The phosphorus spectrum of the compound *trans*-$Rh[(C_6H_5)_3P]_2COCl$ in chloroform, after proton decoupling, consists of a doublet split by *J*(Rh–P). Both lines in the phosphorus spectrum are equally perturbed into triplets by irradiation at rhodium frequencies of 2.843420 and 2.843668 MHz and into doublets at a frequency of 2.843544 MHz. This confirms that the rhodium spectrum consists of the expected 1:2:1 triplet and gives the rhodium chemical shift directly.

The rhodium chemical shifts listed in Table II are arbitrarily reported relative to the resonance frequency of rhodium metal which was reported *vs.* D_2O.[8] This frequency (2.840104 MHz) has been calculated for a field strength such that TMS falls directly at 90 MHz by measuring the chemical shift of D_2O from TMS. A detailed discussion of the rhodium chemical shifts will be presented when additional compounds have been studied.

(8) P. B. Sogo and C. D. Jeffries, *Phys. Rev.*, 98, 1316 (1955).

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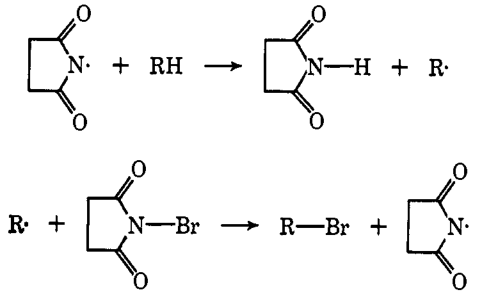
Oxidation of 1-Phenylethanol by the Succinimidyl Radical

Sir:

In 1942 Ziegler[1] first demonstrated the allylic brominating ability of N-bromosuccinimide (NBS). Two years later Bloomfield[2] proposed a radical chain mechanism which involved the succinimidyl radical in a chain-carrying sequence.



Goldfinger[3] in 1953 proposed an alternative mechanism whereby the chain-propagating step involved a bromine atom as the hydrogen-abstracting species rather than the succinimidyl radical. Bromine was formed in the reaction mixture by the reaction of NBS with traces of HBr in the reaction mixture.

$$Br\cdot + RH \longrightarrow HBr + R\cdot$$

$$R\cdot + Br_2 \longrightarrow RBr + Br\cdot$$

A series of articles[4] appeared in 1963 giving experimental evidence that supported the proposal of Goldfinger. For example, Russell[4b] studied competitive photobromination of aralkyl hydrocarbons by NBS and molecular bromine, and both reactions appeared to involve the bromine atom as the hydrogen-abstracting species.

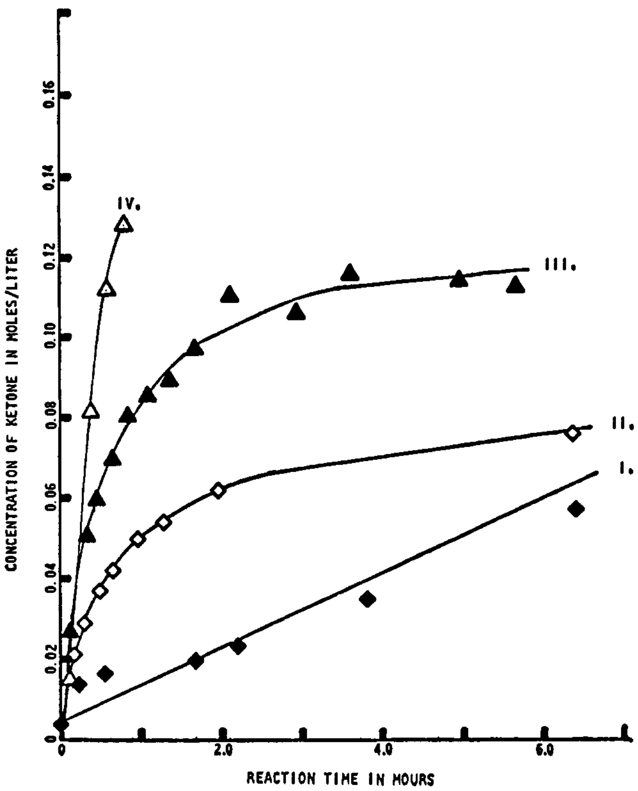


Figure 1. Rates of oxidation of 1-phenylethanol by NIS in benzene at reflux. All rates are with 0.004 mol (0.4 *M*) of alcohol and 0.002 mol of NIS: (I) chloranil inhibited; (II) benzoyl peroxide initiated; (III) benzoyl peroxide initiated, with silver acetate present; (IV) irradiated, with silver acetate present.

