potassium *t*-butoxide in ether was smoothly converted to the conjugated diene **5**, $\lambda_{\max}$ 238 m$\mu$ ($\epsilon$ 14,160). It may be noted that the bicyclo[2.2.2] structure **8** could not have provided a conjugated diene. Treatment of the bromoxide **3** itself with potassium *t*-butoxide yielded the olefinic alcohol **4** *in lieu* of the bisoxide **7**, again, presumably, for reasons of steric constraint (chair → boat) connoted in the latter system.

The diene **5** absorbed 2 moles of hydrogen to give the saturated system **6**. The unsaturated alcohol **4** in the form of its tosylate derivative **4a** was found to be stable to conditions employed for solvolysis of homoallylic systems, namely, potassium acetate in refluxing aqueous 80% acetone.[3] In the presence of potassium *t*-butoxide in ether suspension, on the other hand, **4a** was converted exothermically to the diene **5**.

### Experimental Section

Vpc determinations were carried out employing a 5 ft × 0.25 in. 20% S.E. 30 on Chrom W Column. The uv spectrum was determined in methanol on a Cary Model II PMS spectrometer and ir spectra on a Perkin-Elmer Infracord instrument. Nmr spectra were recorded on a Varian A-60 spectrometer using TMS as an internal standard.

**1,2-Bishydroxymethylcyclohex-4-ene** (1) was prepared by lithium aluminum hydride reduction of $\Delta^4$-tetrahydrophthalic anhydride in ether–tetrahydrofuran solution and purified *via* its acetonide 2 (see below); lit.[4] bp 106–107° (1–1.5 mm) and mp 34.5°.

**Acetonide of 1,2-Bishydroxymethylcyclohex-4-ene** (2).—A solution of crude diol 1 (25 g) (see above) in 500 cc of acetone and 25 g of anhydrous copper sulfate was stirred for 18 hr followed by filtration and evaporation of the filtrate. The residue from concentration was extracted with petroleum ether (bp 30–60°) and the latter extract was washed several times with water, dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. Distillation of the residue, bp 60–61° (2 mm), afforded 18–20 g of acetonide 2: single peak by vpc, 4-min retention time at 180°; nmr ($CDCl_3$), $\delta$ 1.3.

*Anal.* Calcd for $C_{11}H_{18}O_2$: C, 72.53; H, 9.89. Found: C, 72.82; H, 10.10.

Regeneration of diol 1 from acetonide 2 was effected by brief shaking with 10% hydrochloric acid and concentration *in vacuo* followed by treatment with sodium chloride and extraction with ether. Evaporation of the dried ($MgSO_4$) ether solution yielded diol 1 which was single peak by vpc with a retention time of 5.5 min at 180°.

**Reaction of 1,2-Bishydroxymethylcyclohex-4-ene with N-Bromsuccinimide. Formation of Transannular Oxide 3.**—A solution of 15.6 g of diol 1, purified *via* its acetonide, in 165 cc of *t*-butyl alcohol and 33 cc of water was treated at 0–5° with 19.6 g of N-bromsuccinimide with stirring. The reaction mixture was allowed to stir until complete solution of the N-bromsuccinimide (*ca.* 1 hr) and stored for 16 hr in the refrigerator. Any excess positive bromine was destroyed with aqueous bisulfite and the reaction mixture was concentrated *in vacuo* to an oil. The latter was treated with water and extracted with ether. The ether extract was washed several times with water, dried over magnesium sulfate, filtered, and concentrated to give the bromoxide **3** as a colorless oil, 20 g, essentially single peak by vpc with a retention time of 7 min at 200°. This material is unstable to high-vacuum distillation and a sample for analysis was prepared by submitting a film to high vacuum for 18 hr.

*Anal.* Calcd for $C_8H_{13}O_2Br$: C, 43.44; H, 5.88; Br, 36.15. Found: C, 43.19; H, 5.86; Br, 36.15.

***p*-Toluenesulfonate 3a of Bromoxide.**—A 1.75-g sample of the above bromoxide **3** in 5 cc of pyridine was treated with 1.61 g of *p*-toluenesulfonyl chloride at 0° for 18 hr. The reaction mixture was treated with ice–water and the crystalline tosyl derivative was filtered, washed with water, and dried; 2.9 g, mp 74–76°, crystallization from ether gave mp 80–82°, ir of crude and crystallized material were the same.

