Atropisomeric Alkenyl Cobaloximes. Stereochemical Study of the Vinyl Halide Substitution by Transition-Metal Complexes

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Abstract: The first example of chiral atropisomeric cobaloximes in which the cobaloxime substituent inhibits the rotation around the naphthyl–vinyl bond is reported. These complexes were obtained by a substitution reaction of one of the enantiomers of methyl β-chloro-β-(2-methylnaphthyl)acrylate with cobaloxime(I). The reaction occurs with complete retention of the absolute configuration. A similar retention of chirality also occurs during the reaction of this β-chloro ester with lithium dimethylcuprate. The most likely mechanism for these reactions is a direct insertion of the transition-metal atom into the carbon–halogen bond.

A few examples of cobalt complexes made chiral because of hindered rotation of one of the ligands are already known: one of these contains an atropisomeric chiral *o,o'*-diaminodiphenyl group.[1] In a second example, the chirality results from the restricted rotation of an asymmetrically substituted aromatic group which lies perpendicular to the β-diketonate ring present in the complex.[2] More recently, an optically unstable chiral cobalt complex having a fixed propeller conformation was resolved as a diastereomer with an optically active acid.[3]

We report here the synthesis of atropisomeric complexes of a different type, in which the rotation of the atropisomeric ligand is inhibited by the cobaloxime substituent. These complexes were obtained by a nucleophilic substitution reaction between one of the optically active atropisomers of the β-chloroacrylic ester **1a** and the highly nucleophilic cobalt(I) complex: (pyridine)bis-(dimethylglyoximato)cobalt(I) or (pyridine)cobaloxime(I) (Scheme I). It is well-known that a number of d^8 and d^{10} transition-metal complexes, in particular cobalt(I) complexes, readily substitute vinyl halides[4] with retention of the *Z* or *E* configuration of the halide double bond.[5]

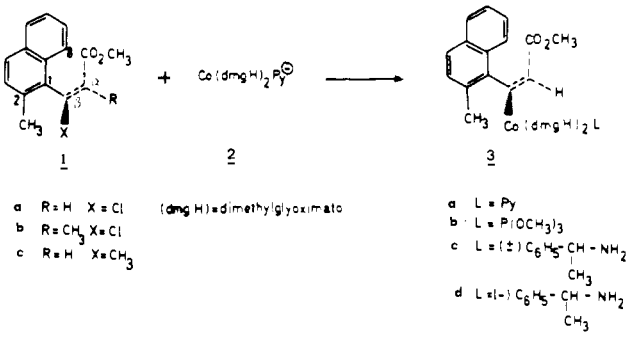
The reaction of **1a** with lithium dimethylcuprate was previously reported;[6] product **1c** was obtained in which the axial chirality was retained but its optical purity was not known. In order to clarify the genuine implications of these stereochemical results, we also tried more conventional nucleophiles than the Co(I) and Cu(I) complexes in this reaction, namely sodium iodide and dimethylamine. Study of the substitution reactions of vinylic halides showing restricted rotation[7] and/or optical activity[6,8] is expected to provide useful mechanistic information on this type of reaction.

Results

Both the enantiomers of the vinyl halides **1a** and **1b** are easily available with use of a slight modification[6] of the original procedure,[9] and the optical purity of the enantiomers of **1a** has been accurately measured.

Reactions of Lithium Dimethylcuprate with Esters 1a and 1b. $(CH_3)_2CuLi$ reacts with the levorotatory isomer of **1a** to give (−)-**1c** (see Table I for rotation and NMR data) and with the dextrorotatory isomer (85% enantiomeric purity) to give (+)-**1c** which has 83.5% of the rotation of the previously obtained (−)-**1c**. These results show that lithium dimethylcuprate reacts with the two enantiomers of **1a** with the same high stereospecificity. The enantiomeric purity of (−)-**1c** was determined by ^1H NMR with use of $Eu(dcm)_3$ as chiral shift reagent;[10] in the presence of the latter, the methoxy and the aromatic methyl protons of racemic (±)-**1c** both give rise to two singlets (Figure 1), whereas with (−)-**1c** only one singlet was observed for each group, showing an optical purity for this product higher than 95% (Figure 2). The substitution of the atropisomeric vinyl chloride (−)-**1a** by $(CH_3)_2CuLi$ thus occurs with *complete retention of the axial chirality*.

Scheme I



Substitution reactions on atropisomeric vinylic halides can occur either with retention of the absolute configuration or with racemization, depending on whether an intermediate is formed which can undergo free rotation.[11] Net inversion of configuration is not possible, and this feature has already been used to establish a chemical correlation between the absolute configuration of several atropisomeric diaryl compounds.[12] Compounds (−)-**1a** and (−)-**1c** have consequently the same absolute configuration, in agreement with the nearly identical CD curves of the two products (Table I).

