an increase in the rate of photodegradation of 4-chlorobiphenyl in isooctane by a factor of 2.8.

Studies with Chlorobiphenyls in the Presence of Dienes. (i) Literature Reports[4,39] in Methanol with 1,3-Cyclohexadiene. Quenching of the photodegradation of several chlorobiphenyls, by using cyclohexadiene and illumination at 290–300 nm, was used to estimate triplet lifetimes.[4] We found that 1,3-cyclohexadiene has λ_{max} = 256 nm in methanol (ϵ 9000) and ϵ_{290nm} = 150. We take as an example the reaction of 2,2′,6,6′-tetrachlorobiphenyl (TCB) with diene, as this represents an extreme case. In cyclohexane,[39] ϵ_{290nm} is given as 50. The data from Table 20 of ref 39 for reaction quenching are given in Table VII together with some absorption data, with the assumption of a 1-cm path length. Thus we see that competing light absorption by the diene more than compensates for any reduction in ϕ_r and hence that the data are not readily interpreted.

(39) L. O. Ruzo, Thesis, Michigan State University, 1974.

(ii) Reaction of Chlorobiphenyls at 254 nm in Cyclohexane in the Presence of 2,5-Dimethyl-2,4-hexadiene. The extinction coefficients at 254 nm for the indicated compounds were as follows: 2,5-dimethyl-2,4-hexadiene, 16 000; 4-chlorobiphenyl, 21 500; 2,4,6-trichlorobiphenyl, 2800; 2,2′,5,5′-tetrachlorobiphenyl, 1700. The solutions to be irradiated contained 1.0×10^{-3} M chlorobiphenyl and varying amounts of diene. Because some of the conversions are high, the data are given as the percent of compound reacted (Table VIII).

Acknowledgment. We thank the NSERC of Canada for financial support.

Registry No. 1, 63635-59-6; 3, 74366-01-1; chlorobenzene, 108-90-7; 1-bromo-2-phenylethane, 103-63-9; *p*-chlorobenzaldehyde, 104-88-1; 4′-chloro-3-phenylpropiophenone, 5739-37-7; 1-(4-chloro-1-naphthyl)-3-(1-naphthyl)-2-propen-1-one, 74366-02-2; 1-chloronaphthalene, 90-13-1; 4-chlorobiphenyl, 2051-62-9; 2,2′,6,6′-tetrachlorobiphenyl, 15968-05-5; 2,4,6-trichlorobiphenyl, 35693-92-6; 2,2′,5,5′-tetrachlorobiphenyl, 35693-99-3.

Diels–Alder Addition of 1,1′-Thiocarbonylbis(1,2,4-triazole) to Dienes. A Useful Preparation of Bicyclic Sulfides and Related Derivatives[1]

Charles Larsen*

Department of General and Organic Chemistry, University of Copenhagen, H. C. Ørsted Institute, Copenhagen, Denmark DK 2100

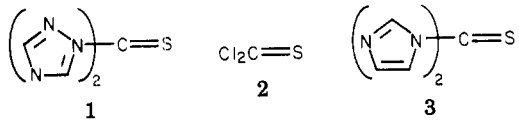
David N. Harpp*

Department of Chemistry, McGill University, Montreal, PQ, Canada H3A 2K6

Received February 12, 1980

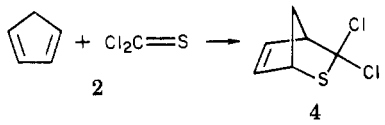
1,1′-Thiocarbonylbis(1,2,4-triazole) adds in a Diels–Alder fashion to a variety of dienes to give high yields of bicyclic sulfides. Alcoholysis of some of these derivatives provided cis-3,5-fused mercapto esters.

