

Scheme I

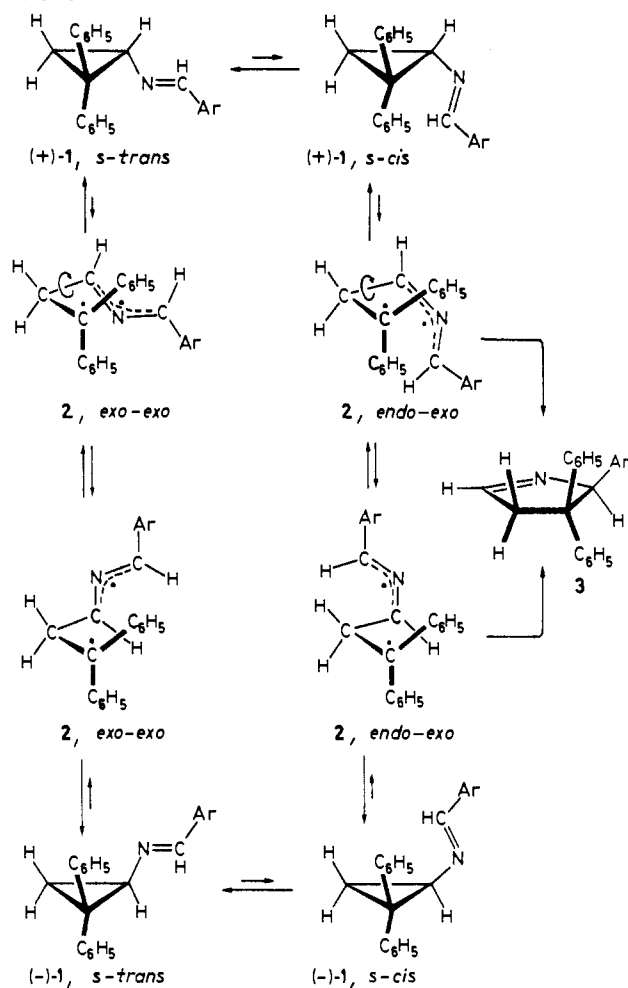


Table II. Comparison of kinetic data for *N-p*-Methoxybenzylidene-2,2-diphenylcyclopropylamine and 2,2-Diphenyl-1-*trans*-styrylcyclopropane in Decalin

	I	II
Racemization		
10^7k , sec ⁻¹ (at 101°)	550	546
ΔH^\ddagger , kcal mol ⁻¹	26.8 ± 0.2	27.5 ± 0.8
ΔS^\ddagger , eu	-7 ± 1	-5 ± 2
Ring expansion		
10^7k , sec ⁻¹ (at 101°)	5.00	2.91
ΔH^\ddagger , kcal mol ⁻¹	33.2 ± 0.9 ^a	30.9 ± 1.2
ΔS^\ddagger , eu	1 ± 2 ^a	-6 ± 2.6

^a In benzonitrile.

ment of N by CH affects rate constants and Eyring parameters⁶ of racemization and ring expansion. Of course, the nitrogen is located in the central position of the allyl radical where the electron density of the unpaired electron is zero.

The ring expansion rates of *N*-cyclopropylazomethines reflect number and positions of the aryl substituents at the cyclopropane ring, as shown by follow-

(6) The activation parameters are apparent values; they concern multistep reactions.

ing half-reaction times. It is impressive that the three phenyls, in addition to the azomethine group, activate the ring opening to such an extent that the half-life at 50° is less than 1 hr.

$t_{1/2}$ (min)	95	79	50
Temp.	190°	151°	50°
Solvent	Decalin	Decalin	Cyclohexane

The optical antipodes of 2,2-diphenylcyclopropane-carboxylic acid⁷ are converted to 1 as described for the racemic acid.⁵ Optical rotations are high, as $[\alpha]^{22}_{486} + 1483^\circ$ and -1514° for the enantiomers of 1, Ar = C₆H₄-N(CH₃)₂-*p*, testify.

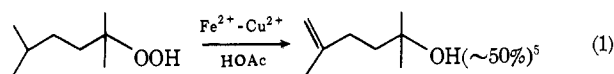
(7) H. M. Walborsky and F. M. Hornyak, *J. Amer. Chem. Soc.*, **77**, 6026 (1955). We express our gratitude to Professor H. M. Walborsky for providing us with a modified and improved procedure of resolution.

