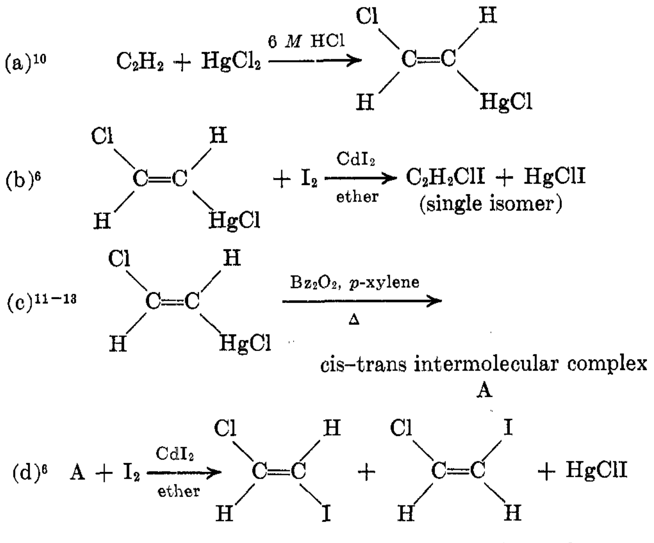
Method I



trans-**2-Chlorovinylmercuric Chloride (Ia).**[10]—The product was recrystallized from chloroform: mp 122° (lit.[12] 123°); tlc R_f 0.52; uv max (EtOH) 212 nm (lit.[14] 212 nm); ir (KBr pellet) 3050–3100 (CH), 1570 (C=C), 940 cm^{-1} (CH, trans).

trans-**Chloroiodoethene (Ib).**[6]—The product was vacuum distilled from HgClI and CdI_2: bp 113° (755 mm) (lit.[1] 113–114° (760 mm) (trans), 116–117° (cis)]; vpc retention time 1.12 min; ir (KBr) 3080 (CH), 1545 (C=C), 1600 and 1630 (Fermi resonance of the C=C fundamental at 1545 and the first overtone of the strong band at 797), 902 cm^{-1} (CH, trans); nmr (acetone-d_6, TMS) δ 6.57 ppm (AB, δ° 10.7 Hz, J_{AB} = 13.5 Hz); mass spectrum *m/e* 188 ($C_2H_2ClI^+$) with prominent P + 2 at 190, characteristic of Cl, 61 (base), and 63 ($C_2H_2Cl^+$).

Cis–Trans Intermolecular Complex of Chlorovinylmercuric Chloride (Ic).[11–13]—*trans*-Chlorovinylmercuric chloride was isomerized in dry *p*-xylene with benzoyl peroxide catalyst at 95° for 10 hr. The hot mixture was filtered. The filtrate was cooled to give (75%) the complex (A) which was recrystallized from CCl_4: mp 74.5° (lit.[11,13] 76°); tlc R_f 0.73; uv max (EtOH) 211 nm; ir (KBr pellet) 3000–3075 (CH), 1585 (C=C), 930 (CH trans), and 692 cm^{-1} (CH, *cis*); nmr spectrum is identical with that reported by Wells and Kitching.[12]

cis- **and** *trans*-**Chloroiodoethene (Id).**[6]—The iodination of the intermolecular mercury complex (A) was carried out by a modification of the method of Beletskaya, Reutov, and Karpov.[6] Ten grams of the complex (A) and 8.40 g (0.0331 mol) of I_2 with 0.5 g of CdI_2 catalyst were stirred for 36 hr in 100 ml of diethyl ether. After removing the ether by distillation, the reaction mixture was treated with an equal volume of 1-propanol, and the azeotropic mixture of the *cis*- and *trans*-chloroiodoethene was resolved by distillation on a spinning-band column. The 87.5–88.5° fraction was found to contain the trans isomer, with properties identical with those of the product of Ib. The 93.6–94.0° fraction contained the cis isomer: vpc retention time 1.36 min; nmr (acetone-d_6, TMS) δ 6.81 ppm (AB, δ^0 4.4 Hz, J_{AB} = 5.8 Hz); gc–mass spectrum is identical with the spectrum of the trans isomer. The preparation was not sufficiently pure for ir or dielectric measurements.

