Reactions of Carbanions with Carbon Tetrachloride in Two-Phase Systems. Chlorinated Products as Nucleophilic and Electrophilic Intermediates[1]

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A variety of carbanions generated in the catalytic two-phase system (aqueous NaOH or K_2CO_3 and tetrabutylammonium bromide catalyst) react with CCl_4 to form chlorinated products that can react as nucleophiles and electrophiles. Thus, chlorinated intermediates generated from arylacetonitriles and propiophenone in the presence of aldehydes and electrophilic alkenes form oxirane and cyclopropane derivatives, respectively. The chlorinated intermediates act as electrophiles toward Cl_3C^- giving (trichloromethyl)oxiranes (from aryl alkyl ketones), α-trichloromethyl nitriles (from phenyl(dialkylamino)acetonitriles), and benzoyldichloro enamines (from α-dialkylamino ketones). From secondary nitroalkanes both chloronitroalkanes and dinitro compounds can be produced.

Perhaloalkanes and particularly carbon tetrachloride are strong electrophiles that react with many types of carbanions in a variety of ways. The main reaction in the system carbanion–CCl_4 is usually chlorination of the carbanion,[2-7] often followed by further transformations of the chlorinated products in the highly basic medium.[6-8] A frequent alternative process is dimerization of the carbanions under the action of CCl_4. The process can be considered as further transformation of the initially formed chlorination products[5,9] or as coupling of carbanions and radicals, the latter resulting from an electron transfer from the carbanion to CCl_4.[10]

Studying reactions of CCl_4 with carbanions generated in the catalytic two-phase system, 50% aqueous NaOH–organic solvent and tetraalkylammonium salt as the catalyst (CTP),[11] we have already observed a variety of processes: simple chlorination of some carbanions (phenylacetylene,[4] 2-phenylalkanenitriles, trichloroethene[2]), dimerization (phenyl- and diphenylacetonitrile[12]), and also the formation of unexpected products containing trichloromethyl group (α-(dialkylamino)phenylacetonitriles[2]). We have shown that the dimerization process of phenylacetonitrile proceeds via initial chlorination to α-chlorophenylacetonitrile, followed by its fast self-alkylation. Thus here the chlorinated product serves as both an electrophilic and, upon deprotonation, nucleophilic reagent. Trapping of α-chlorophenylacetonitrile anion by benzaldehyde and acrylonitrile provided strong evidence for the formation of the chlorinated intermediate in this dimerization process.[2]

Reactions of carbanions with perhaloalkanes in which the initial chlorination products subsequently undergo further transformations could be of practical interest and also give an insight into the complicated problem of the initial step of the carbanion–CCl_4 reaction. Following our preliminary report[2] we would like to present a full paper dealing with these processes.

Results and Discussion

Chlorination Products as Nucleophiles. We have previously reported,[2] that the reaction of phenylacetonitrile with CCl_4 carried out in the CTP system in presence of benzaldehyde or acrylonitrile results in formation of oxirane or cyclopropane derivatives. Further studies have shown that this process is of general character and a number of arylacetonitriles react with various aldehydes and CCl_4 in the CTP system giving glycidonitrile derivatives often in good yields. Also some other compounds containing an "active" methylene group such as previously reported for fluorene[2,13] and propiophenone can react in this way. The results of the reactions of carbanions with CCl_4 and electrophiles are given in Table I.

An interesting question here is a competition between the Knoevenagel condensation of the carbanion and the aldehyde from one side and chlorination of the former followed by the Darzens condensation. Usually the rate of the aldolization is very high, but due to the reversibility of this process the real competition depends on the rate of the dehydration of the aldol and the irreversible chlorination. In order to suppress the former process it is necessary to use a great excess of CCl_4—for instance as a solvent. Thus when the equimolar amount of CCl_4 is used, the Knoevenagel condensation accounts for more than 25% of the product, whereas when CCl_4 is taken in tenfold excess, this fraction drops below 5%.

The process is also sensitive to the presence of the catalyst. In the absence of tetrabutylammonium bromide

(1) Part 122 in the series Reactions of Organic Anions. For part 121, see: Mąkosza, M.; Kwast, A. *J. Chem. Soc., Chem. Commun.* **1984**, 1195.
(2) Jończyk, A.; Kwast, A.; Mąkosza, M. *J. chem.* **1979**, *44*, 1192.
(3) Arnold, R. T.; Kulenovic, S. T. *J. Org. Chem.* **1978**, *43*, 3687 and references cited therein. Gaillot, J. M.; Gelas-Miahle, Y.; Vessire, R. *Can. J. Chem.* **1978**, *57*, 1958. Lauritzen, S. E.; Rømming, Ch.; Skattelbøl, L. *Acta Chem. Scand., Ser. B* **1981**, *B35*, 263. Regis, R.; Doweyko, A. M. *Tetrahedron Lett.* **1982**, 2539.
(4) Mąkosza, M.; Fedoryński, M. *Rocz. Chem.* **1975**, *49*, 1779.
(5) Seux, R.; Morel, G.; Foucaud, A. *Tetrahedron* **1975**, *31*, 1335.
(6) Meyers, C. Y.; Malte, A. M.; Matthews, W. S. *J. Am. Chem. Soc.* **1969**, *91*, 7510.
(7) (a) Meyers, C. Y.; Matthews, W. S.; Ho, L. L.; Kolb, V. M.; Parady, T. E. In "Catalysis in Organic Synthesis—1977"; Smith, C. V., Ed.; Academic Press: New York, 1978; pp 197–278. (b) Meyers, C. Y. In "Topics in Organic Sulfur Chemistry"; Tisler, M., Ed.; University Press: Ljubljana, Yugoslavia, 1978; pp 207–260.
(8) Meyers, C. Y.; Kolb, V. M. *J. Org. Chem.* **1978**, *43*, 1985.
(9) Hauser, C. R.; Kofron, W. G.; Dunnavant, W. R.; Owens, W. F. *J. Org. Chem.* **1961**, *26*, 2627.
(10) Limatibul, S.; Watson, J. W. *J. Org. Chem.* **1972**, *37*, 4491.
(11) Mąkosza, M. In "Survey of Progress in Chemistry"; Scott, A. F., Ed.; Academic Press: New York, 1980; Vol. 1, p 1. Dehmlow, E. V.; Dehmlow, S. S. "Phase Transfer Catalysis"; Verlag Chemie: Weinheim/Bergstr., West Germany, 1980.
(12) Mąkosza, M.; Serafinowa, B.; Gajos, I. *Rocz. Chem.* **1969**, *43*, 671.
(13) Jawdosiuk, M.; Jończyk, A.; Kwast, A.; Mąkosza, M.; Kmiotek-Skarżyńska, I.; Wojciechowski, K. *Pol. J. Chem.* **1979**, 53, 191. Aza analogues of fluorene also form corresponding oxiranes in the reaction with benzaldehyde and CCl_4 in the CTP system: Prostakov, N. S.; Beshchenko, M. A.; Soldatova, S. A.; Konstantinu, E. P.; Lavani-Edogiaverie, S. *Khim. Geterosikl. Soedin.* **1982**, 1393.

