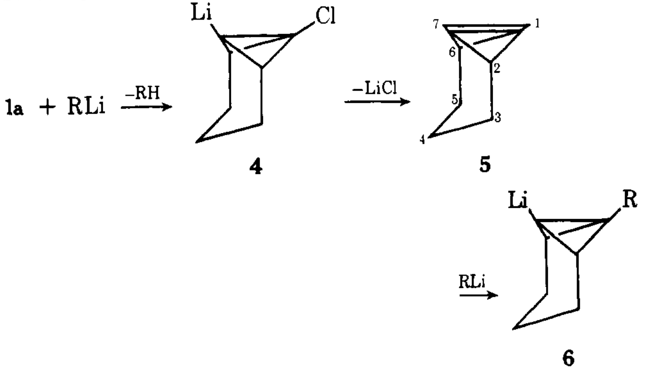
isolated unchanged. This shows that direct coupling as well as chlorine–lithium exchange are insignificant processes and that the absence of a proton at C-7 prevents the substitution reaction to take place. (b) 1-Bromotricyclo[4.1.0.0^{2,7}]heptane (**1b**)[7] and *n*-butyllithium in ether led (via **1d**) to the parent hydrocarbon **1c** as the main product indicating lithium–bromine exchange in this case to be fast and the possible consecutive coupling between **1d** and *n*-butyl bromide, however, under the applied conditions (15 min at 20 °C), to be an inefficient process.[8] As alkyl chlorides need longer reaction times to couple successfully with organolithium compounds than the corresponding alkyl bromides,[9] this result further excludes that the derivatives **2** were produced via route II. (c) When **1a** and *n*-butyllithium were quickly mixed and the mixture was quenched with D_2O after reaction times of 30, 90, and 150 s at 20 °C, 1-*n*-butyltricyclo[4.1.0.0^{2,7}]heptane-7-*d* was obtained, in each case with a deuterium content >96%.[10] The bridgehead metalation of the parent hydrocarbon **1c** with *n*-butyllithium in ether has been shown to occur rather slowly.[11]; Therefore, the introduction of the lithium to the bicyclo[1.1.0]butane unit must have taken place not at the stage of the final product **2a** with the excess of the organometallic base but at an earlier step of the reaction sequence.

Mechanisms I and II are inconsistent with these results; however, all our observations are in accord with III which is outlined in Scheme I.

Scheme I



The chlorine atom in **1a** should enhance the acidity of the proton at C-7 and accelerate the metalation reaction[12,13] to **4**. The consecutive *β* elimination of lithium chloride from **4** leads to tricyclo[4.1.0.0^{2,7}]hept-1(7)-ene (**5**) as a reaction intermediate. This highly strained hydrocarbon adds, as expected, the organolithium reagent with the formation of **6**.[14]

The three-carbon bridge in **5** connecting C-2 and C-6 causes the bicyclo[1.1.0]but-1(3)-ene unit to take a bent structure. It is interesting to note that this might not introduce additional strain into the molecule: calculations predict nonplanarity for the parent olefin.[1]

The proposed scheme for the substitution reaction implies that the carbon atoms 1 and 7 become chemically equivalent on their way from **1a** to **6**.[15] Experiments to test this consequence are in progress. Also, attempts are underway to trap the proposed intermediate **5** with further suitable reagents.

Acknowledgments: This work was supported by Deutsche Forschungsgemeinschaft and by Fonds der Chemischen Industrie.

References and Notes

(1) W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.*, **97**, 6941 (1975).

(2) From the corresponding 1-lithiotricyclo[4.1.0.0^{2,7}]heptane and *p*-toluenesulfonyl chloride. Details will be reported elsewhere.

(3) W. R. Moore, H. R. Ward, and R. F. Merritt, *J. Am. Chem. Soc.*, **83**, 2019 (1961).

