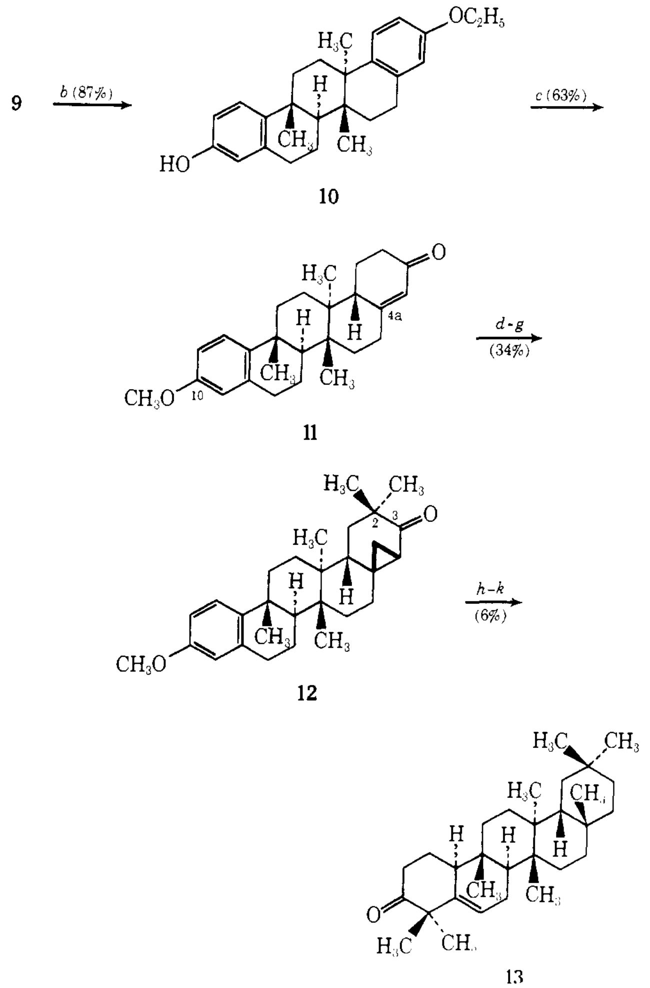
Chart II. The Conversion of the *trans,anti,trans*-Pentacyclic Diether 9 to DL-Alnusenone (**13**)[a]



[a] See Chart I, footnotes *a* and *b*. [b] $LiP(C_6H_5)_2$ (1 equiv), THF. [c] Li, NH_3, C_2H_5OH, THF; CH_3I; H_3O^+. [d] $(i\text{-}Bu)_2AlH$, C_6H_6. [e] CH_2I_2, Zn(Cu), ether–THF. [f] CrO_3–Py_2, CH_2Cl_2. [g] KO-*tert*-Bu, THF, CH_3I. [h] Li, NH_3, THF, NH_4Cl. [i] N_2H_4–2HCl, $N_2H_4 \cdot H_2O$, KOH, TEG, Δ. [j] Li, NH_3, C_2H_5OH, H_3O^+. [k] KO-*tert*-Bu, *tert*-BuOH, C_6H_6, CH_3I.

for the introduction of C-2 *gem*-dimethyl grouping through direct base-catalyzed methylation. In model systems as well as the case at hand, high yields of the bismethylated product were realized.

Of the remaining transformations of the cyclopropyl ketone **12** (mp 177–178°) that led to *dl*-alnusenone (**13**), only the Wolff–Kishner reduction of the highly hindered C-3 ketone formed after lithium–ammonia cleavage[13] of the cyclopropane system afforded a poor yield. The 16% yield of reduced material obtained during this preliminary investigation will undoubtedly be improved by further experimentation. Despite this low yield sufficient material was obtained to allow modification of the aromatic A ring according to the procedures used earlier in the synthesis of *dl*-rimuene,[14] and the high yields realized during these latter transformations provided a sample of the racemic triterpene (**13**): mp 208–208.5°; nmr (220 MHz) ($CDCl_3$) δ 0.82 (3 H), 0.96 (3 H), 1.00 (3 H), 1.03 (3 H), 1.10 (3 H), 1.17 (3 H), 1.23 (3 H), 1.24 (3 H) (s, quaternary CH_3), and 5.71 (m, 1, C-6 H); ir ($CHCl_3$) 3020 (vinyl H), 1700 (>C=O), and 1655 cm^{-1} (>C=C<); glc (0.125 in. × 6 ft 10% W-98 on Chromosorb W at 300° with 50 ml/min He flow) retention time 6.5 min; tlc (silica gel, 10% ether–petroleum ether (30–60°)) R_f = 0.41. *Anal.* Found: C, 84.83; H, 11.40. This material, obtained after 17 steps, was identical with an authentic sample of (+)-alnusenone, mp 245–247°, kindly provided by Professor Robert Stevenson as determined by comparison of the glc and tlc retention times and solution ir and nmr (220 MHz) spectra. Further work is in progress to refine and develop the later stages of this successful reaction scheme and to investigate its utility for the synthesis of other pentacyclic triterpenoid systems.