To our knowledge evidence for the involvement of the succinimidyl radical in chain-propagating steps as a species capable of abstracting hydrogen atoms has not been demonstrated. In fact, when N-iodosuccinimide (NIS) was heated[5] at reflux with toluene in CCl_4 in the presence of benzoyl peroxide and strong light no radical reactivity was found.

We wish to report a set of experiments to establish the ability of the succinimidyl radical to propagate a radical chain reaction. We have investigated the oxidation of 1-phenylethanol to acetophenone with N-iodosuccinimide (NIS) in dry benzene at reflux. Using 0.002 mol of NIS and 0.004 mol of 1-phenylethanol in all runs but varying reaction conditions we obtained four different ketone formation rates. Reactions III and IV (see Figure 1) were initiated with 1 mol % benzoyl peroxide and tungsten light, respectively, and both reactions showed very fast initial rates as compared with reaction 1 which was inhibited with 5 mol % chloranil. This suggests that the oxidation of the alcohol in runs III and IV was a radical-chain reaction. In runs III and IV silver acetate was used to prevent the hydrogen iodide product from reacting with the NIS to form molecular iodine. No iodine color was observed in these reactions.

In runs I and II no silver acetate was used and an immediate iodine color appeared. This iodine formation consumed NIS and should result in lower yields

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(1) K. Ziegler, A. Spaeta, E. Schaaf, W. Schumann, and E. Winkelman, *Ann.*, 551, 80 (1942).

(2) C. F. Bloomfield, *J. Chem. Soc.*, 14 (1944).

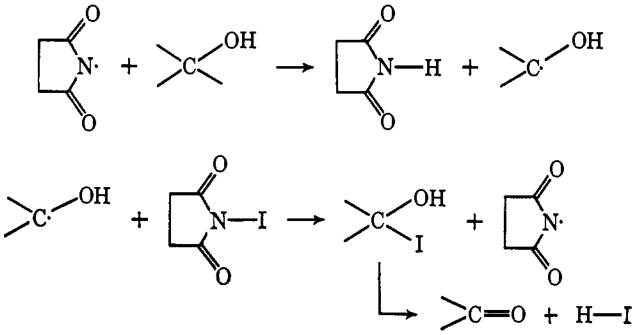
(3) J. Adams, P. A. Gosselain, and P. Goldfinger, *Nature*, 171, 704 (1953); *Bull. Soc. Chim. Belges*, 65, 533 (1956).

(4) (a) C. Walling and A. L. Rieger, *J. Am. Chem. Soc.*, 85, 3134 (1963); (b) G. A. Russell and K. M. Desmond, *ibid.*, 85, 3139 (1963); (c) R. E. Pearson and J. C. Martin, *ibid.*, 85, 354 (1963).

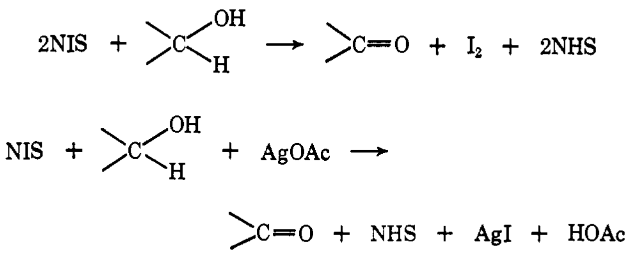
(5) C. Djerassi and C. T. Lenk, *ibid.*, 75, 3494 (1953).

of ketone based upon total NIS, as was observed. Although run II also appeared to be a radical-chain reaction, the formation of iodine slowed the rate of ketone production. This was expected since iodine itself is a known scavenger of free radicals[6] and should decrease the chain length of the radical reaction. Attempts to oxidize the alcohol under the same free-radical conditions but using iodine rather than NIS failed to yield ketone, which supports the idea that the hydrogen-abstracting radical is the succinimidyl radical and not the iodine atom. If the iodine atom were the chain-propagating radical in the NIS reactions, then it would be expected that photolytic or peroxide initiation of the iodine reaction would also oxidize the alcohol. Furthermore, if the iodine atom were the chain-propagating radical, then run II, where iodine was produced as a side product, should have a faster rate than run III, where no iodine was produced due to the presence of silver acetate.