Reaction of (Pyridine)cobaloxime(I) (2) with the β-Chloro-

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(1) Lions, F.; Martin, K. V. *J. Am. Chem. Soc.* **1957**, *79*, 1273. O'Connor, M. J.; Ernst, R. E.; Holm, R. H. *Ibid.* **1968**, *90*, 4561. Holm, R. H. *Acc. Chem. Res.* **1969**, *2*, 307 and references cited therein.
(2) Nakano, Y.; Seki, H. *Chem. Lett.* **1976**, 611. Nakano, Y.; Sato, S. *Bull. Chem. Soc. Jpn.* **1982**; *55*, 1683.
(3) Utsuno, S. *J. Am. Chem. Soc.* **1982**, *104*, 5846.
(4) Parshall, G. W.; *J. Am. Chem. Soc.* **1974**, *96*, 2360. Mc Keon, J. E. *J. Chem. Soc. D* **1968**, 4 and 6. Ibers, J.; Rajarah, J.; Pearson, R. *J. Am. Chem. Soc.* **1974**, *96*, 2103. Fahey, D. R.; Mahan, J. E. *Ibid.* **1977**, *99*, 2501. Morrell, D. G.; Kochi, J. K. *Ibid.* **1975**, *97*, 7262. Stille, K. H.; Lau, K. S. Y. *Acc. Chem. Res.* **1977**, *10*, 434. Halpern, J. *Ibid.* **1970**, *3*, 386. Semmelhack, M. F.; Hequist, P.; Jones, L. D.; Keller, L.; Mendelson, L.; Ryono, L. F.; Smith, J. G.; Stauffer, R. D. *J. Am. Chem. Soc.* **1981** *103*, 6460 and references cited therein.
(5) (a) Schrauzer, G. N.; Windgassen, R. J. *J. Am. Chem. Soc.* **1967**, *89*, 1999. (b) Duong, K. N. V.; Gaudemer, A. *J. Organomet. Chem.* **1970**, *22*, 473. (c) Johnson, M. D.; Meeks, B. S. *J. Chem. Soc. B* **1971** 185. (d) Dodd, D.; Johnson, M. D.; Meeks, B. S.; Titchmarsh; Duong, K. N. V.; Gaudemer, A. *J. Chem. Soc. Perkin Trans. 2* **1976**, 1261.
(6) Cabaret, D.; Maigrot, N.; Welvart, Z. *J. Organomet. Chem.* **1979**, *182*, 257.
(7) Leung, P. T.; Curtin, D. Y. *J. Am. Chem. Soc.* **1975**, *97*, 6799.
(8) Rappoport, Z.; Greenblatt, J. *J. Am. Chem. Soc.* **1979**, *101*, 1343.
(9) Adams, R.; Binder, L. O. *J. Am. Chem. Soc.* **1941**, *63*, 2773.
(10) McCreary, M. D.; Lewis, D. W.; Wernick, D. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 1038.
(11) Detar, D. F.; Haward, J. C. *J. Am. Chem. Soc.* **1955**, *77*, 4393.
(12) Mislow, K. *Angew. Chem.* **1958**, *70*, 683.

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Table I. ^{1}H NMR, Optical Rotation, and Circular Dichroism Data

compd	chemical shifts ($CDCl_3$, Me_4Si), ppm					$[\alpha]^{22}_{546}$, deg	$[\alpha]^{22}_{578}$,[a] deg	D.C. λ, nm (Δε)
	H_α	CO_2CH_3	$CH_3(C_\beta)$	$CH_3(C_\alpha)$	CH_3(dmgH)			
1a	6.67	3.40	2.47			−108.3	−89.5	206 (+88), 228 (−116)[b]
1b		3.21	2.40	2.38		98.8	83.4	
1c	6.54	3.60	2.45			−208	−178	207 (−151), 229 (+119)[b]
(±)-1c[c]	9.72–9.84	6.07–6.14	3.00–3.05					
(−)-1c[c]	9.60	6.05	2.97					
3a	6.08	3.42	2.08		1.81–2.08	+110	+182	230 (−25.4), 332 (+3.3) 370 (+5.1), 458 (−1.50)
3b	5.85[d]	3.40	2.04		1.85–1.95			
3c	5.89–5.90	3.30	1.98		1.67–1.71–1.96–1.98			
3d	5.90	3.30	1.95		1.68–1.98	+136	+160	

[a] c = 0.6–2, EtOH 95%. [b] c = 0.22 g L^{-1}, MeOH. [c] Plus 1 equiv of $Eu(dcm)_3$, CCl_4. [d] J_{PH} = 12 Hz.

