A(g) + e⁻(g)	+3.5	+14.7[e]	+14.7
M(g) → M(s)	−25.9	−25.9	−21.4
M⁺(g) + e⁻(g) → M(g)	−118.5	−118.5	−100.1
A⁻·(g) + M⁺(g) → A⁻·,M⁺(THF)	−171.8 ± 1.9	−174.4 ± 1.7	−163.3 ± 1.4

[a] The enthalpy for reaction 1 can be obtained by summing the reactions 5–8 in this table. [b] These enthalpies were obtained by subtracting the heat of solution of I₂ from that of MI in THF and adding the heat of formation of MI. [c] These values are simple heats of solution and were measured in our laboratory using previously published techniques.[8] [d] The best literature values for these four reactions have been recently compiled.[2] [e] The EA of BZO is taken from ref 9.

from the anion radical and its addition to iodine, it is a direct measurement of the relative solution EA, and the solution electron affinity of A can be very simply obtained as shown in Table I.

Crushing glass bulbs containing the sodium salt of either the naphthalene anion radical [NP⁻·,Na⁺(THF)] or benzophenone ketyl [BZO⁻·,Na⁺(THF)] under 100 mL of dry THF containing 0.6 g of I₂ results in a rise in the temperature of the calorimeter due to reaction 2, where A = NP or BZO. The change in the heat content of the calorimeter varies linearly with the amount of anion radical salt in the bulbs, and the slopes of the lines are −59.1 ± 1.4 and −51.2 ± 1.2 kcal/mol for A = NP and BZO, respectively. This means that the ketone has a solution electron affinity that is about 8 kcal/mol more than that of naphthalene. In the gas phase, on the other hand, BZO has an EA that is 11.2 kcal/mol greater than that for NP. It was expected that the benzophenone would have a larger solution EA than does naphthalene. However, it is very surprising that the difference in the EA's of benzophenone and naphthalene is not augmented but is attenuated by the solvent.

Utilizing Table I the solvation enthalpy of BZO⁻· + Na⁺ was found to be −174.4 ± 1.7 kcal/mol. To be certain that this new technique is operating correctly, it was applied to the NP system yielding a solvation enthalpy for NP⁻· + Na⁺ of −171.8 ± 1.7 kcal/mol, which is in excellent agreement with that previously reported[5] of −172.5 ± 4.0 kcal/mol. The heat of generation of the BZO anion radical from the neutral molecule and the metal in their standard states in THF (solvated neutral molecule and solid metal), reaction 3, is more negative than that for the naphthalene system by about 8 kcal/mol.

The solvation enthalpy of BZO⁻·(g) + K⁺(g) was found to be −163.3 ± 1.4 kcal/mol,[6] which is considerably lower than that for the sodium system. This is consistent with the earlier observation by M. Szwarc[7] that the smaller cations involved in ion association are better solvated than are the larger cations involved in ion association. That is, the solvent has better cation contact wih BZO⁻·,Na⁺ than with BZO⁻·,K⁺. It is, however, surprising that a change in the cation from Na⁺ to K⁺ yields a much more dramatic change in the thermodynamics of solvation of the anion radical salt than does the alteration of the anion from a ketyl to a hydrocarbon anion radical. It should be noted that the more

exothermic generation of the K–BZO ion pair than that of the Na–BZO ion pair, reaction 3, is due to the smaller ionization

$$A(THF) + M(s) \rightarrow A^{-\cdot},M^+(THF) \qquad (3)$$

M = Na; A = benzophenone; ΔH° = −24 kcal/mol

M = K; A = benzophenone; ΔH° = −35 kcal/mol

M = Na; A = naphthalene; ΔH° = −16 kcal/mol

potential of K. Thus, BZO⁻·,K⁺(THF) is lower in energy relative to the metal and BZO in their standard states in THF than is BZO⁻·,Na⁺(THF), despite the poorer solvation of the former system.

We have described the only calorimetric technique for the direct measurement of relative solution electron affinities of neutral molecules, and this technique will be applicable to all persistent anion radicals.

