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(19) In benzene, at least, this argument would not apply, since the rate of S_1 relaxation in the fast region (k_{nr} ~ 10^{11} sec^{-1}) is too fast for an intersystem crossing.[17]

Systematic Structural Modifications in the Photochemistry of β,γ-Unsaturated Ketones. II. Acyclic Olefins and Acetylenes

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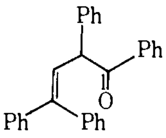
Abstract: The photochemical reactions of six acyclic β,γ-unsaturated ketones have been investigated. Direct irradiation of those with a simple olefin (**11**, **15**, **16**) leads to an α-cleavage, cyclobutanol, or oxetane, with the quantum yield of ketone disappearance decreasing when the olefin is more heavily alkylated. Although β,γ-acetylenic ketone **12** also exhibits α-cleavage, an overwhelming preference for turning around of the allylic moiety is found in ketone **14**, in which the two modes of cleavage are allowed to compete. Ten unsaturated C_{10} hydrocarbons have been determined from irradiation of **14**. Photolysis of bis-β,γ-unsaturated ketone **13** gives turnaround ketone **24** and a mixture of three C_{10} hydrocarbons, probably via the very short-lived acyl radical **33**. **11**, **12**, and **16** show no products on triplet photosensitizaton, but **15** exhibits olefin cis-trans isomerization. The triplet state of **13** and **14** undergoes intramolecular [2 + 2] cycloaddition, followed by ring opening in the case of **14**. Two new simple carboxylic acids have been prepared during the course of the work: 2,2-dimethylbutynoic acid (**36**) and 2,2,3,4-tetramethylpent-3-enoic acid (**51**).

The photochemistry of β,γ-unsaturated ketones (β,γ-UK's) has become an actively researched area in recent years, particularly in regard to the oxadi-π-methane (ODPM) rearrangement.[1] Although most of the compounds which have been examined to date are cyclic, the ODPM rearrangement was actually discovered[2] in an open chain compound (**1**). Like compound **1**, many of the other acyclic cases contained an aromatic ring conjugated with either the carbonyl group or double bond.[3-6] No pattern in photochemical behavior is apparent on examining the limited data available; for example, triplet sensitization[3] of **2** gives ODPM rearrangement but **3** does not.[4]



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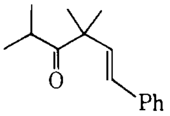

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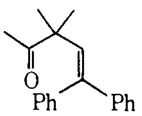
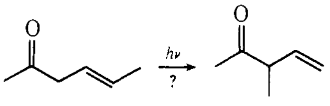


3

We have been interested in compounds with no conjugating substituents, an area in which published work is also scarce. In 1964 Morrison[7] reported that direct irradiation of **4** gave olefin trans-cis isomerization plus products from acetyl and 2-butenyl radicals; however, no mention was made of the expected **5**. More recent work[8] on **4** showed that olefin isomerization could also be sensitized by triplet acetone. Direct irradiation of compounds **6**[9] and **8**[10] gave products of α-cleavage and γ-hydrogen abstraction. Although these three cases are the only simple, acyclic β,γ-UK's which have been studied, they do show the other principal reactions known for this class of compounds as a whole.

The purpose of the present study was twofold: to elucidate the factors which govern the competition between the various pathways, and to examine the effect of a second unsaturated group on the photochemistry. We were also concerned with the α-cleavage process and the fate of the radicals produced. Two reactions which are new to the acyclic series have been found in the course of this work: intramolecular triplet [2 + 2] cycloaddition of bis-β,γ-UK's, and oxetane formation from simple, electron-rich β,γ-UK's.



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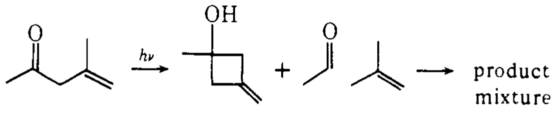

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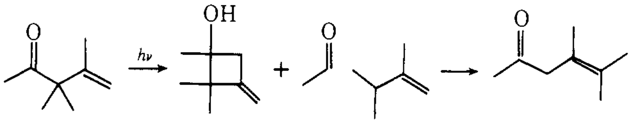
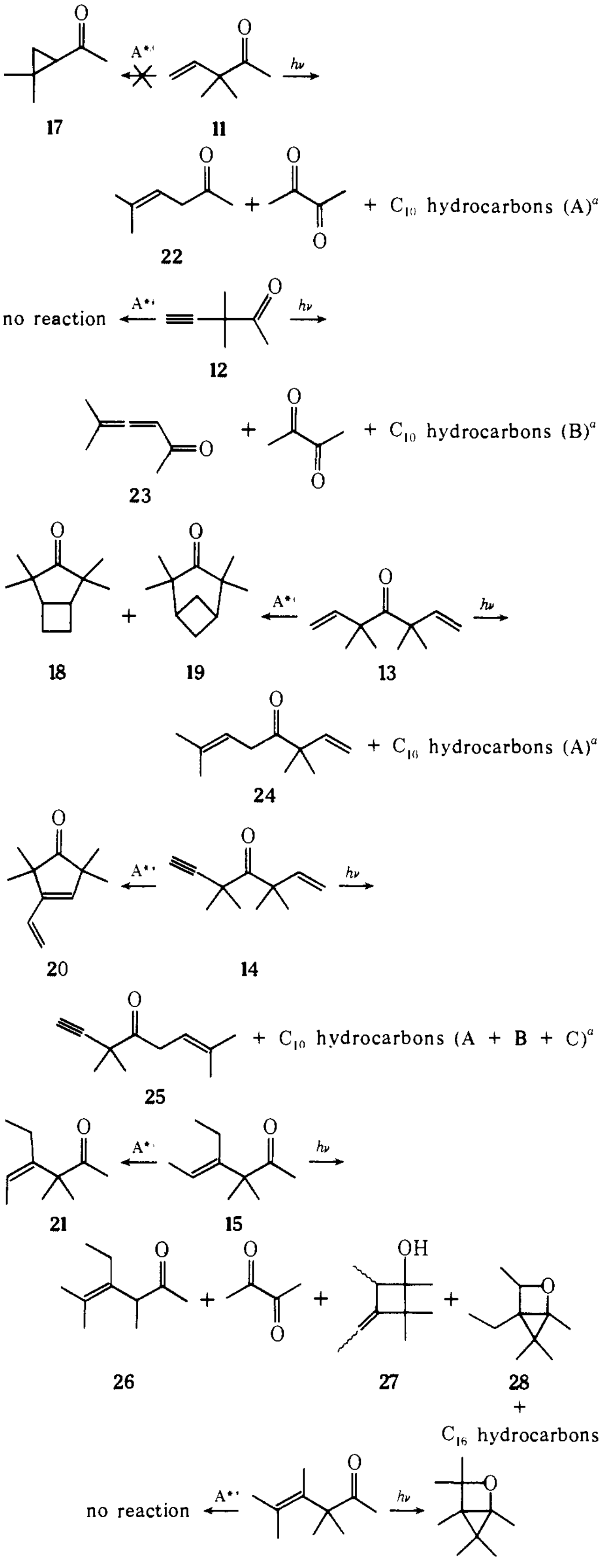


8 9 10 + others

Results

Acetone Sensitization. As mentioned in a preliminary report,[11] irradiation of 3,3-dimethyl-4-penten-2-one (**11**) in acetone did not produce the ODPM product **17** (cf. Scheme I). **11** was not inert, however, because cis-trans isomerization of the double bond could be demonstrated when a deuterium atom was substituted for one terminal olefinic pro-

Scheme I. Direct and Acetone (A) Sensitized Photoreactions of 11–16.



^{a}See Table II for identification of hydrocarbons.

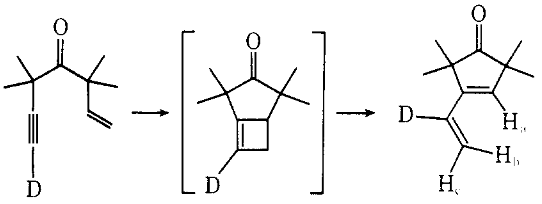
Table I. Quantum Yields for β,γ-Unsaturated Ketones

	Direct		Sensitized^c	
Compound	$\Phi_{-k}{}^a$	$\Phi_p{}^b$	$\Phi_{-k}{}^a$	$\Phi_p{}^b$
11	0.68	22, 0.14	<0.04	
12	0.67	23, 0.12	0.07	
13	0.36	24, 0.06	0.19	18, 0.10; 19, 0.04
14	0.25	25, 0.06	0.12	20, 0.055
15	0.23	26, 0.08 27, 0.01 28, 0.05	0.24	21, 0.20
16	0.12	29, 0.04	0.01	

^{a} Ketone disappearance. ^{b} Product appearance. ^{c}In acetone.

ton. None of the other compounds gave ODPM products either, but cis-trans isomerization was found in the other case (**15**) in which the isomers were distinguishable. These results are in accord with the previous conclusion[12] that ODPM rearrangement is most efficient in rigid cyclic olefins whereas cis-trans isomerization takes over in the flexible cases.

