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.

Acknowledgment.—The authors are grateful to Professor L. Friedman and Dr. R. H. Reitsema for some helpful correspondence during the course of this work. They are also pleased to acknowledge financial assistance from the National Research Council of Canada and one of us (U. A. S.) gratefully acknowledges the receipt of the Goodfellow Scholarship for 1968.

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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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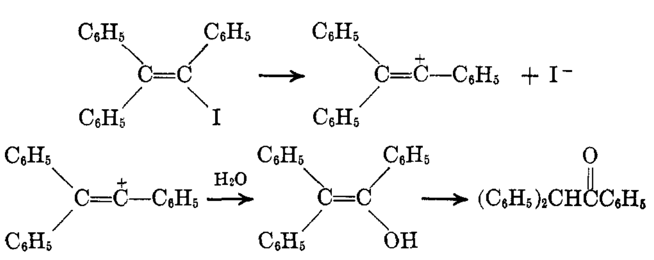
In earlier work, triarylvinyl halides were shown to solvolyze in aqueous dimethylformamide to yield halide ion and benzhydryl ketones *via* an SN1 mechanism.[2] Our work showed that the intermediate vinyl cations exhibited a high degree of selectivity, implying that they are not more reactive than alkyl 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).

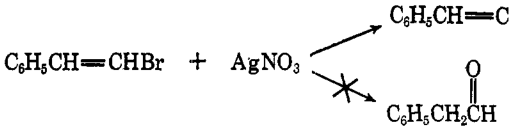
(5) W. M. Jones and F. W. Miller, *ibid.*, **89**, 1960 (1967).

(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.

vinyl cation were involved in these reactions, one would expect to obtain a carbonyl product by analogy with our earlier work.[2] The formation of nitro compounds



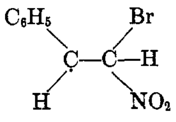
and no carbonyl products, therefore, suggested that silver assisted heterolytic cleavage was not involved in this reaction. Two further observations appear to vitiate the possible intermediacy of vinyl cations: (1) 1,1-diphenyl-2-bromoethylene gave 1,1-diphenyl-2-nitroethylene and not the rearranged product, 1,2-diphenyl-1-nitroethylene, expected for carbonium ion participation;[3-5] (2) triphenylbromoethylene reacted much more slowly with silver ion than did any of the other halides. The α-aryl group present in the triphenyl compound should have stabilized an intermediate carbonium ion and led to a rate enhancement, not deceleration.

Addition–elimination mechanisms with various nitrogen oxide species as addends were then considered. Nitrite ion was eliminated as an intermediate on the basis of the reaction of β-bromostyrene with sodium nitrite. After a reaction time of 2.5 hr at 130°, nmr did show approximately 20% consumption of the starting material and the appearance of a corresponding amount of β-nitrostyrene. However, during this reaction time β-bromostyrene is allowed to react quantitatively with silver nitrate. Thus nitrite ion cannot be a reacting intermediate. Similarly, nitrate was eliminated since heating with β-bromostyrene for 2 hr at 130° gave only starting material. Finally, nitronium ion involvement was rendered unlikely by our inability to trap it with anisole.

The participation of nitrogen dioxide as the nitrating species seems quite plausible. Silver nitrate is known to decompose with heat according to the following equation[9] and a brown irritating gas was produced in

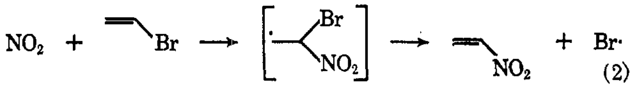
$$2AgNO_3 \xrightarrow{\Delta} 2Ag + 2NO_2 + O_2$$

our reaction tubes when excess silver nitrate was used. The ability of NO_2 to serve as a vinyl nitrating agent was shown by Stevens,[10] who prepared β-nitrostyrene by passing NO_2 through an ethereal solution of β-bromostyrene. It was proposed that products arise *via* the following radical intermediate.