Pierluigi Caramella, Rolf Huisgen,* Bernd Schmolke
Institut für Organische Chemie der Universität
8 Munich 2, Germany
Received December 7, 1973

Formation of Remote Double Bonds by Ferrous Sulfate-Cupric Acetate Promoted Decomposition of Alkyl Hydroperoxides¹

Sir:

The ferrous sulfate-cupric acetate promoted formation of olefinic alcohols from alkyl hydroperoxides (1) proceeds well in tertiary systems^{2,3} while primary and secondary hydroperoxides have been reported, in closely related reactions, to yield only cleavage and oxidation products.⁴



The synthetic attractiveness of forming remote least substituted olefinic alcohols, combined with the easy availability of primary and secondary hydroperoxides of variant structure⁶⁻⁸ as well as the lack of theoretical justification for the restriction of this reaction (1) to tertiary hydroperoxides,⁹ prompted us to carry out the current investigation. As may be seen in Table I, our expectations were justified thereby setting the stage

(1) We are grateful to the National Institute of General Medical Sciences (GM-16638) for support of this project.

(2) J. K. Kochi, *J. Amer. Chem. Soc.*, **85**, 1958 (1963).

(3) B. Acott and A. L. J. Beckwith, *Aust. J. Chem.*, **17**, 1342 (1964).

(4) (a) W. Pritzkow and K. A. Müller, *Justus Liebigs Ann. Chem.*, **597**, 167 (1955); W. Pritzkow and I. Hahn, *J. Prakt. Chem.*, **16**, 287 (1962); (b) The work in ref 4a is reviewed by G. Sosnovsky and D. J. Rawlinson, Chapter II in "Organic Peroxides," Vol. 2, D. Swern, Ed., Wiley-Interscience, New York, N. Y., 1971, Chapter 2, p 153 ff.

(5) See ref 3. The internal (4, 5) olefin is formed in one-tenth this yield.

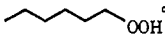
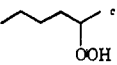
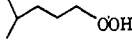
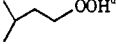

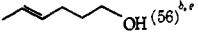
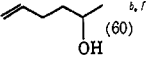
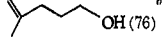
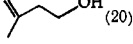
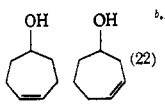
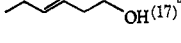
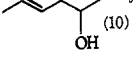
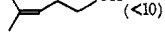
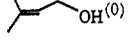
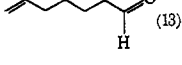
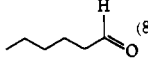
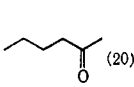
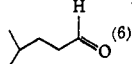
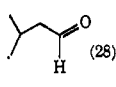

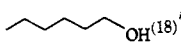
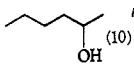
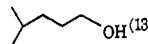
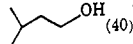

(6) H. R. Williams and H. S. Mosher, *J. Amer. Chem. Soc.*, **76**, 2984 (1954).

(7) C. Walling and S. A. Buckler, *J. Amer. Chem. Soc.*, **77**, 6032 (1955).

(8) M. M. Midland and H. C. Brown, *J. Amer. Chem. Soc.*, **95**, 4069 (1973).

(9) J. K. Kochi, "Free Radicals," Vol. I, J. K. Kochi, Ed., Wiley-Interscience, New York, N. Y., 1973, Chapter 11, and references therein.

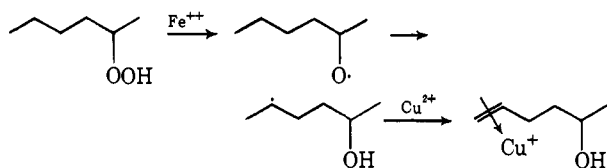
Table I.^{a,b} Products (yield %)

Hydroperoxide				
				
				
				
				
				

