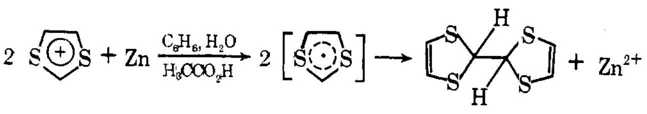
probable route for formation of the desired compound is shown in Scheme I.

Scheme I



1

The first reported procedure for the synthesis of $(C_3H_3S_2)_2$ from 1,3-dithiole-2-thione is that of Challenger et al.[1] However, no overall yield was given. The use of zinc for reductive couplings of six-membered heterocyclic cations has been reported previously[2-4] to give rise to dimers coupled in the γ,γ' positions. More recently, however, Siedle and Johannesen[5] reported the synthesis of 2,2′-bi(1,3-dithiolyl), in moderate yield, via the exotic reducing agent sodium bis(diglyme)hexacarbonyl vanadate. The advantages of our method are (1) it involves the use of an inexpensive, common reducing agent; and (2) the yield is much higher.

Experimental Section[6]

In a 250-mL Morton flask fitted with a magnetic stirrer were placed 50 mL of benzene, 50 mL of distilled water, 50 mL of glacial acetic acid, 1.725 g (6.96×10^{-3} mol) of 1,3-dithiolium hexafluorophosphate,[7] and 0.920 g (1.41×10^{-2} g-atom) of zinc dust. After the reaction mixture was stirred vigorously for ca. 12 h, the layers were separated, and the aqueous layer was extracted once with 50 mL of benzene. The organic layers were combined, washed with 150 mL of dilute potassium chloride (three times, 50 mL each), dried (potassium carbonate), filtered, and concentrated to dryness on the rotary evaporator. The semicrystalline residue was crystallized from cold acetone to give 0.660 g (92%) of 2,2′-bi(dithiolyl) as white needles (mp 150.9–151.6 °C; lit.[5] mp 150–151 °C). The IR and ^1H NMR spectra of this compound were in substantial agreement with those reported by Siedle and Johannesen.

Registry No.—**1,** 23625-38-9; 1,3-ditholium hexaflurophosphate, 55298-73-2; zinc, 7440-66-6.

References and Notes

(1) F. Challenger, E. A. Mason, E. C. Holdsworth, and R. Emmott, *J. Chem. Soc.*, 292 (1953).
(2) Z. Yoshida, S. Yoneda, T. Sugimoto, and O. Kikukawa, *Tetrahedron Lett.*, 3999 (1971).
(3) S. Hünig, B. J. Garner, G. Ruider, and W. Schenk, *Justus Liebigs Ann. Chem.*, **685**, 1036 (1973).
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(5) A. R. Siedle and R. B. Johannesen, *J. Org. Chem.*, **40**, 2002 (1975).
(6) Melting points were taken on a Mettler thermal microscope apparatus and are corrected. The benzene and glacial acetic acid were electronic grade and used as received. The zinc dust was Eastman practical grade.
(7) Prepared by the method of L. R. Melby, H. D. Hartzler, and W. A. Sheppard, *J. Org. Chem.*, **39**, 2456 (1974). However, *m*-chloroperoxybenzoic acid was used as the oxidizing agent.

Oxygen Transfer Reaction in Acetonylation of 2-Methylcyclohexane-1,3-dione with 2-Nitropropene

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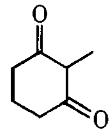
In the previous paper, we (T.Y., M.K., and A.Y.) reported that the KF-catalyzed reaction of 2-methylcyclohexane-1,3-dione (**1**) and 2-nitropropene in hot xylene resulted in the formation of 2-methyl-2-acetonylcyclohexane-1,3-dione (**3a**) in good yield.[3] Obviously, the Michael addition of **1** and 2-nitropropene occurred first to yield nitrodione **2a**, which was then converted into **3a** under the prolonged reaction conditions, as demonstrated by the fact that **2a** was isolated from the reaction mixture at the initial stage and then converted into **3a** under similar conditions. 2-Nitrooctane and 2-methyl-2-(β-nitroethyl)cyclohexane-1,3-dione[3] (**2b**), however, were unchanged on similar treatment. The fact that 2-nitrooctane, a typical secondary nitroalkane, is inert under the above reaction conditions indicates that the nitro group in **2a** would be activated by the keto group on the cyclohexane ring to be converted into a keto group. Unsuccessful conversion of **2b** into the corresponding keto aldehyde **3b** demonstrates that a nitro ketone intermediate is required to have a secondary nitro group.[4]



