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CONVERSION OF NITROALKENES INTO β-(TRICHLOROMETHYL)NITROALKANES

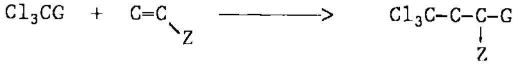
Robert F. Cunico* and Cui-ping Zhang

Department of Chemistry
Northern Illinois University
DeKalb, IL 60115

Abstract: The cesium fluoride-catalyzed reaction of (trichloromethyl)-trimethylsilane with conjugated nitroalkenes affords β-(trichloromethyl)nitroalkanes.

Since trichloromethyl carbanion, at least in its form as trichloromethyllithium, is only stable at -100°C,[1] protocols have been sought to effect its transfer to electrophiles under ambient conditions. Generally these efforts have involved the in situ trapping of the trichloromethyl carbanion, generated from chloroform under basic conditions (eq. 1, G = H), by aldehydes or ketones.[2] More recently, treatment of (trichloromethyl)-trimethylsilane (1) (eq. 1, $G = SiMe_3$) with fluoride ion in the presence of aldehydes has proven highly successful.[3] However, few reports exist concerning the "conjugate" addition of

$$Cl_3CG + C{=}O \longrightarrow Cl_3C{-}C{-}O{-}G \qquad \text{(eq. 1)}$$



$$Cl_3CG + C{=}C{\diagdown}Z \longrightarrow Cl_3C{-}C{-}\underset{Z}{\underset{|}{C}}{-}G \qquad \text{(eq. 2)}$$

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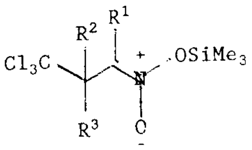
*To whom correspondence should be addressed trichloromethyl carbanion to carbon-carbon double bonds activated by electron-withdrawing groups (eq. 2). Along these lines, chloroform itself has been added to α,β-unsaturated esters and nitriles using sodium hydroxide under phase-transfer conditions,[4] and a triethylamine-trichloroacetic acid system has been used for similar additions.[5] Included in these latter reactions is the transformation of eq. 3, which to our knowledge is the only example of "trichloromethyl carbanion" addition to a conjugated nitroalkene.[6] We wish to report here on a more efficient method to effect this general transformation.

$$PhCH{=}CHNO_2 \quad + \quad Cl_3CCO_2H \quad \xrightarrow{Et_3N} \quad PhCH(CCl_3)CH_2NO_2 \qquad \text{(eq. 3)}$$

(6% yield)

When a mixture of cesium fluoride, 1, and certain nitroalkenes (2) are allowed to react at 25°C in tetrahydrofuran, synthetically useful yields of β-(trichloromethyl)nitroalkanes (3) are formed (Table). The products 3a-e presumably arise via the intermediacy of the hydrolytically unstable trimethylsilyl nitronates (4).[7] Significant amounts of a monomeric by-product only appeared in the



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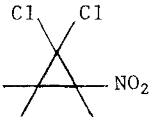

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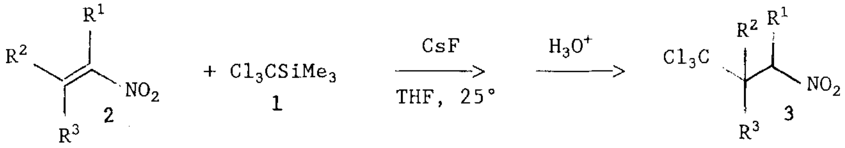
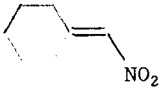
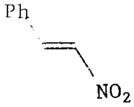
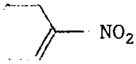
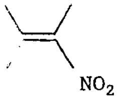
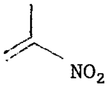
instance of 2e, where the cyclopropane 5 was produced in 9% yield. Higher molecular weight materials were produced to some extent in

TABLE: β-(Trichloromethyl)nitroalkanes (3) obtained from the reaction of (1) with nitroalkenes (2).[a]



Nitroalkene		Time(h[b])	Product	Yield(%)
2a		6	3a	59
2b		15	3b	61
2c		6	3c[c]	67
2d		24	3d	46
2e		240	3e[d]	32
2f		6	--[e]	--[e]

[a] All runs were heterogenous using a 1:5 weight ratio of CsF to 2 and equimolar amounts of 1:2.