*Anal.* Calcd for $C_{15}H_{19}SO_4Br$: C, 48.00; H, 5.07; Br, 21.33. Found: C, 48.12; H, 5.12; Br, 21.20.

**Conversion of Tosylate 3a to Diene 5.**—A solution of 650 mg of **3a** in 25 cc of ether was treated with 780 mg of potassium *t*-butoxide and stirred for 2 hr. At the end of this period water was added, the ether layer was separated and washed with water until neutral. Evaporation of the solvent yielded an oil exhibiting a single peak in the vpc with retention time of 1.5 min at 180°. The oil was evaporatively distilled at 75–80° (32 mm); $\lambda_{\max}$ 238 m$\mu$ ($\epsilon$ 14,160); $\lambda_{\max}^{\text{film}}$ 6.12, 6.28 $\mu$; nmr, $\delta$ 4.69, 4.79 (each d, $J$ = 1.5 cps, $>C{=}CH_2$), 6.05 (m, $CH{=}CH$).

*Anal.* Calcd for $C_8H_{10}O$: C, 78.69; H, 8.20. Found: C, 78.45; H, 8.48.

Hydrogenation of diene **5** (0.3 g) in 5 cc of ether employing 150 mg of 5% Pd–C catalyst resulted in absorption of 2 molar equiv of hydrogen and formation of the saturated analog **6** which was evaporatively distilled at 70° (32 mm), nmr, $\delta$ 0.85 ($J$ = 6 cps, $CH_3$ doublet).

*Anal.* Calcd for $C_8H_{14}O$: C, 76.19; H, 11.11. Found: C, 76.26; H, 11.11.

**Reaction of Bromoxide 3 with Base to Give 4.**—A solution of 1.7 g of bromoxide **3** in 15 cc of anhydrous ether was treated with 2 mole equiv of potassium *t*-butoxide. An exothermic reaction occurred which was allowed to continue with stirring at ambient temperature for 48 hr. The reaction mixture was treated with saturated salt solution and the ether extracts were washed with salt solution until neutral. Product distilled at 85° (0.02 mm); $\lambda_{\max}^{\text{film}}$ 2.8, 6.12 $\mu$.

*Anal.* Calcd for $C_8H_{12}O_2$: C, 68.57; H, 8.57. Found: C, 68.07; H, 8.47.

Tosylation of **4** as described for the preparation of **3a** yielded an oily tosylate, which was recovered unchanged after refluxing 18 hr in 80% acetone–water containing 4 mole equiv of potassium acetate. Treatment of this derivative with potassium *t*-butoxide as described for the preparation of **5** proceeded exothermically to give this diene.

**Registry No.**—**2**, 19639-98-6; **3**, 19639-92-0; **3a**, 19639-99-7; **4**, 19642-96-7; **5**, 19642-97-8; **6**, 19642-98-9.

---

[3] E. M. Kosower and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 4347 (1956).

[4] E. L. Eliel and C. Pillar, *ibid.*, **77**, 3600 (1955); see also D. C. Ayres and R. A. Raphael, *J. Chem. Soc.*, 1779 (1958), and references cited therein.

---

## Reactions of Hydroxymethylferrocene. II. Sulfides[1]

CHARLES S. COMBS, CHARLES I. ASHMORE, ALEC F. BRIDGES,
CANDACE R. SWANSON, AND WILLIAM D. STEPHENS[2]

*Thiokol Chemical Corporation, Huntsville Division,*
*Huntsville, Alabama*

*Received October 16, 1968*

Alkyl ferrocenylmethyl sulfides have been prepared by reduction of alkyl ferrocenethiolcarboxylates with lithium aluminum hydride in the presence of aluminum chloride.[3] Nesmeyanov has reported the preparation of these compounds from ferrocenylmethanethiol,[4] and by decomposition of ferrocenylmethyltrimethylammonium iodide in the presence of aqueous sodium sulfide.[5]

We wish to report a new preparation of alkyl ferrocenylmethyl sulfides directly from hydroxymethylferro-

---

[1] This work was supported by the Propellant Division of the Air Force Rocket Propulsion Laboratory, Edwards Air Force Base, Calif., under Contract F-04611-67-C-0034.

[2] To whom inquiries should be addressed.

