hyperfine interaction with two equivalent hydrogens. Futhermore, another orientation was found to give a well-resolved triplet substructure in the center of the absorption envelope, as shown in Figure 2. As well as providing important structural information, these details clearly verify the radical anion assignment.

The hyperfine and *g* parameters deduced from the spectra obtained at the three canonical orientations are collected in Table I. These are unlikely to be the principal tensor components, since the magnetic field directions corresponding to these canonical orientations are limited to those for which the two hydrogens (and the two fluorines) are magnetically equivalent. Despite this restriction, the values of the ^{19}F and ^{1}H hyperfine parameters so obtained are diagnostic for the structural analysis given below.

If we assume that the 1,1-difluoroethylene radical anion adopts a planar geometry as in the case of the neutral molecule,[13] it is difficult to reconcile the combination of large ^{19}F and small ^{1}H couplings in Table I. Thus, the uniformly large ^{19}F couplings appear to rule out a π^* radical and are strongly indicative of a σ^* configuration as in $C_6F_6^-$ (ref 4) [$^{19}a(6) = 134$ G[14,15]] or $C_2F_4^-$ (ref 6 and 12) [$^{19}a(4) = 94$ G], whereas the very small ^{1}H couplings would not be expected for a σ^* radical but are typical of a π^* configuration as in $C_6H_6^-$ (ref 16) ($^{1}a(6) = 3.75$ G). There is also a serious problem in explaining the results in terms of a slightly pyramidal radical with most of the spin density concentrated on the carbon of the CF_2 group, since the average fluorine couplings are much larger than the range of values (68–94 G) reported for isotropic ^{19}F couplings in CF_2X radicals.[1-3]

On the other hand, the results are readily accommodated by the assumption of a perpendicular geometry for the radical anion, and the $5B_2$ orbital shown in Figure 3 satisfies the requirements for the singly occupied molecular orbital (SOMO) imposed by the ^{19}F and ^{1}H hyperfine parameters. INDO calculations[17] show that this orbital is built primarily from the σ^* (or π'^*) group orbital in the (yz) plane of the CF_2 group which is antibonding with a smaller contribution from the p_y orbital of the CH_2 group. This is just the combination demanded by the experimental results, as mentioned earlier. While the ordering of antibonding molecular orbitals predicted by INDO calculations for $CF_2{=}CH_2^-$ gives the sequence, in increasing energy, $3B_1 < 6A_1 < 7A_1 < 5B_2$, the $3B_1$ and the two A_1 orbitals can be ruled out as candidates for the SOMO on the basis of their unsuitable compositions. Thus, each of these molecular orbitals possesses a direct contribution from the 1s orbitals of the two hydrogens, suggesting a much larger ^{1}H coupling than that which is observed. Also, it should be noted that the ordering of antibonding molecular orbitals predicted by INDO calculations is also incorrect for both $C_6F_6^-$ (ref 4) and $C_2F_4^-$.[18]

Finally, the present assignment for $CF_2{=}CH_2^-$ makes good sense if $C_2F_4^-$ is a σ^* radical[6] and $C_2H_4^-$ is a π^* radical. Although the EPR spectrum of the ethylene radical anion has not been reported,[19] a π^* assignment would be expected from the results of optical spectroscopy.[20] Also, the σ^* assignment for $C_2F_4^-$ (ref 6) is consistent with the results of electron transmisssion spectroscopy which show that the temporary π^* anions of the fluoroethylenes are increasingly destabilized by fluorination relative to the π^* anion of ethylene.[21] We conclude, therefore, that the perpendicular geometry of the 1,1-difluoroethylene radical anion enables it to avoid the π^*–σ^* crossover problem[4,5] by adopting the π configuration at the CH_2 group and σ^* configuration at the CF_2 group.[22,23]

Acknowledgment. This research has been supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy (Report DOE/ER/02968-133).

---

[13] Carlos, J. L., Jr.; Karl, R. R., Jr.; Bauer, S. H. *J. Chem. Soc., Faraday Trans 2* **1974**, 177.

[14] Wang, J. T.; Williams F. *Chem. Phys. Lett.* **1980**, *71*, 471.

[15] Anisimov, O. A.; Grigoryants, V. M.; Molin, Yu. N. *Chem. Phys. Lett.* **1980**, *74*, 15.

[16] Jones, M. T. *J. Am. Chem. Soc.* **1966**, *88*, 174.