Method II[1]

$$C_2H_2 + ICl \xrightarrow{6\,M\,HCl} C_2H_2ClI + \text{other products}$$

A mixture of *cis*- and *trans*-chloroiodoethene was prepared by the direct addition of iodine monochloride to acetylene as described by Van de Walle and Henne.[1] The vpc retention times, nmr AB spectra, and gc–mass spectra of the cis and trans isomers were found to be identical with those of the products of reactions Ib and Id.

The dielectric constant and density data used for the calculation of the dipole moment of *trans*-chloroiodoethene in benzene and cyclohexane are summarized in Table III.

TABLE III
DIELECTRIC CONSTANT AND DENSITY OF *trans*-CHLOROIODOETHENE

Benzene			Cyclohexane		
N_2	d	ϵ	N_2	d	ϵ
0.00980	0.8781	2.280	0.01088	0.7826	2.036
0.01429	0.8831	2.282	0.01443	0.7851	2.039
0.02037	0.8906	2.286	0.02011	0.7922	2.042
0.03080	0.9027	2.290	0.03066	0.8034	2.048
0.03630	0.9095	2.293	0.04107	0.8148	2.054
α = 0.469, β = 1.19 $P_{2\infty}$ = 35.0 CC ϵ_1 = 2.276, d_1 = 0.8663			α = 0.580, β = 1.08 $P_{2\infty}$ = 35.0 CC ϵ_1 = 2.030, d_1 = 0.7703		

Registry No.—*trans*-2-Chlorovinylmercuric chloride, 1190-78-9; *trans*-chloroiodoethene, 28540-81-0; *cis*-chloroiodoethene, 31952-74-6.

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O-Triphenylmethylhydroxylamine (Trityloxyamine), a Useful O-Protected Form of Hydroxylamine

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In connection with other work, a protected form of hydroxylamine was required in which substitution would be rigorously restricted to the nitrogen atom and which would be soluble in aprotic solvents.[1] It was also necessary that the protecting group be readily cleaved under mild acidic conditions. This report describes the preparation and some properties of *O*-triphenylmethylhydroxylamine (trityloxyamine), $(C_6H_5)_3CONH_2$, an O-protected hydroxylamine which fulfills these requirements.

Acylation of the amine function of hydroxylamine does not usually require protection of the hydroxyl group. The conditions under which such reactions are usually carried out give the *N*-acyl derivative as the only isolable product. Jencks[2] has described a number of cases, however, wherein certain acylating agents under controlled conditions can give high yields of the *O*-acyl derivative. Evidently, *O*-acylhydroxylamines are often the initial product. Unless the conditions of the reaction and work-up are carefully controlled, rearrangement to the more stable *N*-acyl form occurs.

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[1] The preparation of solutions of free hydroxyamine of appreciable concentration usually requires the use of aqueous or alcoholic solvents due to the polar characteristics of hydroxylamine and the salts from which it is usually prepared.

[2] W. P. Jencks, *J. Amer. Chem. Soc.*, **80**, 4581 (1958).

Similarly, alkylation of hydroxylamine usually occurs at the nitrogen atom due to the greater nucleophilicity of the amino group in this type of reaction. However, when dialkylation with highly reactive halides is carried out, O,N disubstitution can occur in addition to the usual N,N-dialkylation.[3,4]

Trityloxyamine was readily prepared by the hydrazinolysis of *N*-trityloxyphthalimide[5] which was in turn prepared by the tritylation of *N*-hydroxyphthalimide according to the method of McKay, *et al.*[6] It is a stable solid which gives *O*-trityl oximes with reactive aldehydes and ketones. The reactions of trityloxyamine with benzaldehyde and with acetone were essentially complete in a few minutes. With the less reactive fluorenone, no reaction could be detected even after a long reflux period. The usual acid catalyst was necessarily avoided in these reactions. Examples of the facile acylation reactions which trityloxyamine undergoes will be published in connection with other work.

As expected, trityloxyamine and related compounds were readily detritylated by hydrogen chloride in benzene at room temperature.[7] The cleavage products were obtained in excellent yield (see Experimental Section).

Compounds described in the literature which have received some use as O-protected forms of hydroxylamine include *O*-benzylhydroxylamine (benzyloxyamine) and *O*-(2-tetrahydropyranyl)hydroxylamine. In the respective cases, reductive methods[8,9] and ethanolic hydrogen chloride[10] were used to remove the protecting groups.

