

Reaction of Diacetyl Peroxide with Phenyl Alkyl Ketones. A Re-examination

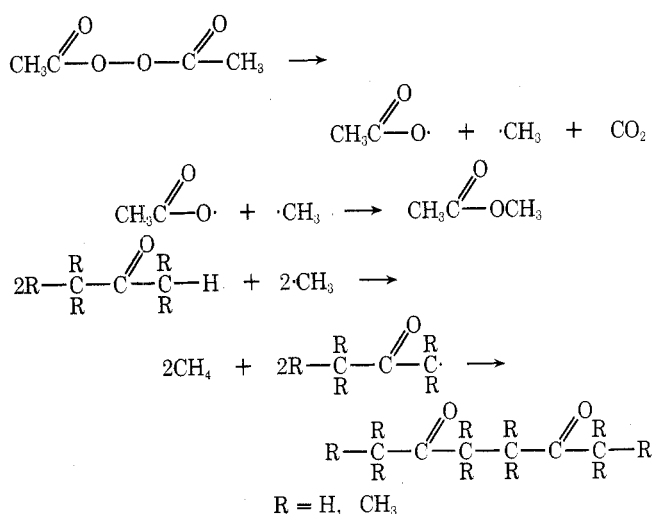
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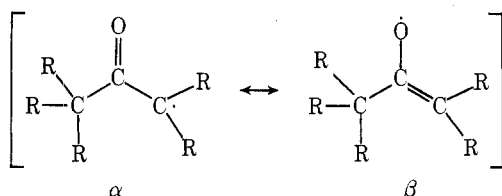
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The re-examination of an old reaction is reported. Based on new evidence regarding the structure of the phenacyl free radical a more detailed interpretation of the mechanism of the reaction is presented. The failure of phenacyl radicals to dimerize is explained by the delocalized, nonclassical nature of its structure. The suggested structure consistent with both physical and chemical evidence is that of the 1-keto spiro[2.5]octadienyl radical. The low methane to peroxide ratios obtained are accounted for by methyl substitution to form methyl acetophenones. The collective data are explainable in terms of the postulate that the methyl free radical is solvated by acetophenone into a spin-correlated π -complex which is the principal doublet species in these reactions.

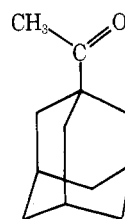
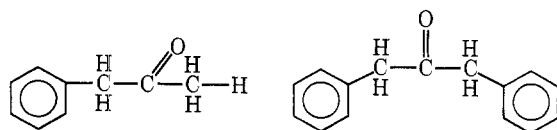
The progress which has been made during the past 25 years in the chemistry of organic free radicals is dramatically exemplified by ref 1 and 2. An earlier study^{1b} of the reactions of diacetyl peroxide with ketones showed that the methyl free radical generated by the thermolysis of the peroxide formed 1,4-diketones from aliphatic ketones through dehydrodimerization. While the existence of 2-alkanonyl



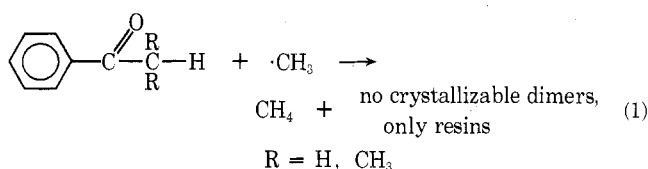
radicals was confidently postulated as intermediates in these dimerization reactions, the evidence (product isolation) was purely chemical and thus indirect. The structures of these intermediate 2-alkanonyl radicals which are involved in these successful dimerizations have recently been determined by electron spin resonance spectroscopy. They have been reported^{2c} to have the following structure, with



85% contribution from canonical α and 15% from canonical β . Among aliphatic ketones which have subsequently been dimerized³ by this technique are the following.



In striking contrast to this free-radical dimerization of aliphatic ketones, the phenyl ketones with the phenyl group attached directly to the carbonyl group give no crystallizable dimers, only resinous polymeric material, under identical conditions.^{1b}



Results and Discussion

There are several aspects of this latter reaction (eq 1) which appeared worthy of further investigation.