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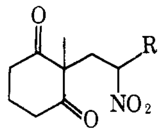
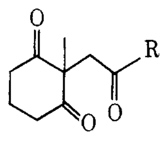
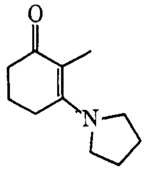


2a, R = Me
b, R = H



3a, R = Me
b, R = H



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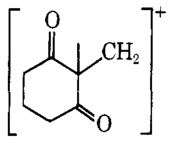


9

$[CH_3C\equiv O]^+$

10

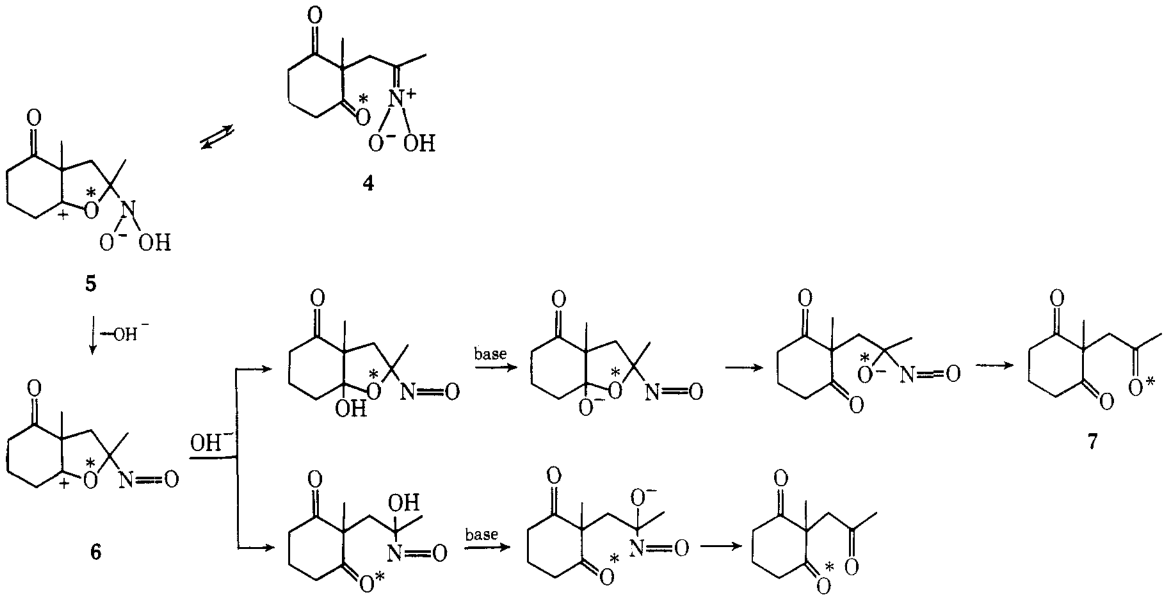
Initially we assumed an equilibration between an aci form (**4**) of **2a** and structure **5** which would probably be responsible to such activation of the nitro group by the keto group (Scheme I). If this is the case, the attack by a nucleophile such as hydroxide anion, a probable nucleophilic species in this case, could occur in two ways, i.e., in **6**, on the carbon adjacent to the nitrogen atom and on the carbonium carbon on the cyclohexane ring. Our provisional transformation into the final product after this stage is shown in Scheme I. Provided that the transformation is limited to the pathway in which the carbonium carbon in **6** is attacked by hydroxide anion, an oxygen transfer from the keto group in **4** to the side chain in the product may occur as shown by asterisked O in the scheme, while no one can anticipate such oxygen transfer in the alternative pathway.

