Decarbonylation of Some Unsaturated Cyclic Aldehydes[1]

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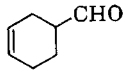
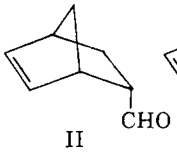
Cyclic aldehydes I–IV were decarbonylated using di-*t*-butyl peroxide. The major products in all cases were dimeric or polymeric residues. Of these aldehydes, only II exhibited rearrangement, giving a hydrocarbon fraction consisting of norbornene and nortricyclene. The composition of this hydrocarbon fraction was relatively unchanged upon dilution of II, indicating possibly a pair of radicals in rapid equilibrium or a delocalized species as the hydrocarbon progenitor. Only IV decarbonylated well (80%) and it is felt that this is a significant example of radical anchimeric assistance.

Our interest in the radical decarbonylation of aldehydes[2] led us to attempt this reaction with the following four aldehydes:


I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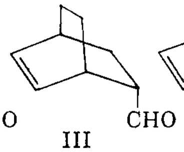
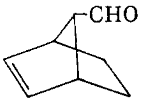
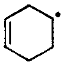

III


IV

We sought to determine: (1) whether homoallylic rearrangement occurs in the unsubstituted radicals shown,[3] (2) whether such rearrangement (if any)


V


VI


VII


VIII

proceeds *via* classical or delocalized species, (3) whether anchimeric assistance by a suitably located double bond is possible in decarbonylation, and (4) whether decarbonylation in these systems can compete successfully with the known aldehyde-olefin addition reaction.[4] While the major result of this work was to confirm the difficulty of decarbonylating unsaturated aldehydes,[5] some information was obtained on each point above.

Aldehydes I–III are known, but a synthesis of IV had to be devised. Norbornene-*anti*-7-carboxylic acid[6] was converted to IV by reduction of its acid chloride with lithium tri-*t*-butoxyaluminohydride.[7] IV so prepared was an unstable substance and necessitated its characterization as a derivative. The aldehydes were decarbonylated using di-*t*-butyl peroxide as the initiator, and the results of these studies are summarized in Table I. The decarbonylations uniformly gave little hydrocarbon. The major products were residues which were investigated to some degree in each case.

TABLE I

DECARBONYLATION OF ALDEHYDES I–IV

Aldehyde	Time (hr.)	Yield (%) CO	Yield (%) Hydrocarbons	R[a]
I(A)[b]	4.5	25.0	27.0[c]	20.3
I(B)[d]	6.5	29.6	33.4[c]	6.25
II(A)	3.0	13.6	8.6[e]	1.90
II(B)	4.75	28.0	9.4[f]	1.17
III(A)	4.75	19.8	5.1[g]	8.62
III(B)	7.0	24.0	4.8[g]	3.29
IV(A)	2.0	80.0	2.3[h]	2.89

[a] *t*-Butyl alcohol/acetone yield ratio. [b] Without solvent, bath temperature 170–175°, reaction procedure A (see Experimental). [c] Pure cyclohexene. The lower carbon monoxide values are considered due to experimental error. [d] Aldehyde 1 *M* in chlorobenzene at reflux, reaction procedure B (see Experimental). [e] Norbornene (41.5%), nortricyclene (58.5%). [f] Norbornene (38.3%), nortricyclene (61.7%). [g] Pure bicyclo[2.2.2]octene. [h] Pure norbornene.

Rearrangement in Radicals V–VIII.—Of these radicals, apparently only VI rearranged, although the low hydrocarbon/carbon monoxide ratios from II–IV preclude any definite conclusions in this regard, since rearranged structures from these radicals could be present as moieties in the residues. In any event, the hydrocarbons that were detected from I, III, and IV were completely unrearranged, even upon dilution of two of the aldehydes (procedure B). The rearrangement of VI is certainly expected in view of the results of others on substituted 5-norbornenyl carbonium ion and radical systems.[3,8] The lack of rearrangement ascribed to V and VII also finds some substantiation in the literature. On the basis that carbon radicals rearrange less

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[1] Taken from the M. Sc. thesis of A. A. L., January, 1962. The initial investigation of cyclohexene-4-carboxaldehyde was done by Allen J. Wysocki as a senior research problem in 1958.

[2] J. W. Wilt and Bro. H. Philip, *J. Org. Chem.*, **25**, 891 (1960); J. W. Wilt and C. A. Schneider, *ibid.*, **26**, 4196 (1961).