(I) The marked decrease in methane to peroxide ratios observed with phenyl ketones as contrasted with results obtained with completely aliphatic ketones.

(II) The failure of phenyl ketones with benzoyl functions in their structure to form dimeric 1,4-diketones in the manner similar to that of purely aliphatic ketones.

(III) The occurrence of wine-colored resinous polymeric material as the principal product of the reactions of these phenyl ketones and the absence of such resins among the products of the purely aliphatic ketones.

(IV) The persistence in the polymer of the $(\text{C}=\text{O})$ breathing frequency at 5.94μ while the doublet at 6.24 and 6.32μ attending the $\text{C}_6\text{H}_6 \leftrightarrow (\text{C}=\text{O})$ breathing has nearly vanished. (This evidence is specifically consistent with the interpretation that the intermediate phenacyl free radicals rearrange to 1-keto spiro[2.5]octadienyl radicals before they are trapped by acetophenone and thus incorporated into the polymer.) The interpretation here proposed is that the $\text{C}_6\text{H}_6 \leftrightarrow (\text{C}=\text{O})$ doublet has completely vanished in the spectrum of the polymer leaving exposed the much less intense aromatic $>\text{C}=\text{C}<$ stretching frequency. The fact that ESR studies⁵ indicate complete rearrangement of the radical tends to support this interpretation.

(V) The occurrence in the ir spectra of these polymers of broad and intense ether bands at 8.05μ , actually 7.65 – 8.40μ , is here interpreted as ketal linkages. (These cannot be

methyl ketals. Zeisel methoxy determinations⁶ on the gunks show essentially no methoxy groups in the structure.)

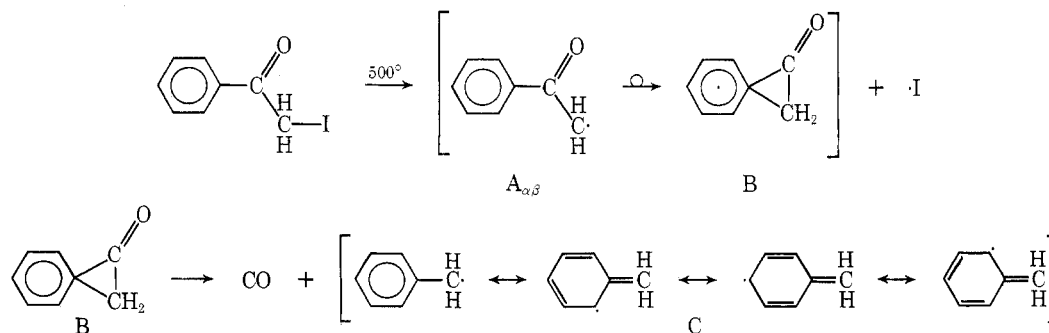
Evidence supporting this assignment in the infrared spectra of these resins is the fact that these polymers have been partially degraded by acid-catalyzed hydrolysis to regenerate the free derivatizable keto groups, thus restoring the intensity of the composite carbonyl band in the infrared absorption spectrum.

We have demonstrated that those methyl free radicals which have failed to appear as methane gas were actually substituted into the aromatic ring of the phenyl ketone substrate. Methyl acetophenones have been isolated from the reaction mixture when acetyl peroxide is decomposed in acetophenone. It has been demonstrated that methyl benzophenone appears among the products of the reaction of diacetyl peroxide with benzophenone. The mixture of methyl acetophenones has been resolved by gas chromatography into the ortho, meta, and para methyl components with a ratio of approximately 26:14:60, respectively.

Preliminary ESR studies⁵ suggest that the phenacyl free radical which was the expected intermediate in these reactions is a delocalized species under the conditions of the reaction. The spin density at the specific α carbon at which dimerization might be expected to occur is greatly reduced by delocalization, and failure to couple at this position is no longer difficult to understand. It has been demonstrated that there are two discrete isomeric free radicals with the molecular formula $C_6H_5COCH_2$. The radical with high spin density at the α carbon atom is thus far known only at 4 K in an argon matrix.