To test on the basis of the above presumption whether or not the ketonic oxygen atoms on the cyclohexane ring could indeed migrate, we decided to use 2-methylcyclohexane-1,3-dione labeled with ^{18}O as the starting material in the acetonylation and to examine the resultant product by mass spectrometric analysis.

Acid hydrolysis of 2-methyl-3-(1-pyrrolidinyl)cyclohex-2-en-1-one (**8**)[5] in water enriched with $H_2{}^{18}O$ gave the requisite 2-methylcyclohexane-1,3-dione with one of its ketonic oxygen atoms labeled with the isotopic oxygen. No double labeling of **1** took place during the hydrolytic treatment since no molecular ion peak corresponding to $C_7H_{10}{}^{18}O_2$ was detectable in the mass spectrum of the labeled **1**.

The molecular ion peak enhancement at *m/e* 128 relative to that at *m/e* 126 showed a 28.9% incorporation of ^{18}O into **1**.[6] The labeled dione **1** was made to react with 2-nitropropene under standard conditions (Experimental Section) affording the labeled trione **3a** with little loss in ^{18}O content (26.9%). No doubly labeled species was detectable in the mass spectrum of the labeled **3a**.

Scheme I



We selected the fragment ions **9** and **10** in the mass spectra for examination to estimate the ^{18}O content in **3a**. Quantitative comparison of the mass spectra of the unlabeled and labeled triones **3a** showed that isotopic contents of fragment ions at *m/e* 141 (labeled **9**) and 45 (labeled **10**) are 18.2 and 7.9%, respectively.[7] These results indicate that significant migration of the oxygen atoms on the cyclohexane ring to the acetonyl side chain had occurred.

Neglecting an isotopic effect, two oxygen atoms on the ring of the labeled **1** are equally probable to migrate. Calculating on this assumption, migration ratios of the oxygen atoms based on the labeled ions **9** (*m/e* 141) and **10** (*m/e* 45) amount of 64.6 and 58.7%, respectively.[8]

The migration ratio calculated on the basis of the ion **9** is somewhat higher than that estimated from **10**, and this difference is attributable to a contamination due to $C_3H_7^+$ ion in the fragment ion **10**. High-resolution mass spectrometry of the unlabeled and labeled triones **3a** demonstrated that the ion **9** involves no contamination, while the ion **10** is fairly contaminated as anticipated. This result indicates that the migration ratio calculated from the isotopic content of the latter ion is less reliable.

Possible oxygen scrambling between the *aci*-nitro and keto groups in **4** through an equilibration process may be ruled out since neither significant loss of the isotopic content nor doubly labeled species was observed in the labeled **3a**. On similar account, scrambling between the ketonic oxygen on the cyclohexane ring and the acetyl oxygen in the labeled **3a** during the reaction may also be neglected.

Although it is, as a matter of course, difficult to give a discussion on the detailed mechanism with only the above results, the significant oxygen transfer observed allows us to propose the pathway from **4** to **7** via **6** as a probable mechanism for this oxygen transfer reaction.

The necessity of secondary nitro group in the nitrocarbonyl conversion would be explained in terms of a difference in acidity of nitroalkanes depending on their substitution; since primary nitroalkanes are fairly less acidic than secondary ones,[9] in a nitro-aci equilibration of the Michael adduct of **1** and nitroethylene, the low acidity of the former would favor the nitro form **2b** rather than its aci form which accelerates the adduct to undergo further transformation to **3b**.