(4) Ether solutions of **1a** were added to 3 equiv of the halide-free solution of the organolithium compound in ether. The isolated yields (not optimized) were 30% for **2b**, 30% for **2c** (reaction at −40 °C), 62% for **2d**.

(5) L. A. Paquette and G. Zon, *J. Am. Chem. Soc.*, **96**, 203 (1974).

(6) K. Fujita, T. Nakamura, K. Matsui, and T. Shono, *Tetrahedron Lett.*, 2441 (1975).

(7) From **1d** and *p*-toluenesulfonyl bromide. Details will be reported elsewhere.

(8) This corresponds to an observation of Paquette who found that **1d** and isopropyl bromide did not give a tricyclo[4.1.0.0^{2,7}]heptane derivative.[5]

(9) K. Ziegler and H. Colonius, *Justus Liebigs Ann. Chem.*, **479**, 135 (1930).

(10) These results were obtained from the mass spectra of the final products. Also, the spectra indicated that after a reaction time of 150 s **1a** was totally consumed.

(11) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **85**, 2022 (1963). The authors found that *n*-butyllithium and **1c** at 25 °C in ether and in concentrations of 1 mol/L needed 3 h to reach the half reaction point for the formation of **1d**.

(12) A related effect has been observed in the ortho metalation of the halobenzenes: R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes", Academic Press, New York and London, 1967, p 9 ff.

(13) This is further indicated by the fact that **1a** and an excess of **1d** led to bis(1-tricyclo[4.1.0.0^{2,7}]heptyl) as the major product. Details will be reported elsewhere.

(14) Organolithium compounds are known to add to cyclopropene: J. G. Welch and R. M. Magid, *J. Am. Chem. Soc.*, **89**, 5300 (1967).

(15) This is only true if the conformational change of the three-carbon bridge in **5** is fast compared with the addition of the organolithium reagent to the double bond.

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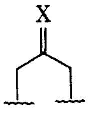
Synthesis of *β*,*γ*-Unsaturated Esters. Direct Generation of Ester Dienolates from *β*-Keto Ester Tosylhydrazone Trianions

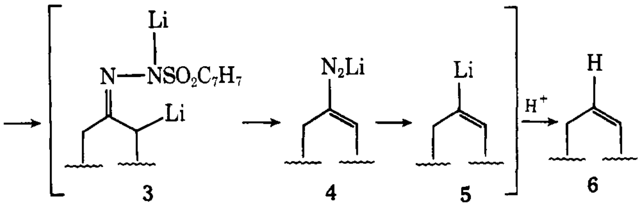
Sir:

An excellent and frequently used procedure for the ketone → olefin (**1** → **6**) transformation is the Shapiro reaction.[1] The ketone **1** is converted to its tosylhydrazone derivative (**2**) which, in turn, is allowed to react with ≥2 equiv of strong base (CH_3Li, $LiNR_2$) to yield ultimately olefin **6** via the successive intermediacy of tosylhydrazone dianion (**3**), vinyldiazinyl anion (**4**), and vinyllithium (**5**).[2]



1, X = O

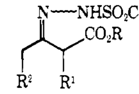
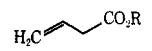
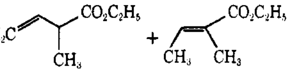
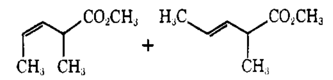
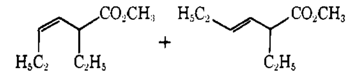
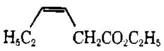
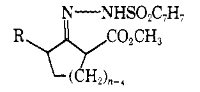
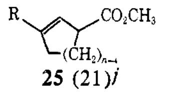
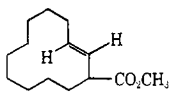
2, X = $NNHSO_2C_7H_7$



In connection with one of our programs, we are evaluating the synthetic potential of deprotonation reactions of more highly functionalized tosylhydrazones.[3] We are pleased to report that reaction[4] of a series of *β*-keto ester tosylhydrazones **7–18** with 3.1 equiv of lithium diisopropylamide[5] (LDA) in tetrahydrofuran at −78 °C, followed by warming to room temperature (4–24 h), quenching with ammonium chloride, and distillation, provides an exceptionally convenient synthesis of *β*,*γ*-unsaturated esters **19–30** (Table I).