Preparation, Structure, and Coordination Chemistry of Mo[S-2,4,6-C₆H₂(CHMe₂)₃]₄

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The coordination chemistry of monomeric MoX₄ complexes (X = a monodentate anion) is relevant to the reduction of molecular nitrogen by nitrogenase, since it is generally agreed that at least one end of dinitrogen binds to molybdenum and that the molybdenum is in a relatively high oxidation state, perhaps Mo(IV).[1] There are only two well-characterized examples of MX₄ species, Mo(SCMe₃)₄[2] and Mo(NMe₂)₄.[3,4] The former is the more

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(6) A plot of the change in the heat content of the calorimeter vs. the millimoles of BZO⁻·,K⁺(THF) is linear and has a slope of −49.4 ± 0.7 kcal/mol. All three such plots described in this paper represent at least seven separate experiments (points), and the errors reported in the enthalpy of reaction 2 represent the standard deviations of the slopes of these lines. All three plots have intercepts of 0,0. Any water or other protic impurity in the THF containing the I₂ in the calorimeter would yield Birch reduction products. NMR analysis of the calorimeter contents did not yield detectable amounts of dihydro materials.

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(4) Several Mo(OR)₄ species are known. Mo(OCHCMe₂)₄ is a dimer.[5a] Others, such as Mo(OCMe₃)₄,[5b] are poorly characterized. However, related adducts such as Mo(O-adamantyl)₄(py)[5c] and Mo(OSiMe₃)₄(Me₂NH)[5b] are well characterized.

(5) (a) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Reichert, W. W. *Inorg. Chem.* 1978, *17*, 2944. (b) Chisholm, M. H.; Reichert, W. W.; Thornton, P. *J. Am. Chem. Soc.* 1978, *100*, 2774. (c) Bochmann, M.; Wilkinson, G.; Young, G. B.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* 1980, 901.

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Communications to the Editor
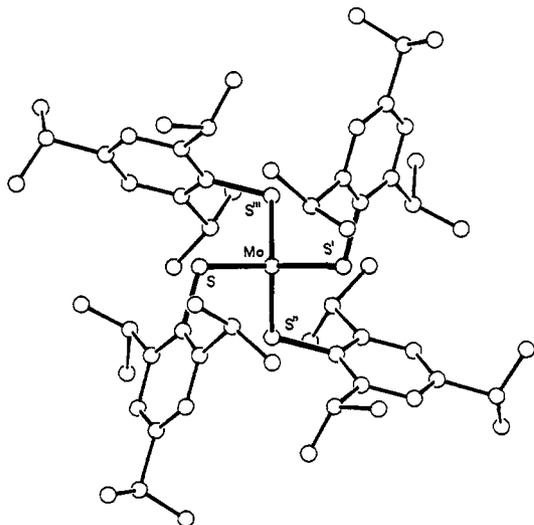
Figure 1. Diagram of $Mo[S-2,4,6-C_6H_2(CHMe_2)_3]_4$ showing the atom labeling.[13] $S-Mo-S' = S''-Mo-S''' = 114.1 (1)°$; all other $S-Mo-S = 107.2 (1)°$; $Mo-S = 2.262 (1)$ Å; $Mo-S-C = 107.6 (2)°$. Thermal ellipsoids are not shown so that details of the crowded coordination sphere are clearer.

biologically relevant, but unfortunately it is readily reduced by a simple substrate such as an isonitrile,[6] thus raising a question concerning the stability of molybdenum(IV) tetrathiolate complexes.[7] Here we show that a diamagnetic $Mo(SR)_4$ species containing the bulky thiolate, 2,4,6-triisopropylbenzenethiolate (TIPT), can be prepared, and that it forms monoadducts with several small molecules.