Acknowledgment. Support of this research by the National Science Foundation is gratefully acknowledged.

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* Author to whom correspondence should be addressed.

Robert E. Ireland,* Steven C. Welch[15]
Contribution No. 4136
Gates and Crellin Laboratories of Chemistry
California Institute of Technology
Pasadena, California 91109

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tert-Butyl Peroxyformate. A Convenient Source of Hydrogen Atoms in Solution. Reactions of the Hydrogen Atom. V[1,2]

Sir:

Recently we reported detailed kinetic studies of the reactions of the hydrogen atom in solution.[2] This species is important both because of theoretical considerations[3,4] and also because it has been implicated in radiation chemistry and biology.[5–7] In our previous studies[2] the hydrogen atoms were generated by the solution photolysis of thiols (eq 1), and relative values

$$\mathrm{RSH} \xrightarrow{h\nu} \mathrm{RS}\cdot + \mathrm{H}\cdot \tag{1}$$

of k_H were reported for a series of organic hydrogen donors QH.

$$\mathrm{H}\cdot + \mathrm{QH} \xrightarrow{k_H} \mathrm{H_2} + \mathrm{Q}\cdot \tag{2}$$

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We have now found that photolysis of *tert*-butyl peroxyformate (BUP), *tert*-BuOOOCH, produces appreciable quantities of hydrogen gas; reactivity data and other considerations discussed below suggest that the H_2 arises from the reactions of hydrogen atoms produced by the photolysis of BUP. The products from a typical photolysis experiment are shown in Table I. The results obtained by Pincock[8] from thermal decomposition of BUP are included for comparison.

Table I. Products of Decomposition of *tert*-Butyl Peroxyformate[a]

Product	Method of decomposition Photolysis[b]	 Thermolysis[c]
Hydrogen	0.46	0.00
Carbon dioxide	0.93	0.68
Formic acid	0.04	0.14
tert-Butyl alcohol	0.90	0.88
Acetone	0.09	0.18
Methane	0.06	0.20

[a] In moles per mole of performate decomposed. [b] [BUP] is 0.141 *M* in cyclohexane; photolysis was effected by 3000-Å lamps in a Rayonet reactor; the temperature was 40°. [c] Data of R. E. Pincock, *J. Amer. Chem. Soc.*, **86**, 1820 (1964); [BUP] is 0.366 *M* in cumene; the temperature was 140°.

Photolysis of BUP at 40° in deuterated solvents such as acetone-d_6, benzene-d_6, chloroform-d_1, toluene-α,α,α-d_3, and 2-methyl-2-propanethiol-d_1 gives HD (and also some H_2). Identical solutions heated to 40° for extended periods, but not photolyzed, are free of noncondensible gases. Thermal decomposition at 100° in these solvents does yield minor amounts of HD and H_2, but not enough for quantitative analysis.

The photolysis of a solution containing BUP, a deuterated compound RD as a standard reactant, and a hydrogen donor (QH) may give H_2 and HD by the following reactions (eq 3–7), where ·BUP and ·RD

$$\mathrm{BUP} \xrightarrow{h\nu} \mathrm{H}\cdot + \text{other products} \qquad k_i \tag{3}$$

$$\mathrm{H}\cdot + \mathrm{BUP} \longrightarrow \mathrm{H_2} + \cdot\mathrm{BUP} \qquad k_1 \tag{4}$$

$$\mathrm{H}\cdot + \mathrm{QH} \longrightarrow \mathrm{H_2} + \mathrm{Q}\cdot \qquad k_\mathrm{H} \tag{5}$$

$$\mathrm{H}\cdot + \mathrm{RD} \longrightarrow \mathrm{H_2} + \cdot\mathrm{RD} \qquad k_2 \tag{6}$$

$$\mathrm{H}\cdot + \mathrm{RD} \longrightarrow \mathrm{HD} + \mathrm{R}\cdot \qquad k_3 \tag{7}$$

are the radicals which result when a hydrogen atom is abstracted from BUP and RD, respectively, and the other symbols have their usual meaning. We will comment on the nature of the photolysis step (eq 3) in more detail at a later date.