Experimental Section

Melting points were uncorrected. IR spectra were taken on a Hitachi EPI-S 32 spectrophotometer. NMR spectra were obtained on a JEOL Model C-60HL spectrometer (60 MHz) using Me_4Si (δ 0) as an internal standard and $CDCl_3$ as the solvent. Mass spectra were obtained on a JEOL JMS-D 100 gas chromatograph–mass spectrometer, and for quantitative measurements a JMS-PD1 multi-ion detector was utilized together. Operating conditions of the mass spectrometer are as follows: (mass spectrometer) ionizing voltage, 22 eV; ionizing current, 300 μA; chamber temperature, 200 °C; accelerating voltage, 3 kV; (gas chromatograph) column, 2% OV-17 (2 mm × 3 m); column temperature, 180 °C; helium pressure, 2.5 kg/cm^2; injection temperature, 280 °C. A JEOL JMS-01SG-2 high-resolution mass spectrometer was used for accurate mass measurements.

Reaction of 2-Methylcyclohexane-1,3-dione (1) and 2-Nitropropene. Formation of the Nitrodione 2a and the Trione 3a. A suspension of the dione **1** (63 mg, 0.5 mmol) and KF (38 mg, 0.65 mmol) in dry xylene (0.7 mL) was stirred at room temperature for 40 min under nitrogen. A solution of 2-nitropropene[10] (87 mg, 1.0 mmol) in the same solvent (0.5 mL) was added and the mixture was stirred at 120 °C for 13 h. The reaction mixture was filtered and the filtrate was concentrated in vacuo giving a brown oil, which showed two main spots in TLC. The product was separated by silica gel thick layer chromatography using methylene chloride as the eluent, and the trione **3a** (65 mg) and the crystalline nitrodione **2a** (21 mg) were obtained from polar and less polar fractions, respectively. The trione **3a** slowly solidified to give low-melting crystals (mp 54–57 °C): IR (supercooled liquid) 1723 (shoulder), 1700, and 1692 cm^{-1}; NMR δ 1.22 (s, 3 H), 1.9–2.5 (m, 2 H), 2.10 (s, 3 H), 2.75 (br t, 4 H), and 3.30 (s, 2 H).

Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 66.15; H, 7.89.

Recrystallization of **2a** from ether–petroleum ether gave crystals melting at 62–63 °C: IR ($CHCl_3$) 1725, 1693, and 1552 cm^{-1}; NMR δ 1.30 (s, 3 H), 1.50 (d, 3 H, J = 6.5 Hz), 1.8–3.0 (m, 8 H), and 4.65 (m, 1 H).

Anal. Calcd for $C_{10}H_{15}O_4N$: C, 56.32; H, 7.09; N, 6.57. Found: C, 56.02; H, 7.15; N, 6.54.

Longer reaction times resulted in increased yields of **3a** at the expense of **2a** (vide post).

Conversion of the Nitrodione 2a into the Trione 3a. A mixture of the nitrodione **2a** (95 mg, 0.45 mmol), KF (34 mg, 0.59 mmol), and dry xylene (1.5 mL) was stirred at 100 °C for 26 h under nitrogen. The reaction mixture was worked up as usual to leave a yellow oil, which was homogeneous in TLC. The oil was purified by silica gel thick layer chromatography using methylene chloride as the eluent and afforded the trione **3a** (60 mg), which was identified by IR and NMR.

Attempted Conversion of 2-Nitrooctane into 2-Octanone. A mixture of 2-nitrooctane[11] (159 mg, 1 mmol), KF (70 mg, 1.2 mmol), and dry xylene (1 mL) was stirred at 100 °C for 24 h under nitrogen. Workup gave an oil showing no carbonyl absorptions in IR. Purification of the oil by silica gel thick layer chromatography gave the unchanged nitroalkane (154 mg) as identified by IR and NMR.

2-Methyl-2-(β-nitroethyl)cyclohexane-1,3-dione (2b). After a suspension of the dione **1** (189 mg, 1.5 mmol) and KF (104 mg, 1.8 mmol) in dry xylene (2 mL) had been stirred at room temperature for

30 min under nitrogen, a solution of nitroethylene[10] (219 mg, 3 mmol) in dry xylene (1 mL) was added, and then the resultant mixture was heated at 100 °C for 4 h with stirring. The reaction mixture was worked up as usual to give an oil, which showed no formyl signals in the NMR spectrum. The crude product was purified by silica gel thick layer chromatography using ether–petroleum ether (2:1) as the eluent, giving an oil (245 mg, 82%): IR ($CHCl_3$) 1726, 1698, 1556, and 1378 cm^{-1}; NMR δ 1.42 (s, 3 H), 1.8–3.0 (m, 8 H), and 4.38 (t, 2 H, J = 7 Hz).