[3] D. E. Bublitz, *J. Organometal. Chem.*, **6**, 436 (1966).

[4] A. N. Nesmeyanov, E. G. Perevalova, L. I. Leont'eva, and Y. A. Ustynyuk, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1696 (1965); *Chem. Abstr.*, **63**, 18146 (1965).

[5] A. N. Nesmeyanov, E. G. Perevalova, L. S. Shilovtseva, and V. D. Tyurin, *Izv. Akaa. Nauk SSSR, Otd. Khim. Nauk*, 1997 (1962); *Chem. Abstr.*, **58**, 9132 (1963).

TABLE I

EXPERIMENTAL RESULTS

| Compd | R | Conditions | Yield, % | Mp, °C | $n^{20}D$ | Calcd, % C | Calcd, % H | Found, % C | Found, % H |
|---|---|---|---|---|---|---|---|---|---|
| IIa | $C_2H_5$ | Reflux (72 hr) | 60 | 8–14 | 1.6245 | 60.03 | 6.20 | 60.22 | 6.33 |
| IIb | $C_3H_7$ | Reflux (1.5 hr) | 99[a] | 6–8 | 1.6045 | 61.32 | 6.62 | 61.24 | 6.35 |
| IIc | $C_4H_9$ | Reflux (1.5 hr) | 82 | 3–7.5 | 1.5815 | 62.50 | 6.99 | 62.18 | 6.86 |
| IId | $HOCH_2CH_2$ | Reflux (3.5 hr) | 81 | 1–5 | 1.6355 | 56.53 | 5.84 | 56.38 | 5.99 |
| IId | $HOCH_2CH_2$ | Reflux (3.5 hr) | 81[b] | 2–5 | | 56.53 | 5.84 | | |
| IIe | $HO_2CCH_2$ | Reflux (2 hr) | 74 | 125–126 | | 53.81 | 4.87 | 53.91 | 5.27 |

[a] Crude yield. [b] No acetic acid catalyst was used.

cene by reaction with alkanethiols in the presence of acetic acid according to the reaction shown. The success of this reaction probably depends on facile formation of ferrocenylmethyl carbonium ion, as did the direct formation of esters from carboxylic acids without mineral acid catalysis, as described previously.[6] The

$$C_5H_5FeC_5H_4CH_2OH + RSH \xrightarrow{HOAc} C_5H_5FeC_5H_4CH_2SR$$

Ia, R = $C_2H_5$ IIa, R = $C_2H_5$
b, R = $C_3H_7$ b, R = $C_3H_7$
c, R = $C_4H_9$ c, R = $C_4H_9$
d, R = $HOCH_2CH_2$ d, R = $HOCH_2CH_2$
e, R = $HO_2CCH_2$ e, R = $HO_2CCH_2$

ferrocenylmethyl ethyl, *n*-propyl, and *n*-butyl sulfides were prepared in 60–99% yield by heating hydroxymethylferrocene with a 50:50 mixture of water and the thiol in the presence of small amounts of acetic acid as a catalyst. The presence of the acetic acid catalyst is necessary for water-insoluble compounds since 1-butanethiol failed to react on prolonged heating with hydroxymethylferrocene and water. The fact that 2-mercaptoethanol gave high yields of ferrocenylmethyl 2-hydroxyethyl sulfide when heated with water and hydroxymethylferrocene with or without acetic acid indicates that the catalyst is unnecessary for water-soluble thiols. Although it has been reported previously that alcohols react with hydroxymethylferrocene in the presence of acetic acid to give ethers,[7] the only product isolated from the reaction of hydroxymethylferrocene and 2-mercaptoethanol was ferrocenylmethyl 2-hydroxyethyl sulfide.

It has also been reported that carboxylic acids react with hydroxymethylferrocene to give ferrocenylmethyl carboxylates.[6] However, when hydroxymethylferrocene was heated with mercaptoacetic acid, the only product isolated was ferrocenylmethyl carboxymethyl sulfide.

## Experimental Section

Melting points (uncorrected) were determined by obtaining heating curves on compounds IIa–IId. A Büchi apparatus was used for IIe. Infrared (ir) spectra were determined on a Perkin-Elmer Model 21 spectrophotometer.[8] A summary of experimental conditions and results is shown in the Table I.