The unusual intramolecular cycloaddition reaction[13] of **13** prompted us to examine the behavior of **14** under acetone sensitization. The structure of the product (**20**) suggests that the same type of cycloaddition occurred between the olefin and acetylene of **14** but that the initial adduct underwent electrocyclic ring opening. Isolation of **20** was achieved only with difficulty, primarily because it reached a low maximum concentration after rather brief irradiation. Although the structure of **20** presages its photolability, we were unable to obtain this compound in sufficient quantity for an independent study of its photochemistry. The structural assignment of **20** was based upon its NMR spectrum and upon the spectrum of compound **20D** produced by irradiation of **14D.** In the deuterated product, the complex pattern in the olefinic region was replaced by a singlet for H_a and broad singlets for H_b and H_c in which splitting by deuterium was barely discernible.



14D **20D**

Direct Irradiation. Irradiation of **11** in benzene gave biacetyl, dimers of the 1,1-dimethylallyl radical, and turnaround ketone **22,** in which the allylic moiety is attached via its other end to the acyl group. Although the latter product is formally the result of a 1,3-acyl shift reaction, it could equally well be formed from cage or noncage acyl-allyl radical recombination. It is likely that at least some of the turnaround ketone comes from recombination of *free* radicals because both acetyl and dimethylallyl radicals must escape the solvent cage to recombine with their own species. Formation of free radicals was confirmed by isolating products **31** and **32** from irradiation of **11** in the presence of 0.1

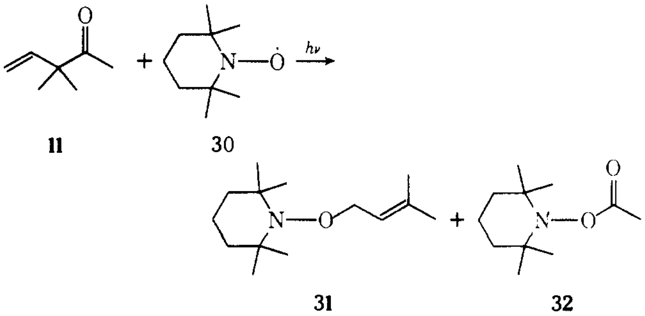


Table II. Distribution (%) of Hydrocarbons from α-Cleavage of β,γ-UK's[a]

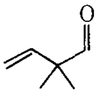
	A			B			C			
Precursor	tata	hata	haha	tptp	hptp	hphp	tatp	tahp	hatp	hahp
Azo-1,1-dimethylpropene	54	30	16							
Azo-1,1-dimethylpropyne				10	57	33				
11	65	25	10							
12				9	60	30				
13	59	27	14							
14	11	6	3	2	13	6	19	16	9	14

[a] The hydrocarbons are grouped according to whether they are dimethylallyl dimers (A), dimethylpropargyl dimers (B), or cross-recombination products (C). Each hydrocarbon is abbreviated by four letters: t = tail, h = head, a = dimethylallyl, p = dimethylpropargyl. For example, tahp is 3,3,6-trimethylhept-1-yn-5-ene.

M 2,2,6,6-tetramethylpiperidine-1-oxyl (nitroxyl, **30**); however, the yield of **22** was still 57% of its value without added nitroxyl (Table I). Approximately the same figure was obtained using 0.0625 or 0.11 *M* thiocresol as scavenger, suggesting that 43% of **22** comes from recombination of free radicals.

Since free radicals produce nearly half of the turnaround ketone, they should also recombine to regenerate starting material **11.** However, independent irradiation of **22** ($\Phi_{-k} = 0.31$) gave biacetyl and C_{10} hydrocarbons but only minute amounts of **11.** It follows that free acetyl and dimethylallyl radicals experience a barrier to recombination at the tertiary site. This is a surprising contrast to 1,1-dimethylallyl radicals which give a moderate yield of tertiary-tertiary (head-head) recombination (cf. Table II).

Nitroxyl trapping experiments were also carried out with **13** but only product **31** was observed. The failure to trap acyl radicals **33** and the constancy of the carbon monoxide yield (Table III) argue that **33** does not survive long enough to escape the solvent cage. Moreover, the yield of turnaround ketone **24** is unaffected by addition of 0.1 *M* nitroxyl. As expected from the great difference in stability between methyl and dimethylallyl radical, we conclude that the lifetime of **33** is much shorter than that of acetyl radical. In fact, **33** is even shorter-lived than phenylacetyl radical ($PhCH_2CO\cdot$, $\tau \sim 10^{-8}$ sec),[14] in accord with the greater stability of dimethylallyl than benzyl radical.[15] Since **33** is virtually nonexistent, irradiation of **13** should lead to a caged pair of 1,1-dimethylallyl radicals, a fraction of which should recombine before diffusing into the bulk of the solution. Indeed, addition of 0.1 *M* nitroxyl reduced the yield of C_{10} hydrocarbons by 63%. Assuming complete scavenging of free radicals, this implies a cage effect of 37%, which is comparable to the 45% found with the analogous azo compound.[16]



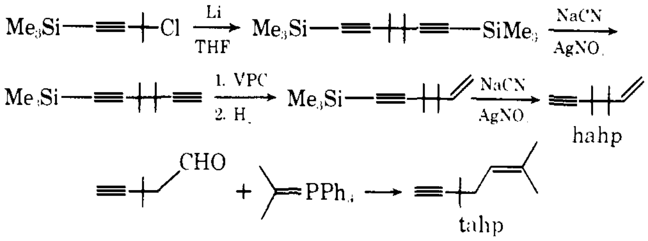
33

The three C_{10} hydrocarbons from photolysis of **11** and **13** were produced in approximately the same ratio as those from decomposition of the azo compound[16] corresponding to **13** (cf. Table II). Similarly, acetylenic ketone **12** gave the dimethylpropargyl radical dimers previously isolated from decomposition of the azo compound.[16] Compound **12** also produced biacetyl and turnaround product **23**, which was identical with the material synthesized by oxidation of 5-methylhexa-3,4-dien-2-ol.[17,18] It is noteworthy that **14** gave **25** but none of the allenic product analogous to **23**. The C_{10} hydrocarbons from **14** are particularly interesting because they provide information on recombination of two delocalized radicals.

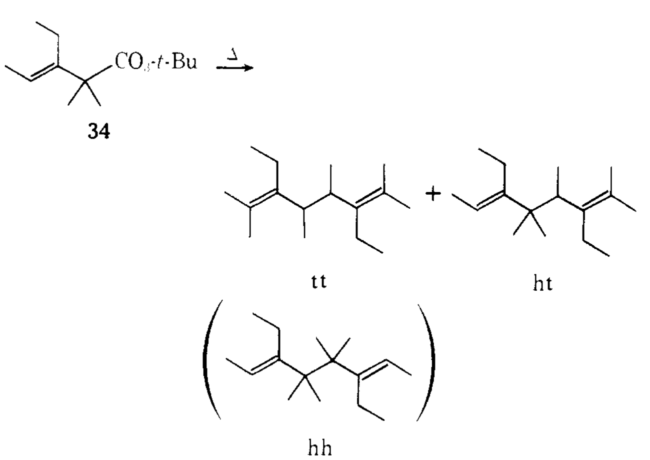
Table III. Nitroxyl Quenching Studies on 3,3,6,6-Tetramethylhepta-1,6,-dien-4-one (13)

Nitroxyl concn, *M*	CO, Φ^0/Φ	Reaction of 13, Φ^0/Φ	CO yield, %
0	(1.0)	(1.0)	70
0.01	1.04	1.15	77
1.0	1.44	1.53	74

These ten hydrocarbons were identified as follows. Five of them (groups A and B in Table II) could be isolated by preparative VPC of decomposed azo-1,1-dimethylpropene and azo-1,1-dimethylpropyne.[16] Although 2,7-dimethylocta-2,3,5,6-tetraene (tptp) was also produced from the azoalkane, it rearranged on preparative VPC. This compound was therefore synthesized independently[19] and its amount estimated by comparison with the figures from thermolysis of azo-1,1-dimethylpropyne. Of the group C products, tahp and hahp were prepared as shown below, while tatp and hatp could be isolated from photolysis of **14** by silver nitrate extraction and preparative VPC. The structure of all ten hydrocarbons was apparent from their NMR and ir spectra. Comparison of authentic materials with the components of the mixture was done by coinjection on a 250 ft × 0.02 in. SF-96 capillary VPC column and a 50 ft × ⅛ in. UCON 50 HB column. In view of the similarity between these products, they were assumed to have the same response factor on the flame ionization detector.



Although the singlet photochemistry of **11–14** arises solely from α-cleavage, the situation with **15** is considerably more complex. This compound is also potentially the most informative because none of its expected photoreactions are inherently undetectable. α-Cleavage was demonstrated unequivocally by characterizing both biacetyl and the expected C_{16} hydrocarbon dimers from irradiated **15.** The latter appeared as three VPC peaks whose retention time and area ratios matched those of thermolyzed perester **34.** The first two peaks were of the same area, but, since they were not



34

tt

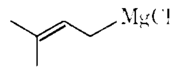
ht

hh

separable on preparative VPC, they were collected together. This fraction showed no olefinic protons in the NMR, suggesting that it was the meso and *dl* isomers of the tail-to-tail recombination product (tt). The third peak was somewhat larger than the sum of the first two and its NMR spectrum was in accord with the ht structure. The mass spectra of the two VPC fractions were nearly identical ($M\cdot^+ = 222$; base peak *m/e* 111). None of the hh product was detected.

