Ten new esters of *p*-methyl- and *p*-isopropylmandelic acid were prepared in order to study the effect of alkyl substitution in the aromatic nucleus on the mosquito repellent action. The esters were prepared as previously described, *p*-tolualdehyde and cuminic aldehyde being used as starting materials for the corresponding mandelic acids. Yields, physical constants, and analytical data are given in Table 1.

None of the esters exhibited any appreciable repellent effect against mosquitoes[2] although the corresponding unsubstituted mandelic esters have shown repellent action.[1]

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(2) Carroll N. Smith, I. H. Gilbert, H. K. Gouck, and others on the staff of the Orlando, Fla., laboratory conducted the repellency tests.

Ultraviolet Absorption Spectra of Nitrostyrene Derivatives[1]

JEREMIAH P. FREEMAN AND TRAVIS E. STEVENS

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Although only scattered references to the ultraviolet spectra of nitroolefins are found in the literature, it appeared that the study of such spectra should allow assignment of stereochemical configuration particularly in the case of ω-nitrostyrene derivatives. The *trans*-ω-nitrostyrene system is characterized by a band of strong intensity in the region of 305–325 mμ, the exact position being affected by the nature of the substituent on the carbon atom bearing the nitro group.[2] The spectra of several nitrostyrene derivatives have been measured in alcohol solution and their characteristics are summarized in Table I.[3]

In each of the three *cis-trans* pairs examined, one of the isomers showed absorption beyond 300 mμ while the other did not. The compounds exhibiting absorption in the 300-mμ region have been assigned the *trans*-nitrostyrene structure. The alternative assignment of this long wave length absorption to the *trans*-stilbene system appears unattractive for the following reason: the α,α′-dinitrostilbene structures are known with certainty[4] and the isomer with the phenyl groups *cis* shows a definite absorption peak at 310 mμ while the *trans* isomer shows only end absorption in this region.[5]

TABLE I

SPECTRAL CHARACTERISTICS OF ω-NITROSTYRENE DERIVATIVES, $C_6H_5CR'{=}CRNO_2$

R	R′	M.P., °C.	λ_{max}	ϵ_{max}
cis-C_6H_5	NO_2	108–109	252 (sh)	7850
			310	4600
trans-C_6H_5	NO_2	187–188	238 (sh)	13300
cis-C_6H_5[a]	I	113–114	240	15200
			310	4400
trans-C_6H_5	I	176–177	242 (sh)	13700
			310	2300
trans-C_6H_5	H	127–128	281	21500
cis-C_6H_5	H	74–75	228	12200
			316	12100
H[b]	Cl	54–55	246 (sh)	8450
			285	5450
H	I	50–51	244 (sh)	14000
			284	9350
			310 (sh)	7750

[a] The intensities listed indicate only the extent of absorption at the wave lengths noted for comparison with the *trans* compound. *cis*-Nitroiodostilbene exhibited only end absorption with no definite peaks or shoulders. [b] The intensities previously reported for this compound [J. P. Freeman and W. D. Emmons, *J. Am. Chem. Soc.*, **79**, 1712 (1957)] are too low apparently due to partial decomposition of the material before the spectrum was measured.

The *cis* and *trans*-α-nitrostilbenes have been known for some time as products of the condensation of benzaldehyde and phenylnitromethane,[6] but little evidence as to their stereochemistry has been assembled.[7] It is known, however, that the lower melting isomer, which is now assigned a *trans*-nitrostyrene structure, is the more readily obtained and appears to be the thermodynamically more stable form. In this study the lower melting isomer was produced preponderently when either *meso* or DL-1,2-dinitro-1,2-diphenylethane was treated with pyridine.[8]

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(1) This research was carried out under Army Ordnance Contract W-01-021-ORD-334.

(2) E. A. Braude, E. R. H. Jones, and G. G. Rose, *J. Chem. Soc.*, 1104 (1947).

(3) In the table the designations *cis* and *trans* refer to the relation of the phenyl groups. It is clear that the *cis* compounds contain the *trans*-nitrostyrene system.

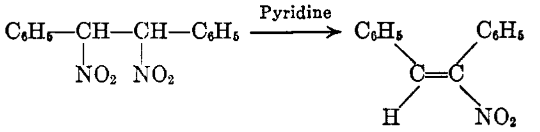
(4) K. N. Campbell, J. Shavel, Jr., and B. K. Campbell, *J. Am. Chem. Soc.*, **75**, 2400 (1953).

(5) The spectra of the dinitrostilbenes as reproduced by Campbell *et al.*[3] appear to be in error as no maximum of an intensity comparable to those reported by them was found nor should one be expected of such a sterically crowded molecule. Since nitrostyrene derivatives partially decompose on standing, it is important that spectra are measured on freshly recrystallized samples. This point has been emphasized previously [M. J. Kamlet and D. J. Glover, *J. Am. Chem. Soc.*, **77**, 5696 (1955).]

(6) F. Heim, *Ber.*, **44**, 2016 (1911).

(7) B. Reichert and W. Kuhn, *Ber.*, **74B**, 328 (1941). These authors assigned the structures of some nuclear-substituted α-nitrostilbenes on the basis that the *cis* isomer had the lower melting point, the greater solubility and the more intense color. Their assignments are the same as ours.

(8) The use of sodium methoxide or piperidine to convert the 1,2-dinitro-1,2-diphenylethanes to α-nitrostilbenes also led to the lower melting isomer; see J. Meisenheimer and F. Heim, *Ann.*, **355**, 269 (1907); A. Angeli and L. Alessandri, *Atti. accad. Lincei*, **19**, I, 784 (1910) [*Chem. Abstr.*, **4**, 2634 (1910)].



