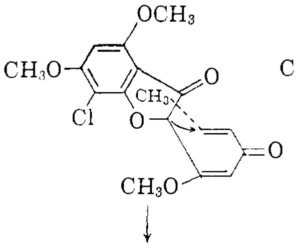
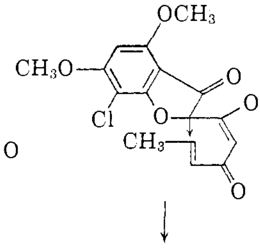
with $\tau = 4.5$. Hydrolysis with 6% aqueous potassium hydroxide gave the known 5-methylcyclohexane-1,3-dione,[9] m.p. 130–132°, undepressed on mixing with an authentic sample. Similarly, the methoxyethynyl ketone IV gave the related adduct with malonic ester. This was hydrolyzed directly with aqueous 10% potassium hydroxide to give a 64% yield of the above dione.

The stereospecificity in the desired sense of the addition of IV to the coumaranone III to produce *dl*-griseofulvin requires comment. Since the two possible C_2' epimers are of roughly the same stability. the formation of *dl*-griseofulvin in our synthesis must be under kinetic control. We believe that it is significant that the product actually obtained is that which would correspond to the greatest overlap of electron donor and acceptor systems in the transition state for the second Michael addition.



dl-griseofulvin



dl-epigriseofulvin

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[9] A. J. Birch and R. W. Rickards, *Austral. J. Chem.*, **9**, 241 (1956).

THE CHANDLER LABORATORY
COLUMBIA UNIVERSITY
NEW YORK 27, N. Y.

GILBERT STORK
MARIA TOMASZ

RECEIVED NOVEMBER 20, 1961

tert-BUTYL PEROXYFORMATE. A HIGHLY STABLE PEROXIDE AND A NEW FORM OF INDUCED PEROXIDE DECOMPOSITION[1]

Sir:

The rate of decomposition of diacyl peroxides and of peresters often is increased by a concurrent series of free radical chain steps involving reaction of a solvent radical with undecomposed peroxide. The induced decomposition of benzoyl peroxide in ether has been shown to involve attack by an α-ethoxyethyl radical on one of the oxygens of the peroxide link.[2] We wish to report a highly stable perester which undergoes a new form of induced radical decomposition.

tert-Butyl peroxyformate (b.p. 41° at 24 mm., $n^{25}\text{D}$ 1.3973) prepared by reaction of *tert*-butyl hydroperoxide and formyl fluoride[3] in ether at 0° was shown to be pure by vapor phase chromatography and by its analysis. *Anal.* Calcd. for $C_5H_{10}O_3$: C, 50.83; H, 8.53. Found: C, 50.62; H, 8.61. Kinetic studies were carried out in dilute solutions using degassed sealed ampoules and the perester decomposition followed by loss of its carbonyl absorption at 1760 cm.$^{-1}$.[4] Representative rate measurements are shown below.

RATES OF DECOMPOSITION OF *tert*-BUTYL PEROXYFORMATE

Solvent	Peroxide concn., *M*	Temp., °C.	$k \times 10^4$, sec.$^{-1}$
Chlorobenzene	0.135	140.8	1.71
	.0274	140.8	1.62
	.0260	140.8	1.67
	.138	130.8	.538
	.0249	130.8	.571
	.0243	130.8	.548
Cumene	.0296	140.8	5.03
	.0300	140.8	5.41
	.097	140.8	5.58
	.141	140.8	6.76

tert-Butyl peroxyformate decomposed in chlorobenzene with first order kinetics and a half-life of 70 min. at 140.8° (ΔH^* 38 kcal., ΔS^* 15 e.u.). This rate of decomposition is only about twice as great as that of *tert*-butyl peroxide[5] and makes this simple *t*-butyl perester the most stable of its class. The products of decomposition in chlorobenzene include 45% carbon dioxide, 33% formic acid as well as products derived from addition of formyloxy radicals to the solvent. No hydrogen was formed by decomposition in chlorobenzene or in cumene. The slow rate and the products of decomposition in chlorobenzene indicate simple unimolecular breakage of the peroxide bond giving rise to formyloxy and *tert*-butoxy radicals. The resonance of the formyloxy radical produced seems to have little accelerative effect but increased stability of the peroxide bond may be a result of electron withdrawal from the peroxide oxygens by the formyl group similar to inductive effects in other peroxide decompositions. In contrast to acetoxy radicals,[6] formyloxy radicals do not quickly decarboxylate presumably because of the higher energy required to break a carbon hydrogen bond.