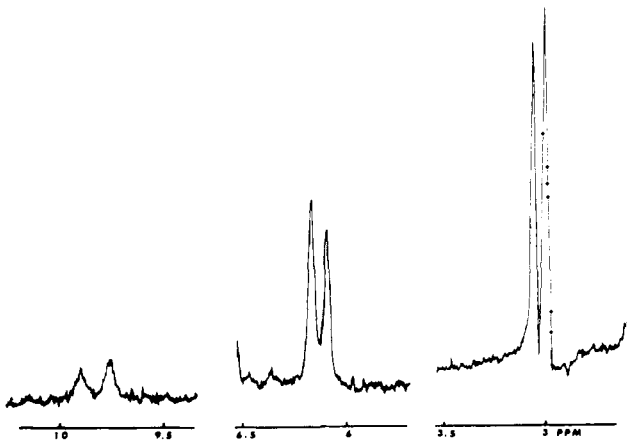


Figure 1. High-field part of the ^{1}H NMR spectrum of (±)-**1c** in the presence of 1 equiv of $Eu(dcm)_3$ (90 MHz).

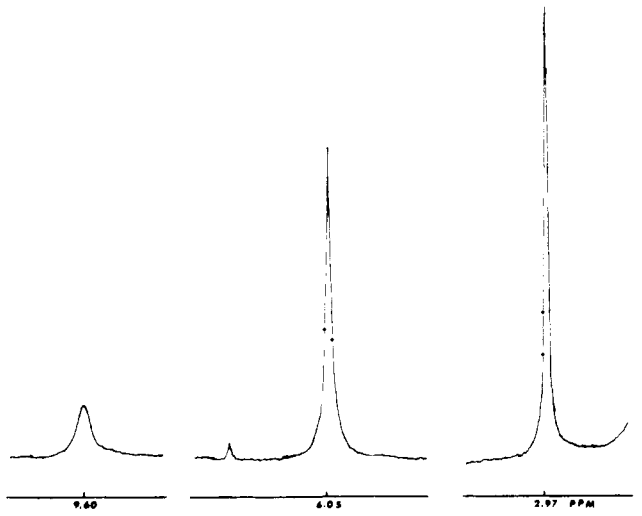


Figure 2. High-field part of the ^{1}H NMR spectrum of (−)-**1c** in the presence of 1 equiv of $Eu(dcm)_3$ (90 MHz).

acrylate (1a). (Pyridine)cobaloxime(I) (**2**), prepared by the method of Schrauzer et al.,[5a] reacts with the chloride (−)-**1a** (90% enantiomeric purity) to give the alkenyl cobaloxime **3a** (yield 88%), the structure of which is unambiguously deduced from its NMR spectrum (Table I).

One set of signals is observed for the methyl, methoxy, and vinyl protons, supporting the presence of only one stereoisomer, in agreement with previous results.[5] As expected for a cobaloxime having a chiral ligand, two singlets corresponding to six protons each are observed for the diastereotopic methyl groups of the dioximato moiety.[13] The shielding of these protons, compared

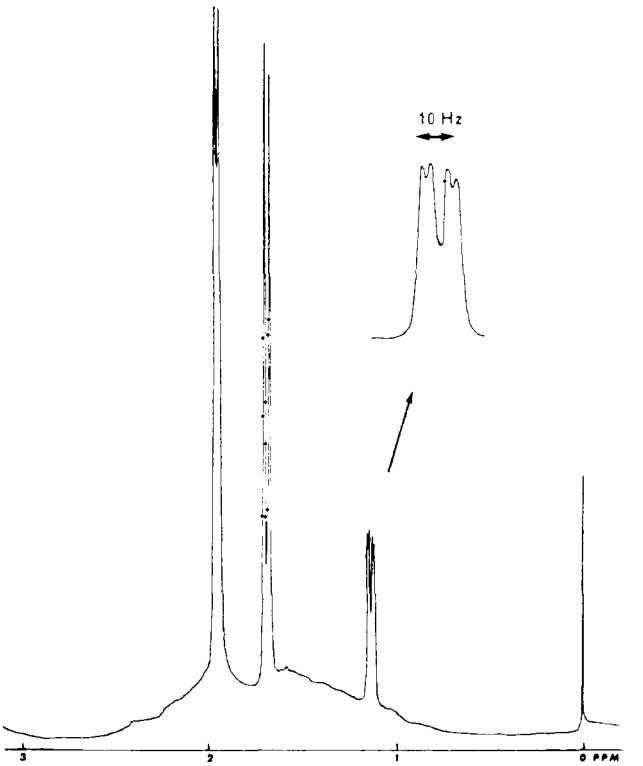


Figure 3. High-field part of the ^{1}H NMR spectrum of **3c** (250 MHz).

to analogous protons in other cobaloximes, arises from their close proximity to the naphthyl group, which according to molecular models lies approximatively parallel to the plane of the equatorial ligands.