Besides α-cleavage products and turnaround ketone **26**, we were also able to isolate oxetane **28** and a trace of two cyclobutanols **27**. By analogy with the interesting results of Dalton and Chan,[20] the cyclobutanols are assumed to be epimers; however, insufficient material was available to examine their stereochemistry. Oxetanes have been obtained previously[12,21,22] from cyclic β,γ-unsaturated ketones, but **28** is the first one found in an acyclic system. Since the number of alkyl groups on the double bond seemed to be the key factor in oxetane formation, it was considered important to examine ketone **16**. The difficulties encountered in preparing this compound were outweighed by a clean experimental result; direct irradiation gave only the oxetane **29**.

Synthesis of β,γ-Unsaturated Ketones and Selected Products. The synthesis of **11** and **13** from Grignard reagent **35** has been outlined previously[13] and a detailed procedure, using an electronic constant-rate addition funnel,[23] appears in the present experimental section. The key intermediate for compounds **12** and **14** is the β,γ-acetylenic acid **36**, which was an unknown compound at the outset of this work. In fact, very few β,γ-acetylenic acids or derivatives had ever been reported.[24-27] Most of the procedures were unsuitable for the synthesis of **36** and the ones which appeared promising were unsuccessful. The sequence by which **36** was finally prepared is shown in Scheme II.



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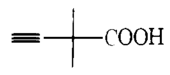
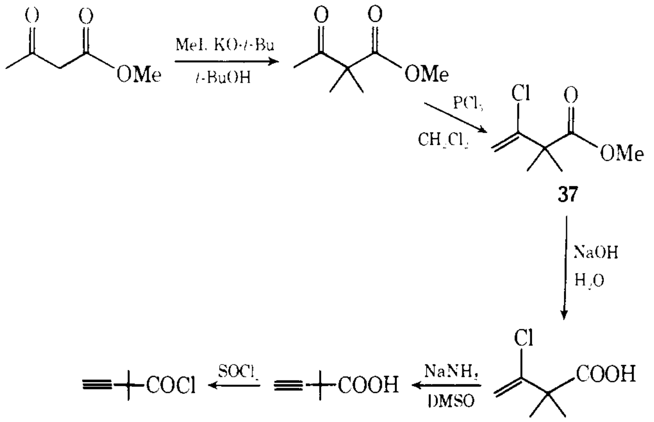


36

Fortunately, neither the reaction of the acid chloride of **36** with Grignard reagent **35** nor the reaction of acid **36** with methyllithium was complicated by involvement of the relatively acidic acetylenic proton. Viola[28] had reported earlier the successful preparation of the alcohol from propynal and allylmagnesium bromide. Very recently, French workers[29] claim to have found ketone **12** in a complex mixture of products from methylation of 3-pentyn-2-one; however, their spectral data are distinctly different from ours.

Scheme II



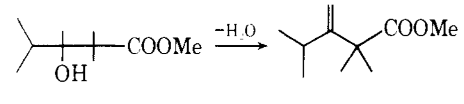
37

36

38

The preparation of **15** from 3-pentanone proceeded smoothly by the route employed previously[12] for cyclic β,γ-UK's. The (*E*) stereochemistry about the double bond is based upon the expected[30] greater stability of the (*E*) isomer and on the NMR spectrum of **15**. As in the case of (*E*)-3-ethylidene-2,2,5,5-tetramethylcyclohexanone,[31] neither allylic nor homoallylic coupling is observed. The (*Z*) isomers of both compounds, on the other hand, show these couplings.

Attempts to prepare **16** by the same sequence starting from methyl isopropyl ketone yielded exclusively the wrong isomer (**40**) on dehydration of the adduct **39**. This result is less surprising when one realizes that the disubstituted olefin **41** is actually more stable than its trisubstituted isomer **42**.[30]



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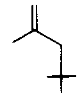

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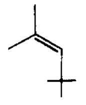
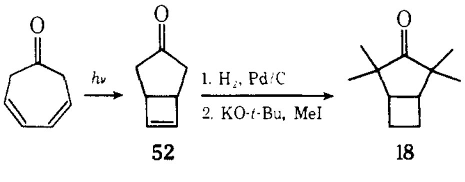


42

A search of the literature revealed that ester **45** had supposedly been made[32] by the route shown with dashed arrows in Scheme III; however, our attempts to repeat this work gave entirely different results. The reaction which was claimed[32] to give **43** actually produced **46** as the major product plus minor amounts of both geometric isomers of the α,β-unsaturated nitrile. Dimethylation of this product gave not **44**, but **47**, whose structure was confirmed by hydrolysis to **48**, which was identical with the acid produced by saponification of ester **40**. The melting point of **48** agreed with that reported for the carboxylic acid in the older work.[32]

To circumvent the problem of the less substituted isomer being the more stable, **46** was hydrolyzed and isomerized to **49** under strongly basic conditions. As expected,[33] this tetrasubstituted isomer constituted over 95% of the equilibrium mixture. Because alkylation[34] of the carboxylic acid **49** was unsuccessful, it was first esterified to **50**, which could be smoothly dimethylated to **45**. Vigorous saponification of the latter afforded the desired carboxylic acid **51**. Conversion of **51** with methyllithium to the methyl ketone **16** was the most stubborn such reaction which we have encountered; however, an acceptable yield could be obtained after 2 days refluxing in ether.

An authentic sample of **18** was prepared by photochemical cyclization[35] of cyclohepta-3,5-dienone followed by hydrogenation and exhaustive methylation. This material was



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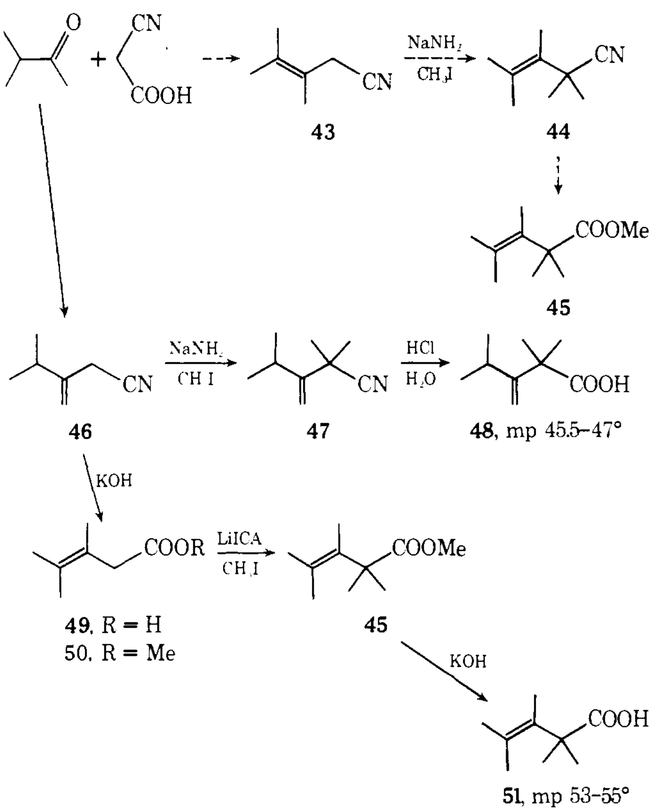
Scheme III

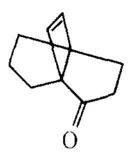


identical with that prepared by irradiation of **13**. Since it was important to establish the absence of **17** in the sensitized irradiation of **11**, an authentic sample was prepared from mesityl oxide and dimethyloxosulfonium methylide.[36] No trace of **17** could be detected in irradiated solutions of **11** under VPC conditions where the known product was easily observed. Ketone **22** was prepared independently by reaction of methyllithium with 4-methyl-3-pentenoic acid while **24** was made from Grignard reagent **35** and the appropriate acid chloride.

Discussion

Triplet Photochemistry. Little needs to be added to what has already been said[12] about the triplet state photochemistry of simple β,γ-UK's. ODPM rearrangment is not observed in any of the compounds examined here because olefin geometric isomerization is faster. Failure to detect an acetylcyclopropene from **12** may be due to its instability or to any number of mechanistic reasons.

The cyclization of triplet **13** and **14** is remarkable since this reaction must be faster than either cis-trans isomerization or ODPM rearrangement. It has been known for some time that β,γ-UK's can react intermolecularly at a rigid double bond; for example, **53** undergoes [2 + 2] cycloaddition with vinyl acetate.[37] On the other hand, attempts to photosensitize the reaction of **11** with vinyl acetate or ethyl vinyl ether led to no cycloadduct. These observations suggest that a large part of the reason why the flexible compounds **13** and **14** undergo cycloaddition is the presence of both partners in the same molecule. (The same reaction has been reported[38] for **56**.) The situation is analogous to that in α,β-enones, which will react with olefins only if the enone is rigid.[39] However, even flexible enones exhibit intramolecular cycloaddition when the second double bond is readily at hand (e.g., **57**).[40] The fact that neither **54** nor **55** showed any tendency to cyclize on irradiation in acetone demonstrates the importance of both the carbonyl and *gem*-dimethyl groups. The carbonyl probably lowers the triplet energy to a region accessible with acetone while the dimethyls would favor ring formation.[41]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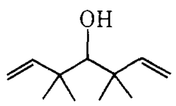
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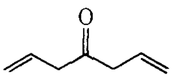
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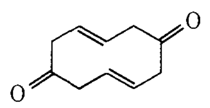
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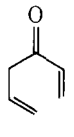
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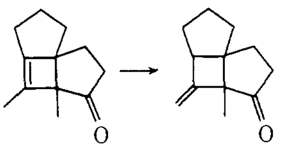
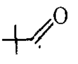
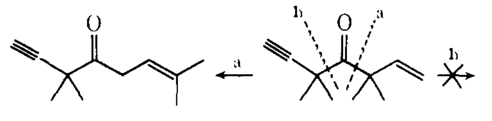
As indicated above, **20** arises by ring opening of the initial [2 + 2] olefin–acetylene adduct. This process normally has an activation energy in the region 31.5–36.1 kcal mol^{-1}; however, the bicyclo[3.2.0]hept-1(7)-ene ring system is known to be especially unstable.[42,43] Cargill and coworkers,[43] for example, found that compound **58** spontaneously rearranged to **59** or underwent an acid-catalyzed 1,3-acyl shift. Since neither of these rearrangements appears especially favorable in the cyclobutene leading to **20** and conrotatory ring opening of **58** would place a trans double bond in a five- or seven-membered ring, the difference in behavior between the two systems is not surprising.