Anal. Calcd for $C_9H_{13}O_4N$: C, 54.26; H, 6.58; N, 7.03. Found: C, 54.48; H, 6.88; N, 6.89.

The oil slowly solidified on standing and gave low-melting crystals.

Attempted Conversion of the Nitrodione 2b into 3b. A mixture of the nitrodione **2b** (77 mg, 0.39 mmol), KF (27 mg, 0.46 mmol), and dry xylene (1 mL) was stirred at 100 °C for 38 h under nitrogen. The reaction mixture was worked up as usual to afford a brown oil. The oil was almost homogeneous as shown by GLC and TLC. A pale yellow, viscous oil (70 mg) obtained by passing through a silica gel column was identified as the starting material **2b** by IR and NMR.

Preparation of the Labeled 2-Methylcyclohexane-1,3-dione (1). A heterogeneous mixture of 2-methyl-3-(1-pyrrolidinyl)cyclohex-2-en-1-one (8,[5] 179 mg, 1 mmol) and $H_2{}^{18}O$-enriched water[12] (assay, over 20%; 1.0 mL) containing hydrogen chloride (55 mg) was stirred at reflux under nitrogen for 15 min. The reaction mixture was cooled to room temperature and the crystalline product was collected by filtration, washed with water, and dried in vacuo giving labeled 1 (91 mg, 72%). Recrystallization from ethanol gave crystals melting at 203.5–204.5 °C, IR (KBr) 1575 cm^{-1}.

A direct insertion probe was used for mass measurements. Relative intensities of peaks at m/e 128 to those at m/e 126 were 0.017 and 0.424 for the unlabeled and labeled diones 1, respectively.[6]

Preparation of the Labeled 2-Methyl-2-acetonylcyclohexane-1,3-dione (3a). A heterogeneous mixture of the labeled dione 1 (252 mg, 2 mmol), 2-nitropropene (251 mg, 3 mmol), anhydrous KF (116 mg, 2 mmol), and dry xylene (3.5 mL) was stirred on a bath (115–120 °C) for 19 h. The resultant mixture was cooled to room temperature and separated by filtration. The filtrate was concentrated in vacuo giving an oil. Silica gel thick layer chromatography gave the labeled trione 3 (351 mg), which was purified further by distillation [110 °C (bath temperature)/(1–2 mm)]. The trione (298 mg, 82%) thus obtained crystallized on cooling (mp 54–57 °C). The IR and NMR spectra of the product were in agreement with those of the unlabeled trione. An exact mass determination gave m/e 184.0979 (calcd for $C_{10}H_{14}O_2{}^{18}O$, 184.0984).

In the mass spectra of the labeled trione, relative intensities of the molecular ion peak at m/e 184 to that at m/e 182 and of the fragment ion peak at m/e 141 to that at m/e 139 were 0.377 and 0.252, respectively. On the other hand, the corresponding relative values for the unlabeled trione were 0.009 and 0.029.[6] Exact masses of the fragment ion **9** were m/e 141.0822 (calcd for $C_8H_{11}O^{18}O$, 141.0801) and 139.0749 (calcd for $C_8H_{11}O_2$, 139.0758) for the labeled and unlabeled triones, respectively.

Acknowledgment. We thank Dr. K. Ogura for his helpful discussion in labeling experiments.

Registry No.—**1**, 1193-55-1; **1**-^{18}O, 62587-14-8; **2a**, 57822-04-5; **2b**, 57822-03-4; **3a**, 32561-57-2; **3a**-^{18}O, 62587-15-9; **7**, 62587-16-0; **8**, 53940-63-9; 2-nitropropene, 4749-28-0; 2-nitrooctane, 4609-91-0; nitroethylene, 3638-64-0.