Attack on BUP by hydrogen atoms (eq 4) can be studied by observing the change of the H_2/HD ratio with variation of the concentration of BUP at a constant QH/RD ratio. This attack becomes important for concentrations of BUP greater than 0.03 *M* in cyclohexane in which a small amount of 2-methyl-2-propanethiol-d_1 (QH/RD = 20) is present as a deuterium donor. When the thiol concentration is increased (QH/RD = 1), however, attack on BUP remains unimportant up to 0.3 *M* BUP. Presumably abstraction from BUP occurs predominantly at the formyl moiety, since the rate constant for abstraction of an aldehyde-type hydrogen by a hydrogen atom is 10^2–10^3 times larger than that from a *tert*-butyl fragment.[9] This mode of induced decomposition of BUP is unique for peresters or peroxides.

Kinetic analysis of eq 5–7 leads to eq 8. Step 4 has

$$\frac{[\mathrm{H_2}]}{[\mathrm{HD}]} = \frac{k_2}{k_3} + \frac{k_\mathrm{H}[\mathrm{QH}]}{k_3[\mathrm{RD}]} \tag{8}$$

been omitted in this analysis since its contribution to hydrogen formation is negligible for [BUP] = 0.02 *M*, the concentration used in the runs from which relative k_H values were obtained. Thus a plot of $[\mathrm{H_2}]/[\mathrm{HD}]$ against [QH]/[RD] should give a straight line with an intercept of k_2/k_3 and a slope of k_H/k_3. We have found that a linear relationship exists over a [QH]/[RD] range of 0–18.0 for the following compounds: hexane, cyclohexane, 2,3-dimethylbutane, methyl alcohol, isopropyl alcohol, *tert*-butyl alcohol, *p*-dioxane, tetrahydrofuran, and diisopropyl ether. In our initial kinetic runs we have used 2-methyl-2-propanethiol-d_1 as the standard reactant, since thiols can be deuterated easily by exchange with D_2O to give RSD, a very reactive deuterium donor. In theory, any donor with suitably reactive deuteriums could be used. The runs were made in Pyrex tubes, and 3500-Å Rayonet lamps were used for irradiation; under these conditions photolysis of thiol is negligible. As Table II shows, the agreement of our results with those obtained by other methods appears to be quite good. The preliminary data illustrate the utility of our system for kinetic purposes.

Table II. Relative Values of k_H in Equation 2 for Various Hydrogen Donors toward the Hydrogen Atom

QH	Method of generation of hydrogen atoms Photolysis BUP	 Thiol-d_1[a]	 Thiol-*t*[b]	 Radiolysis[c]
n-Hexane	(1)	(1)	(1)	(1)
Cyclohexane	1.4	1.2	1.3	1.4
2,3-Dimethylbutane	2.1	2.2	2.0	3.2
Methyl alcohol	0.34	0.42	0.43	0.42
tert-Butyl alcohol	0.05	0.03		0.03
Isopropyl alcohol	2.6	1.9	*d*	*d*
p-Dioxane	2.2	3.0	1.4	1.4
Tetrahydrofuran	8.2	9.1		7.6
Diisopropyl ether	4.9	4.8		

[a] Either 2-methyl-2-propanethiol-d_1 or thiophenol-d_1 gives the same value; this method actually gives $k_\mathrm{H}I$ where $I = k_\mathrm{D}/k_\mathrm{H}$ for $\mathrm{H}\cdot(\mathrm{D}\cdot) + \mathrm{QH} \rightarrow \mathrm{H_2}(\mathrm{HD}) + \mathrm{Q}\cdot$; see ref 2a. [b] An average of the values obtained using propanethiol-*t* (ref 2c) and thiophenol-*t* (unpublished data in the laboratory of Dr. T. H. Lin); this method actually gives $k_\mathrm{H}I'$ where $I' = k_\mathrm{T}/k_\mathrm{H}$ for $\mathrm{Q}\cdot + \mathrm{RSH}(t) \rightarrow \mathrm{QH}(t) + \mathrm{RS}\cdot$; see ref 2b. [c] Taken from a compilation of data in ref 2d. [d] The value obtained by this method appears to be anomalously high; see discussion in ref 2d.