A change in solvent from chlorobenzene to cumene results in a threefold increase in rate of decomposition and leads to increased yields of carbon dioxide (86% carbon dioxide, 8% formic acid). The rate of decomposition is increased slightly at higher concentrations of perester but is decreased toward the rate in chlorobenzene by 0.2 molar quinone or 0.5 molar styrene in cumene.

From these results it appears that the increased decomposition in cumene is caused by attack of solvent derived radicals on the aldehydic hydrogen of *tert*-butyl peroxyformate rather than by attack on either of the peroxide oxygens.

$$\text{R}\cdot + \text{H}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{O}_2\text{C(CH}_3)_3 \longrightarrow \text{RH} + \text{CO}_2 + \cdot\text{OC(CH}_3)_3$$

$$(\text{CH}_3)_3\text{CO}\cdot + \text{RH} \longrightarrow (\text{CH}_3)_3\text{COH} + \text{R}\cdot$$

This type of induced decomposition would give rise to the higher yield of carbon dioxide observed in cumene and the yields of *tert*-butyl alcohol and dicumyl, about 80% and 28%, respectively, are

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[1] Supported by a grant from the National Research Council of Canada.

[2] (a) D. B. Denney and G. Feig, *J. Am. Chem. Soc.*, **81**, 5322 (1959); (b) J. C. Martin and E. H. Drew, *ibid.*, **83**, 1232 (1961); other types of induced decomposition of peroxides have been discussed and reviewed by C. Walling and E. S. Savas, *ibid.*, **82**, 1738 (1960), and by C. G. Swain, L. J. Schaad and A. J. Kresge, *ibid.*, **80**, 5313 (1958).

[3] G. A. Olah and S. J. Kuhn, *ibid.*, **82**, 2380 (1960).

[4] P. D. Bartlett, E. P. Benzing and R. E. Pincock, *ibid.*, **82**, 1767 (1960).

[5] J. H. Raley, F. F. Rust and W. E. Vaughan, *ibid.*, **70**, 88 (1948).

[6] H. J. Shine and D. M. Hoffman, *ibid.*, **83**, 2783 (1961); L. Herk, M. Feld and M. Szwarc, *ibid.*, **83**, 2998 (1961).

consistent with this induced decomposition as the predominant decomposition path. Radicals derived from chlorobenzene are relatively unreactive toward the perester in low concentration and no induced decomposition appears in this solvent.

This mechanism of induced decomposition is also supported by the observation of a small (*ca.* 30%) increase in rate of decomposition in chlorobenzene when 0.5 molar styrene is present. Radicals of the benzylic type, similar in structure to cumyl radicals, would be generated from the styrene and, in part, attack the peroxide by this induced path.

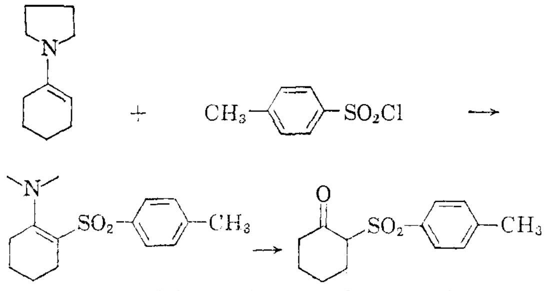
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF BRITISH COLUMBIA
VANCOUVER 8, B.C., CANADA
RICHARD E. PINCOCK

RECEIVED NOVEMBER 17, 1961

FOUR-MEMBERED SULFONES FROM ENAMINES AND ALIPHATIC SULFONYL HALIDES

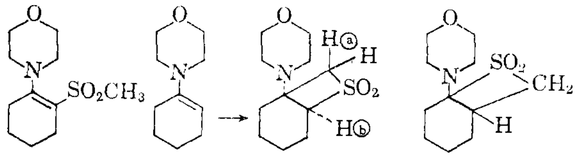
Sir:

Some time ago we reported[1] that enamines such as for instance that from cyclohexanone and pyrrolidine react with aromatic sulfonyl chlorides to produce, after hydrolysis, a β-ketosulfone



In connection with another problem which required the synthesis of β-ketosulfones we have had occasion to examine the reaction of enamines with aliphatic sulfonyl chlorides.