[17] Pople, J. A.; Beveridge, D. L.; Dobosh, P. A. *J. Chem. Phys.* **1967**, *47*, 2026.

[18] Yim, M. B.; Williams, F., unpublished work.

[19] Attempts to generate $C_2H_4^-$ in solid matrices at 77 K have been unsuccessful.

[20] Merer, A. J.; Mulliken, R. S. *Chem. Rev.* **1969**, *69*, 639.

[21] Chiu, N. S.; Burrow, P. D.; Jordan, K. D. *Chem. Phys. Lett.* **1979**, *68*, 121.

[22] It is interesting to note that the average ^{19}F coupling of 196 G (Table I) for the 1,1-difluoroethylene radical anion is approximately twice the isotropic ^{19}F coupling of 94 G for $C_2F_4^-$.[6,12] Also, the average ^{1}H coupling of 4.8 G (Table I) indicates a spin density of 4.8/22.5 = 0.21 in the p orbital of the CH_2 carbon. These results suggest that most of the spin density in $CF_2{=}CH_2^-$ is located in the σ^* (π'^*) CF_2 group orbital, in qualitative agreement with the composition of the $5B_2$ orbital (Figure 3).

[23] The cis–trans isomerization of 1,2-substituted ethylene radical anions is well-known (see, e.g., for the stilbene radical anions: Gerson, F.; Ohya-Nishiguchi, H.; Szwarc, M.; Levin, G. Chem. *Phys. Lett.* **1977**, *52*, 587), but in such cases the perpendicular form of the the radical anion is nonisolable and possibly corresponds to the transition state for the reaction.

Condensation of Enolates with Hexachlorobutadiene

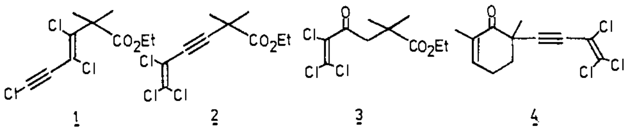
Andrew S. Kende,* Pawel Fludzinski, and John H. Hill

Department of Chemistry, University of Rochester
Rochester, New York 14627

Received November 17, 1980

The formation of carbon–carbon bonds by uncatalyzed condensation of enolates with halo olefins is sufficiently unusual to merit synthetic exploitation and mechanistic scrutiny.[1-3] We have recently described an unprecedented dichlorovinylation of certain enolates as a route to α- and γ-ethynylated carbonyl compounds.[4] We now report novel and synthetically useful direct condensation reactions of enolates with hexachlorobutadiene (HBD) and propose a mechanistic rationale for our observations.

Reaction of 2 equiv of the lithium enolate of ethyl isobutyrate (from 2 equiv each of the ester, LDA, and HMPA at −78 °C in THF) with HBD (from −78 °C to room temperature, 6 h) gave, after kugelrohr distillation at 87–90 °C (0.1 mm), a 63% yield of a $C_{10}H_{11}O_2Cl_3$ oil having intense UV absorption at λ_{max} (MeOH) 245 nm (ϵ 13 500) and 251 nm (ϵ 13 800), ν_{max} (neat) 1740, 1560 cm^{-1}, and MS, ^{1}H NMR and ^{13}C NMR spectra consistent with either structure **1** or **2**.[5] Catalytic hydrogenation of the product (5% Pd/C, H_2, EtOH–Et_3N) to ethyl 2,2-dimethylhexanoate confirmed its carbon skeleton, and hydration of the product under vigorous conditions (saturated $HgSO_4$ in 1% H_2SO_4, EtOH, 75 °C, 21 h) to the highly reactive trichloro enone **3**[5] [λ_{max} (MeOH) 260 nm (ϵ 5500)] established the correct regiochemistry as **2**.[5]



1 2 3 4

The kinetic C-6 lithium enolate of 2,6-dimethyl-2-cyclohexenone reacted with HBD under the above conditions to give in 56% yield the condensation product **4**[5] having spectroscopic properties entirely analogous to the isobutyrate product **2**. In contrast, the sodio derivative (NaH, THF, room temperature, HMPA) from diethyl methylmalonate underwent negligible reaction with HBD. However, in THF at reflux for 35 h a condensation proceeded

---

[1] For examples of nickel-catalyzed vinylation and arylation of enolates by bromides and iodides, see: Millard, A. A.; Rathke, M. W. *J. Am. Chem. Soc.* **1977**, *99*, 4833.