When generated by the ultraviolet photolysis of phenacyl iodide at 4 K in an argon matrix a partially delocalized phenacyl free radical has been detected. The ESR spectrum of this radical indicates that the spin density, ρ_C , on the oxygen is 0.13 while on the methylenic carbon this density, ρ_C , is 0.87. Similar ESR measurements on the analogous pentadeuteriophenacyl radical provide evidence that this particular phenacyl free radical at 4 K has no spin density delocalized into the benzene ring.

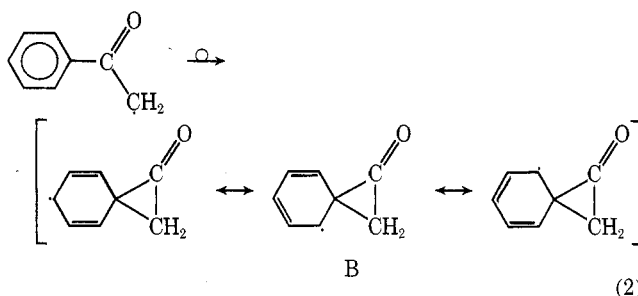
When phenacyl iodide is pyrolyzed at 500° and deposited immediately on a sapphire rod in a matrix of neon at 4 K one obtains the ESR spectrum known for the benzyl radical. When the pyrolysis products of phenacyl iodide under similar conditions are fed directly into the mass spectrometer the results obtained are best interpreted as follows.



The combined results of mass spectrometry and ESR spectrometry clearly support the conclusion that CO is eliminated at 500°. It seems necessary to postulate the occurrence of the rearrangement *before* the loss of CO since neither the mass spectrometry nor the ESR spectrometry shows evidence of a free $\cdot CH_2$ fragment.

The rearrangement of free radicals is a well-known phenomenon.⁷ The 1,2 shift of a phenyl group in a doublet species such as is here described was first demonstrated by Urry and Kharasch.⁸

Results more recently reported⁹ indicate that in specific instances the process of radical rearrangement might be reversible with a critically temperature-dependent free-energy change. The temperature at which the two isomeric structures are at equilibrium, $(\Delta G = 0)_{T=T_i}$, is designated by those authors as the inversion temperature. The inversion temperature at which this presumed rearrangement (eq 2) occurs is not now known nor is the minimum temper-