[3] Studies on the homoallylic rearrangement of substituted derivatives of VI have been reported: (a) S. J. Cristol, G. D. Brindell, and J. A. Reeder, *J. Am. Chem. Soc.*, **80**, 635 (1958); (b) E. S. Huyser and G. Echegaray, *J. Org. Chem.*, **27**, 429 (1962). It is a pleasure to acknowledge valuable discussions with Dr. Huyser concerning various aspects of the present study.

[4] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 273 ff. Aldehydes add readily to some olefins in benzoyl peroxide or acetyl peroxide induced reactions. Interestingly, the palladium promoted decarbonylation of unsaturated aldehydes proceeds excellently. *Cf.*, H. E. Eschinazi, *Bull. soc. chim. France*, 967 (1952); H. E. Eschinazi and H. Pines, *J. Org. Chem.*, **24**, 1369 (1959). Palladium, on the other hand, appears to be a poor reagent for saturated aldehydes. J. O. Hawthorne and M. H. Wilt, *ibid.*, **25**, 2215 (1960).

[5] M. S. Kharasch, W. H. Urry, and B. M. Kuderna, *ibid.*, **14**, 248 (1949).

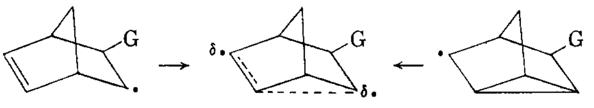
[6] R. R. Sauers, *Chem. Ind.* (London), 176 (1960). We thank Dr. Sauers for sending us experimental details of this preparation.

[7] H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **80**, 5377 (1958).

[8] (a) A. Streitwieser, Jr., *Chem. Rev.*, **56**, 571 (1956); (b) P. von R. Schleyer, *J. Am. Chem. Soc.*, **80**, 1700 (1958) and the many references therein; (c) J. G. Traynham, *J. Org. Chem.*, **25**, 833 (1960).

easily than do the corresponding carbonium ions, the absence of homoallylic isomerization in the Δ^3-cyclohexenyl carbonium ion[9] predicted structural stability in V. Rearrangement (but less than in 5-norbornenyl systems) has been observed in the 5-bicyclo[2.2.2]oct-2-enyl carbonium ion[10] but data appear lacking for the corresponding radical. As a point of interest, the 2-bicyclo[2.2.2]octyl carbonium ion is easily rearranged,[11] while the radical is not.[12] Reactions involving VIII have not previously appeared but reactions producing the corresponding carbonium ion from *anti*-7-norbornenyl compounds retain the norbornene skeleton, albeit with some astounding rates.[13] The rearrangement abilities of V–VIII appear then to follow the expected pattern.[14]

The Nature of the Rearrangement of VI.—Several groups have commented on the possible intermediacy of a delocalized radical in the 5-norbornenyl and 3-nortricyclyl systems, *viz.* IX–XI below.[3,8]



IX X XI

Product control by X appears significant in the corresponding carbonium ion,[16] but not in the radical.[3] A test for rearrangement *via* a single, delocalized species as opposed to two classical species is to note the effect of changing the substrate concentration on the product ratio.[17] The results of such a test are given in Table II.

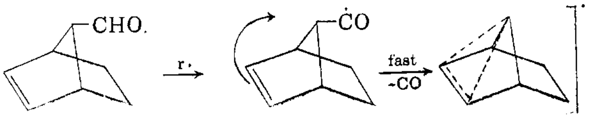
TABLE II
EFFECT OF CONCENTRATION ON HYDROCARBON PRODUCT RATIO FOR ALDEHYDE II

Molar[a]	Norbornene, %[b]	Nortricyclene, %[b]
0.8	43.7	56.3
1.2	46.5	53.5
2.3	47.1	52.9
4.1	46.9	53.1

[a] In chlorobenzene at reflux. [b] Percentage composition of product by gas chromatography after 3.0 hr. The yield of combined product was ~9% (see procedure C in Experimental).

While the yield of mixed hydrocarbon is low, the product composition over this fivefold change in concentration shows significantly less change than that noted by Cristol and co-workers in their radical addition of *p*-thiocresol to norbornadiene.[3a] Subject to the uncertainty inherent in our study, we opine that less change is expected in our case than in Cristol's. As was pointed out by these authors, if a pair of classical radicals equilibrate[18] much faster than they undergo chain transfer, then the product ratio is also unchanged with changing substrate concentration, the same as if one nonclassical radical engenders both products. Since the chain transfer constants of thiols are quite high,[19] while those of aldehydes are undoubtedly lower,[20] the equilibration or nonclassical situation may be involved in our work.

