metry number of one, there is no symmetry effect of its entropy and $\Delta S_{\text{I}\rightarrow\text{III}}$ should be +3.6 e.u., a value in approximate agreement with that found experimentally (Table II). The high symmetry of I is destroyed in its derivatives, such as V, and such derivatives should be favored to a greater extent than the parent hydrocarbon, I, in equilibration processes, *e.g.*, V with VI.[3]

It is novel to find that the course of some organic reactions can be governed largely by symmetry and entropy factors.

Acknowledgment.—The gas chromatography apparatus was purchased with a Grant-In-Aid from the FMC Corporation.

(12) Alfred P. Sloan Research Fellow.

(13) National Science Foundation Predoctoral Fellow.

(14) A. B. Thesis, Princeton University, 1957.

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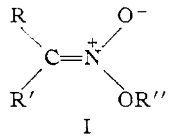
RECEIVED MARCH 8, 1963

THE SYNTHESIS AND CHARACTERIZATION OF NITRONIC ESTERS

Sir:

Hitherto there has been no generally useful way of synthesizing nitronic esters (I).



I

R, R′ = H, alkyl or aryl
R″ = alkyl

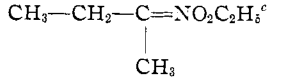
Indeed, those derived from strictly aliphatic nitro compounds are unknown.

We now report a new and general synthesis of nitronic esters which involves treating the salts of nitro compounds with trialkyloxonium fluoroborates[1] at 0°; the reaction is rapid and pure nitronic esters are generally obtained in yields of excess of 90% (*cf.* Table I).

$$RR'CNO_2^-Na^+ + R_3''O^+BF_4^- \longrightarrow \text{I} + NaBF_4 + R_2''O$$

TABLE I

NITRONIC ESTERS PREPARED FROM OXONIUM FLUOROBORATES AND NITRO SALTS[a,b]

Nitronic ester	Yield, %
$CH_3CH{=}NO_2CH_3$	90–95
$CH_3CH{=}NO_2C_2H_5$	94
$CH_3CH_2CH{=}NO_2C_2H_5$	79
$CH_3CH_2CH_2CH{=}NO_2C_2H_5$	95
p-Br—C_6H_4—$CH{=}NO_2C_2H_5$	95
p-O_2N—C_6H_4—$CH{=}NO_2C_2H_5$	92
$(CH_3)_2C{=}NO_2C_2H_5$[c]	75–80
 $CH_3{-}CH_2{-}C(CH_3){=}NO_2C_2H_5$[c]	90–95

[a] All the nitronic esters mentioned in this Communication exhibit intense absorption in the 6.05 to 6.2-μ region. [b] The yields of sodium fluoroborate usually exceed 95%. [c] Prepared at −65 to −60°.

As a typical example: to a stirred, ice-cold, slurry of 3.00 g. (24.0 mmoles) of the dry, finely powdered, sodium salt of 1-nitrobutane in 25 ml. of methylene chloride is rapidly added an ice-cold solution of 4.05 g. (21.8 mmoles) of triethyloxonium fluoroborate in 15 ml. of methylene chloride. After being stirred under nitrogen for 15 min., the mixture is filtered rapidly and the solid washed with 5 ml. of ice-cold, anhydrous ethyl ether. The combined filtrate and wash are rapidly evaporated *in vacuo* to constant volume at *ca.* 5 to 15°. The resulting very pale yellow liquid is subjected to a vacuum of *ca.* 1 mm. for another 5 min. at 25° and stored at −78°; $n^{20}\text{D}$ 1.4468; yield 2.72 g. (95%).

Anal. Calcd. for $C_6H_{13}NO_2$: C, 54.94; H, 9.99; N, 10.68. Found: C, 55.16; H, 9.96; N, 11.02.