References and Notes

(1) Tohoku University.
(2) JEOL Ltd.
(3) T. Yanami, M. Kato, and A. Yoshikoshi, *J. Chem. Soc., Chem. Commun.*, 726 (1975).
(4) Similar transformations with other 1,3-dicarbonylic substrates will be published elsewhere.
(5) J. J. Panouse and C. Sannié, *Bull. Soc. Chim. Fr.*, 1374 (1956).
(6) Multi-ion detection techniques were utilized for all quantitative analyses of the mass spectra.
(7) Regarding the calculation, for example, see K. Biemann, "Mass Spectrometry. Organic Chemical Applications", McGraw-Hill, New York, N.Y., 1962, p 204.
(8) Designating the isotopic contents of the labeled trione **3a** and its fragment ions (labeled **9** and **10**) as a, b, and c, the migration ratio of oxygen (x) based on the labeled ion **9** or **10** may be given by eq 1 or 2, respectively.

$$b = a(1 - x/2) \qquad (1)$$

$$c = ax/2 \qquad (2)$$

(9) For example, see G. W. Wheland and J. Farr, *J. Am. Chem. Soc.*, **65**, 1433 (1943).
(10) G. D. Buckley and C. W. Scaife, *J. Chem. Soc.*, 1471 (1947).
(11) N. Kornblum and J. W. Powers, *J. Org. Chem.*, **22**, 455 (1957).
(12) Supplied by the British Oxygen Co., Ltd.

Trichlorosilane-Induced Cleavage. A Mild Method for Retrieving Carbinols from Carbamates

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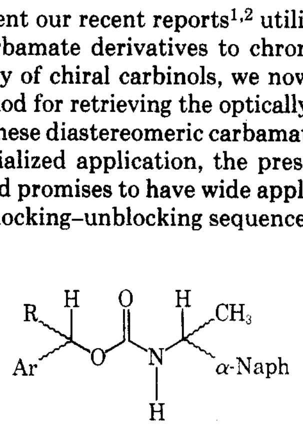
To complement our recent reports[1,2] utilizing type 1 diastereomeric carbamate derivatives to chromatographically resolve a variety of chiral carbinols, we now report a mild, high-yield method for retrieving the optically active carbinol moieties from these diastereomeric carbamates. Beyond this somewhat specialized application, the presently described retrieval method promises to have wide applicability as part of a hydroxyl blocking–unblocking sequence in organic synthesis.



R = alkyl or fluoroalkyl

1

Carbamates are generally hydrolyzed by means of either strong base or strong acid. However, such harsh conditions do not always furnish the desired products. For example, ethoxide treatment of either of the diastereomeric carbamates derived from 1-(1-naphthyl)ethyl isocyanate and 2,2,2-tribromophenylethanol affords decomposition products rather than retrieval of carbinol. Moreover, hydrolysis of carbamates derived from allylic alcohols could conceivably occur by an S_N2' process with attendant rearrangement or racemization, and thermal reactions of such carbamates have been noted[3] (albeit at somewhat higher temperatures than might normally be used during hydrolysis).

Several chlorosilanes have been used to prepare isocyanates from carbamates.[2,4] We have explored modifications of the "silanolysis" reaction as an alternate means for retrieving alcohols from carbamates.

Treatment of carbamates 2–16 with trichlorosilane–triethylamine in any of several dry solvents[5] followed by aqueous workup affords the liberated carbinol in high yield. Table I contains representative examples of carbamates which have been successfully cleaved as well as the reaction conditions utilized. Note that, in all cases, the silane retrieval sequence is essentially independent of the structure of the alcohol and works equally well for primary, secondary, tertiary, or allylic, propargylic, and benzylic alcohols. Most importantly, no racemization or rearrangement of the carbinols has been observed. Further evidence of the mildness of the overall sequence was obtained by applying it to a cyclic hemiacetal. Reduction of γ-valerolactone with diisobutylaluminum hydride at −78 °C in hexane affords a 70:30 mixture of the dia-