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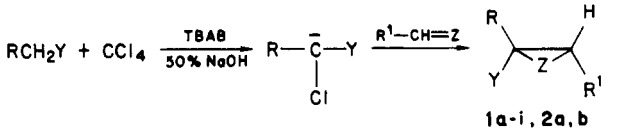
Table I. Reactions of Carbanions with CCl_4 and Electrophiles[a]



1a-i, 2a, b

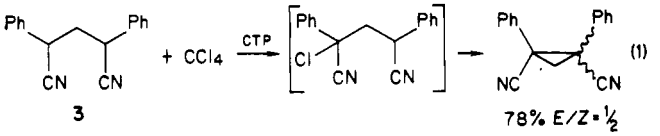
expt	R	Y	R^1	Z	temp, °C	reactn time, min	product	yield,[b] %
1	Ph	CN	Ph	O	20	60	**1a**	80
2	Ph	CN	*i*-Pr	O	15	30	**1b**	55
3	Ph	CN	4-ClC_6H_4	O	25	45	**1c**	56
4	Ph	CN	4-$MeOC_6H_4$	O	25	30	**1d**	55
5	Ph	CN	4-*i*-PrC_6H_4	O	25	30	**1e**	60
6	3-BrC_6H_4	CN	Ph	O	25	45	**1f**	30
7	4-$MeOC_6H_4$	CN	Ph	O	40	90	**1g**	64
8	1-$C_{10}H_7$	CN	Ph	O	20	90	**1h**	60
9	CH_3	COPh	Ph	O	25–30	75	**1i**	42
10	Ph	CN	H	CHCN	15	60	**2a**	10[c]
11	Ph	CN	H	CHCN	20	70	**2a**	52[d]
12	Ph	CN	H	CHCOO-*t*-Bu	20	150	**2b**	45[d]

[a] Unless otherwise noted all reactions were performed with the molar ratio CH-acid/electrophile/CCl_4 of 1.0/1.1/10 and were not optimized. [b] Isolated yield. Only one isomer in pure product was detected by GLC and ^1H NMR. [c] 41% of 1-chloro-1,2-dicyano-2-phenylcyclopropane was formed.[2] [d] Equimolar amount of CCl_4 and benzene as a solvent was used.

the reaction occurs at the phase boundary since carbanions stay there in an adsorbed state, where their reactivity is reduced, so they can react only with a very active electrophile—the aldehyde.[14] On the other hand the dehydration of the aldol at the phase boundary is probably facilitated; consequently the Knoevenagel condensation dominates even when a large excess of CCl_4 is used.

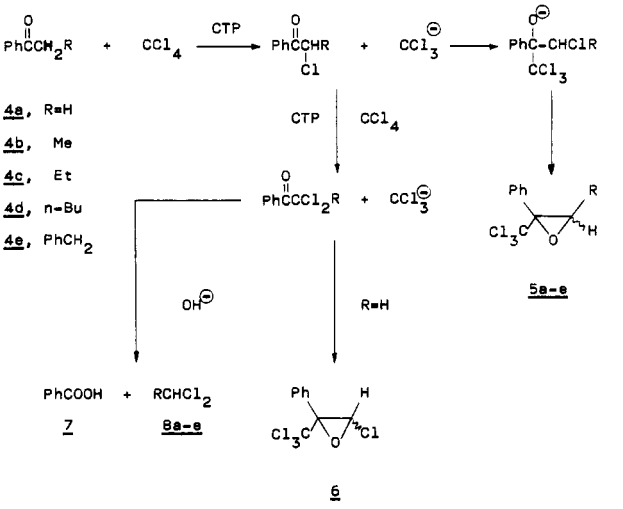
When acrylonitrile is used for trapping of the transient α-chlorophenylacetonitrile carbanion generated in the reaction of phenylacetonitrile with CCl_4, a competition between two irreversible processes chlorination and cyanoethylation[15] of phenylacetonitrile take place. The latter can be suppressed by use of an excess of CCl_4. In such a case, however, 1-chloro-1,2-dicyano-2-phenylcyclopropane is the main product, formed by chlorination of the anionic adduct of α-chlorophenylacetonitrile anion to acrylonitrile before its cyclization.[2] The yield of the desired product **2a** can be increased when the reaction is carried out with an equimolar amount of CCl_4, for in such conditions formation of chlorocyclopropane is much subdued. Similarly, the reaction of *tert*-butyl acrylate with phenylacetonitrile and CCl_4 occurs.

Cyclopropanes are also formed in the CTP system via chlorination of 1,3-diphenyl dinitrile **3** with CCl_4 followed by fast cyclization of the monochlorinated intermediate, which is simultaneously an electrophile and nucleophile (eq 1).

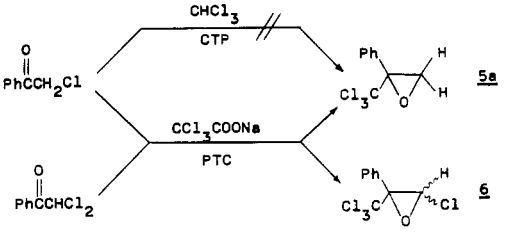


Chlorination Products as Electrophiles. Chlorination of carbanions leads as a rule to compounds of electrophilic character. In many cases reactivity of chlorinated products is so high that they react rapidly with nucleophiles present in the reaction medium. This type of transformation includes the previously reported dimerization of phenylacetonitrile,[2,12] the Ramberg–Bäcklund reaction of sulfones,[6,7] and such reactions of chlorinated ketones in strongly basic media as the Favorski rearrangement, haloform-type reaction, and hydrolysis to α-hydroxy ketones.[6-8]

Scheme I



Scheme II



Studying the reaction of alkanophenones with CCl_4 in the CTP system, we have observed a quite new process—formation of (trichloromethyl)oxirane derivatives, along with the haloform-type reaction leading to benzoic acid and dichloroalkanes[16] (Scheme I).