Anchimeric Assistance in the Loss of Carbon Monoxide.—The aldehydes I–III were not decarbonylated well, either with or without solvent. With these, the addition reaction[4] preponderated. IV, however, evolved 80% of the carbon monoxide and the rate of this evolution was significantly greater than with I–III. We suggest that the decarbonylation of IV is anchimerically assisted by π-electrons, advantageously located in XII as in the ion.[13] While the present study was in progress, Story[21] reported similar π-bond assistance at the 7-position of norbornadiene. From the available information, anchimeric assistance in radical formation may be expected only when such assistance is known to be extremely effective in the cationic analogs. If this is true, striking differences may then be expected between *exo*- and *endo*-II and *anti*- and *syn*-IV in decarbonylation.



IV XII VIII

Self-addition of the Aldehydes.—The residues obtained in these reactions were viscous oils or resinous solids. These materials were difficult to study and at best some of our results are only qualitative. The molecular weight and elemental analysis indicated that the majority of the residue

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[9] E. E. van Tamelen, *J. Am. Chem. Soc.*, **77**, 1704 (1955).

[10] A. Gagneux and C. A. Grob, *Helv. Chim. Acta*, **42**, 1753 (1959).

[11] W. von Doering and M. Farber, *J. Am. Chem. Soc.*, **71**, 1514 (1949).

[12] W. von Doering, M. Farber, M. Sprecher, and K. B. Wiberg, *ibid.*, **74**, 3000 (1952).

[13] S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *ibid.*, **77**, 4184 (1955). The result in the *syn*-7-norbornenyl system does lead to rearrangement, though VIII-carbonium ion probably is not involved, S. Winstein and E. T. Stafford, *ibid.*, **79**, 505 (1957).

[14] LCAO-MO calculations (neglecting strain energies) indicate that for V–VII as cations the delocalization energy DE_π equals $2(\sqrt{k^2 + 1} - 1)\beta$, where k is the fraction of the standard resonance integral (β) allowed for nearest neighbor transannular interaction. For VI, with $k = 0.25$,[15] $DE_\pi = 0.06\beta$ (~1.2 kcal./mole). V and VII would be expected to have $k < k_{VI}$, since the transannular distance in each is greater than in VI. Their DE_π values, therefore, should be less than that for VI. For DE_π of VIII, see W. G. Woods, R. A. Carboni, and J. D. Roberts, *ibid.*, **78**, 5653 (1956). The calculations indicate that the electron added to change these ions to radicals enters a nonbonding orbital, so that similar considerations should hold for the radicals V–VIII.

[15] J. D. Roberts, "Molecular Orbital Calculations," W. A. Benjamin, Inc., New York, N. Y., 1961, p. 72.

[16] J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **77**, 3034 (1955).

[17] F. H. Seubold, Jr., *ibid.*, **75**, 2532 (1953). For a penetrating discussion, see C. Rüchardt, *Chem. Ber.*, **94**, 2599 (1961). Dr. Seubold has informed us that he decarbonylated II some time ago and also obtained norbornene and nortricyclene in unpublished work.

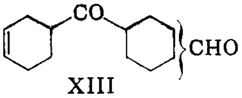
[18] The interconversion of 3-nortricyclyl and 5-norbornenyl radicals has yet to be demonstrated, however. The equilibrium has apparently been heretofore assumed.

[19] Text ref. 4, p. 156.

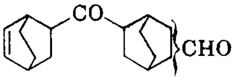
[20] Witness the decreased rearrangement of aldehyde-derived neophyl radicals in the presence of thiols.[2]

[21] P. R. Story, *J. Am. Chem. Soc.*, **82**, 2085 (1960); *J. Org. Chem.*, **26**, 287 (1960).

from I and III was a dimeric substance, for which the respective structures XIII and XIV are proposed (position and stereochemistry of the aldehyde group uncertain). The formation of XIII and XIV