The penultimate intermediate in this unsaturated ester synthesis is presumed to be a dienolate, which undergoes kinetic protonation *α* to the ester moiety; thus, the simple expedient of quenching the reaction mixture with various electro-

Table I

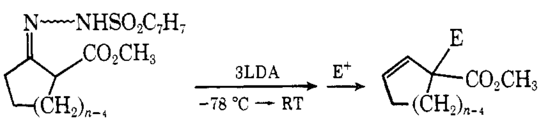
Tosylhydrazone, mp, °C[a–c]	β,γ-Unsaturated ester (% yield)[d,e]
 7 ($R = CH_3$; $R^1 = R^2 = H$), 126–129 8 ($R = t\text{-}Bu$; $R^1 = R^2 = H$), 115–118	 19 ($R = CH_3$) (40)[f] 20 ($R = t\text{-}Bu$) (65)
9 ($R = C_2H_5$; $R^1 = CH_3$, $R^2 = H$), 103–104	 21a (34)[f,g] + 21b (17)[f,g]
10 ($R = R^1 = R^2 = CH_3$), 91–93	 22a (27)[f] + 22b (14)[f]
11 ($R = CH_3$; $R^1 = R^2 = C_2H_5$), 103–104	 23b (10) + 23b (20)
12 ($R = C_2H_5$; $R^1 = H$; $R^2 = C_2H_5$), oil	 24 (56, 95% cis)[h,i]
 13 ($R = CH_3$; $n = 5$), 120–124 14 ($R = H$; $n = 5$), 144–147 15 ($R = H$; $n = 6$), 129–132 16 ($R = H$; $n = 7$), 149–153 17 ($R = H$; $n = 8$), 144–147	 25 (21)[j] 26 (68) 27 (79) 28 (73) 29 (<5)
18 ($R = H$; $n = 12$), 155–161	 30 (51, >95% trans)[k]

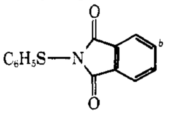
[a] Prepared from the corresponding β-keto ester and p-toluenesulfonylhydrazine in ether (**7**, **8**, **10**, **11**, **12**, **18**), methanol (**15**, **16**), or 95% ethanol (**9**, **13**, **14**, **17**) in an average yield of 80%. [b] These materials exhibit combustion analysis (C, H, N, S), IR, ^{1}H NMR, and ^{13}C NMR spectral data in accord with the assigned structures. [c] The crystalline tosylhydrazones are produced as a mixture of syn and anti isomers (containing as well, in some cases, substantial amounts of the ene–hydrazine[6] form as assayed by ^{13}C NMR[7]) and are used as such in all subsequent reactions. [d] Yields are nonoptimized and refer to distilled material of >95% purity (10–25-mmol reactions). [e] These esters exhibit IR, NMR, and exact mass spectral data in accord with the assigned structures. [f] Losses incurred because of product volatility. [g] The same 1.4:1.0 ratio of **21a**/**21b** was obtained by NH_4Cl quenching of the enolate prepared via reaction of **21b** with LDA in THF at −78 °C. [h] The cis stereochemistry of **24** was established by direct comparison (IR, ^{1}H NMR, ^{13}C NMR) of authentic *cis*- and *trans*-ethyl 3-hexenoate.[8] [i] ^{13}C NMR analysis indicated that <5% of the trans isomer was present, as judged by comparison with an authentic mixture. [j] The factors responsible for the low yield in this case appear to be more complex than the recurrant findings that trisubstituted olefins are difficult to synthesize using the standard Shapiro reaction (CH_3Li as base),[9] since the tosylhydrazone of isobutyrophenone can be converted to 1-phenyl-2-methyl-2-propene in 80% yield using LDA as base. [k] The trans stereochemistry of **30** is assigned on the basis of IR (10.3 μ), the proton-decoupled, Eu(FOD)$_3$-shifted 90-MHz ^{1}H NMR spectrum, and the ^{13}C NMR spectrum.

philic reagents allows direct access to α-functionalized β,γ-unsaturated esters **31**–**33**[10,11] (see Table II).