The configuration of the double bond in **3a** was deduced from the NMR spectrum of complex **3b** obtained by substitution of the pyridine ligand by $P(OCH_3)_3$. In this spectrum the vinyl proton appears as a doublet due to the spin–spin coupling with ^{31}P, and the value of the coupling constant (J_{PH} = 12 Hz) is compatible only with a *cis* orientation of this proton with respect to the cobalt atom.[14]

Optical rotation measurement shows that complex **3a** is optically active. We were able to estimate the optical purity of complex **3a** by substituting either racemic or optically active (−)-phenyl-1-ethylamine (ee 95%) (respectively complexes **3c** and **3d** (Scheme I)).

The NMR spectrum ($CDCl_3$ 250 MHz) of complex **3c** (with racemic amine) showed, as expected, four singlets of equal intensity for the diastereotopic dimethylglyoxime methyl groups, this compound being a 1:1 mixture of diastereomers (Figure 3). This was confirmed also by observation of two doublets for the amine CH_3 group and of two singlets for the vinylic H_β proton.

(13) Naumberg, M.; Duong, K. N. V.; Gaudemer, F.; Gaudemer, A. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1970**, *270*, 1301.

(14) Naumberg, M.; Duong, K. N. V.; Gaudemer, A. *Tetrahedron Lett.* **1970**, 231.

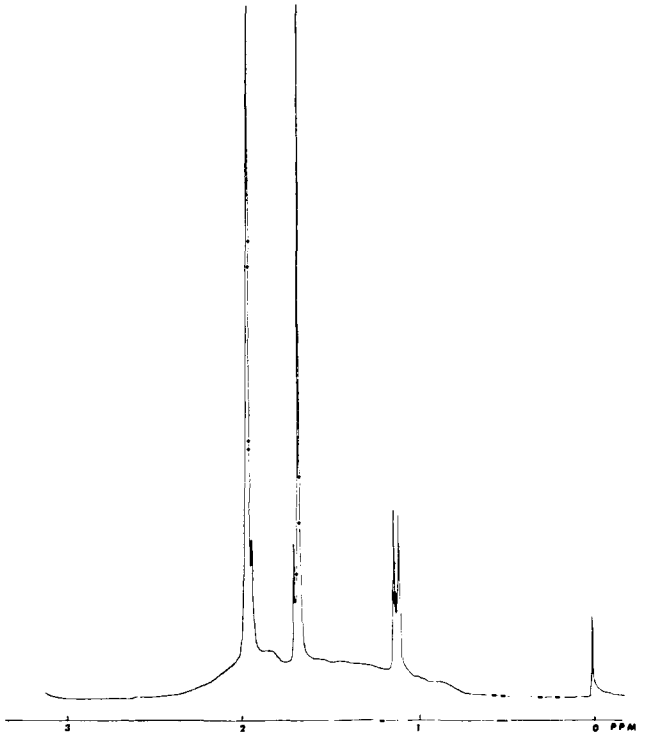


Figure 4. High-field part of the ^1H NMR spectrum of **3d** (250 MHz).

By contrast complex **3d** with (-)-phenyl-1-ethylamine showed in its spectrum two intense and two weak (ca. 10% of the former ones) CH_3 (dmg H) singlets and unsplit signals for the amine methyl group and the vinylic protons. We can therefore conclude that the enantiomeric excess of complex **3** must be at least 80% (Figure 4).

The expected retention of configuration in this substitution of an atropisomeric reagent[11,12] is confirmed by the CD curves of reagent **1a** and product **3a** which show the Cotton effect of the same sign at 230 nm (Table I).

Finally, we attempted the substitution of the reagent **1a** with the more conventional nucleophiles sodium iodide and dimethylamine and also the substitution of vinyl halide **1b** with the Co(I) and Cu(I) complexes, but these reactions proved unsuccessful even after several hours (however, the recovered unreacted chloride **1a** had racemized probably because of prolonged heating).

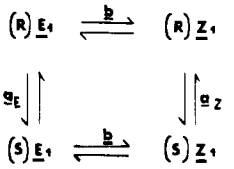
In conclusion, our results demonstrate that the substitution reaction of reagent **1a** either by lithium dimethylcuprate or by (pyridine)cobaloxime(I) occurs with complete retention of configuration whereas the vinylic substitution failed with other nucleophiles and also with reagent **1b**.

