Electrochemical Synthesis of 4,4,4-Trifluoro-2-butanone

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Electrolysis of solutions which contain trifluoroacetate ions generates trifluoromethyl radicals which may either combine to form hexafluoroethane or react with suitable organic cosolutes to form mixtures of trifluoromethylated derivatives.[1-7] When the cosolute is an olefin, it is often found that the principal product is either the corresponding 1,2-bis(trifluoromethyl) derivative[4,5] or a dimeric species resulting from the coupling of two radicals each formed from the olefin by addition of a trifluoromethyl radical at one end of the double bond.[4,6,7] However, it was found in this laboratory that the anodic trifluoromethylation of substrates containing the isopropenyl group leads mainly to monomeric products containing only one trifluoromethyl group.[8] Typically one obtains a mixture of saturated and unsaturated materials, the latter consisting of several isomers, e.g. eq 1 where X = alkyl, CH_2Cl, or $COOCH_3$. If desired, such a mixture can be hydrogenated to convert **3** and **4** to **2** which can then be isolated with a total yield of 15-20%, based on the olefin.

$$\underset{\mathbf{1}}{CH_2{=}C(CH_3)X} \rightarrow \underset{\mathbf{2}}{CF_3CH_2CH(CH_3)X} + \underset{\mathbf{3}\text{ (two isomers)}}{CF_3CH{=}C(CH_3)X} + \underset{\mathbf{4}}{CH_2{=}C(CH_2CF_3)X} \quad (1)$$

It is now reported that when partially neutralized trifluoroacetic acid is electrolyzed in the presence of isopropenyl acetate, the trifluoromethylated material is almost entirely 4,4,4-trifluoro-2-butanone (**5**). Fluorine NMR spectra of samples taken during the electrolysis indicate that possible intermediates such as the enol acetate of **5** are too short-lived to be easily detected and that only trace amounts of fluorine-containing byproducts are formed if the electrolysis is not excessively prolonged. Compound **5** has been made previously by the hydration of 1,1,1-trifluoro-2-butyne,[9] which, however, is not readily available. The electrochemical method now provides a convenient one-step synthesis of this ketone.

As reported earlier,[9] **5** promptly forms a 2,4-dinitrophenylhydrazone, but it failed to condense with malonic acid or malonic ester under mild conditions in which the unfluorinated analogue, 2-butanone, would react. However, by use of the procedure of Cragoe et al.,[10] **5** could condensed with ethyl cyanoacetate, and hence it can serve as the starting material for the preparation of a variety of other trifluoromethylated compounds.[11]

Experimental Section

Commercial trifluoroacetic acid, isopropenyl acetate, and acetone were used as received. In a typical run, 33 mL (300 mmol) of isopropenyl acetate and 30 mL (389 mmol) of trifluoroacetic acid were dissolved in 180 mL of acetone and 20 mL of water containing 1.6 g (40 mmol) of sodium hydroxide. If the water was not included in the mixture, electrolysis soon caused it to turn dark brown, and the electrodes became coated with a brown resinous material. Electrolyses were carried out with stirring in a 500-mL bottle loosely stoppered with a plug of cotton and cooled in a water bath to keep the temperature from rising much above 25 °C. The electrodes consisted of two spirals of no. 20 platinum wire mounted coaxially and about 0.6 cm apart. It was usually convenient to pass a current of 0.6-0.7 A through the cell for 24 h, providing about 0.6 faradays. The current density could be varied over a wide range without significantly affecting the course of the reaction.