We recently reported the synthesis and properties of 1,1′-thiocarbonylbis(1,2,4-triazole) (1).[1] As a thiocarbonyl



1 2 3

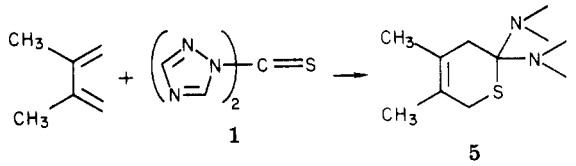
transfer reagent 1 appears to be superior in many ways to the parent thiophosgene (2) or the 1,1′-thiocarbonyldiimidazole analogues (3).[2] For instance, reagent 1 reacts with primary amines in a selective fashion,[3] thus permitting the facile synthesis of unsymmetrically substituted thioureas.[1] This unexpected chemistry prompted us to explore its behavior as a dienophile. Parent thiophosgene (2) is well-known to react with various dienes to give cyclic and bicyclic adducts such as 4.[4] In general, however, these



2 4

derivatives are unstable and must be stored in the cold. For instance, sulfide 4 decomposes to a black tar if not kept at dry ice temperatures.[4a,c]

We have found that triazole reagent 1 not only adds smoothly and in excellent yield (isolated ca. 90%) to a variety of dienes[5] but also provides crystalline adducts which are moisture stable at room temperature. Thus, further chemistry can be carried out directly, which is not the case with the thiophosgene derivatives.[4c] While a variety of thiocarbonyl dienophiles have been investigated,[4a,6] none appear to give consistently high yields of stable adducts as reagent 1. For example, 2,3-dimethyl-1,3-butadiene reacts with 1 to give 5 in 99% isolated yield.



1 5

(1) Thiocarbonyl Transfer Reagent Chemistry, Part 2. For Part 1 see: Larsen, C.; Steliou, K.; Harpp, D. N. *J. Org. Chem.* **1978**, *43*, 337.

(2) For a recent paper on this and related derivatives, see: Walter, W.; Radke, M. *Justus Liebigs Ann. Chem.* **1979**, 1756.

(3) When 2 and 3 are treated with amines, the monosubstituted derivatives (*N*-thiocarbamoyl chloride or imidazole) are unstable and are converted to isothiocyanates. A similar versatility of 1 vs. 2 or 3 obtains for a variety of reactions of 1 with several nucleophiles: Larsen, C.; Harpp, D. N., manuscripts in preparation.

(4) (a) Middleton, W. J. *J. Org. Chem.* **1965**, *30*, 1390. (b) Laban, G.; Mayer, R. *Z. Chem.* **1967**, *7*, 227. (c) Johnson, C. R.; Keiser, J. E.; Sharp, J. C. *J. Org. Chem.* **1969**, *34*, 860. (d) Reich, H. J.; Trend, J. E. *Ibid.* **1973**, *38*, 2637.

(5) 1,3-Cyclooctadiene and furan did not react with reagent 1.

(6) Yamada, K.; Yoshioka, M.; Sugiyama, N. *J. Org. Chem.* **1968**, *33*, 1240. Zwanenburg, B.; Thijs, L.; Strating, J. *Tetrahedron Lett.* **1969**, 4461. Ohno, A.; Ohnishi, Y.; Tsuchihashi, G. *Tetrahedron* **1969**, *25*, 871. Raasch, M. S. *J. Org. Chem.* **1970**, *35*, 3470. Vyas, D. M.; Hay, G. W. *Can. J. Chem.* **1971**, *49*, 3755. Friedrich, K.; Zamkanei, M. *Tetrahedron Lett.* **1977**, 2139. Friedrich, K.; Zamkanei, M. *Chem. Ber.* **1979**, *112*, 1867.

(7) Allgeier, H.; Winkler, T. *Tetrahedron Lett.* **1976**, 215.

0022-3263/80/1945-3713$01.00/0

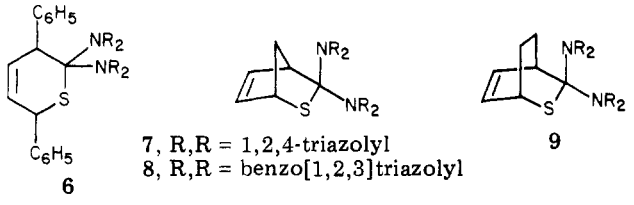
Table I

$$10 \xrightarrow{ROH} 11 + 12$$

R	11, % yield	12, % yield
CH_3	84[9]	*a*
CH_3CH_2	71	8
$CH_3CH_2CH_2$	66	*b*
$(CH_3)_2CH$	47[11]	40
$(CH_3)_3C$	*a*	78

[a] Not detected. [b] Not isolated.