[2] For examples of nickel- and palladium-catalyzed arylation and vinylation of Reformatsky reagents, see: Fauvarque, V. F.; Jutand, A. *J. Organomet. Chem.* **1978**, *177*, 273.

[3] For examples of iron-assisted vinylation of enolates, see: Chang, T. C. T.; Rosenblum, M.; Samuels, S. B. *J. Am. Chem. Soc.* **1980**, *102*, 5930.

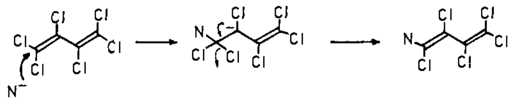
[4] Kende, A. S.; Benechie, M.; Curran, D. P.; Fludzinski, P.; Swenson, W.; Clardy, J. *Tetrahedron Lett.* **1979**, 4513.

[5] UV, MS, ^{1}H NMR, and ^{13}C NMR spectra and elemental analyses are submitted as supplementary information.

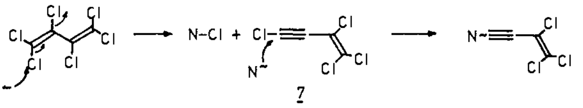
0002-7863/81/1503-2904$01.25/0

J. Am. Chem. Soc. 1981, 103, 2905-2907

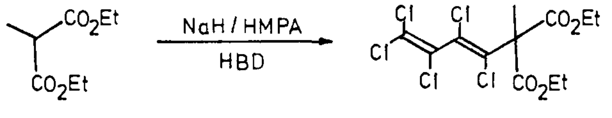
Scheme I



Scheme II

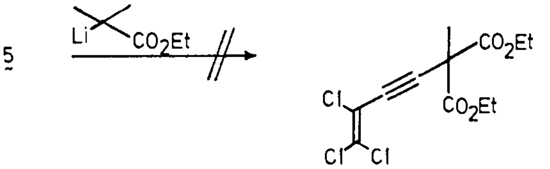


cleanly to yield 61% of a homogenous product having λ_{max} (MeOH) 220 nm (ϵ 12 000) and a molecular formula of $C_{12}H_{13}O_4Cl_5$. The structure of this adduct was shown from spectroscopic data and by catalytic reduction to diethyl methyl-*n*-butylmalonate to be the pentachlorodienylmalonate **5**.[5,6]



5

The formation of pentachlorodienylmalonate **5** is readily explained on the basis of an addition–elimination mechanism (Scheme I) whereby the enolate nucleophile (N^-) adds to the HBD acceptor to give an inductively and resonance stabilized perchloroallyl anion, which then ejects halide. The observed formation of the trichloro enyne **2** from ethyl isobutyrate is less straightforward. For example, the primary formation of a pentachlorodienylisobutyrate adduct (cf. **5**) followed by reductive dechlorination of the internal dichloro olefin is formally possible, but such high regioselectivity for the hindered internal dichloro olefin in a secondary reduction step is unreasonable. Indeed, treatment of the pentachlorodienylmalonate **5** with the lithium enolate of ethyl isobutyrate fails to yield any of the internal acetylene **6** corresponding to **2**.

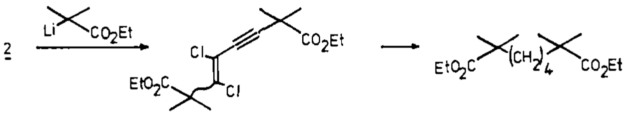


6

We propose that perchlorobutenyne (*7*) *is an obligatory intermediate in the formation of 2* (Scheme II). Thus the initial step in the condensation is attack by the isobutyrate enolate (N^-) on chlorine to give ethyl α-chloroisobutyrate and perchlorobutenyne (**7**). Reaction of a second molecule of the enolate at the terminal ethynyl carbon, possibly by addition–elimination, would yield the observed product **2**.