The nearly colorless reaction mixture was poured into 700 mL of water and the product extracted into methylene chloride. The resulting solution contained considerable amounts of acetic and trifluoroacetic acids and was washed with 15% aqueous potassium carbonate until the pH of the aqueous layer was between 7 and 8 and then with water and dried. Such solutions from four identical runs were combined and distilled. When most of the low-boiling material (methylene chloride and acetone) had been removed, 150 mL of *n*-butyl ether was added. Unless such a dilutant was present, the yield was reduced owing to partial pyrolysis of the product during the subsequent distillation. A fraction (25.5 g) boiling from 93 to 98 °C (mostly 94.5-96 °C) consisted of nearly pure **5** (lit.[9] bp 95-96 °C): ^1H NMR ($CDCl_3/Me_4Si$) δ 3.24 (q, J = 10.6 Hz), 2.28 (s). The spectrum indicated a purity of better than 90%; the mixture appeared to contain about 5% *n*-butyl ether and traces of unidentified impurities but no isopropenyl acetate. The initially colorless product gradually turns yellow on storage, even at -15 °C. The ^{19}F NMR of a 1% solution, by volume, in $CHCl_3$ showed the expected triplet (J = 10.6 Hz) 0.59 ppm upfield from external 1,1,2-trichloro-3,3,3-trifluoropropene, the exact shift being strongly solvent and concentration dependent. Distillation of the adjacent fractions gave about 5 g more of similar material, bringing the total yield to about 18%, based on isopropenyl acetate. The 2,4-dinitrophenylhydrazone melted at 130.5-131.5 °C uncor (lit.[9] mp 131-132 °C).

Registry No. **5**, 2366-70-3; trifluoroacetic acid, 76-05-1; isopropenyl acetate, 108-22-5.

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(11) Muller, N., paper in preparation.

High Enantioselectivity in Reductions with a Chiral Polymethylene-Bridged Bis(NADH) Model Compound

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Recently, we reported that the *p*-xylylene-bridged chiral bis(NADH) model compound carrying L-prolinamide as the asymmetric center showed virtually complete stereoselectivity in the asymmetric reduction of ethyl benzoylformate and acetylpyridine. The origin of the enantiospecificity was tentatively ascribed to the specific blockage of diastereotopic faces of the dihydronicotinamide nuclei due to the probable C_2 conformation the model adopts in association with the catalyst magnesium.[1]

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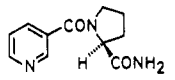
Table I. Physical Constants of Polymethylene Bridged Bis(NAH)s

bis(NAH)	$[\alpha]^{25}_D$ (c, $CHCl_3$)	UV ($CHCl_3$) λ_{max}, nm (ϵ)
8	−59.3 (2.96)	348 (109 00)
9	−37.8 (3.76)	349 (121 00)
10	−42.1 (1.68)	350 (101 80)
11	−8.1 (3.05)	350 (124 30)
12	−22.8 (5.55)	354 (103 40)
13	−10.4 (2.40)	353 (118 30)

To obtain a better insight into the stereospecificity in the asymmetric system, we turned our attention to the novel bis(NADH) model compounds in which two chiral 1,4-dihydronicotinamide units were spanned with a polymethylene bridge of varying chain length, instead of the xylylenes.

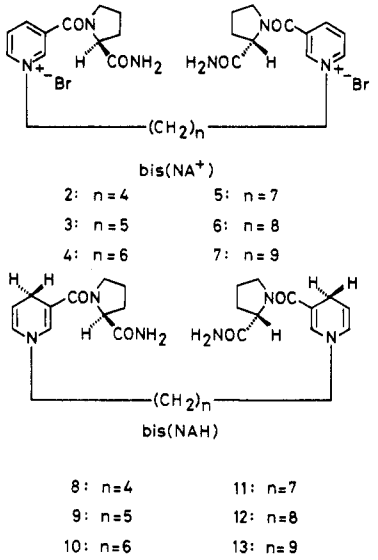
The bis(NAH) derivatives were prepared by quaternization of the nicotinic acid derivative of L-prolinamide (1)



1

with 1,n-dibromoalkanes followed by sodium dithionite reduction. Their physical properties are given in Table I. The ^1H NMR spectra of the models were very similar to that of the p-xylylene-bridged bis(NAH)[1] and are left out in this report.