Several additional observations which are pertinent to this reaction follow. (1) Treatment of tosylhydrazone **14** with 1.9 equiv of LDA in THF produces a stable, homogeneous, deep yellow solution of dianion **34**. VPC examination of this solution after standing at room temperature for 24 h reveals no evidence of the presence of unsaturated esters **26** or **35**. Subsequent treatment of this solution with excess methyl iodide produces only dimethylated tosylhydrazone **36**[10] (>90%) with no evidence of the presence of ester **31a** (<1%).[12] These results implicate a more fundamental role for the third equivalent of LDA than simply serving as a base for ionization of conjugated ester **35**.[13] (2) Treatment of tosylhydrazone dianion **34** with an additional 1.2 equiv of LDA (−78 to −10 °C, 1 h) produces a reddish black solution which is identical in appearance with the solution which results from reaction of **14** with 3.1 equiv of LDA under similar conditions. Although at −10 °C this solution appears relatively stable, further warming to above 0 °C results in the slow evolution of nitrogen, along with the simultaneous appearance of ester **26** as assayed by VPC. As

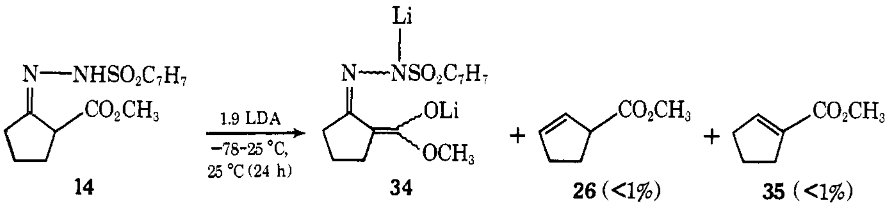
Table II

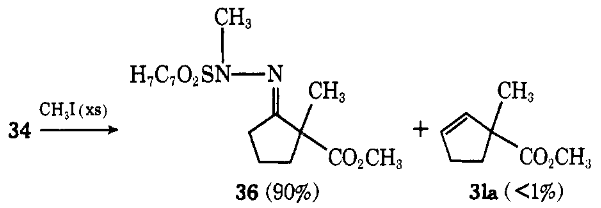


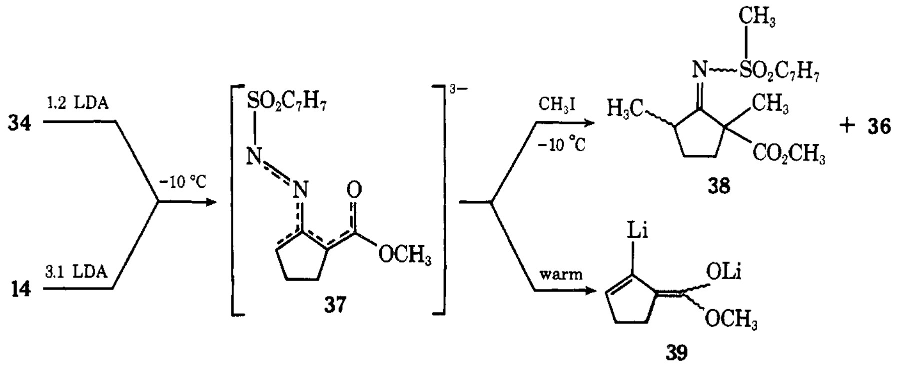
Tosyl-hydrazone	Electrophile	Ester	% yield[a]
14 ($n = 5$)	CH_3I	31a ($E = CH_3$; $n = 5$)	64
14 ($n = 5$)	$C_6H_5CH_2Br$	31b ($E = CH_2C_6H_5$; $n = 5$)	49
14 ($n = 5$)	[b]	31c ($E = SC_6H_5$; $n = 5$)	53
15 ($n = 6$)	CH_3I	32 ($E = CH_3$; $n = 6$)	79
16 ($n = 7$)	CH_3I	33 ($E = CH_3$; $n = 7$)	80