The literature describes two unsuccessful attempts to prepare trityloxyamine. Schumann and coworkers[5] failed to obtain a pure product by essentially the method described here. Leffler and Bothner-By[11] were similarly unable to obtain it by the alkaline hydrolysis of trityl benzohydroxamate.

Experimental Section

Melting points were taken in capillaries and are uncorrected. Infrared spectra were determined on a Beckman IR-8 infrared spectrophotometer. Ultraviolet spectra were determined on a Beckman DK-2A recording spectrophotometer. Microanalyses were performed by the Analytical and Physical Chemistry Section, Warner-Lambert Research Institute, under the direction of Mr. Arnold Lewis.

***N*-Hydroxyphthalimide.**—To a vigorously stirred solution of hydroxylamine prepared by adding a solution of 74.4 g (1.86 mol) of sodium hydroxide in 200 ml of water *to* a solution of 153.5 g (0.935 mol, 1.87 equiv) of hydroxylamine sulfate[12] in 200 ml of water was added 220 g (1.5 mol) of finely powdered phthalic anhydride.[13] As soon as crystals began to appear, an additional 500 ml of water was added and the mixture was allowed to stand overnight at *ca.* 4°. The solid was filtered, washed with ice water containing a little acetic acid, and air-dried. The product, mp 235–237°;[14] ir (mineral oil) 3130, 1790, 1740, 1710 cm^{-1}, weighed 196 g (80%).

***N*-Trityloxyphthalimide.**—Powdered trityl chloride (16.7 g, 60 mmol) was added to a vigorously stirred solution of 9.8 g (60 mmol) of *N*-hydroxyphthalimide and 8.8 ml of triethylamine in 18 ml of *N,N*-dimethylformamide. The mixture was stirred for 20 min and allowed to stand for 36 hr. The solid mass was broken up, made pourable by the addition of 2-propanol, and added to 500 ml of water. The solid was filtered, redispersed with a Waring Blendor in water containing a little sodium carbonate solution, and filtered; the filter cake was washed with water and dried to give 23.6 g (97%) of white powder, mp 180–183.5°, softening above 175°. Analytically pure material, obtained by several recrystallizations from benzene–ligroin, had mp 182–184°;[15] ir (mineral oil) 1770, 1720 cm^{-1}.

Anal. Calcd for $C_{27}H_{19}NO_3$: C, 79.98; H, 4.72; N, 3.46. Found: C, 79.97; H, 4.74; N, 3.70.

Trityloxyamine.—To a stirred solution of 23.6 g (58 mmol) of *N*-trityloxyphthalimide in 75 ml of methylene chloride was added 6.0 ml (120 mmol) of hydrazine hydrate in 10 ml of methanol. After 30 min the solid phthalazine-1,4-dione was dissolved by the addition of 100 ml of 5 *M* ammonium hydroxide. The aqueous layer was removed and extracted with 20- and 10-ml portions of methylene chloride, and the combined extract was washed with brine, dried (K_2CO_3), stirred with decolorizing charcoal (Darco), and filtered, and the filtrate was evaporated on a rotating evaporator. The residue was recrystallized from 25 ml of methanol to give 12.0 g (75%) of white crystals, mp 83–88.5°. Additional recrystallizations from 2-propanol afforded an analytical sample: mp 82.5–85.5°; ir (CCl_4) 1580, 1490, 1450, 1035, 970, 705 cm^{-1}.

Anal. Calcd for $C_{19}H_{17}NO$: C, 82.88; H, 6.22; N, 5.09. Found: C, 83.08; H, 6.22; N, 5.08.

***O*-Tritylacetoxime.**—Trityloxyamine (137 mg) was dissolved in 0.2 ml of acetone. Separation of the crystalline product began within 10 min. After 3 days at −5°, the product was filtered and washed with 2-propanol at −5° to give 140 mg (89%) of product with mp 115.5–118°. Recrystallization of similar material twice from 2-propanol afforded pure material: mp 114–116.5°; ir (CCl_4) 1599, 1492, 1450, 970, 920, 700 cm^{-1}.

Anal. Calcd for $C_{22}H_{21}NO$: C, 83.77; H, 6.71. Found: C, 83.64; H, 6.93.