[b] Time necessary for the total consumption of **2** except **2d** ≤ 24h.

[c] ^{1}H NMR indicated the presence of only one stereoisomer.

[d] Plus 9% of **5**; see experimental.

[e] No 1:1 adduct.

all runs, and these became the predominant product when 2f was employed as starting alkene. These results may be rationalized by postulating a competition between three processes involving 2: (a) nucleophile-induced polymerization, (b) transfer of dichlorocarbene to the C=C bond[8] and (c) 1,4-addition of 1. Anionic polymerization of nitroalkenes is well-known, and would be most facile for terminally unsubstituted species such as 2f. At the opposite extreme, 2e represents the most highly substituted alkene investigated. Deviation from coplanarity within this nitroene system may inhibit conjugate addition, thus allowing its greater nucleophilicity to favor the formation of some 5. We note that the formation of adjacent quaternary sites such as in **3a** is readily accommodated by the method.

Experimental Section

General: Tetrahydrofuran was distilled from benzophenone sodium ketyl as needed. Powdered CsF (99.9%), **2b** and **2c** were obtained from Aldrich Chemical Co. Nitroalkenes **2d** and **2f** were prepared by the phthalic anhydride method;[9] **2a**[10](containing 10% of the β,γ-unsaturated isomer) and **2e**[11] were obtained from the β-acetoxy-nitroalkanes and sodium acetate in hot THF and diglyme, respectively. VPC analyses employed a 2 ft x 0.25 in stainless steel 20% SE-30 on Chromosorb W column. Elution chromatography employed 70-230 mesh silica gel 60. ^{1}H NMR data were obtained in $CDCl_3$ solution ($CHCl_3$ taken as δ 7.24) using an IBM WP200SY spectrometer.

1-(Nitromethyl)-1-(trichloromethyl)cyclohexane (2a). Typical Procedure:

A flask containing CsF (0.2 g, 1.3 mmol) and a magnetic stirrer was evacuated and heated with a flame for about 1 min. When cool, it was backfilled with argon and then charged with **2a** (1.1 g of a 90:10 mixture of α,β and β,γ isomers, 7.1 mmol of **2a**), **1** (1.4 g, 7.3 mmol) and 25 mL of THF. The mixture was stirred under Ar at 25°C for 6 h, after which time VPC analysis indicated that all nitroalkene had been consumed. It was poured into pentane-water containing a drop of HOAc and cross-extracted. The organic phase was dried ($MgSO_4$), evaporated, and the residue chromatographed on 8 in x 0.75 in of silica gel. Elution with CCl_4 gave 1.1 g (59%) of **3a**, mp 76.5-78.0°C (hexane). IR 1555, 763 cm^{-1}; ^1H NMR δ 1.1-2.3 (10 H, m), 4.83 (2 H, s); ^{13}C NMR ($CDCl_3$) δ 22.0, 24.4, 29.5, 56.3, 75.5. Anal. Calcd for $C_8H_{12}Cl_3NO_2$: C, 36.88; H, 4.64; N, 5.38. Found: C, 36.97; H, 4.68; N, 5.40.

1,1,1-Trichloro-3-nitro-2-phenylpropane (2b). Crystals from chromatography, mp 64.8-65.5°C (lit,[5] mp 64-66°C). ^1H NMR δ 4.50 (1 H, dd, J = 11.0, 5.5 Hz), 5.11 (1 H, dd, J = 15.5, 11 Hz), 5.34 (1 H, dd, J = 15.5, 5.5 Hz), 7.4-7.6 (5 H, m).