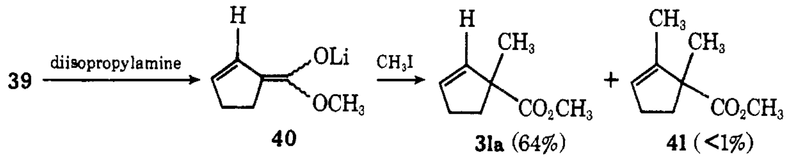
[a] Yield refers to isolated material of >95% purity. [b] T. Kumamota, S. Kobayashi, and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, **45**, 866 (1972).

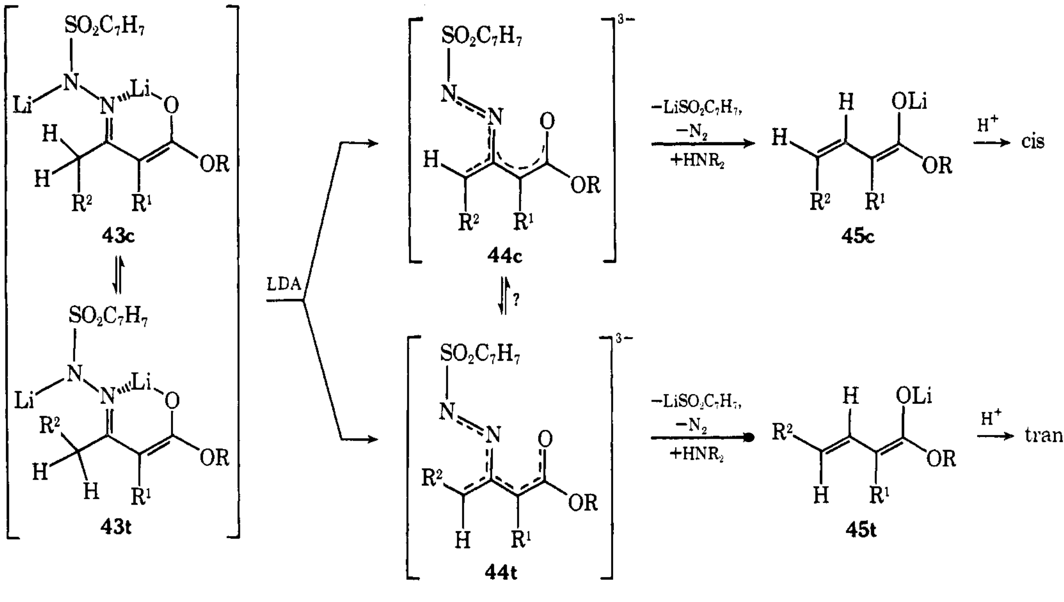
previously indicated, quenching the reaction mixture with methyl iodide, after the nitrogen evolution has ceased, produces











α-methylated ester **31a**; however, careful VPC examination of this solution fails to reveal the presence of dimethylated ester **41**, which was prepared by an independent route for comparison purposes.[14] (3) Addition of excess methyl iodide to the −10→0 °C reaction mixture produces trimethylated hydrazone **38**[15] (~10–15%) as well as dimethyl species **36** (50–55%) and deconjugated ester **31a** (18%).

