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(5) **2b** (cis) was identified by comparison with an authentic sample: see ref 4. Treatment of **1b** with Et_3N in CH_3CN or H_2O gave the corresponding salt (mp, 237–242 °C dec) instead of **2b.** The salt did not give **2b** even under reflux in H_2O.
(6) The products were analyzed as a mixture: molecular distillation 130 °C/1 mm (bath temperature); *m/e* 202 (M^+); NMR ($CDCl_3$, Me_4Si) of one isomer of **2c,** δ 1.41 (3 H, s, C_5-Me), 3.20 (6 H, s, NMe), 3.52 (3 H, s, OMe), and 4.26 (1 H, s, C_6-H); NMR of the other **2c,** δ 1.48 (3 H, s, C_5-Me), 3.20 (6 H, s, NMe), 3.48 (3 H, s, OMe), and 4.26 (1 H, s, C_6-H). Reflux of the mixture in MeOH did not change the ratio. However, heating of the mixture at 160 °C led to the decomposition of the latter isomer.
(7) **2d:** mp 195 °C (from CH_3CN); *m/e* 174 (M^+), 143 ($M - OCH_3$)$^+$, 115 ($M - NHCHOCH_3$)$^+$, 103 ($M - COCH_3OH_2$)$^+$, 101 ($M - COCH_3O$)$^+$, 72 ($COCCH_3OH$)$^+$; NMR (Me_2SO-d_6, Me_4Si) δ 1.40 (3 H, s, C_5-Me), 3.16 (6 H, s, NMe), 4.13 (1 H, d, J = 4.0 Hz, C_6-H), 5.32 (1 H, s, N_3H), 8.52 (1 H, d, J = 4.0 Hz, N_1H), 10.04 (1 H, s, —OH).
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(10) **2e** is a viscous liquid: molecular distillation 160 °C/1 mm (bath temperature); *m/e* 421; NMR ($CDCl_3$, Me_4Si) δ 1.24 (3 H, t, J = 8.0 Hz, —OCH_2CH_3) 1.51 (3 H, s, C_5-Me), 1.97 (3 H, s, COMe), 2.98 (3 H, s, NMe), 3.01 (2 H, d, J = 7.3 Hz, –CH_2–), 3.20 (3 H, s, NMe), 3.57 (1 H, s, OH), 4.11 (2 H, q, J = 8.0 Hz, –OCH_2CH_3), 4.77 (1 H, d + d, J = 8.7 and 7.3 Hz, –CH_2CHNH–), 4.97 (1 H, s, C_6-H), 5.94 (1 H, J = 8.7 Hz, NH), and 6.92 (4 H, m, arom).
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(13) Department of Chemistry, University of California at Los Angeles, Los Angeles, California.
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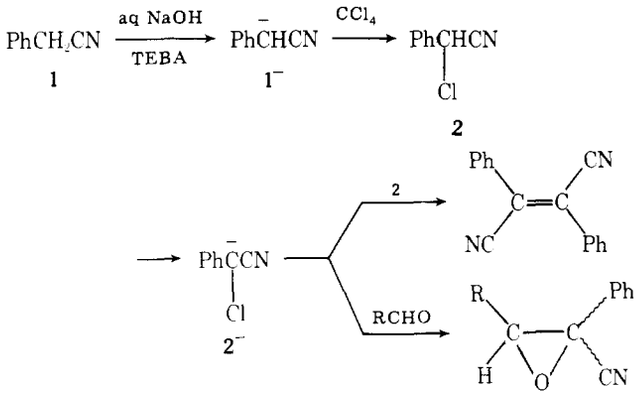
Reactions of Carbon Tetrachloride with Carbon Acids in Catalytic Two-Phase System[1]

Summary: Phenylacetonitrile, its α-substituted derivatives, fluorene, and trichloroethylene react with carbon tetrachloride in the presence of 50% aqueous sodium hydroxide and triethylbenzylammonium chloride as catalyst to form chloro derivatives. The fate of these derivatives depends on the structure of the carbon acid. Carbanions of some of the chloro compounds formed in situ were trapped by suitable electrophiles to give derivatives of glycidic nitrile or dicyanocyclopropane, for example.