^a See the text for the details of a sample reaction. In each case the yield was determined by fractional distillation (Vigreux column) of the entire reaction mixture followed by vpc analysis of the weighed distillates and calculation of the yield from the integrated areas of all the vpc peaks. The nearly quantitative return (Σ yield $\sim 100\%$) precludes the presence of other unidentified products. When the reaction was allowed to stand excessively (see text) the alcohols were converted in part to acetates. ^b All the materials not compared to available authentic material were identified by their nmr, ir, and mass spectra which in each case was commensurate with the structure. ^c Prepared following ref 6 in which they are reported. ^d Prepared as for 1- and 2-hexyl hydroperoxides.⁸ For isohexyl hydroperoxide, bp 30° (0.4 mm), titration by $\text{Na}_2\text{S}_2\text{O}_3$ -KI showed 94% purity. For isoamyl hydroperoxide, bp 28° (0.3 mm), titration as above, 96.8% purity. Cycloheptyl hydroperoxide was prepared from the Grignard reagent,⁷ bp 48 – 50° (4 mm), titration as above, 89% purity. In each case the nmr spectrum was in line with the structure. ^e Carbon-13 nmr showed presence of cis and trans isomers with ratio of 1:10 (trans presumed higher). ^f Converted with H_2SO_4 to 1,5-dimethyltetrahydrofuran identical with authentic material. ^g Produced in equal amounts and separated by vpc on 5' Carbowax 20M. This column served to separate all the olefin isomers reported in Table I. ^h Prepared independently and compared to the reaction mixtures by vpc (see footnote g above) and nmr. These materials are reported by J. B. Rogan, *J. Org. Chem.*, **27**, 3910 (1962) (4-methyl-3-penten-1-ol) and H. Machleidt and W. Grell, *Justus Liebigs Ann. Chem.*, **690**, 79 (1965) (3-methyl-2-buten-1-ol). We prepared the latter material by hypochlorite oxidation of mesityl oxide with subsequent lithium aluminum hydride reduction. ⁱ Identified by vpc and ir comparison to authentic materials and in the carbonyl compounds by conversion to 2,4-DNPH derivatives which gave correct literature melting points. All values in A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, London, 1957; "Dictionary of Organic Compounds," Vol. 4, Oxford University Press, London, 1965. The 6-heptenal is reported in N. A. LeBel and J. J. Whang, *J. Amer. Chem. Soc.*, **81**, 6334 (1959).

for the further development of an unusual reaction of some synthetic potential.

The ferrous sulfate reduction of the hydroperoxides to alkoxy radicals with subsequent 1,4-hydrogen abstraction to yield the carbon radicals is the most probable route to the formation of these materials. Trapping of these carbon radicals with cupric acetate to form olefins (formal oxidation) has been synthetically exploited by Kochi¹⁰ and indeed formed the original mechanistic proposal for the analogous reactions in the tertiary systems.^{2,3} This overall process is schematically presented below.



The formation of the least substituted double bond may arise from the initial production of the complexed (as shown) olefin. The latter is reported to have higher stability on lower substitution.¹¹

(10) R. A. Sheldon and J. K. Kochi, *Org. React.*, **19**, 279 (1972).

(11) See ref 4b herein and ref 211 and 212 in that review. For an up-to-date and comprehensive discussion of the oxidation of alkyl radicals by Cu^{II} see ref 9 herein. See also A. G. Massey in "Comprehensive Inorganic Chemistry," Vol. 3, J. C. Bailar, Jr., H. J. Emeléus, R. Nyholm and A. F. Trotman-Dickenson, Eds., Pergamon Press, Ox-

The importance of the availability and nature of the δ hydrogen is manifested in the lowered yield and intervention of cleavage product (6-heptenal) in cycloheptyl hydroperoxide and the increased yield in the isohexyl system which involves abstraction of an available tertiary hydrogen over the isoamyl system which requires abstraction of an unfavorable primary hydrogen.¹² In addition we have carried out the reaction of 2-hexyl hydroperoxide with cupric chloride and ferrous sulfate, and, following expectation,⁹ the intermediate is converted in 53% yield to cis and trans mixture of 2,5-dimethyltetrahydrofuran.¹³

ford, 1973, pp 34 and 35, and references therein. Alkyl Cu^{I} compounds are known to eliminate CuH to form olefins. See G. M. Whitesides, E. R. Stedronsky, C. P. Casey, and J. San Filippo, Jr., *J. Amer. Chem. Soc.*, **92**, 1426 (1970). In significant contrast, work from this laboratory by Mack Brautigan on lead tetraacetate-cupric acetate promoted decarboxylation of acids¹⁰ shows preferential formation of most substituted olefins from 1-methylheptanoic acid and 1-methylcyclohexanecarboxylic acid.

(12) The yields of the olefinic products (Table I) parallel those obtained in the formation of tetrahydrofurans *via* lead tetraacetate generated alkoxy radicals. See M. L. Mihailović and Ž. Čeković, *Syntheses*, 209 (1970).