Addition of $MoCl_4$ to 2 equiv of $Me_3Si(TIPT)$ in dichloromethane produces a deep red solution from which an oxygen- and moisture-sensitive, pentane-soluble paramagnetic black complex can be isolated routinely in ~40% yield.[10] Elemental analysis[11] and its FD mass spectrum (m/e M^+ 1073 amu) show that the compound is not $Mo(TIPT)_4$, but $Mo(TIPT)_4Cl$ (**1**). The EPR spectrum of **1** shows a peak at $g = 1.98$ with a half-height width of 32 G. A cyclic voltammogram of $Mo(TIPT)_4Cl$ in dichloromethane shows a reversible reduction of $E_{1/2} = -0.40$ V and an irreversible oxidation at $E_p = +0.85$ V (vs. Ag/Ag^+ in CH_3CN). Preliminary observations show that **1** also can be prepared from $MoCl_5$ and 4 equiv of $Me_3Si(TIPT)$ in toluene, but the yield (20%) so far is less than that obtained from $MoCl_4$.

$Mo(TIPT)_4Cl$ is reduced rapidly by 1 equiv of sodium amalgam in pentane to give a brown solution. On a scale of ≳0.5 g of $Mo(TIPT)_4Cl$ exceedingly soluble brown, crystalline, diamagnetic

$Mo(TIPT)_4$ (**2**)[12a] can be isolated from a minimal amount of pentane. The yield must be high on the basis of ^1H NMR spectra and the formation of adducts (see below) in high yield. $Mo(TIPT)_4$ is exceedingly sensitive to moisture and oxygen. It cannot be recrystallized in the presence of coordinating solvents and decomposes slowly in dichloromethane. Its ^1H NMR spectrum in C_6D_6 [12b] is unexceptional, although only under the best conditions is no free thiol observed, presumably the result of hydrolysis.

The X-ray diffraction study[13] of $Mo(TIPT)_4$ showed it to be a slightly flattened tetrahedron (Figure 1) with two $S-Mo-S$ angles of 114.1 (1)° and four of 107.2 (1)°. The $Mo-S$ distance is 2.262 (1) Å and the $Mo-S-C$ angle is 107.6 (2)°. The phenyl rings are turned slightly so that four isopropyl groups lie in the two "holes" created by the two larger $S-Mo-S$ angles.

Addition of 3-hexyne to a pentane solution of $Mo(TIPT)_4$ (generated from $Mo(TIPT)_4Cl$) yields diamagnetic $Mo(TIPT)_4(3-hexyne)$ in high yield.[14] $Mo(TIPT)_4(3-hexyne)$ also can be prepared by treating $Mo(3-hexyne)Cl_4(ether)$ with 4 equiv of LiTIPT in ether.[15] We have also prepared $Mo(TIPT)_4(2-butyne)$[16] and $Mo(TIPT)_4(C_2H_2)$ [17a] by adding the acetylene to $Mo(TIPT)_4$. The latter must be prepared at −78 °C in order to avoid extensive polymerization of acetylene.[17b] ^1H and ^{13}C NMR spectra of all $Mo(TIPT)_4(alkyne)$ complexes are temperature dependent. At 235 K the ends of the acetylene are inequivalent and the signal pattern for the TIPT ligands is extremely complex. At ~300 K or above the acetylene is apparently "rotating" so that the ends are equivalent on the NMR time scale, a process that is qualitatively noticeably faster for C_2H_2 than for 2-butyne. Interestingly, 3-hexyne can replace 2-butyne (eq 1) after 24 h in

$$Mo(TIPT)_4(2\text{-butyne}) + \text{excess } 3\text{-hexyne} \xrightarrow[25\ °C]{\text{pentane}}$$
$$Mo(TIPT)_4(3\text{-hexyne}) + 2\text{-butyne} \quad (1)$$
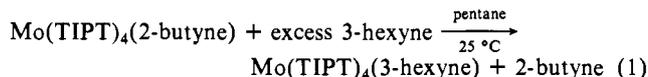
pentane. Although this exchange *may* consist of loss of the 2-butyne from $Mo(TIPT)_4(2-butyne)$ to give $Mo(TIPT)_4$, loss of the acetylene cannot be rapid on the NMR scale, as characteristic TIPT resonances are observed in samples at 300 K that contain a mixture of $Mo(TIPT)_4$ and $Mo(TIPT)_4(RC\equiv CR)$ (R = H, Me, Et).

