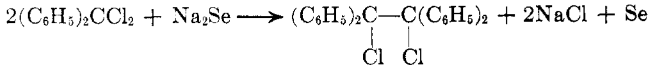
phenylethylene in good yield in accord with the equation[5]

$$2(C_6H_5)_2CCl_2 + 2Na_2Se \longrightarrow (C_6H_5)_2C{=}C(C_6H_5)_2 + 4NaCl + 2Se$$

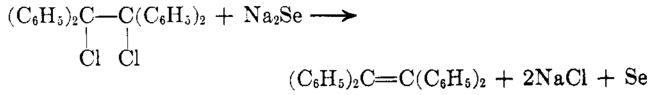
The reaction was conducted with excess sodium selenide in dioxane at the refluxing temperature, 101°, for 24 hr under nitrogen atmosphere.

The formation of the condensed olefin may have involved a carbene intermediate. However, treatment of dichlorodiphenylmethane with sodium selenide in the presence of cyclohexene did not produce the expected carbene-cyclohexene addition product, 7,7-diphenylnorcarane.

The latter reaction was carried out at 80° in the presence of a large excess of cyclohexene. Under these conditions (lower reaction temperature and lower dielectric constant of the medium), dichlorotetraphenylethane was the main product. When the dichlorotetraphenylethane was further treated with sodium selenide in dioxane, tetraphenylethylene was isolated quantitatively. Furthermore, when chlorodiphenylmethane was treated with sodium selenide in dioxane, tetraphenylethane was obtained. Therefore, the dechlorinative coupling reaction may involve two consecutive steps, namely, the intermolecular dechlorination and the intramolecular dechlorination.



$$2(C_6H_5)_2CCl_2 + Na_2Se \longrightarrow (C_6H_5)_2\underset{Cl}{C}{-}\underset{Cl}{C}(C_6H_5)_2 + 2NaCl + Se$$



$$(C_6H_5)_2\underset{Cl}{C}{-}\underset{Cl}{C}(C_6H_5)_2 + Na_2Se \longrightarrow (C_6H_5)_2C{=}C(C_6H_5)_2 + 2NaCl + Se$$

The reaction also was carried out with methyl methacrylate as a solvent at 100° for 1 hr. Dichlorotetraphenylethane was isolated but poly(methyl methacrylate), which would indicate a free-radical intermediate, was not obtained.

A similar reaction was observed with other *gem*-dichlorides. Benzotrichloride with sodium selenide produced *trans*-α,α′-dichlorostilbene. Benzal chloride gave *trans*-stilbene, but in rather poor yield (10%). However, from the reaction of 1,1-dichlorobutane with sodium selenide, the dechlorinative coupling product, octene was not obtained. Methylene chloride gave, instead of ethylene, various cyclic poly(selenomethylenes.[6] Therefore, in order to effect dechlorinative coupling of *gem*-dichlorides, the carbon bonded with the two chlorines must be substituted by at least one, and preferably two, groups such as phenyl.

Experimental Section

The chloride compounds were obtained from commercial sources and purified by distillation or recrystallization. Sodium selenide, a purified grade (>95% pure), was obtained from City Chemical Co., New York, N. Y., and was used as the powder (<100 mesh) without further purification. The products obtained were identified by infrared and mixture melting point measurements with authentic compounds. Melting points were uncorrected. All the reactions were carried out under an atmosphere of nitrogen. Dioxane was distilled over calcium hydride and stored with sodium wire.

A representative experimental procedure is as follows. Dichlorodiphenylmethane (2.4 g, 0.010 mol) in 40 ml of dried dioxane was gradually added to a rapidly stirred suspension (in 40 ml of dioxane) of sodium selenide (4.3 g, 0.035 mol). The reaction was carried out at the refluxing temperature for 24 hr. The solid materials were removed by filtration and the dioxane was distilled off. The yellow solid obtained was recrystallized from a mixture of benzene and ethyl alcohol and gave 1.0 g (60% yield) of pure tetraphenylethylene, mp 215° (lit. mp 220–222,[7] 220°[8]). When an equivalent quantity of sodium selenide was used, the yield was poor (20–30%) and a large amount of unreacted chloride was recovered. The reason for the low yield is not clear at this time, but it may have been due to the heterogeneity of the reaction system. A search for a suitable solvent is currently being made.