The asymmetric reduction with the bis(NAH) reductants **8–13** was carried out in a mixture of dry acetonitrile



bis(NA^+)

2: n=4 5: n=7
3: n=5 6: n=8
4: n=6 7: n=9

bis(NAH)

8: n=4 11: n=7
9: n=5 12: n=8
10: n=6 13: n=9

and dry chloroform in the presence of equimolar amounts of anhydrous magnesium perchlorate and the substrate at room temperature or at 50 °C for 17–96 h in the dark.

As can be seen from Table II, the optical yields of the product mandelate of the R configuration in runs 1–6 varied greatly with the change in the chain length of methylene bridges. Thus in the reduction with **10** (n = 6) the maximum enantiomeric excess (ee; 95.6%) was attained nearly at a 1:1 ratio of $Mg(ClO_4)_2$/**10**, and the ee remained constant with further increases in the catalyst amount (Figure 1) as found with the p-xylylene-bridged bis(NAH).[1] The molar ratio method by UV spectroscopy (Figure 2) corroborated the formation of a 1:1 chelation

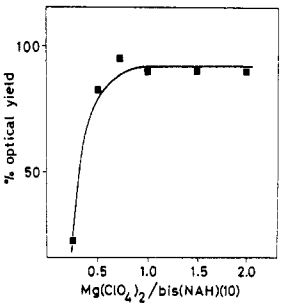


Figure 1. Dependence of the enantiomeric excess on the relative concentration of magnesium perchlorate.

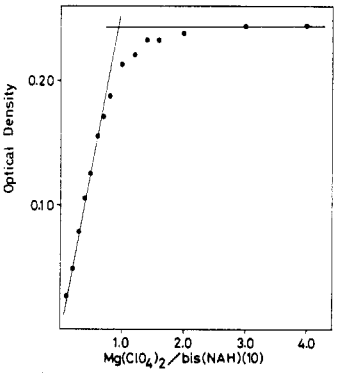


Figure 2. Mole ratio determination for complexation between the bis(NAH) **10** and magnesium perchlorate by UV spectroscopy at 390 nm in a mixture of acetonitrile and chloroform (3:1).

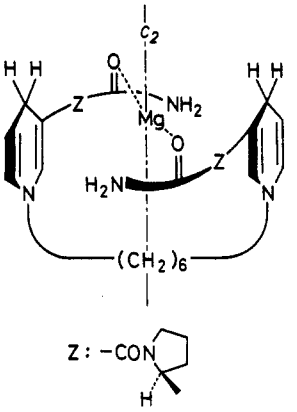


Figure 3. Schematic representation of a reaction species with C_2 symmetry.

complex between **10** and magnesium. The present findings show that the two chiral 1,4-dihydronicotinamide nuclei carrying L-prolinamide in the bis(NAH) molecule do not operate independently but that they interact with each other probably in an *intramolecular* way through the metal ion chelation just as was also the case with the p-xylylene-bridged reductant. The topology must be sensitive to the structural change of the bridging chain and is reflected in the enantioselectivity as observed in the asymmetric reduction of ethyl benzoylformate.

The stereochemical outcome obtained by the application of **10** to other prochiral substrates (Table II) compared very well with respect to configuration (R) and chemical and optical yields with those found for the reduction by the use of the p-xylylene-bridged bis(NAH). However, the enantiomeric excesses observed for the substrates **16** and **18–20** were found to be moderate or poor as compared with other cases. This may be attributable to the difference in mechanism of hydrogen transfer and/or the structural factors inherent in the substrate molecules to control the