Addition of 1 equiv of acetonitrile or *tert*-butylisonitrile to $Mo(TIPT)_4$ prepared in situ in pentane yields paramagnetic complexes in high yield with analyses consistent with the formulae $Mo(TIPT)_4(L)$.[18] Addition of 1 equiv of CO to $Mo(TIPT)_4$ in

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(7) Some other evidence for the instability of $Mo(SR)_4$ complexes is the reaction between $MoCl_4(thf)_2$ and 4 equiv of NaTIPT (TIPT = (S)-2,4,6-triisopropylbenzenethiolate) in THF followed by introduction of CO to give $[Mo(TIPT)_3(CO)_2]^-$.[8] However, note that Koch and Millar[9] have prepared $[Fe(SR)_4]^-$ complexes (e.g., SR = (S)-2,3,5,6-C₆HMe₄), species that were thought to be too unstable toward reduction to dianions to be stable.

(8) (a) Dilworth, J. R.; Hutchinson, J.; Zubieta, J. A. *J. Chem. Soc., Chem. Commun.* **1983**, 1034. (b) Dilworth, J. R. In "Studies in Inorganic Chemistry"; Müller, A., Krebs, B., Eds.; Elsevier: Amsterdam, 1984; Vol. 5, p 141.

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(10) $MoCl_4$ (0.80 g, 3.37 mmol) was added to a solution of $Me_3Si(TIPT)$ (2.10 g, 6.80 mmol) in dichloromethane (20 mL). The solution immediately turned red. After stirring the reaction for 12 h at room temperature a brown precipitate was filtered off and the solvent was removed from the filtrate in vacuo. The residue was dissolved in minimal pentane and the solution was cooled to −40 °C to yield black "crystalline" product. Concentrating and cooling the mother liquor afforded a second crop of crystals, yield 650–780 mg, 36–43% based on $Me_3Si(TIPT)$. Several "crystals" of **1** selected for X-ray study apparently were amorphous, as no diffraction was observed.

(11) Calcd for $MoC_{60}H_{92}ClS_4$: C, 67.18; H, 8.63; Cl, 3.30; S, 11.93; Mo, 8.96. Found: C, 67.64; H, 8.82; Cl, 3.28; S, 11.96; Mo, 8.30 (by difference).

(12) (a) Calcd for $MoC_{60}H_{92}S_4$: C, 69.46; H, 8.94. Found: C, 69.96; H, 9.19; N < 0.04. (b) ^1H NMR (250 MHz, C_6D_6) δ 7.30 (s, 2), 3.45 (br sept, 2), 2.78 (sept, 1, $J = 6.9$ Hz), 1.28 (d, 12, $J = 6.6$ Hz), 1.24 (d, 6, $J = 6.9$ Hz).

(13) Data were collected at −50 °C on an Enraf-Nonius CAD4F-11 diffractometer using Mo Kα radiation. A total of 1510 reflections were collected in the range 3° ≤ 2θ ≤ 50° with 1355 having $F_o > 4\sigma(F_o)$ being used in the structure refinement which was by full-matrix least-squares techniques (150 variables) using SHELX76 to a final $R_1 = 0.040$ and $R_2 = 0.048$. All non-hydrogen atoms were refined anisotropically and an empirical adsorption correction was applied. Thermal ellipsoids are not shown in Figure 1 so that details of the crowded coordination sphere are clearer. $Mo(TIPT)_4$ possesses crystallographically imposed 4̄ symmetry where the axis passes through the midpoints between atoms S,S' and S'',S'''. The S' atom is at −x,−y,z; S'' is at y,−x,−z; S''' is at −y,x,−z.

(14) Calcd for $MoC_{66}H_{102}S_4$: C, 70.80; H, 9.18; S, 11.45. Found: C, 69.99; H, 9.40; S, 11.02. IR, cm^{-1}, 1751 (w, $\nu_{C\equiv C}$).