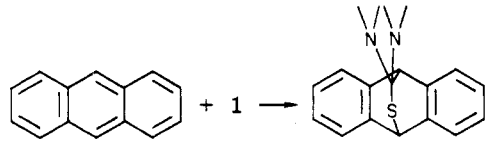
Similarly, 1,4-diphenyl-1,3-butadiene, 1,3-cyclopentadiene, and 1,3-cyclohexadiene gave **6**, **7**, and **9** in 67, 99, and 88%



6 **7**, R,R = 1,2,4-triazolyl; **8**, R,R = benzo[1,2,3]triazolyl **9**

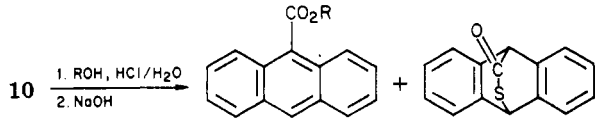
yields, respectively. The bis(benzotriazolyl) analogue **8** was obtained in 98% yield. In constrast to the instability of **4**, adduct **7** has been stored at room temperature without sign of deterioration for several months.

The chemistry of bicyclic adducts **7–10** has been investigated. In the case of the reaction of anthracene with **1**, a stable compound **10** was formed in 85% yield. The



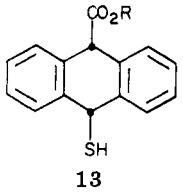
10

behavior of **10** under solvolytic conditions was interesting. The distribution of anthracene derivatives **11** and **12** was



11 **12**

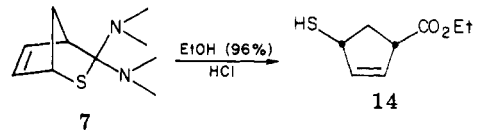
a function of the alcohol used. When methanol was employed, 84% of the 9-methylanthroate was isolated. With *tert*-butyl alcohol, only the thiolactone **12** was produced (Table I). A possible rationale of the above trends is indicated as follows. As the R group of the alcohol becomes progressively larger simple hydrolysis of **10** to give thiolactone **12** is favored relative to alcohol participation in forming ring-opened derivative **13**. Support for this



13

proposal derives from the evidence obtained by treating adduct **10** only with ethanol and aqueous HCl, omitting the treatment with NaOH. In this case mercapto ester **13** was produced in ca. 85% yield. While it was not possible to crystallize this material, ^1H NMR, mass spectra, and IR data leave no doubt as to its structure.[8] Further, when **13** was treated with aqueous NaOH, anthracene derivative **11** was formed in 78% isolated yield, presumably by 1,4-elimination of H_2S.

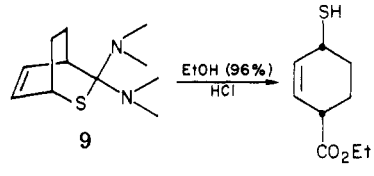
When bicyclic derivative **7** was treated with dry HCl in 96% ethanol an oil was obtained. Infrared analysis indicated SH and C=O absorptions. As in the case of the



7 **14**

conversion of **10** → **13**, we found that adduct **7** was transformed in 70% yield into the novel cis-3,5-fused cyclopentene structure **14**. Proof of the structure derives largely from mass spectra and ^1H and ^{13}C NMR considerations. Exact mass measurement of the parent ion gave a correct molecular formula corresponding to $C_8H_{12}O_2S$. In addition, a number of expected fragmentations were observed and their composition confirmed by high-resolution mass measurements (see Experimental Section). ^{13}C NMR spectroscopy revealed 8 carbon signals in the expected positions. The ^1H NMR spectrum is extremely complex. While the couplings of the ethyl and thiol functions could be clearly defined, the remaining multiplets defied simple interpretation. Hence the groups at ca. δ 5.9, 3.6, and 2.4 were subjected to a detailed computer analysis. It was possible to simulate these three complex regions of the spectrum to match the actual peaks.[9] A similar yield of **14** was obtained by solvolysis of benzotriazole adduct **8**.