The possibility that the hydrogen-abstracting radical was the β-propionyl isocyanate radical[7] ($\cdot CH_2CH_2COCNO$), formed from the succinimidyl radical by ring cleavage, was ruled out as succinimide was recovered in 80–90% yield from the reaction mixtures. Succinimide was recovered from runs where silver acetate was added and from runs where no silver acetate was added. We propose that the oxidation mechanism involves the succinimidyl radical and is similar to that of Bloomfield's original suggestion.



In runs I and II, where silver acetate was absent, 2 mol of NIS was needed for the production of 1 mol of ketone as the hydrogen iodide product reacted with NIS to produce iodine and succinimide. When silver acetate was present the hydrogen iodide formed silver iodide before it could react with the NIS.



The final yield of ketone produced in runs I, II, III, and IV relative to the amount of NIS present in the reaction was 50, 35, 80, and 64%, respectively. Based upon NIS available for oxidation the ketone yield in runs I and II was 100 and 70%.

The leveling off of plots of Figure 1 for runs II and III is attributed to the exhaustion of the supply of benzoyl peroxide which was not added except at the beginning of each reaction. The plot for run IV does not level off, and this is attributed to constant radical production during photolysis.

The rates of reaction were followed by injecting 5-μl samples of the reaction mixture on a 6-ft long vapor-phase chromatograph column holding 3% Carbowax 20-M and 7% SE-30 on Chromosorb P (60–80 mesh).

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(6) W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y. 1966, p 94.

(7) J. C. Martin and P. D. Bartlett, *J. Am. Chem. Soc.*, **79**, 2533 (1957).

Stable Carbonium Ions. XC.[1] The Octamethylbicyclo[3.3.0]octadienyl Dication, a Dihydropentalene Dication

Sir:

We undertook a study of the protonation of derivatives of tetramethylcyclobutadiene dimer in an attempt to prepare the octamethylhomotropylium ion **2**. This study is a continuation of our work on the protonation of hexamethyl Dewar benzene[2] and also the acid-catalyzed opening of cyclobutane rings.

We examined the protonation of *syn*- and *anti*-octamethyltricyclo[4.2.0.$0^{2,5}$]octa-3,7-diene (**1a** and **1b**, respectively), octamethylsemibullvalene (**1c**), and octamethylcyclooctatetraene (**1d**)[3] in $HFSO_3$–SbF_5–SO_2 solution at temperatures ranging from −10 to −60°. In every case the major species produced was the octamethylbicyclo[3.3.0]octadienyl dication (**3**). The structural assignment of ion **3** is based on the remarkable simplicity of its nmr spectrum (Figure 1) which consists of three singlets in the ratio 1.96:1.00:1.04 at δ 3.29, 2.30, and 2.05 (relative to capillary TMS). These chemical shifts are consistent with those of a methyl-substituted allylic cation and indicate that a cyclo-

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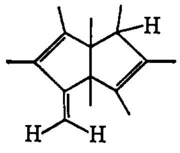
(1) Part LXXXIX: G. A. Olah, J. M. Bollinger, and A. M. White, *J. Amer. Chem. Soc.*, in press.

(2) P. A. Paquette, G. R. Krow, J. M. Bollinger, and G. A. Olah, *ibid.*, **90**, 7147 (1968).

(3) The starting materials were prepared by known methods: *syn*-octamethyltricyclo[4.2.0.$0^{2,5}$]octadiene: R. Criegee and G. Louis, *Chem. Ber.*, **90**, 417 (1957) (we thank Professor Leo A. Paquette for a sample); *anti*-octamethyltricyclo[4.2.0.$0^{2,5}$]octadiene: R. Criegee and G. Schröder *Ann. Chim.*, **623**, 1 (1959); R. Criegee, G. Schröder, G. Maier, and H. G. Fischer, *Chem. Ber.*, **93**, 1553 (1960); octamethylsemibullvalene: R. Criegee and R. Askani, *Angew. Chem. Intern. Ed. Engl.*, **1**, 537, (1968); R. Criegee, W. O. Wirth, W. Engel, and H. A. Brune, *Chem. Ber.*, **96**, 2230 (1963). Octamethylcyclooctatetraene was prepared in 10% yield by the pyrolysis of *anti*-octamethyltricyclooctadiene at 300° (3 mm) in a 38-cm column packed with glass helices. In this reaction 80% of the product was an oil, probably **5**, reported by R.



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Criegee and G. Louis, *Chem. Ber.*, **90**, 424 (1957); 10% of the starting material was recovered unchanged. These materials were readily separated by column chromatography on silica gel.