(15) (a) Mo(2-butyne)Cl_4 and $Mo(PhC\equiv CPh)Cl_4$ were first reported by Greco et al.[15b] Many other Mo(IV) and W(IV) acetylene complexes have been reported relatively recently by Dehnicke.[15c] $MoCl_4$ is slowly added to diethyl ether to yield orange, thermally sensitive crystals of what we believe to be $MoCl_4(ether)_2$. Two equivalents of 3-hexyne are then added and the mixture is stirred overnight to yield $Mo(3-hexyne)Cl_4(ether)$ as a yellow-orange precipitate (~80% yield). The coordinated ether is slowly removed under high vacuum. (b) Greco, A.; Pirinoli, F.; Dall'asta, G. *J. Organomet. Chem.* **1973**, *60*, 115. (c) Hey, F.; Weller, F.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1984**, *514*, 18, 25, and references therein.

(16) Calcd for $MoC_{64}H_{98}S_4$: C, 70.41; H, 9.05; S, 11.75. Found: C, 71.09; H, 9.56; S, 10.80. IR, cm^{-1}, 1742 (w, $\nu_{C\equiv C}$).

(17) (a) Calcd for $MoC_{62}H_{94}S_4$: C, 70.00; H, 8.93. Found: C, 69.90; H, 8.99. IR, cm^{-1}, 1758 (w, $\nu_{C\equiv C}$). (b) Acetone-free acetylene was passed into a pentane solution of $Mo(TIPT)_4$ maintained at −78 °C. After 5 min the excess was flushed out with nitrogen and the polyacetylene was removed by filtration at 25 °C. Crystalline $Mo(TIPT)_4(C_2H_2)$ was isolated in ~40% yield by cooling the filtrate to −40 °C for several hours.

pentane produces a purple-red solution that shows an IR band at 2008 cm^{-1}. Removing the pentane in vacuo yields a brown powder whose ^{1}H NMR spectrum shows it to be pure Mo(TIPT)$_4$ in quantitative yield (vs. an internal standard). Unfortunately, we have not yet been able to isolate what we believe to be Mo-(TIPT)$_4$(CO) due to its extreme solubility and sensitivity to moisture and air.

The addition of diphenyldiazomethane to Mo(TIPT)$_4$ yields a diamagnetic complex with the formula Mo(TIPT)$_4$(Ph$_2$CN$_2$).[19] Its ^{13}C NMR spectrum (C$_6$D$_6$) shows a resonance at 170.4 ppm. We suggest that the diazoalkane has added end-on to the metal to give what could be described as (TIPT)$_4$Mo=N–N=CPh$_2$. Related complexes have been prepared recently by similar methods.[20]

The behavior of Mo(TIPT)$_4$ reported here contrasts strongly with that of Mo(SCMe$_3$)$_4$. We do not yet know if Mo(TIPT)$_4$ is reduced slowly in the presence of a large excess of a ligand such as CO. Also note that we have no evidence for or against formation of Mo(TIPT)$_4$(N$_2$) in solution, but since formation of Mo(TIPT)$_4$(CO) is reversible we would not *expect* a significant amount of Mo(TIPT)$_4$(N$_2$) to be present at ambient pressure.

Registry No. 1, 97731-89-0; **2,** 97731-90-3; Mo(TIPT)$_4$(EtC≡CEt), 97731-91-4; Mo(TIPT)$_4$(MeC≡CMe), 97731-92-5; Mo(EtC≡CEt)-Cl$_4$(thf), 97731-93-6; Mo(TIPT)$_4$(CH$_3$CN), 97731-94-7; Mo(TIPT)$_4$-(*t*-BuCN), 97731-95-8; Mo(TIPT)$_4$CO, 97731-96-9.

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(18) Calcd for MoC$_{62}$H$_{95}$NS$_4$[Mo(TIPT)$_4$(CH$_3$CN)]: C, 69.02; H, 8.89; N, 1.30. Found: C, 68.56; H, 9.11; N, 1.07. Calcd for Mo(TIPT)$_4$(*tert*-BuCN): C, 69.65; H, 9.10; N, 1.25; Mo, 8.56; S, 11.44. Found: C, 69.58; H, 9.05; N, 1.39; Mo, 8.42; S, 11.56 (by difference).