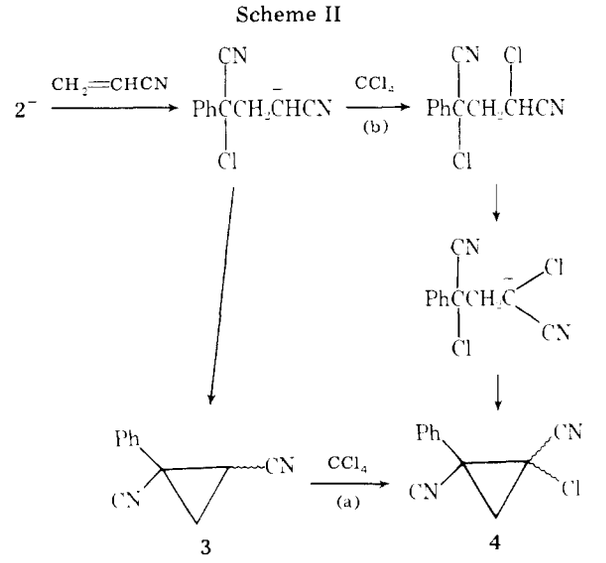
Sir: We have previously shown[2] that phenylacetonitrile (1) reacts with carbon tetrachloride in the presence of concentrated aqueous sodium hydroxide and triethylbenzylammonium chloride (TEBA) (socalled catalytic two-phase CTP system[3]) giving (*E*)-dicyanostilbene. The reaction proceeds via chlorination of 1 α-anion (1^-), and further transformations of phenylchloroacetonitrile (2) (Scheme I). Reactions between CCl_4 and some arylacetonitriles in solid potassium hydroxide/*tert*-butyl alcohol system were subsequently studied by Foucaud et al.,[4] who proposed an electron transfer as a step in these processes. Finally Meyers et al.,[5] on the basis of thorough studies of reactions of CCl_4 and other perhalomethanes with sulfones and ketones, have elaborated on the general mechanistic scheme of these processes which, they suggest, proceed via a radical/anion–radical pair (RARP) pathway.

Scheme I



Our detailed examination of the reaction between 1 and CCl_4 suggested the idea that the intermediate 2 α-anion (2^-) could be trapped by a suitable electrophile. This supposition was fully confirmed in the Darzens condensation with aldehyde. Thus stirring of 1, benzaldehyde, and CCl_4 with aqueous sodium hydroxide and TEBA resulted in an exothermic reaction leading to 1,2-diphenylglycidic nitrile (9:1 trans–cis mixture) in an isolated yield of 65%.[6] Similar reaction takes place with other aldehydes, for example isobutyraldehyde (Scheme I). One could expect that another active electrophile–acrylonitrile would also be able to trap the intermediate 2^-, with the formation of 1,2-dicyano-1-phenylcyclopropane (3). This process indeed takes place, resulting in the formation of two main products in combined yield 51%. However, the major component of the mixture was not 3, but 1,2-dicyano-1-chloro-2-phenylcyclopropane (4) (3 to 4 ratio was 1:4)

Scheme II



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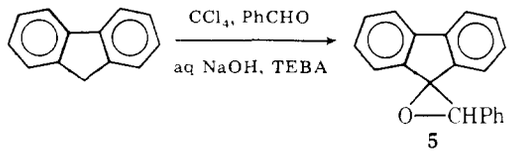
(Scheme II). Two alternative pathways, a and b, for the formation of **4** can be envisaged, namely reaction of CCl_4 with the carbanion produced by the proton abstraction from **3** (a), or reaction of CCl_4 with the carbanion formed by the addition of 2^- to acrylonitrile (b). Although **3** → **4** transformation was indeed observed under CTP conditions, the yield of **4** was much lower than in the direct synthesis. So the second pathway (b) is more plausible.