In a parallel fashion the [2.2.2] derivative **9** was treated with 96% EtOH/HCl. The mercapto ester **15** was isolated as an oil in 91% yield. A correct combustion analysis was obtained; in addition, the ^1H NMR spectrum was consistent with structure **15**.



9 **15**

Thus, not only does **1** form a variety of stable Diels–Alder adducts but **5–10** also provide unique access to bisfunctionalized derivatives such as **13**, **14**, and **15**, whose stereochemistry is known.

Experimental Section

Unless stated otherwise, chemical reagents were obtained from commercial sources and were used directly. Melting points were obtained on a Büchi apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 580 grating spectrophotometer. ^1H NMR spectra were measured with a Varian Associates T-60 A spectrometer and are summarized in Table II. Mass spectra were obtained on an AEI-MS-902 mass spectrometer, using a direct insertion probe. Organic microanalysis were performed by the Microanalysis Department of the H. C. Ørsted Institute, Chemistry Lab II, Copenhagen, Denmark.

(8) In addition to finding infrared bands at 2500 and 1710 cm^{-1}, typical of SH and C=O, an exact mass measurement revealed the parent ion to contain $C_{17}H_{16}SO_2$. The ^1H NMR spectrum ($CDCl_3$) consisted of a triplet at δ 1.02 (J = 7 Hz, 3 H), a doublet at δ 3.05 (J = 9 Hz, 1 H), a quadruplet at δ 4.01 (J = 7 Hz, 2 H), a singlet at δ 5.0 (1 H), another doublet at δ 5.23 (J = 9 Hz, 1 H), and a multiplet at δ 7.31 (8 H). When the solution was shaken with D_2O/pyridine, the signal at δ 3.05 disappeared and the doublet at δ 5.23 collapsed to a singlet.

(9) Information concerning the ^1H NMR spectrum of **14** is available from one of us (C.L.).

Table II. ^{1}H NMR Data for Compounds 5-10

compd	chemical shift, δ
5	1.76 (s, 6 H, CH_3), 3.25 (s, 2 H, CCH_2), 3.72 (s, 2 H, SCH_2), 8.02 (s, 2 H, N=CH), 8.58 (s, 2 H, N=CH)
6	4.55 (d, 1 H, CCH), 5.40 (m, 1 H, SCH), 6.10 (m, 2 H, C=CH), 7.27 (s, 5 H, C_6H_5), 7.47 (s, 5 H, C_6H_5), 7.68 (s, 2 H, N=CH), 8.13 (s, 1 H, N=CH), 8.87 (s, 1 H, N=CH)
7	2.13 (m, 2 H, CH_2), 4.52 (m, 1 H, CCH), 4.88 (m, 1 H, SCH), 5.78 (m, 1 H, C=CH), 6.70 (m, 1 H, C=CH), 7.92 (s, 1 H, N=CH), 8.00 (s, 1 H, N=CH), 8.45 (s, 1 H, N=CH), 8.57 (s, 1 H, N=CH)
8	2.38 (m, 2 H, CH), 4.65 (m, 1 H, CCH), 5.93 (s, 1 H, SCH), 5.87 (m, 1 H, C=CH), 6.83 (m, 1 H, C=CH), 7.45 (m, 6 H, arom), 8.03 (m, 2 H, arom)
9	1.57 (m, 4 H, CH_2CH_2), 3.88 (m, 1 H, CCH), 4.53 (m, 1 H, SCH), 6.10 (m, 1 H, C=CH), 6.65 (m, 1 H, C=CH), 7.85 (s, 1 H, N=CH), 7.93 (s, 1 H, N=CH), 8.45 (s, 1 H, N=CH), 8.70 (s, 1 H, N=CH)
10	5.50 (s, 1 H, CCH), 6.30 (s, 1 H, SCH), 7.23 (m, 8 H, arom), 7.95 (s, 2 H, N=CH), 8.30 (s, 2 H, N=CH)

3,4-Dimethyl-6,6-bis(1,2,4-triazol-1-yl)-5,6-dihydro-2*H*-thiapyran (5). A mixture of 1 (0.01 mol, 1.8 g) and 2,3-dimethyl-1,3-butadiene (0.01 mol, 0.82 g) in dry CH_2Cl_2 (35 mL) was stirred at room temperature for 48 h. Flash evaporation left a faint pink oil, which crystallized upon standing to yield 2.6 g (99%) of pink crystals. The crystals could be recrystallized from benzene (or a mixture of benzene and cyclohexane) to give a nearly colorless product with a melting point of 121–122 °C.