58 **59**

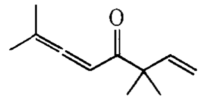
Singlet Photochemistry. The principal singlet reaction of β,γ-UK's **11–14** is a α-cleavage, as evidenced by the formation of hydrocarbon radical recombination products. It is clear from Table II that the dimethylallyl dimers (group A) and the dimethylpropargyl dimers (group B) are produced in essentially the same proportion regardless of the precursor. Thus, the figures reflect the inherent reactivity of such radicals and are not biased by special mechanisms for hydrocarbon production in one case (e.g., a cyclic seven-membered transition state in **13**). Although the factors governing dimethylallyl and dimethylpropargyl radical recombination have been discussed previously,[16] the cross recombination products (groups C) are a new aspect of the present work. Statistical considerations alone would predict a 25:25:50 distribution for hydrocarbons A, B, and C, whereas the observed ratio is 20:21:58. As expected, groups A and B are produced in equal amounts; however, their total is less than 50% of the mixture. This result is most readily explained by a nonzero cage effect for allylic–propargylic radical pairs, as was observed with **13**. The lifetime of acyl radical **60** is therefore not so long that it completely escapes the initial solvent cage.


60

Besides producing an interesting array of hydrocarbons, ketone **14** provides a unique opportunity to examine the competition between α-cleavage of two very similar groups, dimethylallyl and dimethylpropargyl. Irradiation of **14** gave only the dimethylallyl turnaround product **25**, and none of the dimethylpropargyl turnaround product **61**, suggesting that cleavage of bond a is more facile than bond b. However, when no other choice is available, as in **12** or in the



25 **14**



61

previously reported[44] 2-ethynylcycloheptanone, cleavage of the propargyl moiety will occur. By invoking the known sensitivity of α-cleavage to stability of the incipient radical,[45] we could rationalize this behavior if dimethylallyl radical were more stable than dimethylpropargyl. However, our previous studies of azo compound[16] and perester thermolysis[15] suggest that any difference between these groups is so small that even a competition experiment would show some of the less favored cleavage. We therefore choose to interpret the exclusive formation of **25** as a polar effect; that is, α-cleavage is assumed to involve buildup of positive charge at the leaving alkyl carbon. In this instance, the propargyl group would be less prone to cleave, on account of its electron-withdrawing properties.[15] This interpretation is in accord with the recent report of Lewis, Heine, and coworkers[46] that photochemical α-cleavage of deoxybenzoins is characterized by a ρ value of -1.1 for substituents in the benzyl moiety. On the other hand, we cannot strictly rule out a concerted 1,3-acyl shift for formation of **25** and this mechanism need not be governed by the same principles as apply to α-cleavage.

Another problem with which we must deal is the variation in $\Phi_{-\mathrm{K}}$ with ketone structure. In general, photochemical reactions do not proceed with unit efficiency because radiationless decay wastes some of the absorbed photons. It is apparent from the data in Table I that 32% of the light is ineffective in causing reaction of ketone **11** whereas 64% is ineffective in **13**. Four energy-wasting mechanisms which might operate in these ketones are (a) degenerate cis-trans isomerization of the double bonds, (b) noncage recombination of acyl-dimethylallyl pairs to regenerate starting material, (c) cage recombination of these pairs, and (d) radiationless decay of the excited singlet state. Our study[11] of stereospecifically deuterated **11** showed that the quantum yield for cis-trans isomerization under direct irradiation was only 0.02, which does not account for much of the energy lost in **11**, and by analogy, in **13**. Explanation (b) has already been ruled out for **11** since free acetyl and dimethylallyl radicals show little propensity for head recombination. The very short lifetime of **33** mitigates against noncage recombination in **13**.

Consideration of the two remaining alternatives, cage recombination and radiationless decay, leads to a rather detailed picture of the energy-wasting process. This is best understood by first examining the consequences of each process operating to the exclusion of the other, as illustrated in Scheme IV. Case I shows the fraction of excited singlets which would follow each pathway if all inefficiency were due to radiationless decay. The fraction of singlets which decays is set equal to $(1 - \Phi_{-\mathrm{K}})$ and caged radical pairs are presumed to behave like free radical pairs in giving no head recombination (vide supra). The problem with case I derives from our previously suggested[12] correlation of radiationless decay in β,γ-unsaturated ketones with the degree of charge transfer (CT) character in the lowest excited state. This correlation is represented in Figure 1 as a plot of quantum yield for ketone disappearance vs. the ionization potential (IP)[47] of the olefin π orbital. A lower IP leads to more

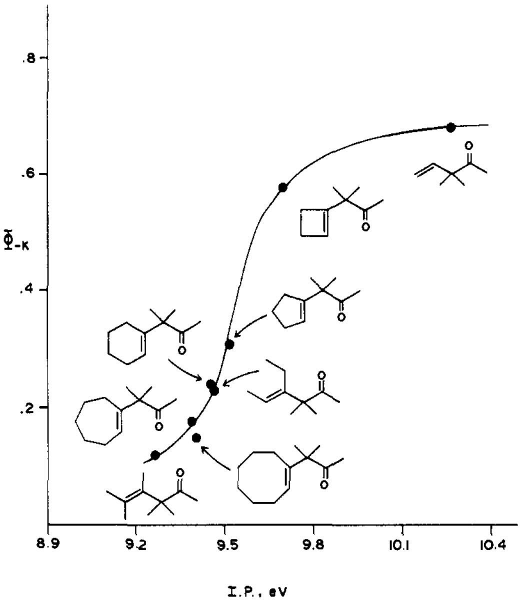
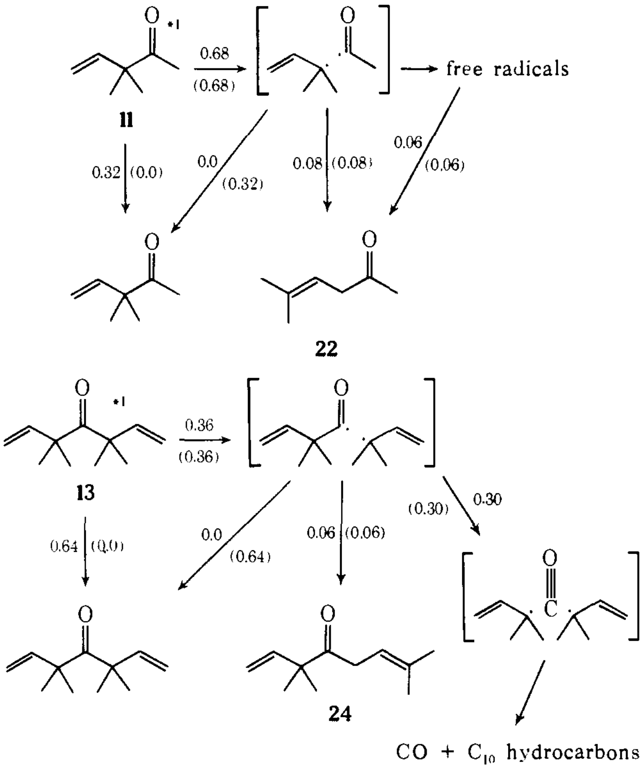


Figure 1. Quantum yield of ketone disappearance as a function of vertical olefin π ionization potential.

Scheme IV. Energy Wasting Pathways in Ketones 11 and 13[a]



[a] Case I, all inefficiency due to singlet radiationless decay; case II (numbers in parentheses), all inefficiency due to cage recombination.

CT character, which is associated with faster radiationless decay and hence a lower quantum yield.[12,48] At the high end of the reactivity scale, we observe a limiting value of 0.68 for $\Phi_{-\mathrm{K}}$. Since it is difficult to imagine why there should be a residual amount of radiationless decay when the π IP is high, we are inclined to seek another explanation. A further argument against case I is the very similar quantum yields for **11** and **12** even though these ketones surely differ in their rate of α-cleavage and the latter has a very high π IP.[49] The most logical alternative is case II, wherein cage recombination of the initial acyldimethylallyl pair is responsible for the quantum inefficiency. Although this process has been demonstrated in other ketones,[50-54] the present results (Scheme IV) require cage recombination with minimal rotation.[55] Thus, α-cleavage followed by extremely rapid radical recombination is the energy-wasting mechanism in ketones **11-13.** In an analogous case, Lewis and Magyar[50] reported that 20% of triplet excited (*S*)-(+)-2-phenylpropiophenone returns to starting material by cage recombination prior to rotation. These authors further concluded that a total of 53% of the initial radical pairs underwent cage recombination, compared with the 40% figure[56] for ketone **11** and the 40% reported by Schaffner et al.[53] for (*R*)-(+)-phenyl 1,2,3-trimethylcyclopent-2-enyl ketone.