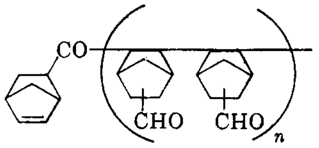


XIII



XIV

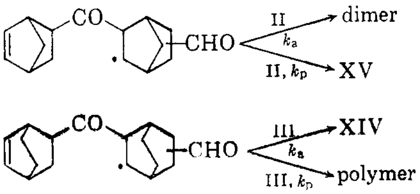
could result from the addition of acyl radicals to the aldehydes followed by chain transfer. The residues from II and IV were soluble only in carbon disulfide. Molecular weights were therefore not obtained, but analysis and infrared data indicated that the residue from II was a polymer with retained carbonyl, while the residue from IV was also a polymer with oxygen present, but not as a carbonyl group. Radical homopolymerization of the norbornenyl system has not been previously reported and the present involving II is therefore of interest. Radical copolymerization, however, is known[22] in this system and recently some examples of homopolymerization in the norbornadienyl system have been published.[23] Structure XV is proposed for the



XV

polymer from II, while the nature of the polymer from IV is unknown. 2,4-Dinitrophenylhydrazone derivatives were obtained from XIII and XIV, the analyses of which correspond reasonably to the suggested structures.

Why polymer formed from II and IV but dimer from I and III can be rationalized in terms of the steric requirement for the addition of these radicals and the reactivity of the double bonds in the various aldehydes toward radical addition. The cases of XIV and XV are treated below.



The ratio k_a/k_p determines in each case whether dimer or polymer will predominate. From the R-values (Table I) for II and III[24] k_a appears some 4.5-fold greater for III.[25] From the known[26] radical addition abilities of norbornene *vs.* bicyclooctene k_p is greater for norbornene and the difference here would be augmented because of the obviously large steric requirement of these reactions.

Experimental

All melting and boiling points are uncorrected for stem exposure. The combustion analyses marked *g* were performed by Galbraith Laboratories, Knoxville, Tennessee; those marked *v* were performed through the courtesy of the analytical laboratories of the Velsicol Chemical Corp., Chicago, Illinois. Infrared spectra were determined on carbon disulfide solutions and recorded on a Perkin-Elmer Infracord using sodium chloride optics. Gas chromatography studies were done on a Perkin-Elmer Model 154 Fractometer using a 10-ft. column packed with tricresyl phosphate (25%) on Celite. Molecular weights were determined by the freezing point depression of benzene solutions. The cyclohexene used was pure commercial material, as was the cyclohexene-4-carboxaldehyde (Aldrich).

Preparation of the Aldehydes II–IV. Bicyclo[2.2.1]hept-2-ene-*endo*-5-carboxaldehyde (II) was obtained by a reported method,[27] (b.p. 60–62° at 15 mm., 93.2%, semicarbazone m.p. 161–163°; lit.,[27] b.p. 70–72° at 20 mm., semicarbazone m.p. 162°). The 2,4-dinitrophenylhydrazone was prepared in the usual manner, m.p. 146–147°.

Anal.^{g} Calcd. for $C_{14}H_{14}N_4O_4$: N, 18.54. Found: N, 18.31.

Bicyclo[2.2.2]oct-2-ene-*endo*-5-carboxaldehyde (III) was similarly prepared[28] (b.p. 84–85° at 12 mm., 24%, semicarbazone m.p. 175–176°; lit.,[28] b.p. 84–85° at 12 mm., semicarbazone m.p. 176–177°). The 2,4-dinitrophenylhydrazone had a m.p. 116.5–117.5°.

Anal.^{g} Calcd. for $C_{15}H_{16}N_4O_4$: N, 17.71. Found: N, 17.90.

Bicyclo[2.2.1]hept-2-ene-*anti*-7-carboxaldehyde (IV).—Bicyclo[2.2.1]hept-2-ene-*anti*-7-carboxylic acid (m.p. 71–73°, lit.,[6] m.p. 70–73°, 2.4 g., 0.017 mole) and purified thionyl chloride (25 ml.) were heated under reflux for 3 hr. Removal of the excess thionyl chloride (water pump) and subsequent short path distillation yielded the acid chloride (b.p. 75–85° at 15 mm., 2.3 g., 85.4%) as an unstable yellow oil. Addition of lithium tri-*t*-butoxyaluminohydride solution (in diethylene glycol dimethyl ether, 1 *M*, 14 ml., 0.015 mole) dropwise to the acid chloride (2.3 g., 0.015 mole) well stirred in freshly distilled diethylene glycol dimethyl ether (15 ml.) at −78°, followed by the customary[7] isolation procedure, yielded IV as a pale yellow oil (0.9 g., 50%) which decomposed readily on attempted distillation under reduced pressure. The material exhibited peaks at 3.7 μ and 5.8 μ, and readily formed a 2,4-dinitrophenylhydrazone, m.p. 150–151°, after recrystallization from ethanol.