(19) Calcd for MoC$_{73}$H$_{102}$N$_2$S$_4$: C, 71.17; H, 8.36; N, 2.27. Found: C, 71.15; H, 8.84; N, 2.14.

(20) (a) Hillhouse, G. L.; Haymore, B. L. *J. Am. Chem. Soc.* **1982,** *104,* 1537. (b) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Ratermann, A. L. *Inorg. Chem.* **1984,** *23,* 2303.

Direct Observation of a 1,3-Biradical

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Because of the predictions of Salem and Rowland[1] that the quantum-mechanical properties affecting intersystem crossing in 1,*n*-biradicals depend on the distance between the biradical termini and thus on *n*, there has been recent interest in experimental determination of the lifetimes of triplet biradicals as a function of $n^{2,3}$ among other measures of distance.[4,5] Although 1,4-bi-

radicals, particularly of the Norrish II type, are well studied,[4-8] only a few direct observations of biradicals with $n \neq 4$ have been reported. The acyl-alkyl series from Norrish I photolyses has so far yielded 1,5,[9] 1,6,[2] and 1,8[10] examples. Wagner and Scaiano have detected certain 1,5-biradicals generated by hydrogen abstraction.[11,12] An elegant generation of a 1,5-biradical from Norrish I photocleavage of 2,2,6,6-tetraphenylcyclohexanone and subsequent decarbonylation has been described.[3] While physical characterization is available for certain special cases,[13] and trapping of others by dioxygen has given important experimental information about the effect of orbital orientation on lifetime,[14] no direct information is available which allows comparison of 1,3-biradicals with the higher members of the series of unconstrained triplet 1,*n*-biradicals of general interest in room-temperature solution photochemistry.

We now report that photolysis of *trans*-1,2-bis(4-acetylphenyl)cyclopropane (**1**) allows the first direct observation of unconstrained 1,3-biradicals in fluid solution. Intermolecular sensitization of 1,2-diphenylcyclopropane geometric isomerization by aryl ketones is believed to proceed through an analogous intermediate.[15] Intramolecular sensitization by the acetophenone chromophore avoids problems of intermolecular sensitization such as sensitizer absorption in the region of expected transient absorption and slow rates of excitation transfer.[16]

Irradiation of *trans*-1,2-bis(4-acetylphenyl)cyclopropane (**1**)[17] rapidly ($\phi = 0.45 \pm 0.02$, benzene, 313 nm) affords the corresponding cis isomer **2** and slowly ($\phi \lesssim 0.005$) affords the E/Z isomers of 1,3-bis(4-acetylphenyl)propene (**3E/3Z**). The reaction was not affected by 0.5 M isoprene, 0.5 M ethyl vinyl ether, 0.5 M ethyl acrylate, or exposure to the atmosphere. The **1/2** photostationary ratio of 45/55 was stable under preparative conditions for up to 30–40 h, over which time period a 60–70% yield of **3E/3Z** built up. Excellent material balance was observed throughout, though small amounts of polymeric material were formed. The reaction sequence below is strongly indicated.

$$\mathbf{1}\ (\mathbf{2}) \xrightarrow{\ h\nu\ } \rightarrow\ ^3\mathbf{I}\ (^3\mathbf{2}) \rightarrow$$

$$p\text{-CH}_3\text{C}(\!=\!\text{O})\text{C}_6\text{H}_4\overset{\uparrow}{\text{C}}\text{HCH}_2\overset{\uparrow}{\text{C}}\text{HC}_6\text{H}_4\text{C}(\!=\!\text{O})\text{CH}_3 \quad (1)$$
$$^3\text{BR}$$

$$^3\text{BR} \rightarrow\ ^1\text{BR} \rightarrow \mathbf{1} + \mathbf{2} \quad\quad (2)$$

$$^1\text{BR} \xrightarrow[1,2\text{-H}\sim]{\text{slow}} \mathbf{3E} + \mathbf{3Z} \quad\quad (3)$$

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