1-Nitro-2-(trichloromethyl)cyclohexane (2c). Obtained as an oil from chromatography; VPC indicated a purity of 98%. ^1H NMR δ 1.5 (4 H, m), 1.92 (2 H, m), 2.4 (1 H, m), 2.6 (1 H, m), 3.32 (1 H, m), 4.85 (1 H, m). Anal. Calcd for $C_7H_{10}Cl_3NO_2$: C, 34.10; H, 4.09; N, 5.68. Found: C, 34.29; H, 4.32; N, 5.60.

1,1,1,-Trichloro-2-(nitromethyl)butane (2d).[12] Obtained as an oil from chromatography, 95% pure by VPC. ^{1}H NMR δ 1.3 (3 H, t), 1.64 (1 H, m), 2.24 (1 H, m), 3.43 (1 H, m), 4.47 (1 H, dd, J = 17, 6.5 Hz), 4.96 (1 H, dd, J = 17, 6.0 Hz).

1,1,1,-Trichloro-2,2-dimethyl-3-nitrobutane (2e). Column chromatography afforded a mixture of **2e** (70%), 1,1-dichloro-2,2,3-trimethyl-3-nitrocyclopropane (**5**) (16%) and various unidentified compounds (14%), as determined from VPC analysis, representing respective yields of 32% and 9% for **2e** and **5**. **2e**: ^{1}H NMR δ 1.50 (6 H, s), 1.77 (3 H, d, J = 8.5 Hz), 5.31 (1 H, q, J = 8.5 Hz). Anal. Calcd for $C_6H_{10}Cl_3NO_2$: C, 30.73; H, 4.30; N, 5.97. Found: C, 30.43; H, 4.46; N, 6.12. **5**: ^{1}H NMR δ1.38 (3 H, s), 1.50 (3 H, s), 1.94 (3 H, s). Anal. Calcd for $C_6H_9Cl_2NO_2$: C, 36.21; H, 4.56. Found: C, 36.32; H, 4.57.

References and Notes

1. Hoeg, D.F., Lusk, D.I. and Crumbliss, A.L., J. Am. Chem. Soc., 1965, 87, 4147.
2. (a) Compere, E.L., Jr., J. Org. Chem., 1968, 33, 2565. (b) Merz, A. and Tomahogh, R., Chem. Ber., 1977, 110, 96.
3. Fujita, M., Obayashi, M. and Hiyama, T., Tetrahedron, 1988, 44, 4135 and references therein.
4. (a) Dehmlow, E.V., Justig Liebigs Ann. Chem., 1972, 758, 148. (b) Makosa, M. and Gajos, I., Bull. Acad. Pol. Sci. Ser. Sci. Chim., 1972, 20, 33.

5. Nanjo, K., Suzuki, K. and Sekiya, M., Chem. Pharm. Bull., 1978, 26, 848.

6. The addition of trihalomethyl carbanions to nitroarenes affords, after in situ elimination, dihalomethyl-substituted nitroarenes: Makosa, M. and Owczarczyk, Z., J. Org. Chem., 1989, 54, 5094.

7. Colvin, W., Beck, A.K., Bastani, B., Seebach, D., Kai, Y. and Dunitz, J.D., Helv. Chim. Acta, 1980, 63, 697.

8. See Cunico, R.F. and Chou, B.B., J. Organometal. Chem., 1978, 154, C45 for the use of 1 as a dichlorocarbene transfer agent towards alkenes under similar conditions.

9. Miyashita, M., Yanami, T. and Yoshikoshi, A., Organic Syntheses, 1981, 60, 101.

10. Svata, B. and Prochazka, M., Coll. Czech. Chem. Commun., 1975, 40, 2315.

11. (a) Hesse, G., Hatz, R. and Konig, H., Justus Liebigs Ann. Chem., 1967, 709, 79. (b) Bordwell, F.G. and Hautala, J.A., J. Org. Chem., 1978, 43, 3116.

12. Colonge, J. and Lartigau, G., Bull. Soc. Chim. France, 1978, 26, 738.

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