Discussion

The easy substitution reaction of the atropisomeric vinyl chloride **1a** with cobaloxime(I) occurs with complete retention of the axial chirality and constitutes a useful method for preparing chiral atropisomeric metal complexes. The alkenyl cobaloximes **3** reported here are the first examples of optically active atropisomers in which the metal atom directly participates in the conservation of the chirality.[15]

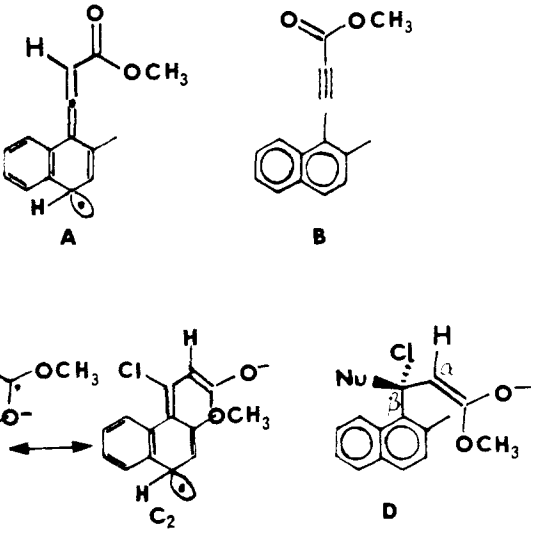
Scheme II depicts the stereochemical changes associated with rotations around the naphthyl–vinyl bond (a) or around the C_α–C_β bond (b): rotation a interconverts the *R* and *S* enantiomers (change of axial chirality), whereas rotation b exchanges the *E* and *Z* configurations of the double bond. Considering the halide **1a**, the rotation process a_Z is expected to be much faster than a_E because the steric interaction between the $COOCH_3$ and the

Scheme II



aromatic methyl group or the peri CH of the second aromatic nucleus is much more severe than the one between H_α and the same groups. Therefore if the configuration of the double bond changes from *Z* to *E* it should be accompanied by a fast racemization. With compounds such as **1a**, the two stereoisomerisms which are present, rotational enantiomerism (atropisomerism) and geometrical isomerism, are not independent from each other. Such systems provide suitable models for the study of the mechanism of displacement reactions occurring at vinylic carbon atoms. The mechanistic pathway for the reactions between the atropisomeric halide **1a** and the Co(I) or Cu(I) derivatives should explain the stereochemical results, i.e., the retention of both the axial chirality and the *E* configuration, but should also take into account the complete lack of reaction of this halide with the more usual nucleophiles: I^- and dimethylamine.

Mechanisms of the Vinylic Substitution. Several mechanisms have been previously considered for vinylic substitutions:[16] nonconcerted mechanisms among which elimination–addition and addition–elimination mechanisms and other mechanisms involving radical[17] or radical-anion intermediates.[18] The various intermediates which could be formed by such mechanisms from **1a** are shown below.



From the retention of configuration observed during the substitution reactions with **1a**, it is possible to preclude radical intermediates such as A, which, like the α-styryl radical[20] and the vinylic cations,[8,21] should have a linear structure in which the axial asymmetry present in the chloride **1a** is lost.

(15) The transformation of the atropisomeric 2,2',4,4'-tetrabromo-3,3'-bithienyl into the dilithiated reagent, followed by carboxylation, involves complete racemization (Hakansson, R.; Wiklund, E. *Acta Chem. Scand.* **1971**, *25*, 2109). Obviously we have no information available on the actual size and role of metals in the hindered rotations.

(16) (a) de la MARE, P. B. D. *Prog. Stereochem.* **1958**, *2*, 90. Patai, S.; Rappoport, Z. "The Chemistry of Alkene"; Interscience: London, **1964**; p 469. (b) Rappoport, Z. *Adv. Phys. Org. Chem.* **1969**, *7*, 1 (c) Modena, G. *Acc. Chem. Res.* **1971**, *4*, 73. (d) Miller, S. I. *Tetrahedron* **1977**, *33*, 1211. (e) Rappoport, Z. *Acc. Chem. Res.* **1981**, *14*, 7.

(17) Whitesides, G. M.; Casey, C. P.; Krieger, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 1379.

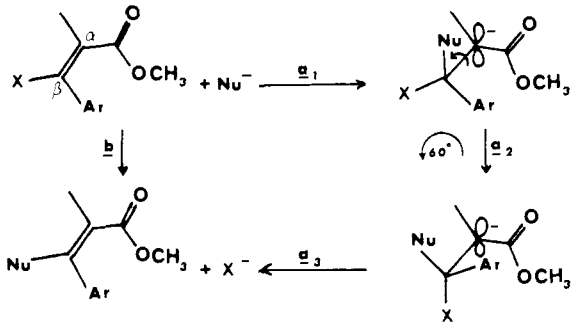
(18) (a) House, H. O. *Acc. Chem. Res.* **1976**, *9*, 59. (b) Rappoport, Z.; Topol, A. *J.* Am. *Chem. Soc.* **1980**, *102*, 406.

(19) (a) Klein, J.; Levene, R. *J. Am. Chem. Soc.* **1972**, *94*, 2520. (b) Chalchat, J. C.; Theron, T.; Vessiere, R. *Bull. Soc. Chim. Fr.* **1973**, 2501. (c) Texier, F.; Henri-Rousseau, O.; Bourgeois, J. *Ibid* **1979**, 86. (d) Stohrer, W. D. *Tetrahedron Lett.* **1975**, 207. Stohrer, W. D.; Schmieder, K. R.; *Chem. Ber.* **1976**, *109*, 285.