We have previously noted[12] that the requirements for efficient oxetane formation from β,γ-UK's are a low olefin π IP and flexibility of the olefin moiety in the excited state. Since **11, 15,** and **16** are acyclic, they all meet the flexibility requirement; however, their IP_v's are 10.26, 9.46, and 9.26 eV, respectively,[47] suggesting that the oxetane yield should increase in this sequence. In fact, we were unable to detect oxetane from **11** whereas it was the only product found from **16.**

Experimental Section

General. Melting points were determined in capillary tubes on a Mel-Temp and are uncorrected. Ir spectra were taken on a Beckman IR8 while NMR spectra were run in CCl_4 on a Varian A-56/60-A or a Perkin-Elmer R-12 spectrometer. A CEC 21-110B was used for both high and low resolution mass spectra. Elemental analyses were performed by Elek Microanalytical Laboratories, Torrance, Calif. Gas chromatography was carried out on a Hewlett Packard Model 700. See Table IV for VPC columns and conditions.

Spectroquality acetone (MCB) was used without further purification in all sensitized irradiations while reagent grade benzene (Fisher) was dried over 4A molecular sieves for use in direct irradiations. A Hanovia 450-W mercury lamp with a potassium chromate filter solution and a corex filter sleeve was the light source in all photochemical experiments.

Synthesis of β,γ-Unsaturated Ketones. Grignard Reagent 35. A solution of 40 g of 2-methyl-4-chloro-2-butene (prepared by hydrochlorination of isoprene)[57] in 150 ml of anhydrous ether was added slowly (10 drops per min) to 100 g of magnesium turnings in 750 ml of anhydrous ether at −15 to −25° under nitrogen. This procedure was reduced from tedious to simple by using an electronically controlled constant rate addition funnel[23] and a refrigerated bath. A small amount of methylmagnesium iodide was used to initiate the reaction. After addition was complete, the gray suspension was stirred in the cold for 3 hr. The concentration of Grignard reagent was determined by adding a 3-cm³ aliquot to 25 cm³ of 0.2 *N* HCl and titrating to pH 7 with 0.2 *N* NaOH. The yield ranged from 60 to 85%.

2,2-Dimethyl-3-butenoic Acid. The above Grignard reagent was added to an excess of finely chopped Dry Ice. This mixture was stirred until all the CO_2 had disappeared, filtered into a separatory funnel, and then acidified. The product was extracted from the ether layer with 2 *N* NaOH, then the aqueous phase was acidified and extracted with ether. The ether was washed with saturated NaCl solution and dried over Na_2SO_4. The residue from ether was distilled to afford a clear liquid, bp 96-98° (30 mm) (lit. 82-83° (10 mm),[58] 184-187°,[59] 185° (760 mm)).[60,61]

2,2-Dimethyl-3-butenoyl Chloride. The above acid was added dropwise to a stirred 20% molar excess of thionyl chloride. After addition was complete, the mixture was heated to 95° for 1.5 hr and then distilled under reduced pressure. The product boiled at 38-39° (30 mm).

3,3,5,5-Tetramethylhepta-1,6-dien-4-one (13). A 15% molar excess of Grignard reagent **35** was forced with nitrogen pressure into an addition funnel mounted on a flask which contained a 20% solution of 2,2-dimethyl-3-butenoyl chloride in ether. The solution of **35** was added rapidly with good stirring and the mixture was then refluxed for 4 hr. After cooling, any suspended magnesium was removed by filtration through cotton, and an excess of 10% HCl was added to the ether solution. Workup in the usual manner, drying over sodium sulfate, rotary evaporation of the ether, and vacuum distillation afforded dienone **13** in 72% yield, bp 74-75° (16 mm). Anal. Calcd for $C_{11}H_{18}O$: C, 79.47; H, 10.91. Found: C, 79.14; H, 10.89.

Table IV. VPC Columns and Conditions

Compound	Column for Φ determination[a]	Temp, °C	Internal standard	Column for product isolation	Temp, °C
11[b]	a(S,T)	130	Chlorobenzene	f(S)	120
12[b]	a(S,T)	130	*m*-Xylene	f(S)	125
13[b]	b(S)	130	Dodecane	f(S)	155
	a(T)	120	Dodecane	f(T)	160
14[c]	a(S,T)	135	Chlorobenzene	f(S,T)	145
15	c(S,T)	110	*m*-Xylene	g(T)	110
	d(S)	115	Dodecane	h(S)	105
16	d(S,T)	115	Dodecane	h(S)	110

[a] (S) = singlet products, irradiated in benzene; (T) = triplet products, irradiated in acetone. [b] Ratio of C_{10} hydrocarbons was measured on column e. [c] Ratio of C_{10} hydrocarbons was measured on columns i and j.

Table V. Identification of VPC Columns

Letter	Column	Letter	Column
a	$^{1}/_{8}$ in. × 10 ft 10% XE-60	f	$^{1}/_{4}$ in. × 10 ft 10% XE-60
b	$^{1}/_{8}$ in. × 6 ft 20% DEGS	g	$^{1}/_{4}$ in. × 20 ft 8% OV-17
c	$^{1}/_{8}$ in. × 15 ft 5% OV-17	h	$^{1}/_{4}$ in. × 6 ft 10% OV-17
d	$^{1}/_{8}$ in. × 18 ft 10% SP-1000	i	0.02 in. × 250 ft SF-96
e	$^{1}/_{8}$ in. × 25 ft 10% Apiezon L	j	$^{1}/_{8}$ in. × 50 ft 10% UCON 50 HB

3,3,5,5-Tetramethylhept-1-yn-6-en-4-one (14). Reaction of Grignard reagent **35** with 2,2-dimethylbutynoyl chloride by the above procedure gave an 85% yield of **14,** bp 77-78° (15 mm). Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.34; H, 9.81.

3,3-Dimethylpent-4-en-2-one (11). 2,2-Dimethylbutenoic acid was treated with methyllithium for 5 hr as previously described,[12] bp 54-56° (70 mm). The NMR data for **11** were in good agreement with those in the literature.[62]

3,3-Dimethylpent-4-yn-2-one (12). 2,2-Dimethylbutynoic acid (**36**) was treated with 3 equiv of methyllithium for 6 hr at ambient temperature as previously described.[12] A 91% yield of **12** was obtained, bp 51-53° (65 mm). Anal. Calcd for $C_7H_{10}O$: $M^{\cdot +}$ 110.0731. Found: 110.0737.

1-Deuterio-3,3,5,5-tetramethylhept-1-yn-6-en-4-one (14D). One gram of ketone **14** was added to a solution of a 5% molar excess of sodium methoxide in 20 ml of D_2O and stirred vigorously for 30 min. The deuterated ketone was extracted out with ether, dried with sodium sulfate, and purified by bulb-to-bulb distillation.

5-Deuterio-3,3-dimethylpent-4-en-2-one (11D). A 3.7-g portion of 2,2-dimethylbutynoic acid (**36**) was stirred for 25 min with a solution prepared by cautiously treating 1.5 g of sodium metal with 45 ml of D_2O. The solution was cooled and nonacidic material removed by ether extraction. The aqueous phase was acidified with 3.5 g of P_2O_5 carefully dissolved in 35 ml of D_2O and the exchanged acid was extracted with ether. After drying over $MgSO_4$ and removing the solvent, an NMR spectrum showed no remaining acetylenic protons.