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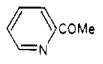
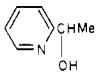
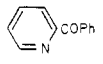
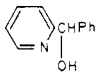
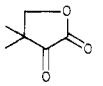
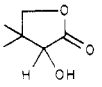
Table II. Asymmetric Reduction of Prochiral Substrates with Bis(NAH)s 8-13

run	bis(NAH)	substrate	product	% chemical yield	$[\alpha]^{25}_D$, (c) deg	config	% ee	ref
1	8	PhCOCOOEt (15)	PhCH(OH)COOEt (21)	50.4	−41.7 (0.37[a])	R	39.9	g
2	9	15	21	73.4	−44.9 (0.46)	R	43.0	
3	10	15	21	63.5	−99.8 (0.46)	R	95.6	
4	11	15	21	57.9	−61.3 (1.50)	R	58.7	
5	12	15	21	63.2	−84.8 (1.92)	R	81.2	
6	13	15	21	65.5	−66.6 (1.34)	R	63.8	
7	10	 16	 22	84.3	−37.8 (9.39[a])	R	66.7	h
8	10	 17	 23	67.0	−114.6 (2.81[b])		92.7[f]	i
9	10	Ph(Me)C=C(CN)$_2$ (18)	PhCH(Me)CH(CN)$_2$ (24)	59.2	+4.3 (0.93[c])	R	24.5	j
10	10	 19	 25	65.7	−17.2 (1.10[d])	R	33.9	k
11	10	PhCOCF$_3$ (20)	PhCH(OH)CF$_3$ (26)	13.7	−1.8 (0.67[e])	R	13.4	l

[a] Dry ethanol. [b] Chloroform. [c] 95% ethanol. [d] Water. [e] Benzene. [f] The specific rotation (−114.6°) found for the carefully purified and fully characterized reduction product, α-pyridylbenzyl alcohol (run 8), was by far higher than the reported maximum value (86.2°).[3] However, the ^{19}F NMR (99.6 MHz) analysis of Mosher's MTPA ester[4] of the alcohol unequivocally established its optical purity to be 92.7%. [g] Roger, R. *J. Chem. Soc.* **1932**, 2168. [h] Imuta, M.; Ziffer, H. *J. Org. Chem.* **1978**, *43*, 3530. [i] Davies, A. G.; Kenyon, J.; Thaker, K. *J. Chem. Soc.* **1956**, 3394. [j] Cabaret, D.; Welvart, Z. *J. Organomet. Chem.* **1974**, *80*, 199. [k] Stiller, E. T.; Harris, S. A.; Finkelstein, J.; Keresztesy, J. C.; Folkers, K. *J. Am. Chem. Soc.* **1940**, *62*, 1785. [l] Jurczak, J.; Konowal, A.; Krawczyk, Z. *Synthesis* **1977**, 258. Peters, H. M.; Feigel, D. M.; Mosher, H. S. *J. Org. Chem.* **1968**, *33*, 4245.

Table III. Analytical Data for the Oxidized Forms 2-7

compd	found, % C	found, % H	found, % N	calcd for	calcd, % C	calcd, % H	calcd, % N
2	47.36	5.93	13.58	$C_{26}H_{34}N_6Br_2O_4$	47.72	5.24	12.84
3	47.71	6.01	13.44	$C_{27}H_{36}N_6Br_2O_4$	48.52	5.43	12.57
4	48.41	6.25	12.57	$C_{28}H_{38}N_6Br_2O_4$	49.28	5.61	12.31
5	48.95	6.28	12.20	$C_{29}H_{40}N_6Br_2O_4$	50.01	5.79	12.07
6	50.10	6.58	12.23	$C_{30}H_{42}N_6Br_2O_4$	50.71	5.96	11.83
7	49.82	6.33	11.47	$C_{31}H_{44}N_6Br_2O_4$	51.39	6.12	11.60

discrimination between the enantiotopic faces to a different extent for individual cases.