In principle, nitronic esters in which $R \neq R'$ should exist as *cis–trans* isomers; such stereoisomerism, however, has not been reported. By the use of nuclear magnetic resonance (n.m.r.) we have now found that such stereoisomers do indeed exist. Thus, the ethyl nitronic ester obtained from 1-nitrobutane has an n.m.r. spectrum in which *two* "vinyl" hydrogen[2] quartets appear. One quartet (at 6.04 δ)[3] has an area about seven times greater than the area of the second quartet (at 5.75 δ). In the same way, all the nitronic esters in Table I which derive from primary nitro compounds prove to be mixtures of the *cis–trans* isomers in proportions varying from 1:1 to 7:1.

The realization that *cis–trans* isomerism is exhibited by nitronic esters clarifies some otherwise puzzling facts. Thus, the *crude* ethyl nitronic ester obtained from *p*-nitrophenylnitromethane (92% yield) gives good carbon, hydrogen and nitrogen analyses, but it melts over a wide range (82–88°). Recrystallization raises the m.p. to 100–101°, but the analyses remain unchanged. This anomaly is resolved by n.m.r.; the spectrum of the "crude" nitronic ester has *two* "vinyl" hydrogen singlets (at. 7.22 δ and 6.95 δ, in approximately a 4:1 ratio) whereas the recrystallized ester shows only the "vinyl" hydrogen singlet at 7.22 δ. Recrystallization has simply separated the stereoisomers.

Of the nitronic esters thus far prepared from secondary nitro compounds, only the ethyl nitronic ester derived from 2-nitrobutane (*cf.* Table I) is capable of exhibiting *cis–trans* isomerism. Here again clear evidence of stereoisomerism is obtained; *two* singlets (at 1.94 δ and 2.00 δ) due to two different "vinyl" methyl groups are found in the n.m.r. spectrum.

Both stereoisomeric nitronic esters are also produced when diazomethane reacts with *p*-nitrophenylnitromethane and *p*-bromophenylnitromethane.[4] Quantitative yields of the "crude" nitronic esters are obtained, but although analytically pure, these products melt over wide temperature ranges. As before, n.m.r. studies demonstrate that in each instance mixtures of both possible stereoisomers are at hand; and, as before, recrystallization serves to separate the stereoisomers.

Nitronic esters are stable indefinitely at −78°, but at room temperature they decompose relatively rapidly, particularly in the liquid state or in solution. Furthermore, for a given nitronic ester, the stereoisomer which is produced in minor proportion proves to be less stable than the isomer produced in major proportion. Thus, the more stable isomer of the methyl nitronic ester of *p*-nitrophenylnitromethane,[5] in deuteriochloroform solution, has a half-life of 5 days, whereas the less stable isomer has a half-life of only several hours. In general, the ethyl nitronic esters

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(1) H. Meerwein, E. Battenberg, H. Gold, E. Pfeil and G. Willfang, *J. prakt. Chem.*, **154**, 83 (1939).

(2) By "vinyl" hydrogen we refer to the hydrogen atom on the unsaturated carbon atom in the compounds listed in Table I.

(3) Chemical shifts from the internal standard, tetramethylsilane, are reported in δ values. The n.m.r. spectra were obtained with a Varian Associates A-60 spectrometer.

(4) F. Arndt and J. D. Rose, *J. Chem. Soc.*, 1 (1935). This reaction is only applicable to nitro compounds which are relatively strong acids. Thus, we have shown that 3-phenyl-1-nitropropane undergoes no reaction whatsoever on treatment with diazomethane even after 5 days.

(5) This is the most stable of the nitronic esters prepared by us. In the crystalline state it only begins to show a lowering of the m.p. after 10 days at room temperature.

derived from primary, purely aliphatic, nitro compounds have half-lives of the order of *ca.* 1 day for the more stable stereoisomer and *ca.* 1 hr. for the less stable stereoisomer. Nitronic esters derived from secondary nitro compounds are apparently less stable than those obtained from primary nitro compounds. Thus, both stereoisomers of the ethyl nitronic ester from 2-nitrobutane (they are produced in equal amounts) in carbon tetrachloride at room temperature have half-lives of only 80 min. Least stable of all is the ethyl nitronic ester derived from nitrocyclohexane which cannot be brought to room temperature without decomposing rapidly.