Anal. Calcd for $C_{11}H_{14}N_6S$: C, 50.35; H, 5.38; N, 32.04. Found: C, 50.30; H, 5.35; N, 32.00.

2,5-Diphenyl-6,6-bis(1,2,4-triazol-1-yl)-5,6-dihydro-2*H*-thiapyran (6). A mixture of 1 (0.01 mol, 1.8 g) and 1,4-diphenyl-1,3-butadiene (0.01 mol, 2.06 g) in benzene (40 mL) was refluxed for 62 h. After the reaction mixture was cooled in an ice–water bath the crystals were collected. The crystals were washed with cold benzene to give 2.6 g (67%) of colorless product, the identity of which was shown by ^{1}H NMR to be **6**. A small portion was recrystallized from benzene and then washed with ether to give an analytically pure compound with a melting point of 195–197 °C.

Anal. Calcd for $C_{21}H_{18}N_6S$: C, 65.26; H, 4.69; N, 21.75. Found: C, 65.10; H, 4.28; N, 21.45.

3,3-Bis(1,2,4-triazol-1-yl)-2-thiabicyclo[2.2.1]hept-5-ene (7). To a stirred solution of 1 (0.02 mol, 3.6 g) in CH_2Cl_2 (25 mL) cooled to 0 °C was added a solution of cyclopentadiene (0.02 mol, 1.32 g) in CH_2Cl_2 (15 mL) dropwise over a 10-min period. Stirring was continued for 15 min to ensure complete reaction. The solvent was evaporated in vacuo, leaving a colorless oil which crystallized after addition of ether to yield 99% of colorless crystals, mp 121–122 °C. An analytical sample recrystallized from benzene gave a melting point of 125–126 °C.

Anal. Calcd for $C_{10}H_{10}N_6S$: C, 48.76; H, 4.09; N, 34.13. Found: C, 48.90; H, 4.21; N, 33.86.

3,3-Bis(1,2,3-Benzotriazol-1-yl)-2-thiabicyclo[2.2.1]hept-5-ene (8). To a sitrred solution of 1,1′-thiocarbonyldibenzotriazole[2] (0.02 mol, 5.6 g) in CH_2Cl_2 (125 mL) was added a solution of cyclopentadiene (0.02 mol, 1.32 g) in CH_2Cl_2 (10 mL) dropwise over a 15-min period. Stirring was continued for 20 h, after which the solution was filtered. The solvent was evaprorated in vacuo, leaving brown grayish crystals (yield, 6.8 g (98%)). The crystals could be recrystallized from ethanol to give a colorless product, mp 184–186 °C dec.

Anal. Calcd for $C_{18}H_{14}N_6S$: C, 62.41; H, 4.07; N, 24.27. Found: C, 62.16; H, 4.58; N, 24.03.

3,3-Bis(1,2,4-triazol-1-yl)-2-thiabicyclo[2.2.2]oct-5-ene (9). A mixture of 1 (0.01 mol, 1.8 g) and 1,3-cyclohexadiene (0.01 mol, 0.80 g) in benzene (25 mL) was refluxed for 18 h. Flash evaporation of the solvent left a pink oil most of which crystallized upon standing. The crystals were collected and washed with cold ether to yield 88% of pale yellow crystals which could be recrystallized from cyclohexane to give an analytically pure product with a melting point of 113–114 °C.

Anal. Calcd for $C_{11}H_{12}N_6S$: C, 50.75; H, 4.65; N, 32.29. Found: C, 50.65; H, 4.66; N, 32.33.