The reaction of dichlorodiphenylmethane (9.5 g, 0.040 mol) with sodium selenide (11.0 g, 0.090 mol) in 80 ml of dioxane was carried out in the presence of cyclohexene (8.4 g, 0.090 mol) at 80° for 20 hr. Recrystallization of the product, from carbontetrachloride, gave 6.0 g (yield 75%) of pure dichlorotetraphenylethane, mp 183° dec (lit.[9] mp 182–184° dec). The reaction in methyl methacrylate at 100° for 1 hr also gave dichlorotetraphenylethane (60%) yield). The reaction of chlorodiphenylmethane (7.1 g, 0.020 mol) with sodium selenide (4.3 g, 0.035 mol) in dioxane gave 4.4 g (yield 70%) of tetraphenylethane, mp 209–211° (lit.[10] mp 207–208°).

Treatment of dichlorotetraphenylethane (1.0 g, 0.0025 mol) with sodium selenide (1.0 g, 0.0080 mol) yielded tetraphenylethylene (0.60 g, yield 80%, after recrystallization).

trans-α,α′-Dichlorostilbene, mp 145° (lit.[11] mp 143–145°), 3.5 g, 52% yield, was obtained from the reaction of benzotrichloride (4.5 g, 0.022 mol) with sodium selenide (10 g, 0.065 mol). The reaction of benzal chloride (3.2 g, 0.020 mol) with sodium selenide (5.9 g, 0.05 mol) gave, upon vacuum distillation of the product, 1.8 g (10% yield) of *trans*-stilbene, mp 120° (lit.[12] mp 124°). The distillation residue contained selenium compounds. Structures have not as yet been established. 1,1-Dichlorobutane (2.3 g, 0.025 mol) was also treated with sodium selenide (7.0 g, 0.056 mol) in dioxane. Gas chromatographic analysis did not show any octene in the reaction product. A dark selenium-containing liquid material was also obtained.

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[5] A similar dechlorinative coupling reaction was reported with gemdihalides by iron pentacarbonyl: C. Eugene Coffey, *J. Amer. Chem. Soc.*, **83**, 1623 (1961).

[6] M. Russo, L. Mortillaro, L. Credali, and C. DeChecchi, *J. Polym. Sci.*, **4**, 248 (1966).

[7] C.-H. Wang and S. G. Cohen, *J. Org. Chem.*, **26**, 3301 (1961).

[8] H. Güsten and L. Horner, *Angew. Chem.*, **74**, 586 (1962).

[9] T. L. Jacobs and D. M. Fenster, *J. Org. Chem.*, **30**, 1808 (1965).

[10] L. L. Alexander and R. C. Fuson, *J. Amer. Chem. Soc.*, **58**, 1745 (1936).

[11] Y. Ogata and H. Nakamura, *J. Org. Chem.*, **21**, 1170 (1956).

[12] O. H. Wheeler and H. N. Battle DuPabon, *ibid.*, **30**, 1473 (1965).

The Oxidation of Ethylbenzene with Aqueous Sodium Dichromate

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Aqueous sodium dichromate has been used by Friedman, Fishel, and Shechter[1] to oxidize alkylated aromatic compounds to the corresponding carboxylic acids in high yields. The procedure is particularly useful with polynuclear aromatic compounds since the side chain can be oxidized without the occurrence of extensive nuclear degradation. For example, 2-methyl-

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[1] L. Friedman, D. L. Fishel, and H. Shechter, *J. Org. Chem.*, **30**, 1453 (1965).