(13) Identical with authentic cis and trans isomers prepared by the oxidation of 2-hexanol with lead tetraacetate.¹⁴ Small quantities ($\sim 5\%$) of 5-chloro-2-hexanol were also recovered. This may be an intermediate in the formation of the tetrahydrofuran or the ether may be formed directly from the Cu^{II} generated carbonium ion. See ref 9. It is significant that no tetrahydrofurans are produced in the reactions with cupric acetate-ferrous sulfate in acetic acid while the 2-hexyl hydroperoxide reaction in acetonitrile gave equal but poor ($\sim 10\%$) yields of olefin and cyclic ether.

In a typical preparation, a solution of 0.97 g of ferrous sulfate hydrate and 1.39 g of cupric acetate hydrate was prepared in 20 ml of glacial acetic acid and 2 ml of water. The hydroperoxide (0.01 mol) was added under nitrogen at room temperature over a 0.5-hr period. The stirring heterogeneous mixture warmed and gradually turned from green to brown and was left overnight. Dissolution in water and extraction to remove acetic acid followed by distillation and/or preparative gas chromatography yielded the olefinic alcohols as well as recoverable alcohols and ketone or aldehyde. These latter materials could, of course, be recycled to increase the yield.

The long-known handleability of primary and secondary hydroperoxides⁶ as well as recent methods to produce these materials in very high yield⁸ clearly suggest this reaction as a useful relative to the variety of other long-range activating alkoxy radical reactions now extant.^{14,15}

(14) See M. M. Green, J. M. Moldovan, and J. G. McGrew, II, *J. Chem. Soc., Chem. Commun.*, 451 (1973), and leading references therein. It could be expected that alkoxy and other hydrogen abstracting radicals formed in other ways would also show this behavior (intervention of Cu^{II}), and we are currently looking into this possibility.

(15) J. W. Wilt, ref 9, Chapter 8.

(16) Visiting senior research associate from the University of Belgrade, Yugoslavia.

Živorad Čeković,¹⁶ Mark M. Green*

Department of Chemistry, University of Michigan
Ann Arbor, Michigan 48104

Received January 9, 1974

Selective Ortho Formylation of Aromatic Amines

Sir:

Relatively few methods for the formylation of aromatic rings are known. Those which do exist fail to offer very much in the way of selectivity. More specifically, methods for the preparation of derivatives of *o*-aminobenzaldehydes, which have extensive value in the synthesis of certain heterocyclics, are generally limited to the reduction of *o*-nitrobenzaldehydes¹ and the oxidation of *o*-toluidines.² We now wish to report two new general methods for the selective ortho formylation of anilines.

Recently, we described a method for the conversion of anilines into *o*-methylthiomethylanilines.³ In principle, the *o*-methylthiomethyl group is a potential precursor of the aldehyde moiety. In practice, we have found that we could prepare a variety of protected *o*-aminobenzaldehydes in good overall yields by an adaptation of our ortho substitution procedure.

Treatment of a mixture of 1.0 equiv of the aniline (1) and 1.6 equiv of thioanisole (2) in 3:1 acetonitrile-methylene chloride at -40° with 1.0 equiv of *tert*-butyl hypochlorite gave the azasulfonium salt 3. These salts were not isolated but were treated with sodium methoxide to yield the phenylthiomethylaniline (4) via intermediate ylid formation and subsequent intra-

(1) F. Sachs and R. Kempf, *Chem. Ber.*, 35, 2704 (1902); F. Sachs and E. Sichel, *ibid.*, 37, 1861 (1904); F. Mayer, *ibid.*, 47, 408 (1914); L. I. Smith and J. W. Opie, "Organic Syntheses," Collect. Vol. 3, Wiley, New York, N. Y., 1955, p 56.

(2) J. J. Brown and G. T. Newbold, *J. Chem. Soc.*, 4878 (1952); J. J. Brown and R. K. Brown, *Can. J. Chem.*, 33, 1819 (1955).

(3) P. G. Gassman and G. Gruetzmacher, *J. Amer. Chem. Soc.*, 95, 588 (1973).