Anal.^{g} Calcd. for $C_{14}H_{14}N_4O_4$: N, 18.54. Found: N, 18.37.

Preparation of Reference Hydrocarbons. Norbornene was prepared as reported[29] (m.p. in sealed tube 43–45°, b.p. 94–97°, 50%; lit.,[29] m.p. 44–46°). The material was chromatographically pure (85° column). **Nortricyclene** was obtained by the isomerization of norbornene[8b] and separated by preparative gas chromatography (85°). Its infrared spectrum was identical with that reported.[30] **Bicyclo[2.2.2]octene-2** was prepared by the method reported[31] from bicyclo[2.2.2]octane-2,3-dicarboxylic acid anhydride (2 g., 0.011 mole, m.p. 187°; lit.,[28] m.p. 187°) as a white, crystal-

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[22] J. J. Judge and C. C. Price, *J. Polymer Chem.*, **41**, 1135 (1959).

[23] V. A. Kargin, N. A. Plate, and L. A. Dudkin, *Vysokomolekulyarnye Soedineniya*, **1**, 420 (1959); P. J. Graham, E. L. Buhle, and N. Pappas, *J. Org. Chem.*, **26**, 4658 (1961).

[24] Text ref. 4, p. 470.

[25] Admittedly, the k_a values would be different for the electron-seeking *t*-butoxy radical attack on II and III and the attack by the electron-donating carbon radicals shown.

[26] M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, **14**, 239 (1949).

[27] O. Diels and K. Alder, *Ann.*, **460**, 98 (1928).

[28] O. Diels, K. Alder, E. Petersen, and F. Querberitz, *ibid.*, **478**, 137 (1930).

[29] L. M. Joshel and L. W. Butz, *J. Am. Chem. Soc.*, **63**, 3350 (1941).

[30] E. R. Lippincott, *ibid.*, **73**, 2001 (1951).

[31] W. von E. Doering, M. Farber, and A. Sayigh, *ibid.*, **74**, 4370 (1952).

line solid (0.18 g., 15.3%, m.p. 111–113°; lit.,[32] m.p. 110–113°). Its infrared spectrum conformed exactly to that reported.[32]

Decarbonylation of the Aldehydes. Procedure A.—A small flask containing the aldehyde (0.05 mole, except for IV which was 0.0087 mole) and di-*t*-butyl peroxide (0.01 mole) under nitrogen was held in a bath maintained at 170–175° and the volatile products collected as they distilled through a small Vigreux column. The gas evolved was passed through two cold traps and then collected over water. Two subsequent additions of peroxide (0.01 mole each) were made when the gas evolution slackened. The carbon monoxide was determined in a Fisher-Orsat apparatus. The times given in Table I are the total times for the three additions of peroxide. The distillates were analyzed by gas chromatography; their composition in the same way through the use of standards. The identity of the eluted hydrocarbons was confirmed by infrared comparison with the knowns. The residues from these reactions were investigated separately (see below). The mass balance for these reactions ranged from 91.6–99%.

Procedure B.—I, II (0.05 mole each) and III (0.025 mole) were separately dissolved in distilled chlorobenzene (50 g. and 36.15 g., respectively) and di-*t*-butyl peroxide (0.01 mole for I, II; 0.005 mole for III) added. The system was flushed with nitrogen and then held at reflux (132°). Second and third additions of peroxide were made as before and the analysis of the products was also the same.

Procedure C.—Samples of II (1.0 g.) and di-*t*-butyl peroxide (0.4 g.) were dissolved in 1, 2.5, 5, and 10-ml. portions of chlorobenzene and the solutions heated at reflux for 3.0 hr. The analysis of products was the same as before, but the gases evolved were not collected.

Investigation of the Residues.—The residues were difficult to study and the analytical results on them are included because they indicate (but not decisively) that these residues are most reasonably dimers or polymers of the starting aldehydes. **XIII** was a viscous, yellow oil.

Anal.[9] Calcd. for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15; mol. wt. 220.3. Found: C, 75.80; H, 8.87; mol. wt. 204.5.