TABLE I

OXIDATION WITH AQUEOUS SODIUM DICHROMATE

Expt no.	Reductant	Reaction time, hr	Temp, °C	Recovd material (%)
1	Ethylbenzene	1.0	246	Acetophenone (48) Benzoic acid (11) Ethylbenzene (41)
2	Ethylbenzene[a]	1.0	254	Acetophenone (27) Benzoic acid (6) Ethylbenzene (67)
3	Ethylbenzene	2.8	254	Acetophenone (54) Benzoic acid (17) Ethylbenzene (28)
4	Ethylbenzene[b]	0.5	256	Acetophenone (45) Benzoic acid (15) Ethylbenzene (40)
5	Ethylbenzene	1.0	258	Acetophenone (47) Benzoic acid (11) Ethylbenzene (42)
6	Ethylbenzene	1.0	270	Acetophenone (47) Benzoic acid (22) Ethylbenzene (31)
7	Ethylbenzene[c]	1.0	275	Acetophenone (30) Benzoic acid (38) Ethylbenzene (32)
8	Ethylbenzene	0.5	275	Acetophenone (52) Benzoic acid (23) Ethylbenzene (25)
9	Ethylbenzene[d]	2.0	250	Acetophenone (68) Benzoic acid (21) Ethylbenzene (11)
10	Ethylbenzene[e]	2.0	275	Acetophenone (6) Ethylbenzene (94)
11	Ethylbenzene[f]	1.0	248	Acetophenone (45) Benzoic acid (11) Ethylbenzene (44)
12	Ethylbenzene[f]	1.0	275	Acetophenone (40) Benzoic acid (21) Ethylbenzene (39)
13	Ethylbenzene[g]	1.0	259	Acetophenone (44) Benzoic acid (20) Ethylbenzene (36)
14	Ethylbenzene[h]	1.0	252	Acetophenone (34) Benzoic acid (7) Ethylbenzene (59)
15	Ethylbenzene[i]	1.0	249	Acetophenone (58) Benzoic acid (7) Ethylbenzene (35)
16	Phenylacetic acid	2.8	250	Benzoic acid (100)
17	Equimolar amounts of ethylbenzene and phenylacetic acid	1.0	270	Acetophenone (10) Benzoic acid (52) Ethylbenzene (33) Phenylacetic acid (4) Benzaldehyde (1)
18	Equimolar amounts of acetophenone and phenylacetic acid	1.0	274	Acetophenone (44) Benzoic acid (52) Phenylacetic acid (2) Benzaldehyde (1)
19	2-Methylnaphthalene[j]	2.0	250	2-Naphthoic acid (100)
20	*n*-Propylbenzene	1.0	195	Propiophenone (4) Benzoic acid (8) *n*-Propylbenzene (88) 1-Phenyl-1,2-propanedione (trace)

[a] A 2 molar excess of ethylbenzene was used. [b] Initial pressure was increased to 90 psi by use of CO_2 gas and a 0.2 molar excess of ethylbenzene was used. [c] The solution was buffered at about pH 7 using NaH_2PO_4 and Na_2HPO_4. [d] The solution contained 6.4 *M* NH_4OH and a 2 molar excess of dichromate was used. [e] The solution contained 1.3 *M* NaOH and a 2 molar excess of dichromate was used. [f] The solution was agitated by shaking rather than stirring. [g] The solution was not agitated. [h] The solution contained 2 g of sulfur/700 ml. [i] The solution contained 2 g of V_2O_5/700 ml. [j] A 1.5 molar excess of dichromate was used.

naphthalene is converted cleanly into 2-naphthoic acid with aqueous dichromate at 250°, whereas use of most other oxidants results in ring degradation and formation of a considerable amount of 2-methylnaphthoquinone. Even more remarkable is the report by Reitsema and Allphin[2] that the oxidation of ethylbenzene by sodium dichromate at 275° for 1 hr leads to the formation of phenylacetic acid in almost quantitative yields. Similarly these authors report that *n*-propylbenzene, isopropylbenzene, and *n*-butylbenzene can be converted into 3-phenylpropionic acid, 2-phenylpropionic acid, and 4-phenylbutyric acid, respectively.