The oxiranes **5a–e** are formed via addition of trichloromethyl anion to the initial chlorination products, i.e., α-chloro ketones, followed by the cyclization of the resulted chlorohydrin anions.

(14) Mąkosza, M. *Pure Appl. Chem.* **1975**, *43*, 439. Mąkosza, M.; Białecka, E. *Tetrahedron Lett.* **1977**, 183.

(15) Actually cyanoethylation is a reversible process but under CTP conditions the retro-Michael reaction of cyanoethylated phenylacetonitrile has not been observed.

(16) When this paper was under preparation a report on the CTP reaction of phenylacetone with CCl_4 in which corresponding (trichloromethyl)oxirane was formed in low yield appeared: Reeves, W. P.; Creswek, M. W. *Synth. Commun.* **1983**, *13*, 945.

Table II. Reactions of $PhCOCH_2R$ 4a–e with CCl_4 in the CTP system

substrate	R	reactn time, h	product yields,[a] % in CCl_4 5a–e	6	7	8	in $CCl_4/CHCl_3$ 5a–e
4a	H	4	30	15	46	*b*	
4b	Me	5	25	*c*	61	*b*	50
4c	Et	5	33	*c*	65	*b*	55
4d	*n*-Bu	7	32[d]	*c*	60	35[d]	57
4e	$PhCH_2$	7	40[d]	*c*	52	44[d]	60

[a] Unless otherwise noted, yields of isolated products. [b] Detected but not isolated. [c] Not detected. [d] Based on NMR and GLC.

Table III. Reactions of $PhCH(NR_2)CN$ with Perhaloalkanes CCl_4R^1 in the CTP System

substrate	R^1	reactn time, h	product	yield, %
9a	Cl	2.5	**10a**	36
9b	Cl	2.5	**10b**	49
9c	Cl	2.5	**10c**	40
9b	Ph	3	**10d**	30
9b	CCl_3	3	**12**	75
			13	12.5

Similarly, addition of Cl_3C^- to an α,α-dichloro ketone can lead to the corresponding dichlorohydrin anion which cyclizes to the chlorooixrane **6**. This is the case, however, only with acetophenone (**4a**, R = H).

In order to confirm this reaction pathway (see Scheme I) α-chloroacetophenone was subjected to the reaction with chloroform in the CTP system. It was expected that Cl_3C^- generated in the system would add to the chloro ketone to form as the final product oxirane **5a**. Contrary to our expectation **5a** was not formed and only based-induced decomposition of chloroacetophenone took place. On the other hand Cl_3C^- generated in the absence of base (via phase-transfer-catalyzed decarboxylation of sodium trichloroacetate[17]) adds to chloroacetophenone, giving **5a** in good yield. Under these conditions also dichloroacetophenone reacts with Cl_3C^-, yielding chlorooxirane **6** (Scheme II).

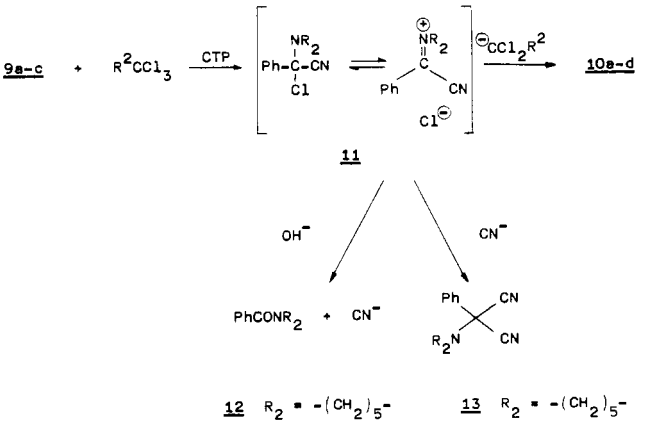
The results show, that under the CTP conditions deprotonation of chloroacetophenone by NaOH at the phase boundary proceeds with higher rate than of chloroform, although a proton transfer between chloroacetophenone and Cl_3C^- is apparently slower than the addition of the latter to the carbonyl group.

Contrary to chloroacetophenone, α-chlorobutyrophenone react with chloroform in the CTP system via addition of Cl_3C^- anion to form (trichloromethyl)oxirane **5c**. Both the lower acidity of alkylated α-chloroacetophenones[18] and their higher stability under basic conditions make the reaction possible.

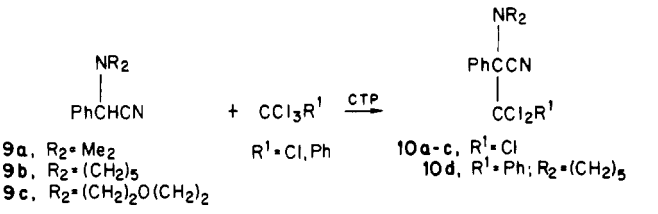
Taking an advantage of this observation we carried out the reaction of alkanophenones **4b–e** in a mixture of CCl_4 and $CHCl_3$ so the yields of oxiranes **5b–e** were improved and the formation of benzoic acid and dichloroalkanes suppressed (Table II).

It is noteworthy, that a chlorooxirane (e.g., **6**) is formed only from acetophenone (**4a**, R = H). Even phase-transfer-catalyzed decarboxylation of sodium trichloroacetate in the presence of $PhCOCCl_2R$ (R = alkyl) failed to give the products of addition of Cl_3C^-. It is now difficult to decide which step of this reaction is responsible for this failure, because both addition of CCl_3^- to the carbonyl group connected with tertiary carbon atom and intramolecular nucleophilic substitution of chlorine in a dichloroalkyl moiety (cyclization step) may be hindered.

Scheme III



We have preliminary reported formation of trichloromethyl derivatives **10a,b** in the reaction of phenyl(dialkylamino)acetonitriles **9a,b** with CCl_4 in the CTP system.[2] Our further studies showed that $PhCCl_3$ also react with carbanions of this type, giving products of "substitution" of chlorine atom (eq 2, Table III).



(2)

There are few reported examples of a similar substitution of halogen in CX_4 by carbanions. Thus, some carbanions (e.g., acetylene, cyanoacetate, etc. derivatives) in reaction with CF_2Br_2 and CF_2BrCl form difluorobromomethyl derivatives; here the reaction proceeds via addition of difluorocarbene to the carbanion and further halogenation of the resulting difluorocarbanion (so-called carbene-chain mechanism).[19]

It is noteworthy, however, that among a variety of carbanions which have been reacted with CCl_4,[2-10] only those containing a dialkylamino group at the carbanionic center gave products of the substitution of halogen. Taking into account that strongly electrophilic chlorinated intermediates can trap Cl_3C^- (see above), one can consider also this substitution process as a combination of initially generated electrophilic intermediate with nucleophilic Cl_3C^- anion. According to the proposed mechanism (Scheme III), which rationalizes the specific function of the dialkylamino group,

(17) Dehmlow, E. V.; Remmler, T. *J. Chem. Res., Miniprint* **1977**, 766.