2,2-Bis(1,2,4-triazol-1-yl)dibenzo[*e*,*h*]-2-thiabicyclo-[2.2.2]octane (10). A mixture of 1 (0.02 mol, 3.60 g) and anthracene (0.02 mol, 3.56 g) in toluene (50 mL) was refluxed for 4 days. After the reaction mixture was cooled in an ice–water bath, 6.10 g of colorless crystals were collected (yield 85%). ^{1}H NMR demonstrated the identity of **10**. An analytical sample was prepared by washing the crystals with several portions of boiling CCl_4. The purified product had a melting point of 213–215 °C.

Anal. Calcd for $C_{19}H_{14}N_6S$: C, 63.67; H, 3.94; N, 23.45; S, 8.94. Found: C, 63.20; H, 3.88; N, 23.57; S, 9.15.

Attempted Preparation of 3,3-Bis(2-imidazoyl)-2-thiabicyclo[2.2.1]hept-5-ene. To a stirred solution of **3** (0.01 mol, 1.78 g) in CH_2Cl_2 (20 mL) cooled to 0 °C was added a solution of freshly distilled cyclopentadiene (0.01 mol, 0.66 g) in CH_2Cl_2 (10 mL) dropwise over a 15-min period. After addition was completed the stirring was continued for 30 min. A ^{1}H NMR spectrum of a sample showed no other peaks than those of the reagents. The solution was left for 40 h at room temperature after which the solvent was removed by flash evaporation, leaving 2.40 g of brown oil which crystallized on standing. ^{1}H NMR of the oily brown crystals in $CDCl_3$ consisted of peaks at δ 2.22 (m, 2 H, $>CH_2$), 4.37 (m, 1 H, >CCH), 4.53 (m, 1 H, SCH), 5.83 (m, 1 H, >C=CH), 6.83 (m, 1 H, >C=CH), 7.17 (m, 4 H, NCHC), 7.78 (s, 1 H, N=CH—N), and 8.10 (s, 1 H, N=CH—N). In addition peaks corresponding to the content of ca. 0.5 mol of imidazole were found. Comparison with the ^{1}H NMR spectrum of **7** leaves no doubt that an addition has occurred; however, all attempts to purify the compound by recrystallization or by TLC were unsuccessful.

Ethyl 4-Mercapto-2-cyclopentenecarboxylate (14). Dry HCl was bubbled through a solution of **7** (0.004 mol, 1.0 g) in ethanol (10 mL) at reflux for 20 min. Reflux was continued for additional 40 min, after which colorless crystals separated on cooling. The solvent was evaporated in vacuo, leaving pink crystals which were extracted with warm CCl_4 (15 mL). The colorless crystals were collected to give 0.8 g of triazole·HCl (95%). The filtrate was flash evaporated and the residue was a pale brown liquid (0.5 g, 76%) with an NMR corresponding to that of **14**. An analytically pure compound was obtained by preparative TLC (top band) on silica gel ($CHCl_3$). The solvent was evaporated in vacuo, leaving a colorless fruity-smelling liquid (n^{25}_D 1.5003). On exposure to air the liquid turned brown and evolved an unpleasant smell.

Anal. Calcd for $C_8H_{12}O_2S$: C, 55.78; H, 7.02; S, 18.61. Found: C, 56.01; H, 6.80; S, 18.61.

Mass spectrum of **14**: *m/e* 172 (50%) $C_8H_{12}O_2S^+ \rightarrow$ *m/e* 139 (67%) $C_8H_{11}O_2^+ \rightarrow$ *m/e* 111 (37%) $C_6H_7O_2$. Another route is *m/E* 172 → *m/e* 127 (10%) $C_6H_7OS \rightarrow$ *m/e* 99 (78%) $C_5H_7S^+ \rightarrow$ *m/e* 67 (91%) C_5H_7. All intensities are relative to the base peak at *m/e* 66 (100%) C_5H_6. The infrared spectrum of **14** shows absorptions at 2578 (w, sh) and 1733 cm^{-1} (s, C=O). Compound **14** was also obtained in 89% yield, using **8** as the starting material. A detailed analysis of the ^{1}H NMR spectrum of **14** is available from the authors on request.

Methyl 4-Mercapto-2-cyclopentenecarboxylate. This compound was formed by using the same procedure as for the preparation of **14**, but with methanol as the solvent. The IR, ^{1}H NMR, and mass spectra of the pale brown liquid were consistent with its structure.