The present findings in the asymmetric reduction with the polymethylene-bridged bis(NAH) provide further evidence that a close face-to-face C_2 conformation (Figure 3) of the two juxtaposed equivalent dihydronicotinamide units, with their specific identical faces disposed toward the outside for the attack on substrates, seems to be the primary steric requirement for a high enantioselectivity in a asymmetric reduction of this type. It is also noted that this specific blockage of the dihydronicotinamide faces is relevant to the stereochemical aspect of alcohol dehydrogenase reaction, in which only one specific dihydronicotinamide face of the coenzyme is accessible to the substrate and thus controls the steric course of the hydrogen transfer in biological systems.[4]

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Experimental Section

UV, IR, ^{1}H NMR, and ^{19}F NMR spectra were recorded on Hitachi 340, Hitachi 215, Varian EM-360, and JEOL JNM FX-100 spectrometers, respectively. The optical rotations were measured on a Perkin-Elmer 241 polarimeter. Shimadzu GC-4B and GC-4CM gas chromatographs with 5% polyethylene glycol succinate were used for VPC analyses. Preparative VPC was performed on a Varian Aerograph Model 920. Elemental analyses were done on a Yanagimoto CHN Corder MT-3. Melting points were uncorrected.

***N*-Nicotinoyl-(*S*)-prolinamide (1).** A solution of *N*-nicotinoyl-(*S*)-proline ethyl ester (50.0 g, 0.20 mol) in dry methanol (400 mL) was saturated with dry ammonia at −5 °C and was allowed to stand for 10 days at 40 °C. Evaporation of the solvent gave the amide 1: 37.4 g (96.2%); colorless crystals; mp 87–88 °C; $[\alpha]^{25}_D$ −104.7° (methanol, *c* 4.085). Anal. Calcd for $C_{11}H_{13}N_3O_2 \cdot H_2O$: C, 55.69; H, 6.37; N, 17.71. Found: C, 55.50; H, 6.34; N, 18.30.

Preparation of the Oxidized Forms 2–7. A solution of *N*-nicotinoyl-(*S*)-prolinamide (1, 2.5 mmol) and 1,*n*-dibromoalkane (1.5 mmol) in acetonitrile (6 mL) was refluxed for 48 h. The

amorphous solid which separated from the reaction mixture was collected on a funnel and washed with acetonitrile. The bromides could not be purified due to their intense hygroscopic nature and were submitted as obtained to the reductions. Analytical data are given in Table III.

Preparation of the Bis(NAH)s 8–13. Sodium dithionite (12.5 g, 85% purity, 61 mmol) was added to a solution of the bis(nicotinium)dibromides **2–7** (2 mmol) in a carbon dioxide saturated solution of sodium bicarbonate (3 g, 36 mmol) in water (50 mL), and the mixture was stirred vigorously. When foaming had ceased, additional water (50 mL), anhydrous sodium carbonate (17.5 g, 165 mmol), and chloroform (100 mL) were added, and the mixture was stirred for 5 h at ambient temperature in the dark. The chloroform layer containing the bis reductant was washed with water, dried over anhydrous sodium sulfate, and used as such for the asymmetric reduction of substrates. The bis reductants showed a single spot on TLC analysis (Kieselgel 60F_{254}, Merck Art. 5714, chloroform–methanol) with characteristic fluorescence of dihydronicotinamide.

Procedure for Asymmetric Reduction of Substrates. A solution of the bis reductant (0.35 mmol), anhydrous magnesium perchlorate (0.35 mmol), and substrate (0.35 mmol) in a mixture of dry acetonitrile (60 mL) and dry chloroform (20 mL) was stirred at room temperature for 17 h in the dark. After the reaction was quenched by addition of water, the reduction product was extracted with methylene chloride or ether. Isolation procedures are as follows: for **21**, see ref. 1; for **22**, purification by preparative VPC (5% polyethylene glycol succinate, 120 °C); for **23**, liquid chromatography (Kieselgel 60, 230–400 mesh) eluted with benzene–ethyl acetate; for **24**, preparative VPC (20% Apiezon L, 170 °C); for **25**, preparative VPC (2% silicon DC QF-1, 150 °C); for **26**, preparative VPC (20% Apiezon L, 130 °C).