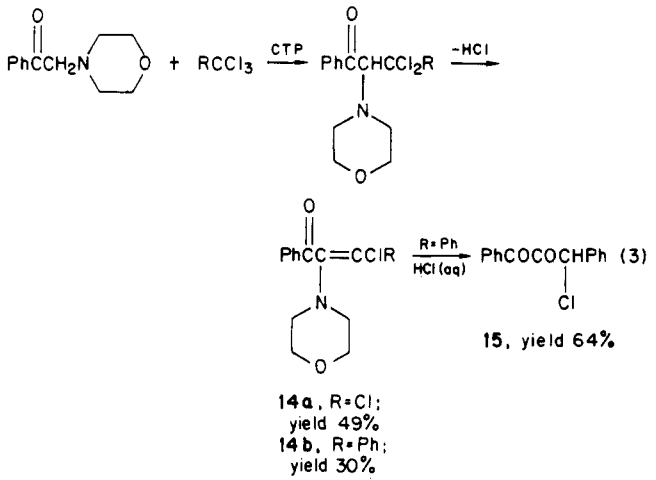
(18) Although we were unable to find data concerning acidities of $PhCOCH_2Cl$ and PhCOCHCl-alkyl, one can expect that similarly to the case of $PhCOCH_2CH_3$ (pK_a = 24.4) and $PhCOCH(CH_3)_2$ (pK_a = 26.3), an alkyl substituent introduced to secondary carbon atom will rather destabilize the enolate anion. Bordwell, F. G.; Bartmess, J. E.; Hautala, J. A. *J. Org. Chem.* **1978**, *43*, 3095.

(19) Rico, I.; Cantacuzene, D.; Wakselman, C. *J. Chem. Soc., Perkin Trans. 1* **1982**, 1063. Bey, P.; Vevert, J.; Dorsselaer, V.; Kolb, M. *J. Org. Chem.* **1979**, *44*, 2732.

chlorination of **9** leads to the α-chloro nitrile actually existing as a highly electrophilic iminium salt **11** which easily adds Cl_3C^- to form the final product **10**.

This mechanistic scheme is strongly supported by the fact that in the reaction of phenylpiperidylacetonitrile (**9b**) with CCl_4 a small quantity (4%) of phenylmalononitrile derivative **13** additionally was isolated. Apparently the intermediate iminium salt adds hydroxy anion, so the amide **12** and CN^- anions are produced. The latter also add to **11** giving **13**. The results of the reaction of **9b** with hexachloroethane ($R^1 = CCl_3$) confirm this supposition. This compound is a chlorinating agent, but it does not form a stable enough carbanion due to the rapid elimination of Cl^- to form tetrachloroethane. Here the main products are the corresponding benzamide **12** and phenylmalononitrile derivative **13**.

Taking into account the ability of Cl_3C^- to add to the carbonyl and the iminium groups, α-(dialkylamino)acetophenone was studied as a precursor of such bifunctional electrophilic intermediate (after chlorination). The results obtained in the reaction of α-morpholinoacetophenone with both CCl_4 and $PhCCl_3$ in the CTP system (eq 3) show



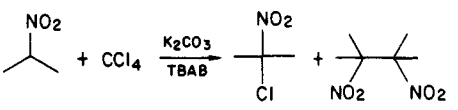
that the chlorinated α-amino ketone adds corresponding carbanions derived from chlorinating agents at the α-position to form, after fast elimination of HCl, keto enamines **14a** (yield 49%) and **14b** (yield 30%). A hydrolysis of **14b** under mild conditions yields the 1,2-diketone **15**.

Products of Chlorination as Acceptors of Electrons. Chlorinated nitroalkanes and particularly 2-chloro-2-nitropropane are known as effective electron acceptors reacting with a variety of nucleophiles to form coupling products. It has been reported, that the sodium or lithium salt of 2-nitropropane in Me_2SO dimerizes upon the reaction with CCl_4 giving 2,3-dimethyl-2,3-dinitrobutane.[10] The authors, however, claimed that it is "unlikely" that the process proceeds via chlorination of 2-nitropropane, and they tentatively "favored" a mechanism via electron transfer from the anion to CCl_4 and direct coupling of 2-nitropropyl radical with the nitronate anion.

We have found that the reaction of 2-nitropropane with an excess of CCl_4 carried out in solid–liquid CTP system (solid K_2CO_3 as a base) results in the formation of 2-chloro-2-nitropropane and only minor amount of the dimer (eq 4).

Similarly, nitrocyclopentane is chlorinated with CCl_4 (yield 70%) and 2-nitropropane brominated with $BrCCl_3$ (GLC yield 90%). Dimers are formed in yields about 5%.

The reaction of equimolar amounts of 2-nitropropane and CCl_4 in benzene under the CTP conditions yields 2-chloro-2-nitropropane (**16**) and the dimer **17** in molar ratio 4.1:1.0. So the larger the excess of CCl_4 used, the



(4)

		16	**17**
1:10	molar ratio (GLC)	9.0	1.0
	yield (isolated)	72%	9%
1:1	molar ratio (GLC)	4.1	1.0
	yield (GLC)	56%	27%
2:1	yield (isolated)		62%

higher ratio of **16** to **17** observed. Consequently when the ratio of CCl_4 to 2-nitropropane is 0.5 the reaction gave the dimer **17** in good yield, although the process requires longer time and/or higher temperature.

Thus one can suppose that formation of the dimer is a slow, subsequent reaction of **16** with 2-nitropropane anion according to $S_{RN}1$ mechanism, and this process is simultaneously competitive to the chlorination of 2-nitropropane anion with CCl_4.

According to the RARP mechanism proposed by C. Y. Meyers for reactions of carbanions with CCl_4, electron transfer from the carbanion to CCl_4 results in formation of radical–anion–radical ion pair (RARP).[7] Active radicals are chlorinated within the RARP via a Cl atom transfer whereas more stable ones are able to escape from it. Therefore one can expect that RARP consisting of relatively stable 2-nitropropyl radicals and $CCl_4^{-\cdot}$ should dissociate to liberate 2-nitropropyl radical which can react with 2-nitropropane anion to form 2-nitropropane dimer bypassing the chlorination step.