This deuterated acetylenic acid was reduced according to Castro[63] by dissolving a 3.7-g portion in a mixture of 110 ml of water and 80 ml of DMF. A 0.75 *N* $CrSO_4$ solution (150 ml) was then added under nitrogen with a syringe. After stirring vigorously for 30 hr, the solution was diluted with water, saturated with ammonium sulfate and extracted three times with ether. The ether was dried over $MgSO_4$ and 1 g of pure *trans*-(*E*)-4-deuterio-2,2-dimethyl-3-butenoic acid was isolated by distillation. More product could be obtained from the aqueous phase by making it basic and saturating with hydrogen sulfide. Removal of chromium sulfides

Table VI. NMR and Ir Spectral Data

Compound	NMR, δ, ppm				Ir, cm^{-1}
	CH$_3$	CH$_2$	Olefinic	Other	
11	1.20 (s, 6 H), 2.02 (s, 3 H)		5.08 (m, 2 q) 5.89 (q, 1 H)		1613 1712
12	1.34 (s, 6 H), 2.30 (s, 3 H)			2.19 (s, 1 H) Acetylenic	1722 2100 3330
13	1.28 (s, 12 H)		5.13 (m, 4 H) 6.22 (q, 2 H)		1696 1635
14	1.40 (s, 12 H)		5.06 (m, 2 H) 6.41 (m, 1 H)	2.38 (s, 1 H) Acetylenic	1628 1703 3325
15	0.96 (t, 3 H), 1.12 (s, 6 H) 1.65 (d, 3 H), 1.90 (s, 3 H)	1.53–2.24, (q, 2 H)	5.43 (q, 1 H)		1710
16	1.18 (s, 6 H), 1.50 (br s, 3 H), 1.73 (br s, 6 H), 2.00 (s, 3 H)				1711
17	1.08 (s, 3 H), 1.20 (s, 3 H), 2.16 (s, 3 H)			0.82 (m, 1 H), 1.0–1.3 (m), 1.82 (dd, 1 H), cyclopropyls	1690
18	1.02 (s, 6 H), 1.05 (s, 6 H)			0.95–2.80 (m, 6 H) ring	1733
19	0.93 (s, 6 H), 1.07 (s, 6 H)			1.95–2.22 (m, 6 H) ring	1737
20	1.11 (s, 6 H), 1.21 (s, 6 H)		5.83 (s, 1 H) ring, 4.95–5.60 (m, 2 H), 6.25 (q, 1 H)		1746
20D	1.11 (s, 6 H), 1.21 (s, 6 H)		5.12 (br s, 1 H), 5.37 (br s, 1 H), 5.83 (s, 1 H) ring		
21	1.09 (dist t, 3 H), 1.19 (s, 6 H), 1.47 (d, fine splitting, 3 H) 2.00 (s, 3 H)	1.91–2.40 (dist q, 2 H)	5.32 (br q, 1 H)		1710
22	1.64 (br s, 3 H), 1.77 (br s, 3 H), 2.01 (s, 3H)	2.99 (br d, 2 H)	5.34 (br m, 1 H)		1719
23	1.82 (d, J = 3 Hz, 6 H), 2.06 (s, 3 H)			5.42 (m, 1 H) allenyl	1683 1952
24	1.18 (s, 6 H), 1.59 (br s, 3 H), 1.73 (br s, 3 H)	3.10 (br d, 2 H)	5.19 (m, 3 H), 6.04 (q, 1 H)		
25	1.35 (s, 6 H), 1.60 (br s, 3 H), 1.72 (br s, 3 H)	3.40 (br d, 2 H)	5.28 (m, 1 H)	2.21 (s, 1 H) acetylenic	1629 1703 3327
26	1.04 (m, 3 H), 1.06 (d, 3 H), 1.76 (br s, 6 H), 1.99 (s, 3 H)	1.50–2.13, (m, 2 H)		3.43 (q, 1 H) methine	1710
27	1.00 (m, 3 H), 1.17 (s, 9 H) 1.57 (m, 3 H)		5.10 (2 overlapping q)	2.63 (m, 1 H) methine	3300–3640
28	0.80 (dist t, 3 H), 0.90 (s, 3 H), 1.18 (s, 3 H), 1.28 (d, J = 7, 3 H), 1.32 (s, 3 H)	1.35 (m, 2 H)		3.94 (q, J = 7 Hz) methine	
29	0.83 (s, 3 H), 1.04 (s, 3 H), 1.13 (br s, 3 H), 1.36 (br s, 9 H)				
C$_{16}$ hydrocarbons					
tt	0.65–1.22 (m), 0.93 (d, J = 7 Hz), 1.55, 1.64 (2s)	1.36–2.20 (m)		2.51 (m) methine	
ht	0.68–1.78 (m, 9 H), 0.91 (s, 6 H), 1.62 (d, J = 7 Hz, 3 H) 1.69 (s, 6 H)	1.45–2.30 (m, 4 H)	5.12 (q, J = 7 Hz)	2.78 (q, J = 7 Hz, 1 H) methine	
C$_{10}$ hydrocarbons					
tata	1.56, (br s, 6 H) 1.66 (br s, 6 H)	1.98 (m, 4 H)	5.10 (m, 2 H)		
hata	0.97 (s, 6 H), 1.56 (br s, 3 H), 1.67 (br s, 3 H)	1.93 (br d, J = 7 Hz, 2 H)	4.80 (m, 2 H), 5.06 (m, 1 H), 5.74 (q, 1 H)		
haha	0.97 (s, 12 H)		4.84, (m, 4 H), 5.98 (m, 2 H)		
tptp	1.70 (narrow m, 12 H)			5.36 (m, 2 H) allenic	
hptp	1.28 (s, 6 H), 1.70 (d, 6 H)			5.05 (sept, 1 H) allenic, 1.98 (s, 1 H) acetylenic	
hphp	1.37 (s, 12 H)			2.02 (s, 2 H) acetylenic	

Table VI *(Continued)*

	NMR, δ, ppm				
Compound	CH_3	CH_2•	Olefinic	Other	Ir, cm^{-1}
hatp	1.08 (s, 6 H), 1.69 (d, 6 H)		4.94 (m, 3 H) allenic and vinyl 5.82 (m, 1 H)		
tatp	1.66 (m, 12 H)	2.61 (br t, 2 H)	5.16 (m, 1 H)	4.85 (m, 1 H) allenic	1630 1963
tahp	1.15 (s, 6 H), 1.58 (br s, 3 H), 1.72 (br s, 3 H)	2.04 (br d, J = 7 Hz, 2 H)	5.18 (br t, J = 7 Hz, 1 H)	1.87 (s, 1 H) acetylenic	2108 3334
hahp	1.09 (s, 6 H), 1.19 (s, 6 H)		4.83 (m, 2 H), 5.92 (m, 1 H)	1.91 (s, 1 H) acetylenic	1634 2110 3334
31	1.09 (s, 6 H), 1.13 (s, 6 H) 1.62 (br s, 3 H), 1.71 (br s, 3 H)	4.17 (br d, J = 7 Hz, 2 H)	5.23 (br t, 1 H)	1.4 (br s, 6 H) ring	
32	1.04 (br s, 12 H), 1.96 (s, 3 H)			1.56 (br s, 6 H) ring	
36	1.52 (s, 6 H)			2.23 (s, 1 H) acetylenic	1712 3333 2500–3545
37	1.47 (s, 6 H), 3.77 (s, 3 H)		5.39 (s, 2 H)		1632 1741
38	1.48 (s, 6 H)		5.30 (s, 2 H)		1625, 1712 2480–3540
39	0.84, 0.98 (2d, J = 6.5 Hz, 6 H), 1.01 (s, 3 H), 1.17, 1.20 (2 s, 6 H), 3.66 (s, 3 H)			1.82 (sept, J = 6.5 Hz, 1 H)	
40	1.28 (s, 6 H), 1.05 (d, J = 7 Hz, 6 H), 3.61 (s, 3 H)		4.89 (s, 1 H), 4.95 (m, 1 H)	2.19 (sept, J = 7 Hz, with fine splitting, 1 H)	1640 1732
45	1.22 (s, 6 H), 1.45 (br s, 3 H), 1.63 (s, 6 H), 3.59 (s, 3 H)				1732
46	1.10 (d, J = 7 Hz, 1 H)	3.00 (m, 2 H)	5.01 (m, 1 H), 5.04 (m, 1 H)	2.33 (sept, J = 7 Hz, 1 H)	1640 2223
47	1.13 (d, J = 6.5 Hz, 6 H), 1.45 (s, 6 H)		4.99 (s, 1 H), 5.13 (d, J = 1 Hz, 1 H)	2.47 (sept, J = 6.5 Hz, 1 H)	1640 2240
48	1.07 (d, J = 7 Hz, 6 H) 1.34 (s, 6 H)		5.00 (s, 1 H), 5.06 (br s, 1 H)	2.28 (sept, J = 7 Hz, 1 H)	1640, 1701 3530–2500
49	1.70 (br s, 9 H)	3.02 (br s, 2 H)			
50	1.67 (br s, 9 H), 3.60 (s, 3 H)	2.97 (br s, 2 H)			1738
51	1.30 (s, 6 H), 1.58 (br s, 3 H), 1.69 (br s, 6 H)				1697 2500–3550

by filtration followed by ether extraction raised the overall yield to 90%.

The above deuterated acid was treated with methyllithium as in the preparation of **11**. The deuterated ketone showed exactly the NMR vinyl pattern expected from its structure.

Methyl 2,2-Dimethyl-3-oxobutanoate. This compound was prepared in 75% yield by alkylation of methyl acetoacetate with methyl iodide and potassium *tert*-butoxide in *tert*-butyl alcohol,[64] bp 65° (14 mm) (lit.[65] 74° (15 mm), 168° (720 mm)).

Methyl 2,2-Dimethyl-3-chloro-3-butenoate (37). A 115-g portion (0.55 mol, 31% excess) of PCl_5 was weighed into a 1-l. flask and 500 ml of CH_2Cl_2 (dried over 4A molecular sieves) were added. Sixty grams (0.42 mol) of methyl 2,2-dimethyl-3-oxobutanoate was added dropwise while stirring, followed by approximately 15 drops of DMF. The dropping funnel was replaced with a reflux condenser equipped with a $CaCl_2$ drying tube and the mixture was refluxed for approximately 24 hr. The reaction was followed by working up aliquots and injecting into column f at 180°. (See Table V for identification of VPC columns.) The desired product (**37**) had the shortest retention time; next came the starting material and finally a by-product, methyl 2,2-dimethyl-3,3-dichlorobutanoate. After the reaction was complete, the solution was cooled and poured into 100 ml of ice water. The CH_2Cl_2 layer was separated and washed twice with 200-ml portions of cold water and two–three times with saturated $NaHCO_3$ solution and dried over $MgSO_4$. The solvent was evaporated and the residue distilled at 17 mm: fr(1) bp 67° (mixture of starting material and **37**); fr(2) 67–69° (**37**, 40 g, 64.5%); fr(3) 71–80° (mixture of chlorinated products); fr(4) 80° (methyl 2,2-dimethyl-3,3-dichlorobutanoate).