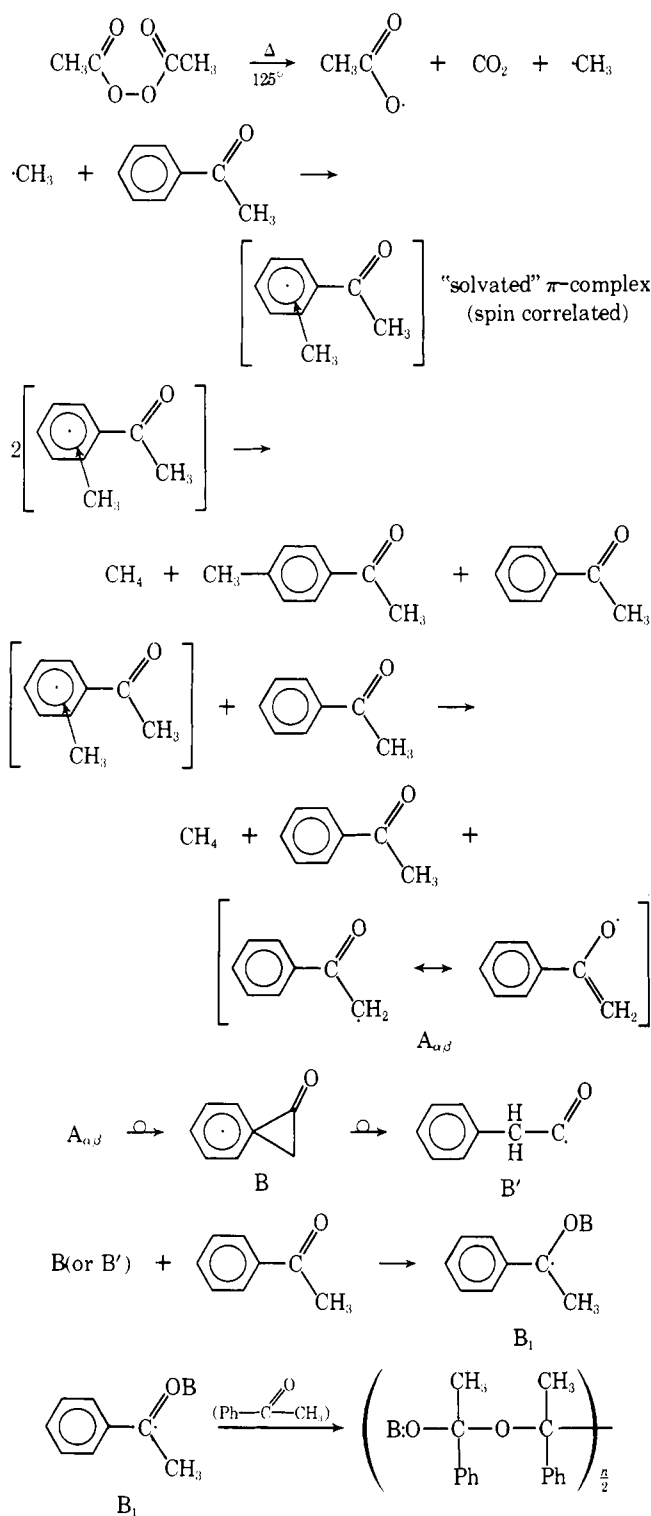


ature known at which the decarbonylation occurs. The absence of bibenzyl among the products of the attempted dimerization together with the persistence of aliphatic carbonyl bands in the infrared spectra of these resins indicate that decarbonylation does not occur at 125°, the temperature of these reactions. The temperature at which the proposed inversion of phenacyl occurs as well as the ESR spectrum of this delocalized and inverted radical are under investigation in these laboratories.

The fact that the quantities of the products, methyl acetophenones, obtained from methyl insertion are extremely small in contrast with the quantities of resins may well be explained in terms of the postulate that the methyl free radical is solvated by acetophenone into a spin-correlated π complex. The concentration of this complex is always extremely low at any time during the reaction because of the fact that the diacetyl peroxide dissolved in acetophenone is added one drop at the time beneath the surface of acetophenone preheated to 125°. In this manner each small portion of diacetyl peroxide is presumably decomposed before the next portion is added. Certainly much care is taken to avoid the build-up of appreciable quantities of diacetyl peroxide during the reaction. (See Experimental Section part of ref 1.) The probability, therefore, of a collision between two particles of π complex, which collision, if effective,¹⁰ is here postulated to lead to methyl insertion, is very

small. On the other hand, the probability that such a solvated methyl radical might collide with a solvent molecule, acetophenone, to generate the phenacyl free radical, B, is much greater. This species denoted by B, the 1-keto spiro[2.5]octadienyl radical, would because of resonance stabilization be expected to have a longer half-life than that of the indicated isomer, A, and in presence of a fairly good scavenger, or "trapping agent", might initiate a chain condensation reaction leading to polymeric resinous material. The initiator, B, or B', is thus incorporated into the