The principle, chlorination of C–H acid with CCl_4 in the CTP system and the subsequent reaction of the in situ produced chloro derivatives with an active electrophile, could be also applied to fluorene. When this hydrocarbon and benzaldehyde were stirred in CCl_4 solution with concentrated aqueous sodium hydroxide and TEBA, the oxirane (**5**) was formed. When recrystallized from methanol, the oxirane



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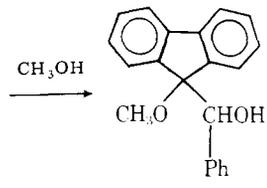
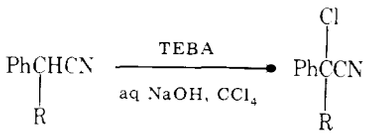


6

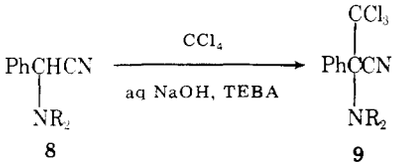
undergoes ring opening to give 9-(α-hydroxybenzyl)-9-methoxyfluorene (**6**). These reactions offer a convenient short cut for the preparation of some oxirane and cyclopropane derivatives.

In contrast to **1**, its alkyl derivatives react with CCl_4 under



R = CH_3	yield 78%
R = C_2H_5	yield 70%
R = OCH_3 (**7**)	yield 49%

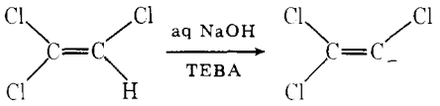
CTP conditions with the formation of stable chlorinated products isolated in good yields. Phenylchloromethoxyacetonitrile (**7**) also can be obtained in this manner. However, as an α-cyano-α-chloro ether it is quite unstable, and cannot be purified sufficiently to eliminate contamination by methyl benzoate and benzoyl cyanide.

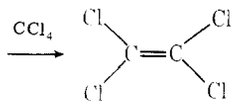


8 **9**

R = CH_3 (**9a**)	yield 36%
R_2 = $(CH_2)_5$ (**9b**)	yield 43%

An entirely different type of product, 2-phenyl-2-(dialkylamino)-3,3,3-trichloropropionitriles (**9**), was obtained when phenyl(dialkylamino)acetonitriles (**8**) were treated with CCl_4 under CTP conditions. The fact these products are formed only from **8** implies a special role of the amino function. Finally we have found that trichloroethylene is very efficiently chlorinated under these conditions. The latter reaction presents to our knowledge the first example of the generation of vinyl anions in CTP systems.





yield 80%

The procedures for all of these reactions are very simple as illustrated by the following examples.

1. 2-Phenyl-3-isopropylglycidic Nitrile. A mixture of **1** (2.34 g, 0.02 mol) and isobutyraldehyde (1.80 g, 0.025 mol) was added dropwise to CCl_4 (15 mL), 50% aqueous sodium hydroxide (10 mL), and TEBA (0.05 g) at 15–20 °C, with stirring. After addition, the mixture was stirred for 15 min and diluted with water and the product (one stereoisomer) was isolated by extraction (C_6H_6) and purified by distillation: bp 94–96 °C (1 mmHg); 2.1 g (56%).

2. 9-(α-Hydroxybenzyl)-9-methoxyfluorene (6). Fluorene (3.32 g, 0.02 mol), benzaldehyde (2.65 g, 0.025 mol), CCl_4 (10 mL), 50% aqueous sodium hydroxide (10 mL), and TEBA (0.05 g) were stirred at 20–25 °C for 1 h under nitrogen. The crude oily product was shown by NMR and GLC to contain the oxirane (**5**) as a main component. The mixture was recrystallized from methanol to give 2.9 g (52%) of **6**, mp 189–190 °C (lit.[7] mp 188–189 °C).

3. 2-Chloro-2-phenylpropionitrile. 2-Phenylpropionitrile (2.62 g, 0.02 mol), CCl_4 (15 mL), 50% aqueous sodium hydroxide (15 mL), and TEBA (0.05 g) were stirred at 20 °C for 1.5 h. The product was purified by distillation: bp 132 °C (33 mmHg); 2.5 g (77%).

4. 2-Dimethylamino)-2-phenyl-3,3,3-trichloropropionitrile (9a). 2-(Dimethylamino)-2-phenylacetonitrile (1.60 g, 0.01 mol), CCl_4 (8 mL), 50% aqueous sodium hydroxide (5 mL), and TEBA (0.05 g) were stirred under nitrogen at 20 °C for 2.5 h. The product (**9a**) was purified by recrystallization from methanol: mp 94–95 °C; 1.0 g (36%).

References and Notes

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compared with authentic samples prepared in another way.

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