extracted with ether. After washing, drying, and removal of the ether, 460 mg of oily 5-carbomethoxycyclopent-2-enone was obtained: nmr (CCl_4) δ 2.0–3.6 (mult), 3.82 (3 H, s, COOMe), 6.45 (1 H, mult, C-2 H), 8.17 (1 H, mult, C-3 H). No carbonyl derivative could be obtained.

Substitution of 1.2 g of 2-bromo-2-carbomethoxycyclopentanone for the 5-bromo isomer in the above procedure gave (nmr analysis) 0.4 g of an oil containing mostly 5-carbomethoxycyclopent-2-enone and some 2-carbomethoxycyclopentanone (contaminant in the starting material), but no 2-carbomethoxycyclopent-2-enone (Ic), since the signal at δ 8.38 was absent.

Other dehydrobromination reagents whose action on the above compounds was investigated include Li_2CO_3–LiBr–DMF; 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU); 5-ethyl-2-methylpyridine; and KOBu-*t*. These reagents gave only polymeric material.

Registry No.—Ic, 36601-73-7; IIb, 18067-33-9; IIb DNP, 36601-75-9; III, 36601-76-0; exo-IV, 36601-77-1; *endo*-IV, 36622-61-4; IV DNP, 36596-59-5; 2-bromo-2-carbomethoxy cyclopentanone, 36596-60-8; 5-bromo-2-carbomethoxycyclopentanone, 36596-61-9; 5-carbomethoxycyclopent-2-enone, 36596-62-0.

Acknowledgments.—Financial support by the Robert A. Welch Foundation is gratefully acknowledged. L. R. N. thanks the National Science Foundation for a traineeship grant, awarded through Texas Tech University.

Carbon Tetrachloride Dimerization of 2-Nitropropane Anion. An Electron-Transfer Process

SUMET LIMATIBUL AND JOSEPH W. WATSON*

Department of Chemistry, University of California, San Diego, La Jolla, California 92037

Received June 27, 1972

The lithium or potassium salts of 2-nitropropane react exothermically with carbon tetrachloride in DMSO saturated with nitrogen to yield 2,3-dinitro-2,3-dimethylbutane in approximately 50% yield. Although a variety of procedures[1,2] are available for producing the synthetically useful vicinal dinitroalkanes[2] in high yields, the carbon tetrachloride oxidative dimerization of nitroalkyl anions reported in this note may prove to be a synthetically useful reaction because of its greater simplicity and speed, especially with *in situ* preparation of the anion by use of commercial potassium *tert*-butoxide.

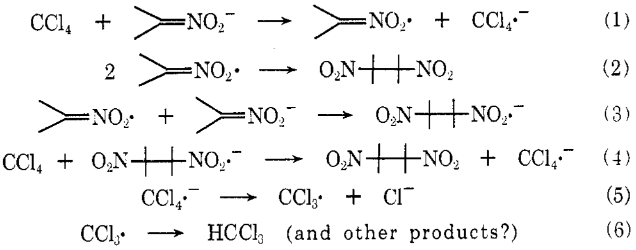
Table I lists the yields of products obtained under several reaction conditions. Since both carbon tetrachloride and the 2-nitropropyl anion are stable to oxygen, the reduction in dimer yield and the formation of acetone when the reaction solution is saturated with oxygen instead of nitrogen suggest that the reaction proceeds *via* 2-nitropropyl radicals which are trapped by oxygen.[3] Quenching the reaction with 6 *N* HNO_3 and Volhard titration of the liberated chloride indicated that the reaction is complete within 1–2 min with DMSO or 2:1 DMSO–cyclohexene as solvent. No detectable reaction occurs in 1 hr with ether, cyclohexene, carbon tetrachloride, ethanol, or 10:2 *tert*-butyl alcohol–water as solvent. Because CCl_4 undergoes nucleophilic substitution with carbanions[4] and is also a good acceptor of electrons, with the intermediate carbon tetrachloride radical anion exothermically decomposing to trichloromethyl radical and chloride anion,[5] two mechanisms for the reaction are immediately conceivable: mechanism A, consisting of nucleophilic substitution on carbon tetrachloride by 2-nitropropyl anion to form trichloromethyl carbanion and 2-chloro-2-nitropropane, which reacts with 2-nitropropyl anion by a radical anion process to form the dimer,[3] and mechanism B (eq 1–6).