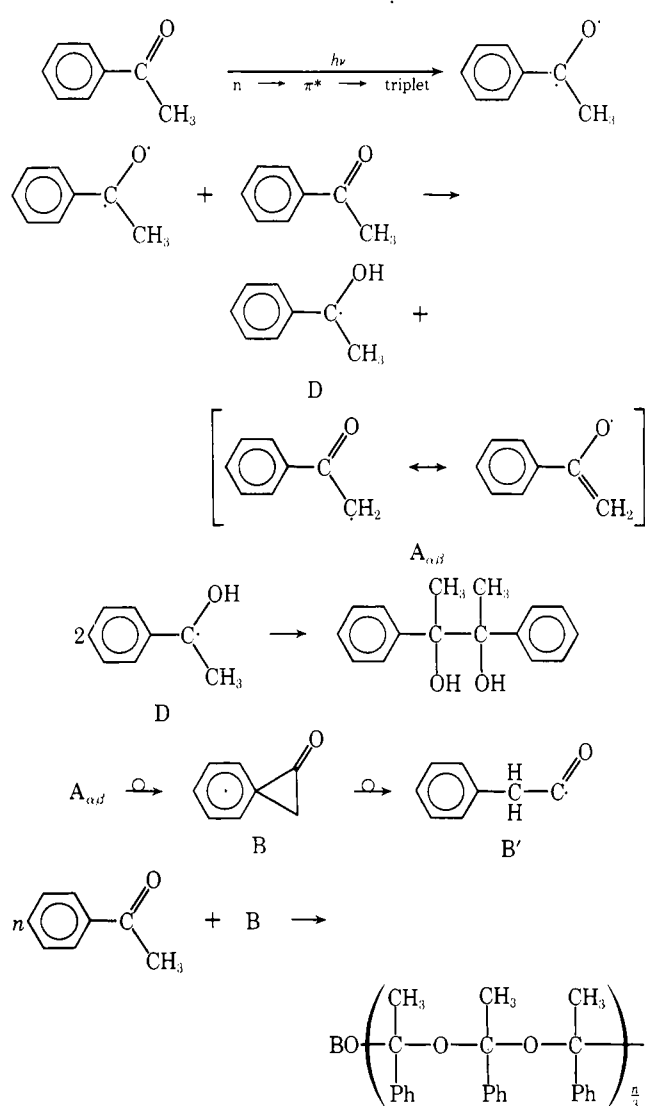
Scheme I



polymer, and the greatly diminished, but still present, carbonyl band in the infrared absorption spectrum of the polymer is thereby explained. These polymers have average molecular weights of ca. 648, indicating an average of 5.33 monomer units per molecule of polymer. The yields of polymer are in every case good, indicating that the initiator is quite effective but these radical chains are indeed not very long.

These results suggest also that as the polymer builds itself through successive attacks on carbonyl by residual radicals of n th order, the ability to attack carbonyl decreases. When $n = 5$ or 6 the condensation process no longer com-

Scheme II



petes successfully with chain termination probably via disproportionation.

The reaction scheme shown in Scheme I for the overall reaction of diacetyl peroxide with acetophenone is consistent with these collective facts.

Note that although B_1 is a benzyl-type free radical its dimerization is sterically retarded. In the absence of the less hindered carbonyl function in acetophenone providing an alternate reaction path this radical would be expected to dimerize.

As a further test for the validity of this composite interpretation an attempt was made to generate the phenacyl free radical in solution of acetophenone by yet another method. The triplet state of acetophenone would be expected to act as a hydrogen abstractor in the presence of hydrogen atoms on a carbon adjacent to the carbonyl function. The cogency of the argument here presented provides the following distinctly predictable interpretation of the results which would be expected when acetophenone is subjected to ultraviolet irradiation either neat or in solution of a relatively inert solvent. The reaction scheme shown in Scheme II outlines that interpretation.

When a dilute solution (0.5 N) of acetophenone in n -heptane was irradiated with the unfiltered mercury arc of a high-pressure ultraviolet lamp, the results obtained were precisely those predicted and outlined here. Both meso and

racemic forms of the glycol, 2,3-diphenyl-*n*-butanediol-1,2, were isolated. The resinous polymer which was obtained exhibited properties identical with those attending the resin obtained from the reaction of diacetyl peroxide with acetophenone described earlier.

It is apparent from Scheme II that there might be competition between B and D for addition to the carbonyl group of the acetophenone to initiate the chain polymerization reaction. One must conclude from the results that B adds much faster to the carbonyl than does D. This is not surprising since benzyl-type free radicals are well known to dimerize with great facility.

When a series of alkyl phenyl ketones are irradiated in 2-propanol,¹¹ a solvent with an easily abstractable tertiary hydrogen, the meso and racemic forms of the corresponding glycols are obtained *without* the accompaniment of the polymeric resins derived from the ketones. These results are consistent with the interpretations here presented.