Equations 1–3 are consistent with both our experimental work and the above reactions.

$$2AgNO_3 \xrightarrow{\Delta} 2Ag + 2NO_2 + O_2 \tag{1}$$



$$NO_2 + \text{β-bromostyrene} \longrightarrow [\text{radical adduct}] \longrightarrow \text{β-nitrostyrene} + Br\cdot \tag{2}$$

$$2Br\cdot + 2NO_3^- \longrightarrow 2Br^- + 2NO_2 + O_2 \tag{3}$$

It is possible that reaction 1 is necessary only to initiate a radical chain and that the main source of NO_2 is from eq 3. In agreement with this possibility, silver ion was found to react catalytically. As was previously noted, sodium nitrate did not react with β-bromostyrene. In the presence of catalytic amounts of silver nitrate, however, sodium nitrate produced much more β-nitrostyrene than could be accounted for by the stoichiometric amount of silver ion. The catalytic effect could also be explained by replacing eq 1 with a more complex set of reactions involving hydroxyl radicals. Participation of acetonitrile in the radical chain is an additional complicating possibility.

As a conclusion to our investigation, silver fluoroborate was substituted for silver nitrate in an attempt to avoid the complicating addition-type reaction found with silver nitrate. However, reaction of β-bromostyrene with silver fluoroborate for 6 hr at 130° and for 24 hr at 100° showed no silver bromide formation. It seems apparent, therefore, that, although silver nitrate does give a silver bromide precipitate with vinyl bromides, this sort of reaction is not a useful route to vinyl cations.

Experimental Section

1,1-Diphenyl-2-bromoethylene was prepared according to the method of Elderfield[11] with a 70% yield of recrystallized product. Recrystallization was successful using Skellysolve H after attempts with methanol had failed. The nmr spectrum showed singlets at τ 3.32 (1 H), 2.84 (5 H), and 2.72 (5 H).

1,1,2-Triphenylbromoethylene was prepared according to the method of Koelsch[12] in 96% yield with mp 116° (lit.[12] mp 114–115.5°).

1,1,2-Triphenyliodoethylene was prepared according to the method of Koelsch[12] *via* addition of iodine to the Grignard of the corresponding bromide in 78% yield, mp 126–128° (lit.[12] mp 125–126°).

1-Bromo-2-phenylpropene was prepared by dehydrobromination of the dibromide through refluxing with 40% alcoholic KOH for 10 hr. The product was purified by vacuum distillation [81–84° (3.5–4.0 mm)] with a 75% yield. The dibromide was obtained by slow addition of Br_2 to an ethereal solution of α-methylstyrene.

β-Nitrostyrene was prepared by the method of Worrall[13] in which nitromethane was condensed with benzaldehyde in the presence of sodium hydroxide. The intermediate carbinol was dehydrated by dropwise addition to dilute hydrochloric acid. Recrystallization from Skellysolve gave yellow needles, mp 55.5–57° (lit.[13] mp 56–58°).

Cleavage Reactions (General).—All reactions of the vinyl halides with silver nitrate were carried out in 80% aqueous acetonitrile in heavy-walled sealed tubes at 130–135° unless otherwise noted. Aqueous ethanol was rejected as a solvent system for blank runs with silver nitrate gave considerable amounts of elemental silver when heated at 130° for periods of 2 hr or longer. A small molar excess of the intended nitrating agent was used. Reaction work-up consisted of filtering off the silver bromide precipitate when present and then concentrating the solution on the rotary evaporator to remove sufficient acetonitrile so as to render the solution extractable with ether. The combined ether layers were extracted with aqueous sodium carbonate to remove any acidic products. The ether layer was then dried and concentrated to yield a crude product which was purified by either recrystallization or column chromatography.