The formation of hydrogen does not, of course, prove the presence of H atoms although this interpretation is clearly the simplest and most attractive. Several other suggestions could be made to explain the formation of H_2, however. For example, it might be suggested that a photoexcited BUP species abstracts H (D) atoms from QH (RD) and then eliminates H_2 (HD). This mechanism is contraindicated by the fact that formic acid, oxalic acid, and ethyl

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formate all fail to give H_2 upon photolysis under the conditions used for BUP. Furthermore, as the data in Table II show, our results from this system agree well with the H-atom data obtained from our thiol systems and from studies of the high-energy radiolysis of aqueous solutions. Also, it might be pointed out that the photolysis of HCO_2O-*tert*-Bu to give $H\cdot$ and CH_3CO_2O-*tert*-Bu to give $CH_3\cdot$ seems quite analogous;[10a] unpublished data from our laboratories[10b] indicate that H atoms and methyl radicals show very similar selectivity in their reactions.[2a]

It is also possible that some as yet unknown type of photolytic interaction between a thiol and BUP could give H_2 or HD. This suggestion appears equally unlikely, since in a subsequent communication[11] we will describe a thiol-free perester system which gives relative k_H values very similar to those obtained when thiol is present.

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[11] W. A. Pryor and R. W. Henderson, in preparation.

[12] NASA Trainee, 1966–1969.

* Address correspondence to this author.

William A. Pryor,* R. W. Henderson[12]
Department of Chemistry, Louisiana State University
Baton Rouge, Louisiana 70803

Received May 16, 1970

Decomposition of Benzene under Electron Impact[1-3]

Sir:

Five primary decomposition reactions are readily discernible in the mass spectrum of benzene: the loss of $H\cdot$, H_2, C_2H_2, $C_3H_3\cdot$, and $CH_3\cdot$ to yield, respectively, $C_6H_5^+$, $C_6H_4\cdot^+$, $C_4H_4\cdot^+$, $C_3H_3^+$, and $C_5H_3^+$.[4] The spectra of variously deuterated benzenes show complete loss of position identity of the six hydrogens in the formation of the four of these products for which the available data permit confident conclusions.[5-7] This finding is, of course, implicit in the loss of $H\cdot$, and it is not too surprising in the loss of $CH_3\cdot$, which necessarily requires some drastic reorganization of the molecule. The loss of C_2H_2 and that of $C_3H_3\cdot$, however, are so easily visualized as proceeding by rupture of appropriate pairs of carbon–carbon bonds in the original ring that the observed randomization has constituted a troublesome problem.

Similar loss of position identity of hydrogens and—although supporting data here are fewer—of carbons as well is widespread in formally benzylic ions, most notably $C_7H_7^+$, under electron impact.[8,9] However, much of this randomization seems to occur, probably *via* ring expansion, in the process of forming the benzylic ions. Perhaps more to the point, such randomization has been shown to occur in the molecular ions of many aromatic and heteroaromatic nuclei with no skeletal substitution.[5,10] In this context, benzene is of particular interest as the prototype aromatic compound and by virtue of its high symmetry.

The discovery in the past few years of the surprising skeletal isomerizations occurring in substituted benzenes[11,12] and thiophenes,[13] and in unsubstituted benzene[14] as well, under ultraviolet irradiation[15] offered an attractive rationale for randomizing processes in the same and related compounds under electron impact. In particular, interconversion and/or rearomatization of Dewar benzenes (**1**), prismanes (**2**), and benzvalenes (**3**) so formed, as is known to occur thermally and photochemically, could effect trans-

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[3] Organic Ions in the Gas Phase. XXV. For paper XXIV in this series, see S. Meyerson, C. Fenselau, J. L. Young, W. R. Landis, E. Selke, and L. C. Leitch, *Org. Mass Spectrom.*, **3**, 689 (1970).

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