Experimental Section

The preparation of the peroxide, its thermolysis in solutions of the alkyl phenyl ketones, and the recommended precautions attending these techniques are all described in the earlier reports.^{1b}

Isolation and Identification of the Methyl Insertion Products. After the acetyl peroxide (32.9 g, 0.28 mol) dissolved in acetophenone (386.8 g) was completely decomposed in acetophenone (103.5 g, 0.86 mol),¹ the unreacted monomeric material was stripped from the polymer by distillation at reduced pressure through a 20-plate column. The collected distillates from three such reactions were combined, and this mixture was carefully distilled through a 100-plate Podbilniak column. The last fraction, bp 60.0° (0.5 mm) (10.0 g), was submitted¹² for ir analysis. This spectrum was superimposable upon the infrared spectrum of an authentic synthetic mixture of 5% *p*-methylacetophenone and 95% acetophenone. This mixture was resolved¹³ by GLC technique. It was shown to be 5% methylated material and 95% acetophenone. The results showed 60:26:14% para:ortho:meta-substituted acetophenones, respectively. The column used was a 4-m, 0.6-cm diameter, glass column packed with 20% Ucon LB-550-X resin on 60/80 mesh Chromosorb operating at 215°.

Ultraviolet Irradiation of Acetophenone.¹⁴ The photolysis vessel was a 3-l, three-necked, cylindrically shaped, flat-bottomed flask. The outer necks were 24/40 outer joints for thermometer and condenser. The middle neck was a 60/50 joint for the quartz water-jacketed immersion well which accommodates the Hanovia high-pressure mercury vapor lamp, 500 W, type 679A. Acetophenone (2.5 l, 0.5 M) (150.2 g) in *n*-heptane was irradiated for 24 hr by the full mercury arc with nitrogen purging and magnetic stirring. The solution acquired a red-brown color and some material was deposited on the surface of the quartz well. No gases were generated. The *n*-heptane was removed by distillation at atmospheric pressure, and the unreacted acetophenone [40.1 g, bp 40° (30 mm), *n*_D²⁰ 1.5330] was removed at reduced pressure. The remaining fractions collected are tabulated below.

Fraction	Bp, °C (0.5 mm)	Weight, g
1	54–104	2.1
2	104–135	28.8
3	135–145	15.9
4	145–146	24.2
5	146–130	11.8

The resinous residue weighed 24.7 g. It had a reddish-brown color and it was soluble with decreasing order in ligroin, ether, acetone, and ethanol. To remove all monomeric materials this residue was subjected to continuous extraction for 30 hr with absolute methanol. It was shown to have properties identical with those of the polymer obtained from the reaction of diacetyl peroxide with acetophenone.

Fractions 2, 3, and 4 deposited crystals and fraction 5 completely crystallized. All of these fractions were pale yellow in color. The crystals from all fractions were collected on a sintered disk by suc-

tion filtering. Recrystallization from 60% aqueous methanol gave needle-like crystals which melted sharply at 116°.

Upon cooling to –80° the mother liquor from this recrystallization gave 2.1 g of material which melted after purification by elution chromatography at 44–45°. Five grams of the yellow oil obtained from the suction filtering was subjected to similar elution chromatography on a column (30 cm long and 2.5 cm i.d.) packed with activated alumina using 25-ml portions of methanol, methanol–2-propanol (1:1), 2-propanol, 2-propanol–benzene (1:1), and benzene. The solvents from each fraction of eluate were evaporated on a steam bath and fraction 2 yielded 2.3 g of crystals. Upon recrystallization from methanol–water these crystals melted at 44–45°. The high-melting (116°) and low-melting (44–45°) crystals gave molecular weights and C and H analyses consistent with 2,3-dihydroxy-2,3-diphenyl-*n*-butane, which exists in two isomeric forms. Neither of these materials depressed the respective melting points of authentic samples of the meso form (mp 117–118°)¹⁵ and the racemic form (mp 45°)¹⁵ of this material.

Registry No.—Diacetyl peroxide, 110-22-5; acetophenone, 98-86-2.

References and Notes

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 - (14) This experiment was performed by Frank C. Greene.
 - (15) These materials were generously provided by C. C. Arrington, who prepared them by action of methyl Grignard with benzil. See J. M. Johlin, *J. Am. Chem. Soc.*, **39**, 291 (1917); Chu and Chu, *J. Chin. Chem. Soc. (Peking)*, **9**, 190 (1942).