Extensions of this new synthesis of nitronic esters are being explored and the chemistry of these compounds is under investigation.

Acknowledgments.—We take pleasure in acknowledging the support of the U. S. Army Research Office (Durham). We are indebted to Mr. William E. Baitinger for determining many of the n.m.r. spectra and to Mr. Baitinger and Professor Norbert Muller for much assistance in interpreting these spectra. Satisfactory analyses for the compounds listed in Table I were obtained by Dr. C. S. Yeh, Mrs. T. Eikeri, Mrs. M. Hudgens, Mrs. V. Keblys and Mrs. A. Seo. We deeply appreciate Dr. Yeh's gracious coöperation in making special arrangements for the analyses of these rather unstable compounds.

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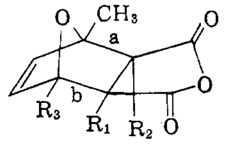
THE MECHANISM OF A DIELS–ALDER REACTION[1]

Sir:

Previously, we reported[2] the isotope effects k_I/k_{II} = 1.16 and k_I/k_{III} = 1.08 in the decomposition of the Diels–Alder adduct from 2-methylfuran and maleic anhydride. It was impossible, from these results, to differentiate between a stepwise or concerted bond breaking. We now show that bonds a and b break simultaneously.



I, $R_1 = R_2 = R_3 = H$
II, $R_1 = R_2 = D, R_3 = H$
III, $R_1 = R_2 = H, R_3 = D$
IV, $R_1 = D, R_2 = R_3 = H$
V, $R_1 = R_3 = H, R_2 = D$

Preparation of pure IV or V is precluded by the high lability ($t_{1/2} \cong$ 28 min. at 50°)[2,3] of this adduct. Fortunately, however, the n.m.r. spectrum of *I* shows protons, R_1 and R_2, to be represented by an AB quartet with $J_{R_1R_3} = 0$ ($J_{R_1R_2} \cong 7.2$ c.p.s., $\tau_{R_1} = 6.71$, $\tau_{R_2} = 6.96$, in $CHCl_3$).[4] The quartet disappears in II, is unaltered in III, and becomes a doublet in a mixture of IV and V. The ratio of the peak areas in the doublet is then equal to the molar ratio of IV to V. Determinations of this ratio initially and after a large extent of decomposition yield[5] the isotope effect, k_{IV}/k_V, which determines[6] the relative amount of bond breaking of a compared to b in the slow step.

Monodeuteriomaleic acid was prepared by electrolytic dehalogenation of sodium bromomaleate in D_2O (lead cathode, ~15°) and converted to the anhydride as reported.[7] Preparation of the IV–V mixture is similar to that for I.[2]

The IV–V mixture (m.p. 75–76°) in 30% dioxane–70% isoöctane decomposed at 50° for a specified time, then was cooled in ice and the solvent (and 2-methylfuran) was removed rapidly at reduced pressure. Maleic anhydride sublimed (oil pump) and the adduct residue was either recrystallized or sublimed under high vacuum. N.m.r. determinations of IV/V before and after a large extent of reaction are recorded in columns 2 and 4 of Table I.

TABLE I
N.M.R. DETERMINATION OF ISOTOPE EFFECT

$[IV + V]_0$	$[IV]_0/[V]_0$[a] obsd.	% Reaction	$[IV]_f/[V]_f$[a] obsd.	$[IV/V]_f\,[IV/V]_0$ calcd. One step	Two steps[b]
0.1132 *M*	1.00 ± 0.02	87	0.99 ± 0.04	1.00	1.31
.0959 *M*	1.02 ± .06	81	1.00 ± .04	1.00	1.24
.0796 *M*	1.01 ± .02	82	1.00 ± .04[c]	1.00	1.25

[a] Each ratio is the average of 20 or more integrations. Errors are average deviations. [b] Calculated by an equation given by Bigeleisen and Wolfsberg.[5] [c] Adduct purified by high vacuum sublimation.