Our results show that anions of secondary nitroalkanes can be chlorinated by CCl_4 despite of their high tendency to the formation of radicals. Also α-(dialkylamino)-phenylacetonitriles and ketones mentioned above, as well as α-methoxyphenylacetonitrile described previously[2] are effectively chlorinated by CCl_4, although the corresponding radicals are relatively well stabilized by the capto-dative effects.[20] So the correlation between stability of the radicals in RARP and direction of their further reactions is not clear yet.

Besides its mechanistic interest, the reaction of nitroalkanes with CCl_4 in the CTP system also has practical value. By simple modification of the reaction conditions the convenient preparation of either chlorinated nitroalkanes or their dimers is possible.

Experimental Section

Melting points are uncorrected. Infrared spectra were recorded on a Specord 71 IR (Karl Zeiss Jena). NMR spectra were recorded on a JEOL JNM-4H-100 (100 MHz) or Varian EM-360 (60 MHz) with Me_4Si as internal standard.

The following compounds were prepared according to the described procedures: 2,4-diphenylglutaronitrile,[21] benzylacetophenone,[22] phenyl(dialkylamino)acetonitriles (**9a–c**),[23] morpholinoacetophenone.[24]

Preparation of Glycidonitriles 1a–h. Standard Procedure for CTP Reactions. Nitrile (0.02 mol) and aldehyde (0.022 mol) in CCl_4 (5 mL) were added dropwise to mechanically stirred 50% aqueous NaOH (15 mL), CCl_4 (15 mL), and TBAB (0.1 g) as the temperature was maintained as specified in Table I. After the addition was complete the stirring was continued for the time

(20) Viehe, H. G.; Merenyi, R.; Stella, L.; Janousek, Z. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 917.
(21) Mąkosza, M.; Serafin, B. *Rocz. Chem.* **1966**, *40*, 1647.
(22) Adams, R.; Kern, J., W.; Shriner, R., L. "Organic Syntheses"; 2nd ed.; Wiley: New York, 1951; Collect. Vol. I, p 101.
(23) Houser, C. R.; Taylor, M.; Ledford, T. G. *J. Am. Chem. Soc.* **1960**, *82*, 1786.
(24) Marvel, C. S.; du Vigneaud, V. *J. Am. Chem. Soc.* **1924**, *46*, 2098.

shown in Table I. Then the mixture was diluted with water, the organic products were extracted twice with CH_2Cl_2, and the extract was thoroughly washed with water and dried with Na_2SO_4 and the solvent evaporated. The crude product was recrystallized or distilled.

(*Z*)-2,3-Diphenylglycidonitrile (**1a**): mp 69–70 °C (from MeOH) (lit.[25] mp 69–70 °C); NMR (100 MHz, $CDCl_3$) δ 4.10 (s, 1 H), 7.50 (m, 5 H).

2-Phenyl-3-isopropylglycidonitrile (**1b**): bp 94–96 °C (1.0 torr); NMR (100 MHz, $CDCl_3$) δ 1.13 (t, 6 H, J = 7.5 Hz), 1.42 (m, 1 H), 2.86 (d, 1 H, J = 8.5 Hz), 7.39 (s, 5 H). Anal. Calcd for $C_{12}H_{13}NO$: C, 76.97; H, 7.00; N, 7.48. Found: C, 76.88; H, 6.91; N, 7.46.

2-Phenyl-3-(4-chlorophenyl)glycidonitrile (**1c**): mp 113–114 °C (from EtOH); NMR (60 MHz, $CDCl_3$) δ 4.08 (s, 1 H), 7.30–7.65 (m, 9 H). anal. Calcd for $C_{15}H_{10}NClO$: C, 70.76; H, 3.94; N, 5.48; Cl, 13.86. Found: C, 70.34; H, 3.80; N, 5.47; Cl, 14.20.

2-Phenyl-3-(4-methoxyphenyl)glycidonitrile (**1d**): mp 96–98 °C (from EtOH); NMR (60 MHz, $CDCl_3$) δ 3.71 (s, 3 H), 3.90 (s, 1 H), 6.65–7.60 (m, 9 H). Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57. Found: C, 76.59; H, 5.14; N, 5.61.

2-Phenyl-3-(4-isopropylphenyl)glycidonitrile (**1e**): mp 66.5–68 °C (from EtOH); NMR (60 MHz, $CDCl_3$) δ 1.22 (d, 6 H, J = 7 Hz), 2.86 (sept, 1 H, J = 7 Hz), 3.93 (s, 1 H), 7.0–7.7 (m, 9 H). Anal. Calcd for $C_{18}H_{17}NO$: C, 82.10; H, 6.51; N, 5.32. Found: C, 82.14; H, 6.48; N, 5.24.

2-(3-Bromophenyl)-3-phenylglycidonitrile (**1f**): mp 112–114 °C (from EtOH); NMR (60 MHz, $CDCl_3$) δ 4.07 (s, 1 H), 7.2–7.8 (m, 9 H). Anal. Calcd for $C_{15}H_{10}NBrO$: C, 60.02; H, 3.36; N, 4.66; Br, 26.62. Found: C, 60.57; H, 3.44; N, 4.72; Br, 26.43.

2-(4-Methoxyphenyl)-3-phenylglycidonitrile (**1g**): mp 114–115 °C (from MeOH); NMR (100 MHz, $CDCl_3$) δ 3.75 (s, 3 H), 4.10 (s, 1 H), 6.7–7.6 (m, 9 H). Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57. Found: C, 76.39; H, 5.30; N, 5.62.

2-(1-Naphthyl)-3-phenylglycidonitrile (**1h**): mp 99–101 °C (form MeOH), NMR (100 MHz, $CDCl_3$) δ 4.15 (s, 1 H), 7.1–8.1 (m, 7 H). Anal. Calcd for $C_{19}H_{13}NO$: C, 84.11; H, 4.83; N, 5.16. Found: C, 84.02; H, 4.78; N, 5.19.

Reaction of Propiophenone with CCl_4 and Benzaldehyde. Propiophenone (0.03 mol, 3.9 g), benzaldehyde (0.035 mol, 3.8 g), CCl_4 (15 mL), 50% NaOH (15 mL), and TBAB (0.1 g) were stirred at 25–30 °C (cold water bath) for 75 min and worked up as described in standard procedure. The crude product (dark oil) was shaken with hexane (150 mL), and the extract was filtered through 5 g of silica gel. After evaporation **1i** (3.0 g, 42%) as a colorless oil was obtained: NMR (60 MHz, CCl_4) δ 1.33 (s, 3 H), 4.03 (s, 1 H), 7.3–7.7 (m, 8 H), 8.0–8.3 (m, 2 H). Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.41; H, 5.84.

