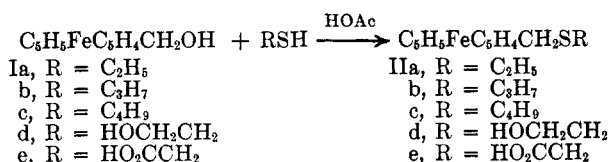


TABLE I
 EXPERIMENTAL RESULTS

Compd	R	Conditions	Yield, %	Mp, °C	n _D ²⁰	Calcd. %		Found, %	
						C	H	C	H
IIa	C ₂ H ₅	Reflux (72 hr)	60	8-14	1.6245	60.03	6.20	60.22	6.33
IIb	C ₃ H ₇	Reflux (1.5 hr)	99 ^a	6-8	1.6045	61.32	6.62	61.24	6.35
IIc	C ₄ H ₉	Reflux (1.5 hr)	82	3-7.5	1.5815	62.50	6.99	62.18	6.86
IIId	HOCH ₂ CH ₂	Reflux (3.5 hr)	81	1-5	1.6355	56.53	5.84	56.38	5.99
IIe	HO ₂ CCH 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



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

(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.

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 (IIId).—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; IIId, 12344-32-0; IIe, 12154-77-7.

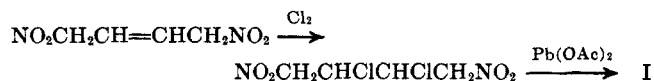
Synthesis of Aliphatic Dinitrodienes

GERALD L. ROWLEY AND MILTON B. FRANKEL

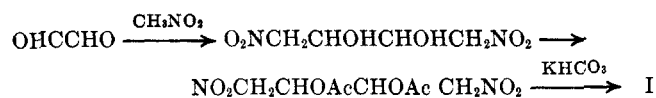
Research Division, Rocketdyne, A Division of
North American Rockwell Corporation,
Canoga Park, California 91304

Received December 13, 1968

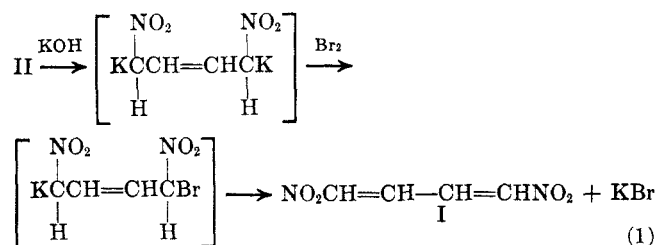
The synthesis of aliphatic dinitrodienes is of interest since there has been very little research done on conjugated dienes with two terminal electrophilic groups. The simplest dinitrodiolefin is 1,4-dinitro-1,3-butadiene (I), and two methods for the preparation of I have been



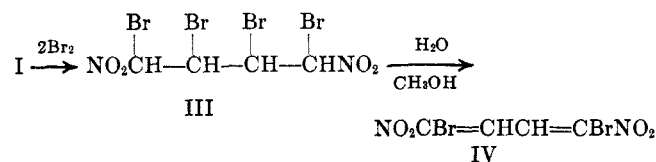
reported. In the first method, I is prepared from 1,4-dinitrobutene-2 (II), via the 2,3-dichloro-1,4-dinitrobutane.¹ In the second method, 2,3-dihydroxy-1,4-dinitrobutane is prepared from nitromethane and glyoxal, converted into the diacetate and deacylated to give I.² A simple one step, high yield reaction for the



preparation of I is now reported. It has been found that the treatment of II with potassium hydroxide and bromine gives a 79% yield of I. A probable mechanism for the formation of I is given in eq 1. Perekalin and



Lerner² reported that I was a highly stable compound and that it was only slowly brominated to a dibromide. We found that 2 mol of bromine can be added to I to yield 1,4-dinitro-1,2,3,4-tetrabromobutane (III). Treatment of III with aqueous methanol quantitatively yielded yellow needles (mp 126–127.5°). This product was identified by elemental and infrared analysis as 1,4-dibromo-1,4-dinitro-1,3-butadiene (IV). Infrared analysis indicated the compound was the 1,4-dibromo isomer as opposed to the 2,3-dibromo isomer by comparison of the wavelengths of its nitro absorptions to those of other analogous nitro compounds.³ Compound IV was apparently obtained by the facile dehydrohalogenation of the tetrabromo derivative (III), similar to the dehydrohalogenations of analogous aromatic substituted compounds.⁴



Experimental Section

Melting points are uncorrected. The infrared spectra were taken on mull samples with a Perkin-Elmer Infracord.

1,4-Dinitro-1,3-butadiene.—Methanolic potassium hydroxide (28.6 ml, 0.98 N) was added in small portions with stirring to 1,4-dinitrobutene-2 (2.05 g, 14 mmol) slurried in 15 ml of methanol, cooled to -10° . A small amount of precipitated dipotassium salt was dissolved by the addition of 15 ml of water to yield a dark solution. This cold solution and an equivalent volume of methanolic bromine solution (2.46 g, 15.4 mmol, 10% excess) were added dropwise simultaneously to 90 ml of water stirred at 0° . The solution became yellow and a yellow solid precipitated after several minutes. An excess of bromine was maintained at all times and the temperature was maintained at or somewhat below 0° . Stirring was continued for 1 hr after the final addition followed by pouring the mixture into 300 ml of water. The yellow solid was filtered, washed with several portions of water,

(1) V. V. Perekalin and O. M. Lerner, *D. Acad. Nauk SSR*, **129**, 1303 (1959).