β-Bromostyrene with Silver Nitrate.—Quantitative reaction occurred within 2 hr at 130° as judged by recovery of the theoretical amount of silver bromide and by the complete disappearance of starting material *via* nmr. β-Nitrostyrene and benzoic acid were isolated as products in a ratio of 9:1, the benzoic

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(9) T. Moeller, "Qualitative Analysis," 1st ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1958, p 255.

(10) T. E. Stevens, *J. Org. Chem.*, **25**, 1658 (1960).

(11) R. C. Elderfield and T. P. King, *J. Amer. Chem. Soc.*, **76**, 5436 (1954).

(12) C. F. Koelsch, *ibid.*, **54**, 2046 (1932).

(13) D. E. Worrall, *Org. Syn.*, **9**, 66 (1929).

acid probably being an oxidation product of the initially formed nitro compound. Subsequent reactions showed that quantitative reaction could be achieved at 100° within 30 min and that 10% reaction was reached after 30 min at 80°. At these shorter times, β-nitrostyrene was the only reaction product found. Identification of β-nitrostyrene was made through comparison of spectra and melting points with an independently prepared sample.

1,1-Diphenyl-2-bromoethylene with Silver Nitrate.—Quantitative reaction was shown after 5 hr at 130°. The weight of crude product obtained represented quantitative conversion into 1,1-diphenyl-2-nitroethylene. The crude product was recrystallized from Skellysolve H to give yellow needles, mp 86–88° (lit.[14] mp 86–88°), which gave an nmr spectrum which was essentially identical with that of the crude product and as expected for the nitro olefin. Elemental analysis gave results expected for the nitro compound.

1-Bromo-2-phenylpropene with Silver Nitrate.—Complete reaction was reached after 2 hr at 130°. The crude product was initially purified by vacuum distillation [90–100° (0.5–0.75 mm)]. Final purification was achieved through chromatography on silica gel. The 2-phenyl-1-nitropropene was eluted with Skellysolve H. Minimum yield was 75%. The ir spectrum showed prominent peaks at 6.38, 6.61, and 7.46 μ;[15] mass spectrum *m/e* 163 (P, 9%), 129 (P − 34, 33%), 117 (P − 46, 36%), 116 (P − 47, 37%), 115 (P − 48, 100%), 91 (P − 72, 78%), 77 (P − 86, 73%).

Triphenylbromoethylene with Silver Nitrate.—Only a trace of silver bromide was seen after heating for 6 hr at 130°. Reaction work-up yielded only unreacted starting material.

Triphenyliodoethylene with Silver Nitrate.—After 24 hr at 130°, 80% reaction was reached. The crude product obtained in 75% yield was purified by chromatographing over silica gel. Triphenylnitroethylene was eluted with 20% benzene–Skellysolve H. Recrystallization from Skellysolve yielded yellow needles with mp 176-178° (lit.[16,17] mp 175–176°); mass spectrum *m/e* 301 (P − 48%), 255 (P − 46, 100%), 253 (P − 48, 33%), 178 (P − 123, 22%).

1-Bromo-2-methylpropene.—The reaction of this vinyl bromide with silver nitrate resulted in a rather violent explosion approximately 10 min after the sealed tube was immersed in the oil bath at 130°. The magnitude of the explosion appeared to be too large to be accounted for by simple increased vapor pressure of the solvent system. A preliminary run with small amounts (~250 mg) of the halide gave no explosion and a silver bromide precipitate formed. The explosion occurred when larger amounts (3.0 g) of halide were used for product study.

Registry No.—Silver nitrate, 7761-88-8; 2-phenyl-1-nitropropene, 15795-70-7.

(14) R. Anschutz and A. Hilbert, *Ber.*, **54**, 1854 (1921).
(15) J. F. Brown, Jr., *J. Amer. Chem. Soc.*, **77**, 6341 (1955).
(16) E. A. Shilov, *J. Russ. Phys. Chim. Soc.*, **62**, 95 (1930).
(17) L. Hellerman and R. Garner, *J. Amer. Chem. Soc.*, **57**, 139 (1935).