Alkyl 9-Anthroates. General Procedure. A mixture of **10** (0.002 mol) in the corresponding alcohol (10 mL) and 1 mL of 4 N HCl was refluxed for 1 h. After the mixture cooled, an excess of 2 N NaOH was added and the crystals were collected. In this way the following compounds were obtained.

Methyl 9-Anthroate. Recrystallization from ethanol yielded colorless crystals, mp 107–108 °C (lit.[10] mp 112 °C).

Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.55; H, 5.20.

(10) Laur, K. *Chem. Ber.* **1937**, *70*, 1288.

Ethyl 9-Anthroate. Recrystallization from ethanol yielded colorless crystals, mp 108–109 °C (lit.[11] mp 102 °C).

Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.52; H, 5.67.

This compound was also prepared by adding ethanolic KOH to a solution of **13** (0.78 mmol, 0.220 g) in hot ethanol (5 mL). The mixture was heated to boiling for 2 min and then cooled in ice. Addition of water gave crystals which were collected and recrystallized twice from ethanol to yield 0.150 g (77%).

Isopropyl 9-Anthroate. Recrystallization from ethanol/water yielded colorless crystals, mp 93–94 °C (lit.[12] mp 95 °C).

Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.54; H, 6.02.

Propyl 9-Anthroate. After cooling, the refluxed solution was taken to dryness by flash evaporation. The residue was dissolved in ethanol and 2 N NaOH added. The precipitated crystals were collected and recrystallized from ethanol to give pale yellow crystals, mp 68–69 °C.

Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.99; H, 6.11.

Dibenzo[*e*,*h*]-1-thiabicyclo[2.2.2]octan-2-one (12). A mixture of **10** (0.002 mol, 0.716 g) in *tert*-butyl alcohol (10 mL) and 1 mL of 4 N HCl was refluxed for 1 h. After the mixture cooled the crystals were collected. Recrystallization from ethanol gave 0.370 g (78%) of colorless crystals which were recrystallized once more from benzene/petroleum ether, mp 135–137 °C; this was followed by solidification and remelting at 210–214 °C (melting point of anthracene) in accordance with the literature.[7]

Anal. Calcd for $C_{15}H_{10}OS$: C, 75.60; H, 4.23. Found: C, 75.63; H, 4.42.

Ethyl 4-Mercapto-2-cyclohexenecarboxylate (15). The same procedure as above, using **9** (0.0038 mol, 1.0 g), yielded a light yellow liquid (0.68 g, 95%). Purification by TLC gave a colorless liquid with the same characteristics as those mentioned for **14**: n^{23}_D 1.5080; ^{1}H NMR (CCl_4) δ 1.27 (t, 3 H, CH_3), 1.60 (d, 1 H, SH), 1.96 (m, 4 H, CH_2), 3.00 (m, 1 H, CH), 3.50 (m, 1 H, CH), 4.17 (q, 2 H, OCH_2), and 5.83 (m, 2 H, CH=CH).

Acknowledgment. We thank the Natural Sciences and Engineering Council of Canada, Imperial Oil of Canada, and the Danish Natural Science Research Council for financial support of this work. We are grateful to Dr. Ole Manscher (Chem. Lab. II, H.C. Ørsted Institutet, University of Copenhagen) for technical and interpretive help concerning the ^{1}H NMR spectrum of **14**.

Registry No. 1, 63976-76-1; **3**, 6160-65-2; **5**, 74346-63-7; **6**, 74346-64-8; **7**, 74356-05-1; **8**, 74346-65-9; **9**, 74346-66-0; **10**, 74346-67-1; **11** (R = CH_3), 1504-39-8; **11** (R = CH_3CH_2), 1754-54-7; **11** (R = $CH_3CH_2CH_2$), 71942-30-8; **11** (R = $(CH_3)_2CH$), 30536-62-0; **12**, 59102-55-5; *cis*-**13**, 74356-06-2; *cis*-**14**, 74346-68-2; *cis*-**15**, 74346-69-3; 1,4-diphenyl-1,3-butadiene, 886-65-7; cyclopentadiene, 542-92-7; 1,1′-thiocarbonyldibenzotriazole, 4314-19-6; 1,3-cyclohexadiene, 592-57-4; anthracene, 120-12-7; methyl *cis*-4-mercapto-2-cyclopentenecarboxylate, 74346-70-6; methanol, 67-56-1; ethanol, 64-17-5; propanol, 71-23-8; 2-propanol, 67-63-0.