2,2-Dimethyl-3-chloro-3-butenoic Acid (38). Ten grams (0.061 mol) of **37** were refluxed with 2.4 g (0.061 mol) of NaOH in 100 ml of water for 3–5 hr until most of the organic phase had dissolved. The solution was cooled to room temperature and extracted once with ether to remove unreacted starting material. The aqueous layer was acidified with cold 20% HCl solution and extracted three times with ether. The ether was dried over $MgSO_4$ and concentrated to yield 8.5 g of white solid. The acid was recrystallized from hexane: yield 93%, mp 60.5–63°. Anal. Calcd for $C_6H_9O_2Cl$: C, 48.49; H, 6.10. Found: C, 48.42; H, 6.12.

2,2-Dimethyl-3-butynoic acid (36). Sodium amide (17.8 g, 0.456 mol) was weighed into a 250-ml one-neck flask and 100 ml of anhydrous DMSO was added. The mixture was stirred at room temperature under a drying tube for approximately 2 hr or until no more NH_3 was given off. Chloroacid **38** (17 g, 0.114 mol) dissolved in 50 ml of DMSO was added dropwise. The mixture was stirred and warmed at 50° for 5 hr, then stirred at room temperature overnight. The cloudy, olive green solution was poured into cold 20% HCl solution, then extracted three times with ether. The ether extracts were washed with saturated NaCl solution, dried over $MgSO_4$, and concentrated to yield 12 g of crude acetylenic acid **36**. Purification was effected by distillation: bp 77–78° (5 mm), yield 11 g, 88%. Anal. Calcd for $C_6H_8O_2$: C, 64.30; H, 7.19. Found: C, 64.08; H, 7.19.

3,3-Dimethyl-4-ethylhex-4-en-2-one (15). The lithium enolate of methyl isobutyrate was treated with 3-pentanone as described previously[12] to give methyl 2,2-dimethyl-3-ethyl-3-hydroxypentanoate in 94% yield. This material was dehydrated with thionyl chloride in pyridine.[12] Methyl 2,2-dimethyl-3-ethyl-3-pentenoate was obtained in 85% yield, bp 89° (22 mm). Saponification[12] with refluxing KOH in ethanol for 4 hr afforded the carboxylic acid in 93% yield, bp 101-103° (1.7 mm) (lit.[58] 102-103° (2 mm)). The acid was treated with methyllithium for 14 hr at ambient temperature as described previously:[12] yield 90%, bp 63-65° (7.5 mm). Anal. Calcd for $C_{10}H_{18}O$: $M\cdot^+$ 154.1357. Found: 154.1354.

3-Methylene-4-methylpentanenitrile (46). The procedure of Van Heyningen[32] using cyanoacetic acid and 3-methylbutan-2-one gave a 79% yield of a mixture of **46** (85%) and the α,β-unsaturated nitriles (15%), bp 170-175°. Anal. Calcd for $C_7H_{11}N$: C, 77.01; H, 10.16. Found: C, 77.03; H, 10.05.

2,2,4-Trimethyl-3-methylenepentanenitrile (47). Methylation of **46** was carried out with CH_3I and $NaNH_2$ in liquid NH_3, according to the published procedure,[32] bp 72-75° (20 mm).

2,2,4-Trimethyl-3-methylenepentanoic Acid (48). One gram of **47** was refluxed in 20% HCl for 5 hr. Extraction with ether and recrystallization from petroleum ether gave **48**, mp 45.5-47°. This product gave spectra identical with the material prepared by saponification of **40**. Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 68.92; H, 10.14.

3,4-Dimethyl-3-pentenoic Acid (49). A mixture of 44 g (0.404 mol) of **46** and 55 g (0.97 mol) of KOH was heated in ethylene glycol at reflux for 16 hr. The solution was cooled and poured into 1 l. of water. This was extracted with ether to remove any unreacted nitrile. The aqueous layer was then acidified and extracted three times with benzene. The benzene extracts were washed twice with saturated NaCl solution and once with H_2O and dried over $MgSO_4$. After removal of the benzene, the acid was distilled through a 2 in. helices packed column: bp 86-90° (5 mm), yield 34 g (stench). Anal. Calcd for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.30; H, 9.47.

Methyl 3,5-Dimethyl-3-pentenoate (50). Acid **49** (40 g) in 500 ml of MeOH with a trace of H_2SO_4 was refluxed for 3 hr. The solution was cooled and dried over Na_2SO_4. After removal of the MeOH, the residue was distilled to afford **50** in 78% yield, bp 61-62° (10 mm).

Methyl **2,2,3,4-Tetramethyl-3-pentenoate (45).** Lithium isopropylcyclohexylamide (LiICA) (70.5 mmol) was prepared from 11.3 g of isopropylcyclohexylamine in 75 ml of anhydrous THF and 33.0 ml of 2.1 *M* *n*-BuLi in hexane at 0° under N_2. After 30 min stirring, 10 g (70.4 mmol) of ester **50** was added. After another 30 min at 0°, 11.5 g MeI was added and the mixture was stirred for 2 hr at 25°. An aliquot taken at this point showed monoalkylated ester. The reaction mixture was cooled to 0° again and a second equivalent of LiICA added via a syringe. A white precipitate formed. This was stirred 45 min and the second portion of 11.5 g MeI was added. After stirring 4 hr at room temperature, the reaction mixture was poured into ice water and acidified. The usual workup procedure was followed. Distillation of the residue gave **45:** bp 72-74° (6 mm), yield 88%.

2,2,3,4-Tetramethyl-3-pentenoic Acid (51). Ten grams of ester (**45**) and 6.5 g KOH in 250 ml of ethylene glycol were heated at 200° for 2 hr. After cooling to room temperature, the solution was diluted with 1 l. of H_2O and extracted with ether to remove byproducts and unreacted ester. The aqueous layer was next acidified and carried through the usual workup (as with **49**). On attempted distillation of the residue at 1 mm, it solidified on the cold finger. It could be recrystallized from pentane to give a white solid, mp 53-55°, yield 80%. Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.07; H, 10.23.

3,3,4,5-Tetramethylhex-4-en-2-one (16). Methyllithium was refluxed for 24 hr with an ether solution of acid **51** as described[12] for analogous compounds. The yield of **16** was 55%, bp 83° (15 mm), but 35% of unreacted **51** could be recovered by extraction with aqueous hydroxide. Anal. Calcd for $C_{10}H_{18}O$: 154.1357. Found: 154.1355.

Synthesis of Authentic Products. 4-Methyl-3-pentenenitrile. Cyanoacetic acid (52 g), isobutyraldehyde (43.2 g), benzene (65 ml), NH_4OAc (9.3 g), and glacial acetic acid (18 g) were allowed to react according to Van Heyningen's procedure.[32] The final distillation at 30 mm afforded the desired nitrile in 61% yield, bp 75-77° (lit.[66] 66° (24 mm)).

4-Methyl-3-pentenoic Acid. Thirty grams of the above nitrile were heated with 3 equiv of KOH in ethylene glycol at 180° for 22 hr. The reaction was worked up as with **49**. After distillation, the product contained approximately 10% of the α,β-unsaturated isomer: yield 85%, bp 77° (2.2 mm) (lit.[67] 99° (10 mm)).

5-Methyl-hex-4-en-2-one (22). The methyllithium reaction on 4-methyl-3-pentenoic acid was carried out according to the usual procedure.[12] After stirring for 24 hr at room temperature, the crude product was distilled at 26 mm, bp 59-60°. Separation of the β,γ- from the α,β-unsaturated ketone was effected on a cold (2°) fluorsil column, eluting with 10% EtOAc-hexane. The β,γ isomer was further purified by bulb to bulb distillation. Anal. Calcd for $C_7H_{12}O$: 112.0877. Found: 112.0891.

3,3,7-Trimethylocta-1,6-dien-4-one (24). 4-Methyl-3-pentenoic acid was treated with thionyl chloride, as in the preparation of 2,2-dimethyl-3-butenoyl chloride (vide supra): yield 96%, bp 65-72° (25 mm) (lit.[67] 60° (15 mm)). Grignard reagent **35** was treated with the resulting mixture of α,β- and β,γ-unsaturated acid chlorides in the usual manner. After 3 hr reflux, a mixture of **24** and 3,3,7-trimethylocta-1,5-dien-4-one was obtained. The desired product was isolated by preparative VPC on column f at 140°. Its spectral properties were in excellent agreement with those of **24** isolated from irradiation of **13**.