TABLE I

REACTION OF CCl_4 WITH 2-NITROPROPYL ANION IN DMSO

	[2-Nitro-propane], *M*	[*t*-BuOK], *M*		Products, mol %		
[CCl_4], *M*			Gas	Dimer	Cl^-	Other
1.8	0.3 (Li salt)		N_2	50	70	60 ($CHCl_3$)
1.8	0.3 (Li salt)		O_2	30	40	$CHCl_3$, acetone
1.8[a]	0.3 (Li salt)		N_2	40	70	50 ($CHCl_3$)
0.4	0.22	0.22	N_2	50	80	
0.22	0.22	0.22	N_2	50	80	
0.4	0.22	0.22	O_2	30	40	

[a] Solvent: 2:1 DMSO–cyclohexene.



We tentatively favor mechanism B as the mechanism of the reaction for the following reasons. (a) Mechanism A involves the formation of trichloromethyl carbanion, which should rapidly decompose to dichlorocarbene which is trappable by cyclohexene.[4] When the reaction was conducted in 2:1 DMSO-cyclohexene solvent no dichloronorcarane was detectable. (b) The yield of dimer in the carbon tetrachloride reaction was reduced from 50 to 30% when the reaction was carried out in the presence of oxygen instead of nitrogen (Table I). In mechanism A dimer is formed *via* the reaction of 2-nitropropyl anion with 2-chloro-2-nitropropane. When this reaction was conducted in oxygen- instead of nitrogen-saturated DMSO solutions, the yield of dimer decreased from 65 to ≤5% at 22° and from 80 to 10% at 60° (Table II) (see also ref 3). It therefore appears unlikely that 2-chloro-2-nitropropane is an intermediate in the carbon tetrachloride mediated dimerization of 2-nitropropyl anion as required by mechanism A. (c) The dimerization of 2-nitropropyl

---

[1] (a) N. Kornblum, S. D. Boyd, and F. W. Stuchal, *J. Amer. Chem. Soc.*, **92**, 5783, 5784 (1970); (b) W. S. Lindsay and R. J. Hardy, *Chem. Abstr.*, **63**, 13075*h* (1965); (c) H. Schechter and R. B. Kaplan, *J. Amer. Chem. Soc.*, **75**, 3980 (1953); (d) A. H. Pagano and H. Schechter, *J. Org. Chem.*, **35**, 295 (1970); (e) G. A. Russell, R. K. Norris, and E. J. Panek, *J. Amer. Chem. Soc.*, **93**, 5839 (1971).

[2] N. Kornblum, S. D. Boyd, H. W. Pinnide, and R. G. Smith, *ibid.*, **93**, 4316 (1971).

[3] G. A. Russell, *ibid.*, **76**, 1595 (1954); G. A. Russell and W. C. Danen, *ibid.*, **88**, 5663 (1966); G. A. Russell and W. C. Danen, *ibid.*, **90**, 347 (1968).

[4] C. Y. Meyers, S. D. Boyd, H. W. Pinnide, and R. G. Smith, *ibid.*, **91**, 7510 (1969).

[5] R. E. Fox and R. K. Curran, *J. Chem. Phys.*, **34**, 1595 (1961); W. E. Wentworth, R. S. Becker, and R. Tang, *J. Phys. Chem.*, **71**, 1652 (1967).