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Registry No. **1**, 85084-02-2; **2**, 85084-03-3; **3**, 85084-04-4; **4**, 85084-05-5; **5**, 85096-99-7; **6**, 85097-00-3; **7**, 85097-01-4; **8**, 85084-06-6; **9**, 85084-07-7; **10**, 82946-92-7; **11**, 82946-93-8; **12**, 82946-94-9; **13**, 82946-95-0; **15**, 1603-79-8; **16**, 1122-62-9; **17**, 91-02-1; **18**, 5447-87-0; **19**, 13031-04-4; **20**, 434-45-7; **21**, 10606-72-1; **22**, 27911-63-3; **23**, 5583-33-5; **24**, 61925-48-2; **25**, 599-04-2; **26**, 10531-50-7; *N*-nicotinoyl-(*S*)-proline ethyl ester, 85097-02-5.

Nitromethylation of Alkenes

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Radical additions to alkenes have been studied extensively, in large part due to their importance to the polymer industry.[1] Carbon radicals, generated by manganese(III)- or cerium(IV)-promoted oxidative deprotonation of carboxylic acids,[2,3] acetone,[4,5] and other carbonyl compounds[5–7] have been added to olefins to give a variety of products with a larger carbon skeleton.[8] A number of these same radicals have been substituted onto simple aromatic compounds under similar conditions.[5,9–11] Recently we discovered that a similar oxidative deprotonation process could be used to generate nitromethyl radicals from nitromethane and successfully substitute them onto aromatic hydrocarbons.[12–14] The goal of this study was to explore the reaction of nitromethyl radicals, generated by way of oxidative deprotonation, with various olefins.

Table I. Nitromethylation of Alkenes[a]

alkene	products	yield, % $Mn(OAc)_3$ + $Cu(OAc)_2$	yield, % $Mn(OAc)_3$
cyclohexene	3-(nitromethyl)-cyclohexene	38	
	1-(nitromethyl)-cyclohexene	2	
	cyclohexen-3-yl acetate	8	8
cyclopentene	3-(nitromethyl)-cyclopentene	11	
	1-(nitromethyl)-cyclopentene[a]	3	
	cyclopenten-3-yl acetate	3	
	cyclopenten-3-ol	7	
1-pentene	pentenyl acetates	9	8
1-octene	minor products[b]		
styrene	minor products[b]		
α-methyl-styrene	1-nitro-3-phenyl-3-butyl acetate	35	32[c]
	nitromethylated α-methylstyrene[d]	8	6

[a] Tentative identification based on product mixture spectral properties. [b] Unidentified. [c] With $Ce(NH_4)_2(NO_3)_6$ (10 mmol) instead of $Mn(OAc)_3$ this product was found in 13% yield, and additional byproducts were produced. [d] Tentative, could be side chain or nuclear substitution product.

Results

Excess alkene, nitromethane, and acetic acid were refluxed with manganese(III) acetate as the limiting reagent until complete reduction to manganese(II) occurred. A second series of reactions with a copper(II) acetate additive (equimolar to manganese(III) acetate) was also carried out. The products and yields obtained after the workup are summarized in Table I.

Cycloalkenes. Low yields of products not containing a nitro group resulted when either cyclohexene or cyclopentene were reacted with nitromethane and manganese(III) acetate. In the former case the only product formed to any extent (8%) was cyclohexen-3-yl acetate. In the latter, just trace quantities of unidentified compounds resulted. However, when copper(II) acetate was included as a cooxidant the products changed rather dramatically. The major product from cyclohexene was identified as 3-(nitromethyl)cyclohexene (38%) on the basis of its NMR and IR spectra and elemental analysis. A minor amount of 1-(nitromethyl)cyclohexene was also found. The analogous nitromethylated products [3-(ni-

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