**Ferrocenylmethyl *n*-Butyl Sulfide** (IIc).—A mixture of hydroxymethylferrocene (5.0 g, 0.023 mol), water (94 ml), 1-butanethiol (94 ml), and glacial acetic acid (4 ml) was heated at the reflux temperature for 1.5 hr with stirring. The reaction mixture was cooled to 10° and 200 ml of a cold 25% solution of aqueous sodium hydroxide was added slowly. The mixture was extracted with ether and the combined extracts were washed with water to neutrality and dried over magnesium sulfate. The mixture was filtered and the solvent was removed from the filtrate *in vacuo*. The orange liquid which was obtained was placed on a column containing Alcoa F-20 alumina and eluted with hexane. In this manner ferrocenylmethyl *n*-butyl sulfide (5.5 g, 82%) was obtained.

When hydroxymethylferrocene (5.0 g) was heated at the reflux temperature for 12 hr with water (20 ml) and with *n*-butyl mercaptan (20 ml), but without acetic acid, no reaction occurred.

**Ferrocenylmethyl 2-Hydroxyethyl Sulfide** (IId).—Hydroxymethylferrocene (20.0 g, 0.092 mol), 2-mercaptoethanol (200 ml), water (200 ml), and glacial acetic acid (1 ml) were heated at the reflux temperature for 3.5 hr. The reaction mixture was poured into water. The oil which separated was taken up in ether and washed with 2 *N* sodium hydroxide, and then with water. The ethereal solution was dried over magnesium sulfate and concentrated *in vacuo*. The oil which was obtained was chromatographed on Alcoa F-20 alumina, using acetone–hexane mixtures, and 20.64 g of ferrocenylmethyl 2-hydroxyethyl sulfide was obtained (81% yield). Repetition without the acetic acid catalyst gave ferrocenylmethyl 2-hydroxyethyl sulfide in 81% yield. The ir spectra of the two products were identical.

**Ferrocenylmethyl Carboxymethyl Sulfide** (IIe).—Hydroxymethylferrocene (10.0 g, 0.046 mol), mercaptoacetic acid (100 ml), and water (100 ml) were heated at the reflux temperature for 2 hr. The reaction mixture was cooled to room temperature and poured into 800 ml of water. The precipitate was washed with water, taken up in ether, and extracted into 5% aqueous sodium hydroxide. Ferrocenylmethyl carboxymethyl sulfide (9.8 g, 74%) was isolated by neutralization (acetic acid), filtration, washing of the precipitate with water, and drying *in vacuo* (mp 125–126°). An authentic sample of ferrocenylmethyl carboxymethyl sulfide was prepared as reported in the literature (mp 126–127°, lit. mp 120–121°).[4] The identity of IIe was established by mixture melting point, 125–127°, and by comparison of ir spectrum with that of an authentic sample.[4]

**Registry No.**—Hydroxymethylferrocene, 1273-86-5; IIa, 12344-33-1; IIb, 12344-34-2; IIc, 12344-35-3; IId, 12344-32-0; IIe, 12154-77-7.

---

[6] C. S. Combs, C. I. Ashmore, A. F. Bridges, C. R. Swanson, and W. D. Stephens, *J. Org. Chem.*, **33**, 4301 (1968).

[7] A. N. Nesmeyanov, E. G. Perevalova, and Y. A. Ustynyuk, *Dokl. Akad. Nauk SSSR*, **133**, 1105 (1960); *Chem. Abstr.*, **54**, 24616 (1960).

[8] The authors wish to thank Mr. R. D. Giles and Mr. J. W. Blanks for technical assistance.

---

# Synthesis of Aliphatic Dinitrodienes

GERALD L. ROWLEY AND MILTON B. FRANKEL

*Research Division, Rocketdyne, A Division of*
*North American Rockwell Corporation,*
*Canoga Park, California 91304*

*Received December 13, 1968*

The synthesis of aliphatic dinitrodienes is of interest since there has been very little research done on conjugated dienes with two terminal electrophilic groups. The simplest dinitrodiolefin is 1,4-dinitro-1,3-butadiene (I), and two methods for the preparation of I have been

$$NO_2CH_2CH{=}CHCH_2NO_2 \xrightarrow{Cl_2} NO_2CH_2CHClCHClCH_2NO_2 \xrightarrow{Pb(OAc)_2} I$$