We feel these facts are most consistent with the presence of *trianion* **37** as a discrete intermediate in the −10→0 °C solution. The rate of formation of trianion **37** and its subsequent decomposition to dilithiodienolate **39**[16] are apparently competitive under these conditions. The absence of dimethylated ester **41** in the methyl iodide quenching experiment suggests that dilithio intermediate **39** is protonated in situ by the diisopropylamine present in the reaction mixture.[17]

This trianion reaction appears to allow considerable stereochemical control over olefin geometry in the formation of ester dienolates from "acyclic" substrates. It is striking to note (cases **10**, **11**, **12**, and **18**, Table I) that the resultant olefin geometry varies from *stereoselectively* cis (**12** → **24**) to completely trans (**18** → **30**). These results seem to be best rationalized on the basis of kinetic deprotonation of the least sterically destabilized dianion rotomer (**43c** ⇄ **43t**) to produce trianion **44c** or **44t** which, in turn, decomposes to dienolate **45c** or **45t,** respectively. Geometrical equilibration at the trianion stage (**44c** ⇄ **44t**) is an additional rationale which makes parallel stereochemical predictions for this trianion reaction.[18]

The product stereochemistry seems to be primarily determined by minimization of steric interactions in intermediates **43** or **44.** In the case where $R^1 = H$ (**12**), the R^2 group apparently prefers to be orientated away from lithiosulfonamide group resulting in formation of cis olefin **24.** When R^1 is an alkyl group (**10, 11**), the situation appears more balanced and a cis-trans mixture of olefins is formed (**21a,b, 22a,b**). Where R^1R^2 are part of a large ring (**18**), the cis orientation (**43c** or **44c**) is further destabilized by additional interactions between the ring methylenes and the alkoxy group of the ester. This cumulative effect presumably overcompensates for the R^2-sulfonamide interaction which, in turn, results in the formation of trans olefin (**30**). This latter effect is consistent with the observed shift toward trans olefin in the acyclic case where an additional methylene group was added to the R^1 and R^2 moieties (c.f. **10** vs. **11**).[19]

Acknowledgment. This investigation was supported by Grant No. CA-19689-01, awarded by the National Cancer Institute, DHEW.

References and Notes

(1) For a recent review of this subject, see R. H. Shapiro, *Org. React.*, **23,** 405 (1976).

(2) Synthetic procedures based upon use of the vinyllithium intermediates produced by this reaction are also known: (a) R. H. Shapiro, M. F. Lipton, K. J. Kolonko, R. L. Buswell, and L. A. Capuano, *Tetrahedron Lett.*, 1811 (1975); (b) J. E. Stemke and F. T. Bond, *ibid.*, 1815 (1975); (c) P. C. Traas, H. Boelens, and H. J. Takken, *ibid.*, 2287 (1976); (d) R. T. Taylor, C. R. Degenhardt, W. P. Melega, and L. A. Paquette, *ibid.*, 159 (1977).

(3) Several examples of olefin synthesis using functionalized tosylhydrazones have been reported using Bamford–Stevens-type conditions (RONa/ROH),[3a–d,13] but to our knowledge this work represents the first extension of the Shapiro reaction to a more highly functionalized substrate: (a) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952); (b) B. Loev, M. F. Kormendy, and K. M. Snader, *J. Org. Chem.*, **31,** 3531 (1966); (c) Y. Gaoni and E. Wenkert, *ibid.*, **31,** 3809 (1966); (d) R. R. Whittekind, C. Weissman, S. Farber, and R. I. Meltzer, *J. Heterocycl. Chem.*, **4,** 143 (1967).

(4) General procedure for preparation of β,γ-unsaturated esters follows. To the tosylhydrazone (20 mmol) in 100 mL of THF at −78 °C was added 3.1 equiv of LDA, prepared from diisopropylamine and *n*-butyllithium in THF at −20 °C. The deep yellow solution became red, then black, when allowed to warm to room temperature. At ~0 °C gas evolution was noted in most cases. The dark mixture was stirred at room temperature for 24 h or until starting material was absent by TLC (SiO_2, 30% THF/hexane). The reaction mixture was poured into 200 mL of cold saturated NH_4Cl solution and the layers were separated. The aqueous phase was extracted with ether (2 × 100 mL) and the combined organic portions were washed with H_2O (200 mL) and saturated NaCl (100 mL) and then dried ($MgSO_4$). Solvent was removed by careful rotary evaporation or, in the case of the more volatile compounds, distillation (1 atm) through a Vigreux column. Kugelrohr distillation gave the reported yields of purified β,γ-unsaturated esters.