(20) Bennett, J. E.; Howard, J. A. *Chem. Phys. Lett.* **1971**, *9*, 460.

(21) Masamune, S.; Sakai, M.; Morio, K. *Can. J. Chem.* **1975**, *53*, 784.

Scheme III



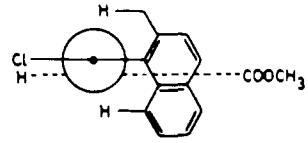
Similarly, retention of the chirality excludes the elimination–addition mechanism which would involve the achiral acetylenic intermediate B.

Radical anions such as C were postulated as intermediates in certain vinylic substitutions;[18] formation of such an intermediate from **1a** may not result necessarily in a complete loss of the chirality since only one mesomeric structure, C_2, is achiral. However, the fast racemization observed during reduction of chiral binaphthyl compounds into the corresponding radical anions is well-documented[22] and suggests that the radical anion should also undergo an easy racemization. Nevertheless, the most convincing argument against formation of this radical anion lies in its expected fast conversion into the achiral radical A by loss of the chloride ion. This is quite analogous to the evolution of the aromatic radical anions which are the postulated intermediates in S_RN1 aromatic substitutions.[23,24]

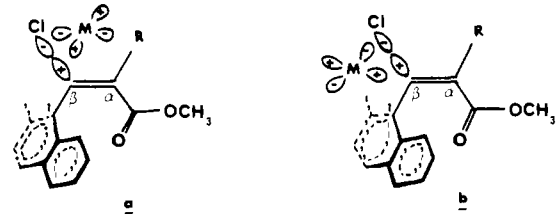
$$ArCl^- \rightarrow Ar\cdot + Cl^-$$

If we now consider the addition–elimination mechanism which is well-documented for vinylic substitution,[16b,c,18b] carbanion D should be an intermediate. Experimental evidence for the formation of such carbanions can be obtained from several methods provided they are long-lived species, which is the case if the vinylic substrate contains a poor leaving group. In the case of vinylic halides having good leaving groups, experimental proof for carbanionic intermediates is lacking. With these halides, retention of the configuration of the double bond is generally observed[16b,c,28] (Scheme III path a_1, a_2, a_3). The same stereochemical result is also in agreement with a concerted pathway b (Scheme III).

Substitution of the atropisomeric halide **1a** by an addition–elimination mechanism involves the carbanion D in which rotation around the C_β–naphthyl bond must occur simultaneously with the 60° rotation around the C_α–C_β bond which is essential to allow for the carbon–halogen bond breaking.[16b,c,28] Rotation of the naphthyl group leads to racemization (Scheme II) which will thus be observed even if the configuration of the double bond is retained. Partial or total loss of axial chirality during substitution can then provide a new type of experimental evidence for a carbanionic intermediate.[29] However, the complete retention of configuration observed in the substitution reaction with the halide **1a** does not favor an addition–elimination mechanism which can also be ruled out on steric grounds. In compound **1a** the naphthyl CH_3 group and the H at C_8 are located on opposite sides of the plane of the double bond and will render the approach of the C_β atom by the nucleophile very unfavorable, the more so if the nucleophile is itself very bulky, e.g., cobaloxime(I).



At this point of the discussion, it is significant to recall that dimethylamine and sodium iodide, which are known to react by addition–elimination mechanisms with halogeno acrylic esters,[16] are inert toward halide **1a**, in contrast to the smooth reactions observed between **1a** and the cobalt or copper nucleophiles. Obviously, the reactivity of the latter must be the consequence of some peculiar feature, for example, the presence of filled bonding d orbitals. Concerted processes have been proposed both for vinylic[31] and aromatic[4] substitution by organometallic compounds which differ from previously proposed concerted pathways[19] as they do not consider the approach of the nucleophile at right angle to the plane of the double bond, which is very unfavorable in the case of compound **1a**, but an in-plane insertion of the metal atom into the C–X bond involving a favorable interaction between a filled d orbital of the metal and the antibonding σ^* orbital of the C–X bond.



Such a mechanism is fully compatible with the stereochemical results reported above with halide **1a**. It also agrees with the lack of substitution by nucleophiles having no filled d orbitals or when the double bond bears a methyl substituent on the α-carbon atom (compound **1b**, R = CH_3). The replacement of a vinylic hydrogen by a methyl group will slow down vinylic substitutions because of inductive and steric effects.[16] Obviously, steric hindrance of the methyl group of **1b** will be of prime importance to an "in-plane" attack from the methyl side as well as from the naphthyl side; results concerning the racemization of atropisomers[9,32] suggest that the replacement of the H_α hydrogen by a methyl group opens the Cl–C_β–C_α bond angle, making the naphthyl side approach b of the nucleophile also more difficult.