A strong absorption at 5.82 μ (C=O) characterized the infrared spectrum and a bis-2,4-dinitrophenylhydrazone derivative was accordingly prepared, m.p. 128–130°. Recrystallizations from ethanol improved neither the melting point nor the analysis.

Anal.[9] Calcd. for $C_{26}H_{28}N_8O_8$: N, 19.30. Found: N, 18.88.

XV was a brown, vile-smelling, resinous solid, insoluble in all the usual solvents except carbon disulfide and was on this basic considered a polymer.

Anal.[9] Calcd. for $(C_8H_{10}O)_x$: C, 78.65; H, 8.25. Found: C, 78.30; H, 9.00.

A standardized study of XV and II (each in carbon disulfide) revealed that the areas under the C—H stretching region (*ca.* 3.4 μ) and carbonyl region (5.85 μ) in each were in the same ratio (1:1.8, respectively), a further indication that the recurring unit in XV was II.

XIV was a brown, viscous, malodorous oil which showed carbonyl absorption (5.85 μ) in its infrared spectrum.

Anal.[9] Calcd. for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88; mol. wt. 272.3. Found: C, 79.72; H, 9.26; mol. wt. 264.0.

A brick red 2,4-dinitrophenylhydrazone derivative was prepared. The material, m.p. 110–111.5°, was exceedingly difficult to purify. Its analysis favors its formulation as a mono-derivative.

Anal.[9] Calcd. for $C_{24}H_{28}N_4O_5$(mono): N, 12.38. Calcd. for $C_{30}H_{32}N_8O_8$(bis): N, 17.71. Found: N, 12.86.

Residue from IV.—This resinous, black solid was insoluble in organic solvents except carbon disulfide and therefore was considered polymeric. Its infrared spectrum exhibited only weak carbonyl absorption (as expected), but oxygen in some form[33] was nonetheless present in the material, as indicated by the analysis.

Anal.[9] Found: C, 77.80; H, 8.99.

This material was not investigated further.

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(32) J. Hine, J. A. Brown, L. H. Zalkow, W. E. Gardner, and M. Hine, *J. Am. Chem. Soc.*, **77**, 594 (1955).

(33) Story[21] has shown that *t*-butoxy substitution occurs in norbornadiene. The oxygen in the residue from IV might also so arise.

Nitrations with Acetyl Nitrate. II. Nitration of Styrenes and Stilbenes[1]

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Received February 16, 1962

Nitration of styrene, α-methylstyrene, β-methylstyrene, *trans*-stilbene, and *trans*-α-methylstilbene gave 40–70% yields of β-nitro acetates. Judging from the results with *trans*-β-methylstyrene, *trans*-stilbene, and *trans*-α-methylstilbene, these products are formed by *cis* additions of acetyl nitrate to the C=C bond. *cis*-Stilbene and *cis*-α-methylstilbene reacted more slowly than the corresponding *trans* isomers to give β-nitro acetates resulting from apparent *trans* addition. *cis*- and *trans*-α,β-dimethylstilbenes reacted but failed to give nitro acetates.

Acetyl nitrate in acetic anhydride solution reacts rapidly with many alkenes to give mixtures of nitroalkenes, β-nitro nitrates, and β-nitro acetates.[2] The reaction is of limited preparative value when applied to simple alkenes, but is more useful when one or two aryl groups are attached to the C=C bond. The yields of β-nitro acetates are then generally increased and product isolation is facilitated. Application of the reaction to a number of styrenes and stilbenes is reported in the present paper.

Nitration of styrene with acetyl nitrate at low temperatures for short reaction times, according to the directions previously described,[2] gave 50% of β-nitro acetate and 28% of nitrostyrenes (principally *o*-nitrostyrene).[3] Under similar conditions

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(1) Abstracted from the Ph.D. dissertation of Edgar W. Garbisch, Jr., submitted to Northwestern University, August, 1961.

(2) F. G. Bordwell and E. W. Garbisch, Jr., *J. Am. Chem. Soc.*, **82**, 3588 (1960).

(3) Using a longer reaction time and a higher temperature R. S. Schiefelbein (Ph.D. dissertation, Northwestern University, 1950) obtained similar products, but found that the β-nitro acetate decomposed to acetic acid and β-nitrostyrene on attempted distillation. We have confirmed this result.