(5) The use of lithium dialkylamide bases in place of the more highly nucleophilic alkylithium reagents has previously been shown to be advantageous in the Shapiro reaction: (a) G. E. Gream, L. R. Smith, and J. Meinwald, *J. Org. Chem.*, **39,** 3461 (1974); (b) E. Vedejs and R. A. Shepherd, *ibid.*, **41,** 742 (1976); (c) P. L. Fuchs, *ibid.*, **41,** 2937 (1976); (d) S. D. Young and W. T. Borden, *Tetrahedron Lett.*, 4019 (1976).

(6) (a) H. Ahlbrecht and H. Henk, *Chem. Ber.*, **109,** 1516 (1976); (b) T. A. Favorskaya, S. I. Yakimovich and V. A. Khrustalev, *Russ. J. Org. Chem.*, **8,** 64 (1971); (c) T. A. Favorskaya, V. V. Fedorova, S. I. Yakimovich, and A. M. Kutnevich, *ibid.*, **6,** 1184 (1970).

(7) We have recently found ^{13}C NMR to be useful in determining the syn/anti configuration of tosylhydrazones: C. A. Bunnell and P. L. Fuchs, *J. Org. Chem.*, in press.

(8) *cis*- and *trans*-3-hexenoic acids were prepared according to the procedure of M. F. Ansell, J. C. Emmett, and R. V. Coombs, *J. Chem. Soc., C,* 217 (1968). Esterification was accomplished by the method of J. E. Shaw, D. C. Kunerth, and J. J. Sherry, *Tetrahedron Lett.*, 689 (1973). We wish to thank D. A. Konen of the U.S.D.A. Eastern Research Center for an authentic sample of *trans*-3-hexenoic acid.

(9) (a) Reference 1, pp 419, 423; (b) Y. Bessiere-Chretien and J.-P. Bras, *C. R. Hebd. Seances Acad. Sci., Ser. C.*, **268,** 2221 (1969); (c) K. Mori, M. Matsui, *Tetrahedron*, **26,** 2801 (1970).

(10) These materials have IR, ^1H NMR, ^{13}C NMR, and exact mass spectral data in accord with their assigned structures.

(11) Lithium dienolates of α,β-unsaturated esters are known to undergo alkylation predominantly at the α position: (a) M. W. Rathke and D. Sullivan, *Tetrahedron Lett.*, 4249 (1972); (b) J. L. Herrmann, G. R. Kieczykowski, and R. H. Schlessinger, *ibid.*, 2433 (1973).

(12) Treatment of dianion **34** with 1 equiv of methyl iodide yields the C-alkylated tosylhydrazone. Treatment of the tosylhydrazone **14** with 1 equiv of sodium hydride, followed by methyl iodide, yields the *N*-methyl tosylhydrazone (as its ene–hydrazine form as judged by ^{13}C NMR[7]).

(13) Monotosylhydrazones of cyclic 1,3-diketones can be converted into α,β-unsaturated ketones by a mechanism not involving a vinyl carbanion intermediate: G. A. Hiegel and D. Burk, *J. Org. Chem.*, **38,** 3637 (1973).

(14) Prepared by the method of Meyer: W. L. Meyer, A. P. Lobo, and E. T. Marquis, *J. Org. Chem.*, **30,** 181 (1965).

(15) Structure assigned on the basis of ^1H NMR, ^{13}C NMR, and exact mass spectral data.

(16) We are actively engaged in pursuing experimental modifications designed to allow sequential bis functionalization of these dilithio species.