In conclusion, the results described in this paper can be best rationalized by assuming a concerted mechanism involving insertion of the nucleophilic metal atom into the carbon–halogen bond. It must be emphasized that such a mechanism is certainly much less general than the addition–elimination mechanism which is postulated for a large variety of reactions between nucleophiles and vinyl halides. Because σ^* orbitals have a higher energy than

(22) Eisenstein, O.; Mazaleyrat, J. P.; Tordeux, M.; and Welvart, Z. *J. Am. Chem. Soc.* **1977**, *99*, 2230. Ito, O.; Hatano, M. *Chem. Lett.* **1976**, 39.

(23) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413.

(24) It was recently proposed[18b] that during the substitution of a nitrovinyl halide by thiolate, the nucleophilic addition step might involve a one-electron-transfer process. This seems legitimate in this particular reaction, in which similarly to the aromatic nitrohalides[25] the carbon–halogen bond cleavage must be very slow. However, there is no experimental evidence for the two-step formation of the carbanion D. The lack of reliable experimental evidence for the participation of a one-electron transfer in the nucleophilic substitution was already pointed out by Kornblum[26] when other alkylating agents than *p*-nitrobenzyl halides are used for the alkylation. For a stereochemical investigation of this problem see also ref 27.

(25) Rossi, R. A. *J. Chem. Educ.* **1982** *59*, 310; *Acc. Chem. Res.* **1982**, *15*, 164.

(26) For this conclusion see the summary and the footnote at the last page of the review of Kornblum: Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 734.

(27) Bram, G.; Cabaret, D.; Maigrot, N.; Mazaleyrat, J. P.; Welvart, Z. *J. Chem. Res.* **1979**, (S) 196 and (M) 2301. Bram, G.; Cabaret, D.; D'Incan, E.; Maigrot, N.; Welvart, Z. *Ibid.* **1982**, (S) 86.

(28) Apeloig, Y.; Rappoport, Z. *J. Am. Chem. Soc.* **1979**, *101*, 5095.

(29) Some racemization can be expected even with large size nucleophiles which are able to hinder the rotation of aromatic groups having perisubstituents[30] (e.g., the β-methylnaphthyl group of reagent **1**). These nucleophiles must also restrict the rate of rotation around the C_α–C_β bond of the carbanion D which is compulsory for the carbon–halogen bond breaking to occur.[16b,c,28] So the large size of a nucleophile will not only decrease the rate of the racemization but also increase the lifetime of the carbanionic intermediate D. Unfortunately, however, we have no information at hand on the influence of the size of a nucleophile on the relative rate of these two types of rotation.

(30) Oki, M. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 87. Lomas, J. S.; Dubois, J. E. *Tetrahedron* **1981** *37*, 2273.

(31) Pearson, R. G. *Acc. Chem. Res.* **1971**, *4*, 152. Pearson, R. G. "Symmetry Rules for Chemical Reactions"; Wiley-Interscience: New York, 1976; p 287.

(32) Anderson, J. E.; Hazlehurst, C. J. *J. Chem. Soc. Chem. Commun.* **1980**, 1188.

π^* orbitals,[33] this insertion mechanism is probably confined to substrates in which the π^* orbitals of the double bond are not sterically accessible to the nucleophile HOMO which are thus free to interact with the π^* orbital of the carbon-halogen bond.

Experimental Section

All new compounds have correct elemental analyses which were performed by the Laboratoire de Microanalyse du C.N.R.S. de Lyon. The structures and optical purities are unambiguously deduced from the ^1H NMR spectrum measured on a Varian T60, Brucker, 90, or Cameca 250 MHz spectrometer (see Figures 1-4). The optical rotations were measured on a 141 M Perkin-Elmer polarimeter.

Starting Materials. The (+)- and (-)-methyl-β-chloro-β-(2-methylnaphthyl)acrylate (**1a**)[6,9] and methyl-β-chloro-β-(2-naphthyl)methacrylate (**1b**)[9] and (pyridine)cobaloxime(I)[5a] are known compounds.

Reactions with Lithium Dimethylcuprate. Under an atmosphere of dry nitrogen and at -5 °C is added 6 mL of an ethereal 0.67 M solution of CH_3Li (4 mmol) to 20 mg of CuI covered with 3 mL of dry ether. After 15 min, the Gilman test becomes negative and the ethereal solution of the copper reagent becomes limpid and has a light yellow color. After this solution is cooled to -20 °C, 315 mg (2.2 mmol) of acrylate **1a** is added. The clear solution becomes brown and a yellow precipitate is formed. After 1 h, dry air is bubbled into the solution and water is added. After the usual workup and purification on TLC, 160 mg (50%) of (*E*)-methyl-β-(2-methylnaphthyl)crotonate is obtained (see Table I). When the reaction is attempted with the methylacrylic ester **1b**, under the same condition, even after leaving the reaction mixture several hours, only the unchanged starting material **1b** is recovered.