Table II

Reaction of 0.1 *M* 2-Chloro-2-Nitropropane with 0.1 *M* Lithium Salt of 2-Nitropropane in DMSO

Temp, °C	Gas	Products, mol %	
		Dimer	Cl^-
22	N_2	65	80
22	O_2	≤ 5	15
60	N_2	80	95
60	O_2	10	50

anion has been effected by a variety of oxidants,[1c,d] 1,1,1-trinitroethane,[6] and several electrophilic aromatics.[1e] The latter reactions were considered to proceed *via* electron transfer reactions similar to mechanism B.[1e,6]

Because carbon tetrachloride is a common chemical, its electron transfer chemistry with anions is deserving of considerable further investigation.

Experimental Section

Reaction of CCl_4 with the Lithium Salt of 2-Nitropropane.—Nitrogen gas was bubbled through a stirred solution of 2 g of the powdered lithium salt of 2-nitropropane[2] in 30 ml of anhydrous DMSO for at least 15 min. Carbon tetrachloride (5 ml) was then added to the solution. The solution rapidly turned from a frothy suspension of some undissolved lithium salt into a clear, yellowish-orange solution. The reaction was exothermic with the temperature rising as high as 60° within 1–3 min. After 15–30 min, 50 ml of water was added and the reaction mixture was extracted with three 150-ml portions of ether. The ether extracts were combined, washed with 100 ml of water, and dried with anhydrous $MgSO_4$. Evaporation of the ether solution yielded 2,3-dinitro-2,3-dimethylbutane in 50% yield, mp 209–212° on recrystallization from absolute ethanol, mp 212° on sublimation (lit.[1e] mp 216°). The nmr spectrum, a singlet at δ 1.8 in CH_2Cl_2, the elemental analysis, and the mass spectrum[7] all confirmed the structure of the product.

Analysis for Other Products.—The dried ether extract of the reaction mixture was carefully distilled until most of the ether had been removed. Gas chromatographic analysis of the remaining solution on a 6-ft column of 5% SF-96 on Chromosorb W at 80 and 150° showed the presence of chloroform and 2,3-dinitro-2,3-dimethylbutane. The nmr spectrum of the solution showed the presence of chloroform and the dimer. The addition of a known weight of chloroform to a known fraction of the concentrated ether solution and measurement of the increase in the area of the chloroform signal permitted an estimation of the yield of chloroform. When the reaction was conducted in a solution saturated with oxygen, 5 ml of the 55–60° distillate of the dried ether extract of the reaction mixture was collected. The nmr spectrum of this distillate showed the presence of chloroform and acetone. The acetone was further confirmed by precipitating its 2,4-dinitrophenylhydrazone from the solution, mp 124–125° (lit.[8] mp 126°). Chloride was determined by the Volhard method[9] on 1-ml aliquots of the reaction solution.

Potassium *tert*-Butoxide System.—After nitrogen gas was passed through 200 ml of DMSO containing 6.3 g (0.22 mol) of potassium *tert*-butoxide and 5 g (0.22 mol) of 2-nitropropane for at least 15 min, 10 ml (0.41 mol) of CCl_4 was added. The frothy solution rapidly became a clear yellowish-orange with the evolution of heat. Water (200 ml) was added to the reaction mixture. This solution was extracted with three 150-ml portions of ether. The combined ether extracts were dried over $MgSO_4$ and distilled, and the residue was recrystallized from absoluted ethanol. The yield was 2.5 g of dimer, mp 212°.

Registry No.—Carbon tetrachloride, 56-23-5; 2-nitropropane anion, 20846-00-8; lithium salt of 2-nitropropane, 28273-55-4; 2,3-dinitro-2,3-dimethylbutane, 3964-18-9.

---

(6) L. Zeldin and H. Schechter, *J. Amer. Chem. Soc.*, **79**, 4708 (1957).

(7) J. T. Larkins, F. E. Saalfeld, and L. Kaplan, *Org. Mass Spectrom.*, **2**, 213 (1969).

(8) R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, Wiley, New York, N. Y., 1964, p 126.

(9) A. I. Vogel, "Inorganic Quantitative Analysis," 3rd ed, Wiley, New York, N. Y., 1961, p 266.