(2) S. S. Novikov, I. S. Korsakova, and K. V. Babievskii, *Izv. Acad. Nauk SSSR*, 994 (1960).

(3) J. F. Brown, *J. Amer. Chem. Soc.*, **77**, 6341 (1955).

(4) P. Ruggli, *Helv. Chem. Acta.*, **23**, 718 (1940).

and dried *in vacuo* to yield 1.60 g (79%) with a decomposition melting point of 133–142°. Recrystallization from chloroform yielded pale yellow needles with a decomposition melting point of 145.5–147.5° (lit.¹ mp 147–148°). This compound is light sensitive and was stored in the dark, $\lambda_{\text{max}}^{\text{Nujol}}$ 6.7, 7.5 μ .

Anal. Calcd for $\text{C}_4\text{H}_4\text{N}_2\text{O}_4$: C, 33.34; H, 2.80. Found: C, 33.09, 32.96; H, 2.72, 2.89.

1,4-Dinitro-1,2,3,4-tetrabromobutane.—1,4-Dinitro-1,3-butadiene (10.79 g, 75 mmol) and bromine (26.4 g 165 mmol, 10% excess) were refluxed 1 hr in 125 ml of chloroform. (The reaction was protected from light by wrapping with aluminum foil.) An orange syrup was obtained on evaporation of solvent and excess bromine under reduced pressure. This syrup was extracted with multiple portions of boiling hexane until a small quantity of dark residue remained. Evaporation of the hexane under reduced pressure yielded an amber syrup (32.05 g, 92%). The syrup crystallized very slowly in the icebox after being seeded. Two recrystallizations from hexane yielded the analytical sample as colorless prisms: mp 83.5–84.5°; $\lambda_{\text{max}}^{\text{Nujol}}$ 6.4, 7.4 μ .

Anal. Calcd for $\text{C}_4\text{H}_4\text{Br}_2\text{N}_2\text{O}_4$: C, 10.36; H, 0.87. Found: C, 10.48, 10.37; H, 0.89, 0.76.

1,4-Dibromo-1,4-dinitro-1,3-butadiene.—1,4-Dinitro-1,2,3,4-tetrabromobutane (11.6 g, 25 mmol) was dissolved in 50 ml of methanol and 5 ml of water was added. The resulting yellow solution was allowed to stand 20 hr at ambient temperature. The yellow needles which had crystallized from solution were washed once with a small quantity of methanol and dried to yield 5.41 g, mp 125.5–127°. A second crop (0.72 g, mp 124.5–126.5°) was obtained by concentration of mother liquor to yield a total of 6.13 g (81%). One recrystallization of the first crop from methanol yielded the following analytical sample: mp 126–127.5°; $\lambda_{\text{max}}^{\text{Nujol}}$ 6.6, 7.7, 10.6, 12.7 μ .

Anal. Calcd for $\text{C}_4\text{H}_2\text{Br}_2\text{N}_2\text{O}_4$: C, 15.91; H, 0.67; N, 9.28. Found: C, 15.80, 15.76; H, 0.76, 0.65; N, 9.38.

Registry No.—I, 929-11-3; III, 868-21-3; IV, 868-79-1.

Acknowledgment.—The sponsor of this work was Air Force Armament Laboratory (AFATL), ATWT, Eglin AFB, Fla. 32542.

Solvolysis of Optically Active

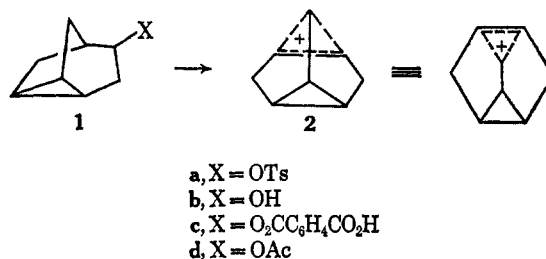
Tricyclo[3.2.1.0^{2,7}]octan-4-yl *p*-Toluenesulfonate

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Recent communications by Berson and coworkers regarding the solvolytic nature of optically active tricyclo[3.2.1.0^{2,7}]octan-4-yl *p*-bromobenzenesulfonate¹ prompted us to report our results of similar studies. We have studied the kinetics and stereochemistry of solvolysis of the optically active *p*-toluenesulfonate **1a** to determine the possible existence of the symmetrical bridged intermediate **2** and have found results in good



(1) (a) J. A. Berson, R. Bergman, G. M. Clarke, and D. Wege, *J. Amer. Chem. Soc.*, **90**, 3236 (1968); (b) *ibid.*, **90**, 3238 (1968).