The Hydrogen-Bonding Basicity of Aryl Alkyl Ketones

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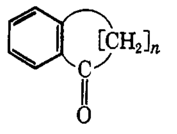
We wish to report the results of experiments which define systems for the study of conjugation effects on the hydrogen-bonding propensity of aryl alkyl ketones,[2,3] and to propose a tentative interpretation of these effects.

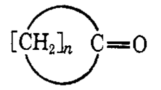
Bellamy and Pace[4] have observed that benzaldehyde and acetaldehyde appear to be hydrogen-bonding bases of comparable strength, and that acetone is a slightly better hydrogen-bonding base than acetophenone. From data pertaining to these and other compounds they were led to the conclusion that conjugation has little effect on the hydrogen-bonding propensity, and that it sometimes produces inexplicable disparities.[4]

It seemed to us that intuitively one would expect that resonance interaction with an aryl group would increase the hydrogen-bonding basicity of a carbonyl group, and we envisaged a system in which the extent of orbital overlap with an aryl group might be controlled without drastically changing the nature of the carbonyl group in other respects.

Hydrogen-bonding basicities were determined for a series of benzocyclanones (**1–4**) and for a corresponding series of cyclanones (**5–8**). The difference ($\Delta\nu_{OH}$) between the O—H stretching frequency of phenol alone in carbon tetrachloride and that of phenol in carbon tetrachloride containing a benzocyclanone or cyclanone was assumed to be proportional to the strength of the $C{=}O\cdots HOC_6H_5$ hydrogen bond.[3] The magnitude of the spectral shift was observed to decrease with increasing ring size in the benzocyclanone series, but increased with increasing ring size in the cyclanone series.[5] The data are summarized in Table I.



1, $n = 2$
2, $n = 3$
3, $n = 4$
4, $n = 5$



5, $n = 4$
6, $n = 5$
7, $n = 6$
8, $n = 7$

TABLE I

HYDROGEN-BONDING AND ULTRAVIOLET SPECTRAL DATA FOR BENZOCYCLANONES AND CYCLANONES

Benzocyclanone	$\Delta\nu_{OH}$, cm^{-1}	λ_{max}, cm^{-1} [a]	ϵ_{max} [a]	Cyclanone	$\Delta\nu_{OH}$, cm^{-1}
1	224	41,900	12,720	5	208
2	215	41,200	11,450	6	209
3	211	41,600	9,000	7	217
4	201	41,100	6,500	8	228

[a] See ref 10.

In an effort to rationalize the behavior of the benzocyclanones a working hypothesis concerning the factors that contribute most significantly to the hydrogen-bonding basicity was adopted. The relative basicity of a benzocyclanone was considered to be dependent upon (1) influences that are an intrinsic function of the ring size of the cyclanone portion, and (2) some factor which is a function of the degree of conjugation

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[1] To whom inquiries should be addressed.

[2] We have terminated research in this area and invite interested researchers to pursue a more complete investigation.

[3] There have been numerous studies of hydrogen bonding between ketones and phenols; yet for several reasons conclusions based on many such investigations must now be considered tentative. T. D. Epley and R. S. Drago [*J. Amer. Chem. Soc.*, **89**, 5770 (1967)] have published a succinct review of the problems involved.

[4] L. J. Bellamy and R. J. Pace, *Spectrochim. Acta*, **19**, 1831 (1963).

[5] The same trend for cyclanones has been observed by others[6] using CH_3OD as a hydrogen-bonding acid. Lactones and cyclic ethers were also studied. The reported trend for ethers[6] was not observed when measurements of Δ*H* for hydrogen-bond formation were made,[7] but the accuracy of similar enthalpy measurements has been questioned.[3]

[6] M. Tamres and S. Searles, Jr., *J. Amer. Chem. Soc.*, **81**, 2100 (1959).

[7] R. West, D. L. Powell, M. K. T. Lee, and L. S. Whatley, *ibid.*, **86**, 3227 (1964).