The suggested reductive dechlorination of HBD to form **7** is consistent with the isolation of 62% of ethyl α-chloroisobutyrate during generation of **2**. Subsequent addition–elimination to **7** is analogous to certain reactions of perchlorobutenyne observed by Roedig for nitrogen[7] and sulfur[8] nucleophiles. Indeed, reaction of the lithium enolate of ethyl isobutyrate (1 equiv each of the ester, LDA, and HMPA at −78 °C in THF) with preformed perchlorobutenyne **7** (from −78 °C to room temperature, 6 h) leads to our product **7** in 76% isolated yield.[9]

It is clear from these results that the formation of a new carbon to carbon bond from enolates with HBD can proceed by at least two mechanisms: direct addition–elimination or a secondary condensation with an intermediate 1-chloroalkyne. The latter mechanism may have general synthetic implications for 1-chloroalkynes as enolate acceptors and be involved in some of our previously reported dichlorovinylations.[4] It is clear, however, that the choice between these two mechanisms is delicately balanced! Thus, reaction of our initial product **2** with 1.1 equiv of the lithium enolate of ethyl isobutyrate leads in 64% yield to a new condensation product **8** (mixture of *E*/*Z* stereoisomers). Analytical and



8 9

spectroscopic data,[5] along with perhydrogenation to diester **9**, establish the structure of **8** as the dichloroenyne addition–elimination product shown.

We see from this that the addition–elimination pathway of Scheme I is not limited to the softer malonate anion but also depends in a subtle manner on the structure of the halo olefin acceptor. The possiblity of electron transfer from enolate to haloolefin (or haloalkyne) in some of the postulated addition–elimination steps cannot be excluded.[10] Futher studies on this point, the scope of these condensations, and the intricate chemistry of compounds **2**, **3**, and **8** will be described elsewhere.

Acknowledgment. Partial support of this work by Grant CA-18846 awarded by the National Cancer Institute, USPHS, is gratefully acknowledged. P. F. thanks the University of Rochester for a Sherman Clarke Fellowship.

Supplementary Material Available: UV, MS, ^{1}H NMR, and ^{13}C NMR spectra and elemental analyses for compounds **2–5** and **8** are available (3 pages). Ordering information is given on any current masthead page.

---

(6) The stereochemistry of compound **5** is assumed as *E* by analogy with the dichlorovinylation adducts described in ref 4.

(7) Roedig, A.; Fauré, M. *Chem. Ber.* **1975**, *109*, 2159.

(8) Roedig, A.; Zaby, G. *Liebigs Ann. Chem.* **1979**, *1979*, 1606, and 1614.

(9) The yield of **2** from HBD drops precipitously when less than 2 equiv of the lithium enolate of ethyl isobutyrate is used. This is in accordance with our mechanism invoking perchlorobutenyne as an intermediate. For the preparation of perchlorobutenyne, see: Jenkins, D. K. *Chem. Ind.* (*London*) **1971**, 254.

(10) A referee's suggestion that perchlorobutenyne reacts with a nucleophile to yield a chlorinated nucleophile and the acetylide, followed by displacment to yield product **7** ("transfer alkylation") appears to be experimentally precluded by our observation that reaction of 1-lithio-1-hexyne with ethyl α-chloroisobutyrate yields no detectable (<10%) ethyl 2,2-dimethyl-3-octynoate.

Selective Functionalization of Doubly Coordinated Flexible Chains

Ronald Breslow,* Raghavan Rajagopalan, and
Joshua Schwarz

Department of Chemistry, Columbia University
New York, New York 10027

Received February 12, 1981

The process of remote oxidation has proven to be remarkably selective and useful with such rigid substrates as steroids.[1] Attack by bound benzophenone reagents[2] and template-directed chlorinations[3] give products determined by and predictable from the relative geometries of reagent and substrate segments. By contrast, remote functionalization of flexible substrates has not so far shown chemically useful selectivity. Mixtures are obtained from benzophenone attack or remote halogenations on long-chain alkyl groups[4] and template-directed epoxidations of flexible,[5] but not

---

(1) For a recent review, see: Breslow, R. *Acc. Chem. Res.* **1980**, *13*, 170.

(2) Breslow, R.; Flechtner, T.; Kalicky, P.; Liu, S.; Washburn, W. *J. Am. Chem. Soc.* **1973**, *95*, 3251.

(3) Breslow, R.; Corcoran, R. J.; Snider, B. B.; Doll, R. J.; Khanna, P. L.; Kaleya, R. *J. Am. Chem. Soc.* **1977**, *99*, 905.

(4) Breslow, R.; Rothbard, J.; Herman, F.; Rodriguez, M. L. *J. Am. Chem. Soc.* **1978**, *100*, 1213. Mixtures are also obtained from the attack of unattached reagents on long-chain esters as in the work of: Eck, C. R.; Hunter, D. J.; Money, T. *J. Chem. Soc., Chem. Commun.* **1974**, 865.