(17) Trapping off the vinyl anion intermediate, **5,** in the Shapiro reaction is not achieved unless TMEDA is used as the solvent.[2]

(18) The rotation barriers for simple allyl and pentadienyl anions vary considerably.[18a–g] The lack of an appropriate model for trianion **44** precludes differentiation of the two possible mechanisms at this stage. Experiments designed to elucidate this point are currently underway. (a) G. M. Whitesides, J. E. Nordlander, and J. D. Roberts, *J. Am. Chem. Soc.*, **84,** 2010 (1962); (b) R. B. Bates, D. W. Gosselink, and J. A. Kaczynski, *Tetrahedron Lett.*, 205 (1967); (c) V. R. Sandel, S. V. McKinley, and H. H. Freedman, *J. Am. Chem. Soc.*, **90,** 495 (1968); (d) D. A. Hutchison, K. R. Beck, R. A. Benkeser, and J. B. Grutzner, *ibid.*, **95,** 7075 (1973); (e) W. T. Ford and M. Newcomb, *ibid.*, **96,** 309 (1974); (f) J. R. Bashby and G. J. Ferber, *Tetrahedron Lett.*, 3701 (1974); (g) D. H. Hunter, R. E. Klinck, R. P. Steiner, and J. B. Stothers, *Can. J. Chem.*, **54,** 1464 (1976).

(19) A similar steric minimization mechanism is consistent with Shapiro's stereochemical results in the *dianion* reaction: R. H. Shapiro, *Tetrahedron Lett.*, 345 (1968).

(20) Postdoctoral Research Associate.

(21) Alfred P. Sloan Fellow 1977–1979.

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Nickel Phosphine Complexes. Crystal and Molecular Structure of a New Nickel(I) Complex: $[Ni(P(CH_3)_3)_4]B(C_6H_5)_4$

Sir:

The interest in Ni(II) phosphine complexes has increased considerably in recent years because of their values as promoters in organic syntheses such as cross-coupling reactions,[1,2] carbonylation,[3] cyclotrimerization of ethylene,[4] . . . . In these reactions, the formation, the stereochemistry, and the oxidation–reduction equilibria of alkylphosphine–nickel complexes are of great importance since they are central to the understanding of the catalytic cycle. On the basis of the 16 and 18 electron rule, it has been assumed[5] that these reactions imply diamagnetic Ni(II) d^8 or Ni(0) d^{10} complexes as active intermediates. Paramagnetic d^9 species (17 electron complexes) have not usually been considered.

Recently, Klein et al.[6] have reported the synthesis of new pentacoordinate $[Ni(CH_3)(P(CH_3)_3)_4]^+X^-$ complexes. Since very few pentacoordinate $[NiXL_4]^+$ compounds have been reported, we planned to determine the x-ray structure of the $[Ni(CH_3)(P(CH_3)_3)_4]BPh_4$ complex. Orange red crystals were obtained by crystallization from a solution of the five-coordinate complex in tetrahydrofuran. It turns out, surprisingly after the crystal structure analysis, that a dissociative reduction of the $[Ni(CH_3)(P(CH_3)_3)_4]BPh_4$ species occurs and that the isolated complex is the unexpected nickel(I) $[Ni(P(CH_3)_3)_4]BPh_4$ compound.[7] We report here the crystal and molecular structure of this Ni(I) complex.

It crystallizes in the monoclinic space group $P2_1/c$ with four units per cell ($\rho_m = 1.145$ (5) g/cm^3) of dimensions $a = 16.153$ (3) Å, $b = 12.540$ (2) Å, $c = 20.880$ (3) Å, $\beta = 111.54$ (2)°. Intensity data were collected from a single crystal sealed in a Lindemann glass capillary mounted on an automatic diffractometer (Enraf-Nonius, CAD-4) using Mo Kα radiation. The structure was solved from Patterson and Fourier synthesis and