+ trace of *trans* isomer

It is clear from a study of models that the isomer with the phenyl groups *cis* allows a closer approach to planarity for the whole molecule and thus the reaction is subject to steric control.

It is interesting to compare the spectra of these nitrostyrene derivatives to those of analogous members of the chalcone and cyanostyrene series. The assignments in the chalcone series[9] are very similar to those made in this study: those compounds exhibiting the longer wave length absorption were assigned the *trans*-chalcone structure. However, in the case of cyanostyrene derivatives[10], such as *cis* and *trans*-α-cyanostilbene or *cis* and *trans*-dicyanostilbene, the isomer with the phenyl groups *trans* absorbed at longer wave lengths than the other isomer. This difference points up the need for reference compounds of known stereochemistry upon which to base spectral assignments particularly in complex systems which contain many chromophores.

Because of the complex nature of the compounds involved it is not possible in this brief examination to assign all the absorption bands. However, it is not unreasonable to assume that the lower wavelength absorption exhibited by all these compounds is probably due to a sterically restricted styrene chromophore. It is interesting, although probably coincidental, that the spectrum of *cis*-α-nitrostilbene is very similar to that of β-methyl-β-nitrostyrene[2] (λ_{max} 226, 305, ϵ_{max} 10300, 12400).

The spectra of the nitroiodostilbenes resemble very closely those of the dinitrostilbenes as might be expected from the similarity of the steric situation. The iodo compounds are probably subject to more steric strains as the *cis*-compound showed only end absorption with no definite peaks or shoulders. The chloro- and iodonitrostyrenes were included for comparative purposes. While both show absorption around 245 mμ and 284 mμ, α-iodo-β-nitrostyrene shows additional absorption at 310 mμ and its absorption is more intense at all three wave lengths. The *trans*-nitrostyrene structure is favored as models indicate a *cis*-nitrostyrene structure is much more sterically crowded.

EXPERIMENTAL[11]

cis and trans-α,α'-Dinitrostilbene. These compounds were prepared and purified by the method previously described.[4]

α-Chloro-trans-β-nitrostyrene. This material was prepared by the addition of nitryl chloride to phenylacetylene and purified as described[12] immediately before measuring the spectrum.

cis- and trans-α-Nitrostilbenes. A mixture containing 25 ml. of benzene, 15 ml. of dioxane, 1 ml. of pyridine, and 1 g. of 1,2-dinitro-1,2-diphenlyethane,[13] m.p. 230-232°, was refluxed for 2 hr. The solution was cooled and washed with dilute hydrochloric acid and water. The residue obtained on removal of the solvent was recrystallized twice from ligroin to give *cis*-α-nitrostilbene as yellow needles, m.p. 74-75°. The filtrates from the recrystallizations were allowed to evaporate slowly, and a mixture of needles and prisms was obtained. Mechanical separation of the small amount of yellow prisms and recrystallization of these from ligroin gave *trans*-α-nitrostilbene, m.p. 127-128°. When the 1,2-dinitro-1,2-diphenylethane, m.p. 149-151°[13] was treated in a similar manner, *cis*-α-nitrostilbene containing a trace of the *trans*-isomer was obtained also.

cis-α-Nitro-α'-iodostilbene, m.p. 113-114°, was obtained in 16% yield from the reaction of tolane and dinitrogen tetroxide in the presence of iodine.[14] Complete details of this reaction will be reported in a future communication.

trans-α-Nitro-α'-iodostilbene, m.p. 176-177°, was obtained in 67% yield from the tolane-dinitrogen tetroxide-iodine reaction.[14]

α-Iodo-β-nitrostyrene, m.p. 50-51°, was obtained from the styrene-dinitrogen tetroxide-iodine reaction.[14]

Spectra. All the samples were measured on a Beckmann DK-1 recording ultraviolet spectrophotometer in absolute alcohol solution.

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[9] W. B. Black and R. E. Lutz, *J. Am. Chem. Soc.*, **75**, 5990 (1953).

[10] D. G. Coe, W. W. Gale, R. P. Linstead, and C. J. Timmons, *J. Chem. Soc.*, 123 (1957); J. F. Codington and E. Mosettig, *J. Org. Chem.*, **17**, 1027 (1952).

[11] We are indebted to Mr. R. D. Strahm for measurement of the spectra.

[12] J. P. Freeman and W. D. Emmons, *J. Am. Chem. Soc.*, **79**, 1712 (1957).

[13] J. Schmidt, *Ber.*, **34**, 3536 (1901).

[14] T. E. Stevens and W. D. Emmons, Abstracts, 131st National AMERICAN CHEMICAL SOCIETY Meeting, Miami, Fla., April 1957, p. 11-O.

Improved Synthesis of Monofluoro- and Monochloropyruvic Acids[1]

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Monofluoro- and monochloropyruvic acids have been obtained in yields of 80 and 28 per cent respectively in a highly pure form by hydrolysis and "ketonic fission" of the diethyl esters of the corresponding halo-oxaloacetic acids. The critical conditions for the "ketonic fission" are described and an inverse relationship is indicated between the enol content of the ester and the extent of "ketonic fission".

In connection with the interest of this laboratory in inhibitors of lactic dehydrogenase,[2,3] it became desirable to have a method for the practical

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[1] These studies were aided by grants from the U. S. P. H. S. (CY-2886C) and the Jane Coffin Childs Fund.

[2] H. Busch, *Fed. Proc.*, **15**, 229 (1956).

[3] H. Busch and P. V. Nair, *J. Biol. Chem.*, **229**, 357 (1957).