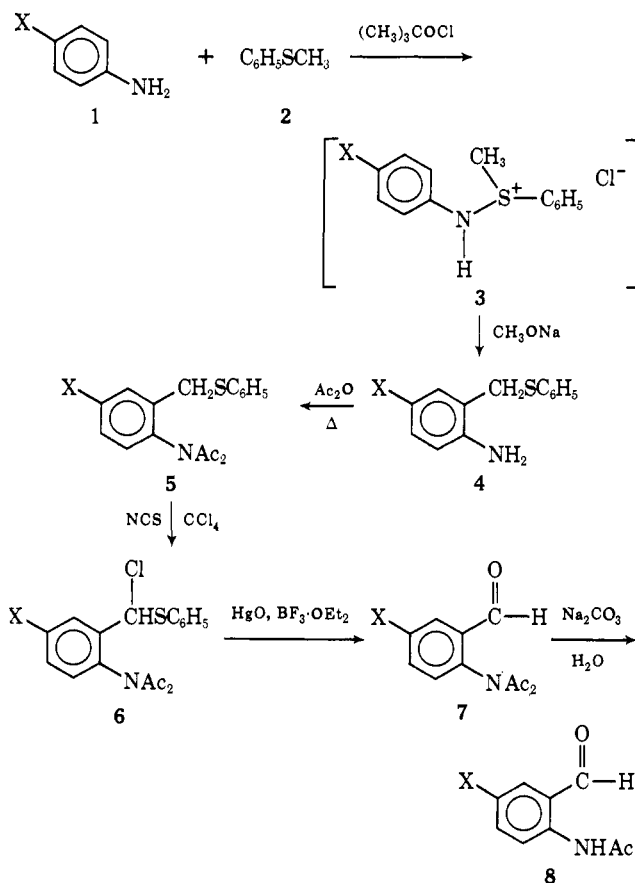


Table I. Yields Obtained in the Conversion of Anilines into *o*-Aminobenzaldehyde Derivatives

Starting aniline	X	% yield of 4	% yield of 8 from 4	Overall % yield of 8 from 1
1a	CH ₃	63	52	33
1b	H	61	73	45
1c	Cl	68	73	50
1d	CO ₂ CH ₃	58	63	37
1e	CN	73	49	36

molecular rearrangement.³ As shown in Table I the yields of 4 ranged from 58 to 73%.⁴

When 4b (X = H) was refluxed with excess acetic anhydride for 24 hr, the *N,N*-diacetyl derivative 5b was obtained in 97% yield.^{2,5} Treatment of 5b with 1.1 equiv of *N*-chlorosuccinimide^{6,7} in carbon tetrachloride

(4) Satisfactory elemental analyses and/or exact mass molecular weights have been obtained on all new compounds for which isolated yields are listed. Infrared and nmr spectral data were consistent with the assigned structures in all cases.

(5) P. G. Gassman and H. R. Drewes, *J. Chem. Soc., Chem. Commun.*, 488 (1973); J. J. Sudborough, *J. Chem. Soc.*, 79, 533 (1901); A. L. Lumiere and H. Barbier, *Bull. Soc. Chim. Fr.*, 33, 783 (1905).

(6) D. L. Tuleen and T. B. Stevens, *J. Org. Chem.*, 34, 31 (1969); D. L. Tuleen, *ibid.*, 32, 4006 (1967); D. L. Tuleen and V. C. Marcum, *ibid.*, 32, 204 (1967); D. L. Tuleen and T. B. Stevens, *Chem. Ind. (London)*, 1555 (1966); G. A. Russell and G. J. Mikol in "Mechanisms of Molecular Migrations," Vol. 2, B. S. Thyagarajan, Ed., Interscience, New York, N. Y., 1968, Chapter 3.

(7) For additional discussions of the α -chlorination of sulfides, see G. E. Wilson, Jr., and R. Albert, *J. Org. Chem.*, 38, 2156, 2160 (1973); H. Böhme, H. Fischer, and R. Frank, *Justus Liebigs Ann. Chem.*, 563, 54 (1949); H. Böhme and H. Gran, *ibid.*, 577, 68 (1952); E. Vilsmaier and W. Sprügel, *ibid.*, 747, 151 (1971); W. E. Truce, G. H. Birum, and E. T. McBee, *J. Amer. Chem. Soc.*, 74, 3594 (1952); F. G. Bordwell and B. M. Pitt, *ibid.*, 77, 572 (1955); E. Vilsmaier and W. Sprügel, *Tetrahedron Lett.*, 625 (1972); and R. Harville and S. F. Reed, *J. Org. Chem.*, 33, 3976 (1968).