Reaction of Phenylacetonitrile with Acrylonitrile and an Excess of CCl_3. Phenylacetonitrile (0.05 mol, 5.9 g) and acrylonitrile (0.06 mol, 3.2 g) were slowly added to the stirred mixture of 50% NaOH (25 mL), CCl_4 (30 mL), and TBAB (0.2 g) maintaining the temperature at 15 °C. The reaction was continued for 1 h and worked up. After flash distillation [120–210 °C (10 torr)] the mixture of **2a** and 1-chloro-1,2-dicyano-2-phenylcyclopropane (5.5 g) was obtained. The products were separated on a silica gel column (2:5) AcOEt/hexane).

(*E*),(*Z*)-1-Chloro-1,2-dicyano-2-phenylcyclopropane: yield 4.1 g, 41%; NMR (100 MHz, $CDCl_3$) δ (*E*) 2.32 (d, 1 H, J = 7 Hz), 2.53 (d, 1 H, J = 7 Hz), 7.35 (m, 5 H), (*Z*) 2.30 (d, 1 H, J = 7 Hz), 2.61 (d, 1 H, J = 7 Hz), 7.35 (m, 5 H). Anal. Calcd for $C_{11}H_7N_2Cl$: C, 65.19; H, 3.48; N, 13.82; Cl, 17.49. Found: C, 65.31; H, 3.50; N, 13.77; Cl, 17.98.

(*E*),(*Z*)-1,2-dicyano-1-phenylcyclopropane (**2a**): yield 0.8 g, 10%; NMR (100 MHz, $CDCl_3$) δ 1.90–2.50 (m, 3 H), 7.33 (m, 5 H). Anal. Calcd for $C_{11}H_8N_2$: C, 78.55; H, 4.79; N, 16.65. Found: C, 78.28; H, 4.85; N, 16.61.

Preparation of 2a and 2b in the Reaction with an Equimolar Amount of CCl_4. Phenylacetonitrile (0.02 mol, 2.35 g), 50% NaOH (15 mL), benzene (15 mL), and TBAB (0.1 g) were stirred, and acrylonitrile (0.024 mol, 1.27 g) or *tert*-butyl acrylate (0.024 mol, 2.1 g) with CCl_4 (0.02 mol, 3.1 g) in benzene (5 mL) was added dropwise at 20 °C (cooling was necessary). After the addition the mixture was stirred for the time specified in Table I and worked up. The crude oil was chromatographed on a silica gel column (5:1 AcOEt/hexane), and a pure fraction of *E,Z* isomer mixture of **2a** (1.75 g, 52%) or **2b** (2.2 g, 45%) was collected.

2b: NMR (60 MHz, CCl_4) (major isomer) δ 1.49 (s, 9 H), 1.5–2.5 (m, 3 H), 7.4 (s, 5 H), (minor isomer) 1.08 (s, 9 H), 1.4–2.6 (m, 3 H), 7.4 (m, 5 H). Anal. Calcd for $C_{11}H_8N_2$: C, 78.55; H, 4.79; N, 16.65. Found: C, 78.28; H, 4.85; N, 16.61.

Preparation of 1,2-Dicyano-1,2-diphenylcyclopropane. 2,4-diphenylglutaronitrile (0.01 mol, 2.5 g), CCl_4 (5 mL), benzene (15 mL), 50% NaOH (7 mL), and TBAB (0.05 g) were stirred without cooling at 20–27 °C for 2 h. After the usual workup a brown solid (2.1 g) was obtained. Recrystallization from ethanol gave the product (*E,Z* mixture, 1.9 g, 78%): NMR (100 MHz, $CDCl_3$) δ (*E*) 2.50 (d, 1 H, J = 7 Hz), 2.59 (d, 1 H, J = 7 Hz), 7.10 (m, 10 H), (*Z*) 2.57 (s, 2 H), 7.48 (m, 10 H). Anal. Calcd for $C_{17}H_{12}N_2$: C, 83.58; H, 4.95; N, 11.46. Found: C, 83.83; H, 4.81; N, 11.23.

Reaction of Acetophenone with CCl_4. Acetophenone (0.02 mol, 2.4 g), CCl_4 (15 mL), 50% NaOH (10 mL), and TBAB (0.1 g) were stirred at ambient temperature for 4 h. After the usual workup the crude product was chromatographed (SiO_2, CCl_4), yielding 2-phenyl-2-(trichloromethyl)oxirane (**5a**; 1.4 g, 30%) and 2-phenyl-2-(trichloromethyl)-3-chlorooxirane (**6**; 0.8 g, 15%).

5a: NMR (60 MHz, CCl_4) δ 2.90 (d, 1 H, J = 5.5 Hz), 3.60 (d, 1 H, J = 5.5 Hz), 7.12–7.72 (m, 5 H). Anal. Calcd for $C_9H_7Cl_3O$: C, 45.51; H, 2.97; Cl, 44.77. Found: C, 45.66; H, 3.10; Cl, 44.28.

6: NMR (60 MHz, CCl_4) δ 5.57 (s, 1 H), 7.12–7.72 (m, 5 H). Anal. Calcd for $C_9H_6Cl_4O$: C, 39.74; H, 2.22; Cl, 52.14. Found: C, 39.70; H, 2.31; Cl, 52.50.

Preparation of (Trichloromethyl)oxiranes 5b–e. Ketone **4b–e** (0.02 mol), CCl_4 (0.03 mol, 4.6 g), $CHCl_3$ (0.03 mol, 3.6 g), 50% NaOH (10 mL), and TBAB (0.1 g) were stirred at 20–30 °C for 5 h. After the ordinary workup the crude products were recrystallized (**5c,e**) or steam-distilled (**5b,d**), yielding the pure oxiranes.

2-Phenyl-2-(trichloromethyl)-3-methyloxirane (**5b**): NMR (60 MHz, CCl_4) δ 1.07 (d, 3 H, J = 5.8 Hz), 3.87 (q, 1 H, J = 5.8 Hz). Anal. Calcd for $C_{10}H_9Cl_3O$: C, 47.75; H, 3.61; Cl, 42.28. Found: C, 47.62; H, 3.66; Cl, 42.51.

2-Phenyl-2-(trichloromethyl)-3-ethyloxirane (**5c**): mp 58–60 °C (from MeOH); NMR (100 MHz, CCl_4) δ 0.9–1.5 (m, 5 H), 3.71 (t, 1 H), 7.2–7.9 (m, 5 H). Anal. Calcd for $C_{11}H_{11}Cl_3O$: C, 49.72; H, 4.14; Cl, 40.11. Found: C, 49.81; H, 4.15; Cl, 40.41.