In the interval between the time of publication of their work and the present it has been assumed that all of these reactions are of a general nature and review articles have presented them in this light.[3,4] However, in an attempt to repeat some of these experiments we have observed that the reactions described by Friedman and coworkers could be easily duplicated, but, to date, after a large number of trials we have not been able to obtain the products reported by Reitsema and Allphin for the oxidation of longer chain arenes.

Experimental Section

The apparatus used for the oxidations was a Parr 4501 stirrer-type, high-temperature hydrogenator of 2-l. capacity equipped with a thermocouple to monitor the temperature of the solution. Typically 0.175 mol of $Na_2Cr_2O_7 \cdot 2H_2O$ in 700 ml of water was placed in the reactor and 0.175 mol of ethylbenzene was added. The solution was brought to the required temperature rapidly with vigorous stirring and the reaction was allowed to continue for the desired time. After cooling, the resulting basic solution was extracted with ether to isolate nonacidic organic products and filtered to remove chromium(III) oxide. This precipitate was boiled in water to dislodge any remaining organic products and refiltered. The combined filtrates were acidified and any products which precipitated were collected by filtration. Finally, any residual products which remained in solution were isolated by ether extraction. The products were identified by comparison with authentic materials through melting and boiling points, ir and nmr spectroscopy, and the use of gas–liquid partition chromatography. Yields were determined gravimetrically for solid products and *via* the use of gas–liquid partition chromatography

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(2) R. H. Reitsema and N. L. Allphin, *J. Org. Chem.*, **27**, 27 (1962).

(3) K. B. Wiberg in "Oxidation in Organic Chemistry," part A, K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, pp 90–92.

(4) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiley & Sons, Inc., New York, N. Y., 1967, p 1061. (These authors note that the reported oxidation of ethylbenzene to phenylacetic acid has not been confirmed.)

for liquid products. The total amount of material recovered by this method was quite high (73-94%).

Results and Discussion

Several attempts were made to find the proper conditions for the conversion of ethylbenzene to phenylacetic acid. In some twenty-four different experiments the temperature was varied from 126 to 282°, the time of reaction was varied from 0.5 to 12 hr, the ratio of oxidant to reductant was varied from 2:1 to 1:2, and the pH was varied from 5 to 11. However, in every experiment the only isolable products obtained were acetophenone and benzoic acid. In general, long reaction times, high temperatures, low pH, and an excess of oxidant tended to favor the production of benzoic acid, while less vigorous conditions decreased the amount of reaction and tended to make acetophenone the main product. Some typical results are presented in Table I, no. 1-10. (Friedman and coworkers[5] have also been unable to reproduce the results reported by Reitsema and Allphin.[2]) Similarly, the only products obtained from an oxidation of *n*-propylbenzene were propiophenone, 1-phenyl-1,2-propanedione, and benzoic acid; no detectable amount of 3-phenylpropionic acid was formed (Table I, no. 20). On the other hand 2-methylnaphthalene was readily converted into 2-naphthoic acid as reported by Friedman and coworkers[1] (Table I, no. 19).

Furthermore the results of expt 17 and 18 indicate that phenylacetic acid is more readily oxidized than either ethylbenzene or acetophenone. Hence it can be concluded that under these conditions phenylacetic acid *could not* accumulate.

A possible explanation for our failure to obtain any appreciable amount of phenylacetic acid may be that a specific catalyst was present in the reactor used by Reitsema and Allphin.[6] In a very cursory investigation of this possibility we carried out the reaction in the presence of catalytic amounts of sulfur and vanadium pentoxide, but were unable to detect any major change in the product composition (Table I, no. 14 and 15). However, the existence of a specific catalyst for the formation of phenylacetic acid cannot be completely ruled out. In any case it is apparent that the applications of this reaction are not so general as was once supposed.