***O*-Tritylbenzaldoxime.**—Trityloxyamine (275 mg) and benzaldehyde (134 mg) in 2 ml of methanol, allowed to stand for 2 hr, afforded 333 mg (92%) of crude product, mp 100–110°. Three recrystallizations from 2-propanol gave material with constant mp 111–114°, uv (cyclohexane) λ_{max} 262 nm (log ϵ 4.27), λ_{min} 236 (3.95). Cope and Haven[3] prepared this compound by rearrangement of the nitrone obtained by condensing *N*-tritylhydroxylamine with benzaldehyde. They report mp 119.5–120.5°, uv λ_{max} 261.5 nm (log ϵ 4.28), λ_{min} 237 (4.0). Stieglitz and Leach[16] found mp 114° for material prepared by the nitrone method.

Cleavage of *N*-Trityloxyphthalimide with Hydrogen Chloride.—*N*-Trityloxyphthalimide (127 mg) in 3 ml of dry benzene was treated with hydrogen chloride gas until precipitation was complete. The mixture was centrifuged and the precipitate was washed several times with benzene by centrifugation. Evaporation of the combined supernatants afforded 87 mg (99%) of trityl chloride, mp 110–112°. The identity was confirmed by mixture mp and ir spectrum.

The residue consisted of 48 mg (104%) of *N*-hydroxyphthalimide, mp 224–229°. The identity was confirmed by the ir and by treatment with aqueous alkali to give an orange-yellow color.

Cleavage of Trityloxyamine with Hydrogen Chloride.—Trityloxyamine (350 mg) in 2 ml of dry benzene was treated with dry hydrogen chloride for 5 min. The precipitate was centrifuged, washed with benzene, and filtered to give 80 mg (90%) of hydroxylamine hydrochloride, mp 154–155.5°. The identity was confirmed by mixture melting point and ir spectrum.

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(4) W. Kliegel, G. Zinner, and R. Vollrath, *Justus Liebigs Ann. Chem.*, **736**, 173 (1970).

(5) E. L. Schumann, R. V. Heinzelman, M. E. Greig, and W. Veldkamp, *J. Med. Chem.*, **7**, 329 (1964).

(6) A. F. McKay, D. L. Garmaise, G. Y. Paris, and S. Gelblum, *Can. J. Chem.*, **38**, 343 (1960).

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(12) The hydrochloride is equally satisfactory.

(13) Commercial phthalic anhydride was ground in a ball mill and passed through a fine mesh sieve.

(14) (a) W. R. Orndorff and D. S. Pratt, *Amer. Chem. J.*, **47**, 89 (1912), report mp 220–226° for crude product prepared by a slightly different procedure. (b) L. Bauer and S. Miarka, *J. Amer. Chem. Soc.*, **79**, 1983 (1957), report mp 227–230° for crude and 233° for recrystallized product.

(15) Schumann, *et al.*,[5] give mp 186–187°.

(16) J. Stieglitz and P. Leech, *ibid.*, **36**, 272 (1914).

Evaporation of the benzene solution afforded 257 mg (72%) of trityl chloride, mp 108–111°. The identity was confirmed by mixture melting point and ir spectrum.

Registry No.—*N*-Hydroxyphthalimide, 524-38-9; *N*-trityloxyphthalimide, 31938-10-0; trityloxyamine, 31938-11-1; *O*-tritylacetoxime, 31938-12-2; *O*-tritylbenzaldoxime, 31938-13-3.

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Electron Spin Resonance Investigation of the 2-Furanylmethyl Radical. Calculation of Its Geometry and Rotational Barrier by INDO

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Because of its great importance in the theory of odd alternant radicals, the benzyl radical has been repeatedly investigated both experimentally and theoretically.[1–4] Heterocyclic analogs of benzylic and similar radical systems have been largely unstudied. One exception is Hudson's[5] report of the esr spectra of both the 2-thenyl and 3-thenyl radicals generated in solution during the steady-state photolysis of di-*tert*-butyl peroxide in the presence of 2-methyl- and 3-methylthiophene, respectively. In both the 2-thenyl and 3-thenyl radicals, the methylene protons were nonequivalent, but π-electron calculations of the McLachlan approximate SCF method did not provide any insight into this nonequivalence.[5] As long as the methylene group's rotational barrier is large, one would expect nonequivalence from a consideration of symmetry. Similar examples of magnetic inequivalence include the allyl[6] and substituted allyl[7] radicals. In these radicals more sophisticated, all-valence electron calculations, such as the INDO technique, correctly predict this inequivalence.[8]

We now report the esr spectrum of the 2-furanylmethyl radical, I, which was obtained during the steady-state photolysis of solutions of di-*tert*-butyl peroxide and 2-methylfuran at temperatures between −30 and −80° in the esr cavity.[9] The spectrum exhibited 32 lines due to the inequivalence of the methylene protons and showed a signal to noise ratio at −80° similar to that observed[5] for the 2-thenyl radical. The inequivalence persisted even at −30° and the only change in the spectrum observed on warming was a drastic decrease in intensity.