(11) Adams-Briers, M.; Fierens, P. J. C.; Martin, R. H. *Helv. Chim. Acta* **1955**, *38*, 2021.
(12) Heller, E.; Schmidt, G. M. J. *Isr. J. Chem.* **1971**, *9*, 449.

Notes

Glutaric and Succinic Acids in the Cobalt Acetate Catalyzed Oxidation of Cyclohexane with Oxygen

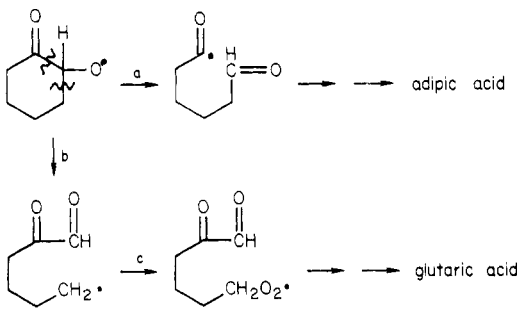
Johann G. D. Schulz and Anatoli Onopchenko*

Gulf Research and Development Company, Chemicals and Minerals Division, Pittsburgh, Pennsylvania 15230

Received January 7, 1980

Radical-initiated autoxidation of cyclohexane was reported by Hendry et al.[1] to proceed predominantly over cyclohexanone as the intermediate which further reacted to form adipic and glutaric acids in a ratio of ~6:1. The same molar ratio was obtained in acetic acid in the presence of a catalytic amount of cobalt acetate. This suggests that (2-ketocyclohexyl)oxy radicals are involved in both cases, which in the latter are formed via ROOH + Co^{2+} → RO· + Co^{3+} + OH^-. The two acids are formed as the result of competing cleavage at two possible locations (paths a and b, Scheme I). No succinic acid was reported at the low ketone conversions investigated. Kamiya and Kotake[2] employed substantial amounts of cobalt acetate to oxidize cyclohexanone in high conversion to adipic and glutaric acids (4.8:1 ratio), but no mention of succinic acid was made. More recently, Druliner[3] studied the cobalt acetate catalyzed oxidation of [1-^{14}C]cyclohexanone in acetic acid

Scheme I



and produced a mixture of C_4–C_6 dicarboxylic acids, with high retention of activity in glutaric and succinic acid. This work suggests little contribution of intermediates, including 1,2-cyclohexanedione[4] and 2,6-dihydroperoxycyclohexanone,[5] and no appreciable oxidative degradation of adipic acid as each of these events was expected to diminish the activity in the products by ~50%.

Earlier, we reported the oxidation of cyclohexane in the cobalt acetate system with high yields to C_4–C_6 dicarboxylic acids.[6] The present work investigates the oxidative degradation of adipic acid to lower dibasics. Lande and Kochi reported on the thermolysis of cobaltic salts of monobasic acids in the absence of oxygen.[7] Reactions of

(1) D. G. Hendry, C. W. Gould, D. Schuetzle, M. G. Syz, and F. R. Mayo, *J. Org. Chem.*, **41**, 1 (1976).
(2) Y. Kamiya and M. Kotake, *Bull. Chem. Soc. Jpn.*, **46**, 2780 (1973).
(3) J. D. Druliner, *J. Org. Chem.*, **43**, 2069 (1978).
(4) I. I. Korsak and V. E. Agebekov, *Dokl. Akad. Nauk SSSR*, **19**, 711 (1975).
(5) G. N. Koshel, M. I. Farberov, T. N. Anmonova, L. V. Bedareva, N. G. Vasil'ev, and L. V. Ob'edkova, *Neftekhimiya*, **14**, 263 (1974).
(6) A. Onopchenko and J. G. D. Schulz, *J. Org. Chem.*, **38**, 3729 (1973).

0022-3263/80/1945-3716$01.00/0