2-Phenyl-2-(trichloromethyl)-3-*n*-butyloxirane (**5d**): NMR (60 MHz, CCl_4) δ 0.6–1.6 (m, 9 H), 3.77 (t, 1 H), 7.2–7.9 (m, 5 H). Anal. Calcd for $C_{13}H_{15}Cl_3O$: C, 53.18; H, 5.15; Cl, 36.22. Found: C, 53.30; H, 5.33; Cl, 37.14.

2-Phenyl-2-(trichloromethyl)-3-benzyloxirane (**5e**): mp 49–50.5 °C (from MeOH); NMR (100 MHz, CCl_4) δ 2.4–2.8 (m, 2 H), 4.08 (t, 1 H), 7.1–7.9 (m, 10 H). Anal. Calcd for $C_{16}H_{13}Cl_3O$: C, 58.67; H, 3.97; Cl, 32.47. Found: C, 58.30; H, 3.89; Cl, 32.56.

Reaction of Ketones 4b–e with CCl_4. Ketone 4 (0.02 mol), CCl_4 (15 mL), 50% NaOH (10 mL), and TBAB (0.1 g) were stirred at room temperature for 4–7 h as specified in Table II. The mixture was then diluted with water (ca. 100 mL) and extracted with CH_2Cl_2 (2 × 30 mL). The water layer was acidified with concentrated hydrochloric acid. Benzoic acid was filtered and dried on air. The organic extracts were worked up as usually, and the crude product was analyzed by GLC and NMR and chromatographed (SiO_2, AcOEt/hexane). Only **5b** and **5c** were isolated quantitatively in pure state.

Reaction of Chloroacetophenone and Dichloroacetophenone with Sodium Trichloroacetate. To a solution of chloro ketone (0.0025 mol) in chloroform (10 mL), sodium trichloroacetate (0.0075 mol, 1.39 g) was added. The suspension was stirred under reflux for 6 h. The reaction mixture was then washed with water (2 × 30 mL) and dried (Na_2SO_4). Chloroform was evaporated and the crude product was purified by column chromatography (SiO_2, 1:1 benzene/hexane), whereupon **5a** (0.39 g, 58%) or **6** (0.44 g, 65%), respectively, was obtained.

Preparation of 2-(Dialkylamino)-2-phenyl-3,3,3-trichloropropionitriles 10a–c. Phenyl(*N,N*-dialkylamino)acetonitrile **9a–c** (0.01 mol) CCl_4 (8 mL), 50% NaOH (7 mL), and TBAB (0.05 g) were stirred under nitrogen at 20–25 °C for 2.5 h. After the ordinary workup the crude crystallizing oil was

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recrystallized from methanol. In case of the reaction of **9b** the filtrate was additionally evaporated and chromatographed (SiO_2, hexane/AcOEt); **10b** (0.1 g, 3%) and phenylpiperidylmalononitrile (**13**; 0.09 g, 4%) were obtained.

10a: mp 94–95 °C; NMR (100 MHz, $CDCl_3$) δ 2.46 (s, 6 H), 7.30–8.0 (m, 5 H). Anal. Calcd for $C_{11}H_{11}N_2Cl_3$: C, 47.60; H, 3.99; N, 10.10; Cl, 47.60. Found: C, 47.50; H, 4.10; N, 10.13; Cl, 47.50. MS, m/e 276 (M^+), 250 ($M^+ - CN$), 232 ($M^+ - NMe_2$), 159 ($M^+ - CCl_3$).

10b: mp 118 °C; NMR (100 MHz, $CDCl_3$) δ 1.57 (m, 6 H), 2.3–3.1 (m, 4 H), 7.30 (m, 3 H), 7.82 (m, 2 H). Anal. Calcd for $C_{14}H_{15}N_2Cl_3$: C, 52.93; H, 4.76; N, 8.81; Cl, 33.48. Found: C, 52.92; H, 4.82; N, 8.75; Cl, 32.66. MS; m/e 316 (M^+), 290 ($M^+ - CN$), 232 ($M^+ - N(CH_2)_5$), 199 ($M^+ - CCl_3$).

10c: mp 138 °C; NMR (100 MHz, $CDCl_3$) δ 2.41–3.10 (m, 4 H), 3.71 (m, 4 H), 7.3–7.5 (m, 5 H). Anal. Calcd for $C_{13}H_{13}N_2Cl_3O$: C, 48.85; H, 4.09; N, 8.76; Cl, 32.27. Found: C, 48.82; H, 4.17; N, 8.68; Cl, 31.77.

13: mp 62–63 °C (hexane); Anal. Calcd for $C_{14}H_{15}N_3$: C, 74.64; H, 6.71; N, 18.65. Found: C, 74.69; H, 6.64; N, 18.43.

Preparation of 2,3-Diphenyl-2-piperidyl-3,3-dichloropropionitrile (10d). **9b** (0.01 mol, 2.0 g) and phenyltrichloromethane (0.01 mol, 1.95 g) in benzene (20 mL) were stirred with 50% NaOH (5 mL) and TBAB (0.05 g) under nitrogen at 20–25 °C for 3 h. Ordinary workup and recrystallization of the crude product from methanol gave **10d** (1.1 g, 30%): mp 108–110 °C; Anal. Calcd for $C_{20}H_{20}N_2Cl_2$: C, 66.85; H, 5.61; N, 7.79; Cl, 19.74. Found: C, 66.86; H, 5.57; N, 7.80; Cl, 19.30.

Reaction of 9b with Hexachloroethane. **9b** (0.01 mol, 2.0 g), hexachloroethane (0.01 mol, 2.5 g), benzene (20 mL), 50% NaOH (5 mL), and TBAB (0.05 g) were stirred under nitrogen at 20–25 °C for 3 h. After workup, the crude product was chromatographed (SiO_2 benzene), whereupon *N,N*-pentamethylenebenzamide (**12**; 1.6 g, 75% oil; GLC, TLC, and IR identical with the original sample) and phenylpiperidylmalononitrile (**13**; 0.28 g, 12.5%; mp 62–63 °C) were obtained.