If the effect, k_I/k_{II} = 1.16, is mainly due to deuteriation at R_1 (*i.e.* bond b breaks in a slow step and a in a prior or latter rapid step) then after large conversion the remaining substrate would be richer in IV than in V. The ratios of final to initial (IV/V) are given in column 6 of Table I for a hypothetical k_V/k_{IV} = 1.15 (*i.e.*, a two-step reaction). For equal amount of bond-breaking of a and b at the transition state (*i.e.*, one-step concerted reaction), this ratio becomes 1.00 (column 5) because the effect, k_V/k_{IV}, would equal 1.00. The results shown indicate that reversion conforms closely to a concerted rupture of a and b.

TABLE II
DETERMINATION OF DEGREE OF REVERSIBILITY DURING DECOMPOSITION OF 4-METHYL-7-OXA-BICYCLO[2.2.1]-2-HEPTENE-EXO-5,6-DICARBOXYLIC ACID ANHYDRIDE

Adduct[a] *M*	Maleic anhydride-2,3-C^{14}[b] $M \times 10^3$	% Reaction	Calcd. %[f] reformed adduct	Sp. activity in remaining adduct mμC/mgC	Observed %[g] reformed adduct
0.0940[c]	5.78	77.7	8.2	0.490	17.9
.0194[d]	1.25	78.8	1.5	.421	14.6
.0743[e]	3.52	78.6	6.9	.411	19.0

[a] Adduct obtained by sublimation of the solid residue after evaporation of solvent, except see *e*. [b] Initial specific activity = 85.7 mμC/mgC. [c] V_0 = 250 ml. (30% dioxane in isoöctane). [d] V_0 = 1200 ml. (27% dioxane in isoöctane). [e] Reaction mixture immediately cooled; solvent lyophillized and adduct sublimed from the solid residue. V_0 = 304 ml. (100% dioxane). [f] Calculated from the amount of reverse reaction as

$$A \xrightarrow{k_1} B + C \quad (1) \qquad A \underset{}{\overset{k_1}{\rightleftharpoons}} B + C \quad (2)$$

From (1), $A_1 = a_0 e^{-k_1 t}$

From (2), $\ln \dfrac{2k_2x + k_1 + k_2b_0 + S}{2k_2x + k_1 + k_2b_0 - S} \times \dfrac{k_1 + k_2b_0 - S}{k_1 + k_2b_0 + S} = St$

where $S = \sqrt{(k_1 + k_2b_0)^2 + 4k_1k_2a_0}$, $A_2 = a_0 - x$ and the other notations have their usual meanings. Then calcd. % reformed adduct = $(A_2 - A_1)/A_1 \times 100$. [g] (Sp. activity in adduct × 9/4 × 100)/(sp. activity in diluted maleic anhydride at –% reaction).

The ratio, $[IV/V]_f$, should refer to unreacted substrate and not to adduct reformed during decomposition. Reversibility was checked for in two ways: (1) by looking for C^{14}-incorporation in the adduct after partial

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(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) S. Seltzer, *Tetrahedron Letters*, **No. 11,** 457 (1962).

(3) See, *e.g.*, R. B. Woodward and H. Baer, *J. Am. Chem. Soc.*, **70,** 1161 (1948).

(4) F. A. L. Anet, *Can. J. Chem.*, **39,** 789 (1961); M. M. Anderson and P. M. Henry, *Chem. Ind.* (London), 2053 (1961).

(5) J. Bigeleisen and M. Wolfsberg, in "Advances in Chemical Physics," Vol. I, I. Prigogine, Ed., Interscience Publishers, Inc., New York, N. Y., 1958, p. 38.

(6) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey and S. Suzuki, *J. Am. Chem. Soc.*, **80,** 2326 (1958); S. Seltzer, *ibid.*, **83,** 2625 (1961); **85,** 14 (1963).

(7) S. Seltzer, *ibid.*, **83,** 1861 (1961).