Reactions with (Pyridine)cobaloxime(I) (2). The reaction was carried out under nitrogen. To a solution of 464 mg (4 mmol) of dimethylglyoxime in 15 mL of MeOH was added 476 mg (2 mmol) of $CoCl_2 \cdot 6H_2O$. After the cobalt salt had dissolved, 0.16 mL of pyridine followed by 0.50 mL of NaOH (8 N) were added. After 20 min, the reaction mixture turned brown. Subsequently 0.25 mL of NaOH (8 N) and 261 mg (1 mmol) of the reagent **1a** was added under hydrogen. The equivalent volume of hydrogen was absorbed (22.4 mL) in about 5 h; the solution had then turned orange-brown. Water was added, and after filtration, the orange solid was washed with water and diethyl ether and dried under vacuum. Complex **3a** was identified by its NMR spectrum (Table I) and its elemental analysis; yield 88%.

Preparation of Complexes 3b-d. The alkenyl(aquo) cobaloxime **3** (L = H_2O) was prepared by the same procedure as for complex **3a**. This complex was dissolved in MeOH and an equimolar amount of α-methylbenzylamine (**3c**) or (-)-α-methylbenzylamine (**3d**) or $P(OCH_3)_3$ (**3b**) was added. After the solution was stirred for 10 min, the orange solution turned brown. The solvent was removed, and the product was purified by chromatography on silica gel (Mallinkrodt CC7) with CH_2Cl_2-acetone (2:1).

Compounds **3b-d** were identified by their NMR spectra.

Reaction with NaI. In a 25-mL single-necked flask filled with a condenser protected by a $CaCl_2$ drying tube, a mixture of 500 mg (2 mmol) of ester **1a** and 300 mg (2 mmol) of dried sodium iodide was dissolved in 6 mL of anhydrous acetone. The mixture was refluxed for 5 days. After the usual workup, the partially racemized ester **1a** was recovered. By using anhydrous DMF instead of acetone and heating the mixture for 5 days we obtained a similar result. Likewise, after heating the ester with a 15-fold excess of dimethylamine in benzene solution in a sealed tube for 1 week at 80 °C, only the racemized starting material **1a** was recovered.

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Registry No. 1a, 89414-95-9; **1b**, 89414-96-0; **1c**, 89414-97-1; (±)-**1c**, 89414-98-2; (-)-**1c**, 89414-99-3; **3a**, 89414-92-6; **3b**, 89414-93-7; **3c**, 89414-94-8; **3d**, 89496-32-2.

(33) Kelsey, D. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 1953. Apeloig, Y., unpublished results, see footnote 14 in ref 28.

On the Mechanism of the Cycloaddition of 1,2,4-Triazoline-3,5-diones with Bicycloalkenes Leading to Rearranged Urazoles

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Abstract: On the basis of product and kinetic data the intervention of an aziridinium ion (mechanism C) is postulated in the formation of rearranged urazole during the cycloaddition of triazolinediones (TAD) with benzonorbornadiene, norbornenes, and related bicycloalkenes. The cycloaddition follows the second-order rate law, first order in each component. It exhibits typically low activation enthalpies and large negative activation entropies. The relative rates and product formation are insensitive to free radical conditions (initiators, scavengers, light) and exhibit a pronounced steric effect. Modest charge transfer from the olefin (nucleophilic partner) to the TAD (electrophilic partner) is detected in the activated complex (small negative ρ values for the Hammett plot of substituted benzonorbornadienes, linear dependence of relative rates with ionization potentials of benzonorbornadiene, small positive ρ values for the Hammett plot of substituted TADs, linear correlation between relative rates and half-wave reduction potentials of TADs, moderate dipole moment of the activated complex relative to reactants and products, and a small solvent effect). No charge-transfer complexes can be detected by UV-vis spectrophotometry, and trapping experiments for 1,4-dipolar intermediates failed. The relative rates of TAD cycloaddition correlate with the relative rates of arenesulfenyl chloride addition, a process for which a three-center mechanism has been established.

In the preparation of azoalkanes for mechanistic and synthetic purposes, the formation of urazoles via cycloaddition of 1,2,4-triazoline-3,5-diones (TAD) and their subsequent hydrolysis has played an important role.[2] Besides the common (4 + 2)-cycloaddition mode of TAD, homo-Diels-Alder reaction, and (2 + 2)-cycloaddition to π bonds and strained σ bonds, numerous

(1) Doctoral Dissertation, University of Würzburg, July 1983.

(2) (a) Adam, W.; De Lucchi, O. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 762-779. (b) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99-150.

0002-7863/84/1506-2874$01.50/0