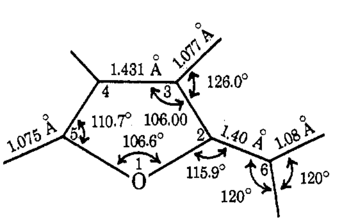


Figure 1.—Geometry of radical I used in INDO calculations.

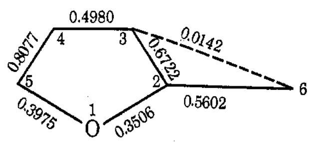
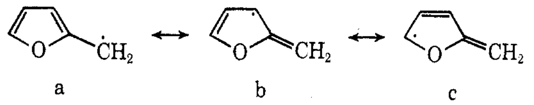


Figure 2.—Calculated π-bond orders of the 2-furanylmethyl radical.



I

The experimental hyperfine splittings, as determined by a computerized best fit to the experimental spectrum, are listed in Table I. Table II summarizes the *g* values determined for the benzyl, 2-thenyl, and 2-furanylmethyl radicals.[10] The *g*-value variation is both a function of the size of the spin–orbit coupling for carbon, oxygen, and sulfur and the energy of the molecular orbital occupied by the odd electron.[11] The 0.0004-*g* value increase for the 2-thenyl over the 2-furanylmethyl radical is a measure of the increase in the size of the spin–orbit coupling constant for sulfur and the amount of sulfur d- and p-orbital contribution to the radical. However, the difficulty of measuring the radical's excitation energy and the number of its excited states contributing to the Δg shift prevents a determination of the sulfur d-orbital contribution. Nevertheless, the larger isotropic *g* value of 2.0061 observed for the thiophene-2-carboxylic acid radical[12] suggests only a small sulfur d- and p-orbital contribution in the thenyl radical.

A series of INDO[8] calculations[13] were performed on I using the bond angles and lengths for the furan portion obtained by Bak[14] in his microwave study of furan. The methylene group was then attached and the parameters used are summarized in Figure 1.[15] The calcu-

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[1] A. Carrington and I. C. P. Smith, *Mol. Phys.*, **9**, 137 (1965).

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[3] A. Carrington, J. R. Bolton, A. Forman, and L. E. Orgel, *Mol. Phys.*, **5**, 43 (1962).

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[6] R. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

[7] R. Livingston and H. Zeldes, *ibid.*, **44**, 1245 (1966).

[8] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967); *J. Amer. Chem. Soc.*, **90**, 4201 (1968).

[9] The uv light from a 500-W PEK 500-2 lamp was filtered by a water filter and was focused on a sample held in a quartz variable-temperature esr dewar by a quartz condenser lens added to the quartz optics of a standard PEK M910 housing. Similar techniques to those previously reported by Kochi and Krusic were used. See J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **91**, 1877, 1879, 3938, 3940, 3942, 3944, 6161 (1969); **93**, 846 (1971).

[10] The benzyl and 2-thenyl radicals were prepared in this study by the same photolysis technique used to generate the 2-furanylmethyl radical.

[11] A. J. Stone, *Mol. Phys.*, **6**, 509 (1963); **7**, 311 (1964). B. G. Segal, M. Kaplan, and G. K. Fraenkel, *J. Chem. Phys.*, **43**, 4191 (1965).

[12] B. Eda, R. J. Cook, and D. H. Whiffen, *Trans. Faraday Soc.*, **60**, 1497 (1964).

[13] The INDO program (cnindo, QCPE No. 141) was obtained from the Quantum Chemistry Program Exchange, Indiana University, and it was modified for use on a Univac 1108 computer.

[14] B. Bak, D. Christensen, W. B. Dixon, L. Hansen-Hygaard, J. R. Anderson, and M. Schottlander, *J. Mol. Spectrosc.*, **9**, 124 (1962).

[15] The only bond which was optimized in the calculations was the 2–6 bond. While the bond distances in the ring will certainly change upon interaction with a $CH_2\cdot$ side chain, these changes would be relatively small.