Registry No.—Ethylbenzene, 100-41-4; sodium dichromate, 10588-01-9.

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[5] L. Friedman, personal communication, 1968. See also footnote 17 on p 1455 of ref 1.

[6] In a private communication Dr. Reitsema has informed us that their reactor, although superficially clean, had been used for Willgerodt reactions as well as numerous other experiments and that they used the same reactor for all of their experiments.

The Reaction of Silver Nitrate with Vinyl Bromides

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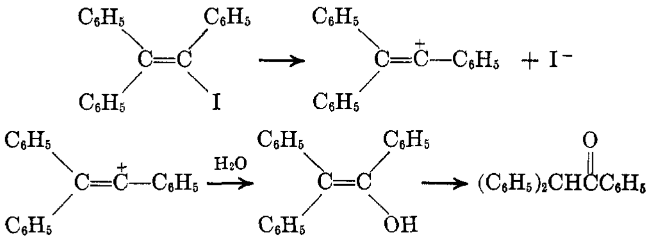
In earlier work, triarylvinyl halides were shown to solvolyze in aqueous dimethylformamide to yield halide ion and benzhydryl ketones *via* an S_N1 mechanism.[2] Our work showed that the intermediate vinyl cations exhibited a high degree of selectivity, implying that they are not more reactive than alkyl cations. Thus we have attributed the substitutional lethargy of vinyl halides to ground-state stabilization rather than to the instability of vinyl cations.



As a continuation of these studies, we sought to prepare vinyl cations that would not be stabilized by an α-aryl group. Such unstabilized vinyl cations have been implicated in the nitrosyl chloride deamination of 1,1-diphenyl-2-aminoethylene,[3] the decomposition of nitroso oxazolidones,[4] and the acid-catalyzed decomposition of vinyl triazenes.[5] The reaction of vinyl halides with silver ion suggested itself as a more general and mechanistically less complicated reaction. While the unreactivity of vinyl halides toward refluxing alcoholic silver nitrate has been noted in numerous organic texts,[6] a literature search substantiated Peterson's conclusion[7] that no definitive study of the reaction of vinyl halides with silver nitrate has appeared in the literature.

Although it is less reactive than alkyl halides with silver nitrate, β-bromostyrene afforded a quantitative yield of silver bromide within 30 min at 100° in 80% aqueous acetonitrile. Quantitative precipitations of silver bromide were also obtained with 1,1-diphenyl-2-bromoethylene and 1-bromo-2-phenylpropene within 2 hr at 130°. Triphenyliodoethylene gave an 80% yield of silver iodide after 24 hr at 130°.

The organic product isolated in all but one[8] case was the corresponding vinyl nitro compound. If a

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[1] National Aeronautics and Space Administration Trainee, 1967-1969.

[2] L. L. Miller and D. A. Kaufman, *J. Amer. Chem. Soc.*, **90**, 7282 (1968).

[3] D. Y. Curtin, J. A. Kampmeier, and B. R. O'Connor, *ibid.*, **87**, 863 (1965).

[4] M. S. Newman and A. E. Weinberg, *ibid.*, **78**, 4654 (1956).

[5] W. M. Jones and F. W. Miller, *ibid.*, **89**, 1960 (1967).

[6] See, for example, R. T. Morrison and R. N. Boyd, "Organic Chemistry," 2nd ed, Allyn and Bacon, Inc., Boston, Mass., 1966, p 828; and J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 321.

[7] P. E. Peterson and J. E. Duddey, *J. Amer. Chem. Soc.*, **85**, 2865 (1963).

[8] See Experimental Section regarding the explosion which occurred when 2-methylbromopropene was heated with silver nitrate.