We have found that, in the presence of triethylamine as a proton acceptor, methanesulfonyl chloride reacts with a variety of morpholine enamines to give an interesting new class of compounds, four-membered cyclic aminosulfones. For example, reaction of the morpholine enamine of cyclohexanone (I) in dioxane at room temperature overnight with one equivalent of methanesulfonyl chloride and one equivalent of triethylamine, gives a very good yield of the cyclic sulfone II, m.p. 139–140°.

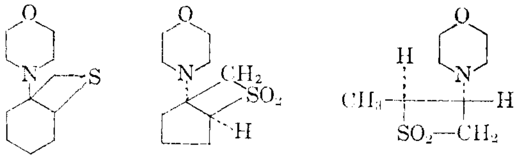


III I II IV

The structure of II follows from its analysis (Calcd. for $C_{11}H_{19}O_3NS$: C, 53.86; H, 7.81. Found: C, 53.56; H, 7.76), its infrared spectrum which shows the presence of the sulfone grouping at 7.62 and 8.60 μ, while the solubility in, and recovery from, dilute acid (as well as the infrared spectrum) exclude the isomeric possibility III. The n.m.r. spectrum is in full agreement with the postulated structure showing (in chloroform) two non-equivalent hydrogens (a) in a typical AB quartet centered at $\tau = 6.1$ with $J = 12.5$ cps., and with the tertiary hydrogen (b) as a broad multiplet centered at $\tau = 5.6$. Absorption from the (a) protons overlapped the absorption of the four hydrogens next to the morpholine oxygen but could be disentangled by putting a positive charge on the nitrogen: solution in aqueous hydrochloric acid moved the protons next to the sulfone about 60 cps. to lower field (5.0 τ for the (a) protons and 4.5 τ for the (b) proton). The CH_2's next to the morpholine nitrogen ($\tau = 7.4$) overlapped some methylene absorption but could be moved to lower field ($\tau = 5.5$) in hydrochloric acid solution.

The orientation of the sulfone with respect to the amino group can, on the basis of the n.m.r. spectrum, only be that shown in II rather than IV. This was confirmed by lithium aluminum hydride reduction[2] of II and acid work up to the amino sulfide V, characterized as its picrate, m.p. 165–167° (Found: C, 46.23; H, 4.86) the alternative arrangement of IV would have produced a sulfide which would have been transformed into an amino or keto mercaptan.

Similar reactions with the morpholine enamine of cyclopentanone gave a 77% yield of the cyclic sulfone VI, m.p. 122–123° (Found: C, 51.97; H, 7.34) while the morpholine enamine of propionaldehyde led in very good yield to the corresponding sulfone VII, m.p. 107–108° (Found: C, 47.12; H, 7.45)



V VI VII

Various mechanisms may be written for these reactions. The interesting possibility that the first step involves the formation of an analog of ketene, $CH_2{=}SO_2$, VIII, followed by reaction with the enamine will have to be explored further.

THE CHANDLER LABORATORY
COLUMBIA UNIVERSITY
NEW YORK 27, NEW YORK
GILBERT STORK
IRVING J. BOROWITZ[3]

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[1] G. Stork, Abstracts of the XVIth National Organic Symposium, Seattle, June, 1959, p. 52; *cf.* H. K. Landesman, Ph.D. thesis, Columbia University, New York, 1956.

[2] *Cf.* P. G. Bordwell and W. H. McKellin, *J. Am. Chem. Soc.*, **73**, 2251 (1951).

[3] Department of Chemistry, The City College, New York.