Preparation of Phenyl 1-Morpholino-2,2-dichlorovinyl Ketone (14a). Morpholinoacetophenone (0.01 mol, 2.05 g), CCl_4 (10 mL), 50% NaOH (5 mL), and TBAB (0.05 g) were stirred at 20–25 °C (ice bath) for 20 min. After the usual workup, the obtained crude brown oil (2.1 g) was passed through a short column (ca. 5 g, SiO_2) in benzene, yielding **14a** (1.45 g, 49%): NMR (60 MHz, CCl_4) δ 2.8–3.15 (m, 4 H), 3.5–3.7 (m, 4 H), 7.4–8.1 (m, 5 H). Anal. Calcd for $C_{13}H_{13}NO_2Cl_2$: C, 54.56; H, 4.58; N, 4.89; Cl, 24.78. Found: C, 54.94; H, 4.68; N, 4.57; Cl, 24.76.

Preparation of 3-Chloro-1,3-diphenyl-1,2-propanedione (15). Morpholinoacetophenone (0.01 mol, 2.05 g) and phenyltrichloromethane (0.01 mol, 1.95 g) in benzene were stirred with 50% NaOH (7 mL) and TBAB (0.05 g) at 25 °C (ice bath) for 30 min and worked up. The crude product was purified by column chromatography (SiO_2, $CHCl_3$), and the resulting orange oil **14b** (1.1 g, 30%) was dissolved in EtOH (10 mL). Aqueous 10% HCl (10 mL) was added and kept at room temperature overnight. The mixture was then poured into water (ca. 200 mL), extracted with CH_2Cl_2 (3 × 30 mL). The extract was dried over Na_2SO_4 and evaporated. The oil (0.8 g) was extracted with hexane and then passed through a short silica gel column (ca. 5 g, SiO_2). After evaporation, **15** (0.6 g, 64%) as a yellow oil was obtained: NMR (60 MHz, CCl_4) δ 6.20 (s, 1 H), 7.0–8.0 (m, 10 H). Anal. Calcd for $C_{15}H_{11}ClO_2$: C, 69.64; H, 4.29; Cl, 13.70. Found: C, 69.64; H, 4.53; Cl, 13.58.

Chlorination of Nitroalkanes with CCl_4 in the Solid–Liquid CTP System. Nitroalkane (0.1 mol), CCl_4 (75 mL), anhydrous K_2CO_3 (21 g), and TBAB (0.6 g) were stirred at 35–40 °C for 3 h. The mixture was then filtered, and the solid was well washed with CH_2Cl_2. Solvents were evaporated, and the crude product was distilled under reduced pressure: 2-chloro-2-nitropropane (8.9 g, 72%), bp 54 °C (50 torr) [lit.[26] bp 48–52 °C (40 torr)]; 1-chloro-1-nitrocyclopentane (10.5 g, 70%), IR and GLC identical with a sample prepared according to literature.[27]

Reaction of 2-Nitropropane with an Equimolar Amount of CCl_4. 2-Nitropropane (0.02 mol, 1.78 g, CCl_4 (0.02 mol, 3.08 g), K_2CO_3 (4.5 g), and TBAB (0.1 g) were stirred in benzene (10 mL) at 35–40 °C for 6 h. Water (50 mL) and CH_2Cl_2 (50 mL) were then added: the organic layer was separated, dried, and analyzed by GLC.

Dimerization of 2-Nitropropane with CCl_4. 2-Nitropropane (0.04 mol, 3.56 g), CCl_4 (0.02 mol, 3.1 g), K_2CO_3 (9.0 g), and TBAB (0.15 g) were refluxed in $CHCl_3$ (10 mL) with stirring for 9 h. The reaction mixture was then diluted with $CHCl_3$ (50 mL) and filtered. The solid was well washed with CH_2Cl_2, solvents were evaporated, and crude crystals were recrystallized from ethanol to yield 2,3-dimethyl-2,3-dinitrobutane: 2.14 g, 62%; mp 210–212 °C (lit.[10] mp 212 °C).

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Registry No. **1a**, 15115-82-9; **1b**, 69573-33-7; **1c**, 97295-13-1; **1d**, 97295-14-2; **1e**, 97295-15-3; **1f**, 97295-16-4; **1g**, 97295-17-5; **1h**, 97295-18-6; **1i**, 15856-60-7; *cis*-**2a**, 70871-50-0; *trans*-**2a**, 70871-52-2; *cis*-**2b**, 97315-05-4; *trans*-**2b**, 97315-04-3; **3**, 1222-47-5; **4a**, 98-86-2; **4b**, 93-55-0; **4c**, 495-40-9; **4d**, 942-92-7; **4e**, 1083-30-3; **5a**, 75590-20-4; **5b**, 97295-22-2; **5c**, 97295-23-3; **5d**, 97295-24-4; **5e**, 97295-25-5; **6**, 97295-21-1; **7**, 65-85-0; **8d**, 820-55-3; **8e**, 4412-39-9; **9a**, 827-36-1; **9b**, 5766-79-0; **9c**, 15190-10-0; **10a**, 69573-36-0; **10b**, 69573-40-6; **10c**, 97295-26-6; **10d**, 97295-27-7; **12**, 776-75-0; **13**, 97295-28-8; **14a**, 97295-29-9; **14b**, 97315-06-5; **15**, 97295-30-2; **16**, 594-71-8; **17**, 3964-18-9; CCl_4, 56-23-5; CH_2=CHCN, 107-13-1; CH_2=CHCOOBu-*t*, 1663-39-4; $PhCOCH_2Cl$, 532-27-4; $PhCOCHCl_2$, 2648-61-5; CCl_3COONa, 650-51-1; $PhCCl_3$, 98-07-7; Cl_3CCCl_3, 67-72-1; $(CH_3)_2CHNO_2$, 79-46-9; $PhCH_2CN$, 140-29-4; 3-$BrC_6H_4CH_2CN$, 31938-07-5; 4-$MeOC_6H_4CH_2CN$, 104-47-2; 1-$C_{10}H_7CH_2CN$, 132-75-2; PhCHO, 100-52-7; *i*-PrCHO, 78-84-2; 4-ClC_6H_4CHO, 104-88-1; 4-$MeOC_6H_4CHO$, 123-11-5; 4-*i*-PrC_6H_4CHO, 122-03-2; *cis*-1-chloro-1,2-dicyano-2-phenylcyclopropane, 70871-51-1; *trans*-1-chloro-1,2-dicyano-2-phenylcyclopropane, 70871-49-7; *cis*-1,2-dicyano-1,2-diphenylcyclopropane, 97295-20-0; *trans*-1,2-dicyano-1,2-diphenylcyclopropane, 97295-19-7; morpholinoacetophenone, 779-53-3; nitrocyclopentane, 2562-38-1; 1-chloro-1-nitrocyclopentane, 931-93-1.

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