1,6-Bis(trimethylsilyl)-3,3,4,4-tetramethylhexa-1,5-diyne. A 19.2-g portion of 1-trimethylsilyl-3-chloro-3-methyl-1-butyne[68] in 200 ml of anhydrous THF was refluxed for 8 hr with 1.4 g (0.20 mol) of lithium dispersion (containing 2% sodium). After cooling, the mixture was filtered to remove any remaining lithium and then washed with water and saturated aqueous NaCl. The THF solution was dried over $MgSO_4$, concentrated on the rotary evaporator, and the residue recrystallized from hexane, mp 27-28°. The yield was close to 100%: NMR (CCl_4) δ 0.13 (18 H, s), 1.22 (12 H, s). Anal. Calcd for $C_{16}H_{30}Si_2$: 278.1885. Found: 278.1888.

3,3,4,4-Tetramethylhex-1-en-5-yne (hahp). The above material was partially cleaved by the procedure of Schmidt and Arens.[69] A 4.5-g portion of 1,6-bis(trimethylsilyl)-3,3,4,4-tetramethylhexa-1,5-diyne was dissolved in 50 ml of ether and 20 ml of ethanol. A solution of 2.7 g (0.016 mol) of silver nitrate in 10 cm^3 of water plus 20 cm^3 of ethanol was added dropwise, yielding a white precipitate. After stirring the mixture for 10 min, a solution of 5.5 g (0.085 mol) of KCN in 20 ml of H_2O was added. The precipitate dissolved immediately. The mixture was extracted three times with ether, and the extracts were washed with aqueous NaCl. After drying the solution with $MgSO_4$ and concentrating it, the residue was allowed to stand in the freezer. The resulting solid, which proved to be recovered starting material, was removed by filtration. The filtrate was diluted with 10 ml of water and extracted three times with pentane. After drying with $MgSO_4$ and removal of the pentane, the residue was bulb-to-bulb distilled. Preparative VPC ($\frac{3}{8}$ in. × 8 ft 10% XE-60 at 110°) was used to separate 3,3,4,4-tetramethylhexa-1,5-diyne from the desired mono(trimethylsilylated) compound: NMR (CCl_4) δ 0.12 (9 H, s), 1.31 (12 H, s), 1.97 (1 H, s); mp 26-27°.

1-Trimethylsilyl-3,3-4,4-tetramethylhexa-1,5-diyne (0.476 g) was hydrogenated in hexane over $Pd-BaSO_4$ with added quinoline.[69] After 50.8 ml of H_2 had been consumed, the catalyst was filtered off and the solvent evaporated: NMR (CCl_4) δ 0.14 (9 H, s), 1.06 (6 H, s), 1.11 (6 H, s), 4.73 (2 H, m), 5.93 (1 H, m).

The above product was cleaved with $AgNO_3$ and KCN as described above[69] to give 3,3,4,4-tetramethylhex-1-en-5-yne. (See Table VI for spectral data.)

3,3,6-Trimethylhept-5-en-1-yne (tahp). Five grams (11.6 mmol) of isopropyltriphenylphosphonium iodide,[70] which had been dried over P_2O_5 at 100° for 12 hr, was placed in a 250-ml three-neck flask under N_2. Addition of 100 ml of anhydrous ether followed by 6.9 ml of 2 *M* butyllithium produced a red color. After 3 hr of stirring, the solution was deep red but some yellow solid remained. The mixture was cooled to −48° and 0.64 g (5.8 mmol) of 3,3-dimethylpent-4-ynal[71] in 10 ml of ether was added dropwise. After warming to room temperature overnight, the mixture was still orange. It was cooled to −40° and water was added dropwise, forming a white precipitate. This was filtered off at ambient temperature and the ether layer of the filtrate was worked up in the usual manner. The residue was bulb-to-bulb distilled, yielding 0.2 g of clear oil. Anal. Calcd for $C_{10}H_{16}$: 136.1251. Found: 136.1239.

2,2,4-4-Tetramethylbicyclo[3.2.0]heptan-3-one (18). One gram of 3,5-cycloheptadienone (prepared according to Schuster)[35] was irradiated in acetone at 313 nm for 3 hr. The solvent was removed and the residue distilled to give bicyclo[3.2.0]hept-6-en-3-one (**52**), bp 58–61° (10 mm). This compound was hydrogenated over Pd-C in EtOH. The bicyclo[3.2.0]heptan-3-one was purified by filtering through celite, evaporating the ethanol, and bulb-to-bulb distilling. *t*-BuOK (11 mmol) in 25 ml of *tert*-butyl alcohol was prepared under N_2. Two hundred milligrams of bicyclo[3.2.0]heptan-3-one was added in 10 ml of *tert*-butyl alcohol. After stirring 15 min, 2 g of MeI was added and the solution was heated to reflux for 3.5 hr. The reaction mixture was cooled and diluted with water, then extracted into $CHCl_3$. The organic phase was washed with dilute HCl and saturated NaCl solution. The residue from $CHCl_3$ was bulb to bulb distilled, then purified further by preparative VPC on column f at 160°. This sample proved identical in VPC retention time, NMR, and ir with that of **18** isolated from irradiation of **13**.

5-Methylhexa-3,4-dien-2-one (23). 5-Methylhexa-3,4-dien-2-ol[72] (5 g) prepared using the method of Cowie and Landor[73] was added dropwise to a 5% solution of 71 g of CrO_3·pyridine in CH_2Cl_2. The black mixture was stirred at ambient temperature for 1 hr and then filtered through a layer of fluorisil. The filtrate was washed twice with cold 10% HCl and dried over K_2CO_3. Rotary evaporation of the solvent followed by distillation of the residue gave a mixture of **23** plus the starting material, bp 36° (5 mm). The product, which was isolated by preparative VPC on a 0.25 in. × 6 ft 10% XE-60 column at 125°, proved identical in retention time and spectral properties with **23** isolated from irradiation of **12**.

C_{16} Hydrocarbons (2,4,5,7-Tetramethyl-3,6-diethylocta-2,6-diene and 2,4,5,5-Tetramethyl-3,6-diethylocta-2,6-diene). 2,2,-Dimethyl-3-ethylpent-3-enoic acid (vide supra) was converted to its acid chloride using thionyl chloride in the conventional manner. This acid chloride (3 g) was treated with 2.4 g of sodium *tert*-butyl peroxide in CH_2Cl_2 according to the published[15] procedure. The crude product showed a carbonyl band at 1778 cm^{-1}, characteristic of the perester group. This material was decomposed by refluxing in benzene for 3 hours, after which no carbonyl band was present. Isolation of the hydrocarbons was carried out by preparative TLC using 10% ethyl acetate in hexane as eluent. The fastest moving band was collected and then subjected to preparative VPC on column h at 140°. The first VPC peak gave an NMR spectrum consistent with an equimolar mixture of meso and *dl* tail-to-tail (tt) dimer while the second proved to be the head-to-tail (ht) dimer. The identity of these materials was confirmed by mass spectroscopy which showed the correct molecular ion (*m/e* 222) and a base peak at *m/e* 111, the characteristic fragmentation mode of such dimers.

Isolation and Quantitative Determination of Photoproducts. Irradiation of ketones **11–16** was carried out as described previously.[12] Nearly all photoproducts were isolated by preparative VPC, using the columns and temperatures listed in Table IV. Since compound **26** did not separate completely from **15**, only an enriched sample could be obtained by VPC. Further purification of **26** was achieved by TLC on silica gel using 10% EtOAc in hexane as eluent.

Column j showed better separation of the C_{10} hydrocarbon mixture from irradiated **14** than did column i, but both revealed several minor, unidentified peaks. After an isothermal period at 60° for 25 min, the temperature with column j was programed at 1°/min to 100°. This gave the following relative retention times: hatp, 1.00; hata, 1.14; haha, 1.21; hptp, 1.46; hahp, 1.54; tahp, 1.63; hphp, 1.85; tata, 2.20; tatp, 2.48. Shaking the photolysate from **14** with concentrated aqueous $AgNO_3$ removed the acetylenes and allowed isolation of five hydrocarbons, including tatp and hatp, by preparative VPC on a 0.25 in. × 20 ft 10% Apiezon L column. The dimethylallyl dimers[74] and the dimethylpropargyl dimers[75] have been characterized by others. Comparison of photoproducts and authentic samples was always done by coinjection.

Trapping of Radicals from Photolysis of 11. A solution of 250 mg of **11** and 375 mg of 2,2,6,6-tetramethylpiperidine-1-oxyl (**30**) in 30 cm^3 of benzene was irradiated in a degassed, sealed Pyrex tube. After 8 hr, the orange color of the radical had disappeared and the solvent was removed by distillation.

The trapped radical products **31** and **32** were isolated by TLC on silica gel, eluting with benzene. **31** moved approximately half way up the plate whereas **32** was found just above the baseline. The structure of **31** was apparent from its NMR spectrum (Table VI) while that of **32** was confirmed by comparison with authentic material made by irradiation of biacetyl with **30**.

Acknowledgment. The authors are grateful to the National Science Foundation and The Robert A. Welch Foundation for financial support of this work.

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CNDO/2 Calculations on Geometries of Tetra- and Pentacoordinated Phosphoranyl Radicals and UHF Calculations on Tetracoordinated π-Ligand Phosphoranyl Radicals

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Abstract: Open shell CNDO/2 calculations have been performed with geometry optimization. The calculated geometries are in agreement with the symmetry as derived from ESR data. Phosphoranyl radicals are found to have trigonal bipyramidal geometries, with the exception of π-ligand phosphoranyl radicals, which have tetrahedron-like geometries, when strong electron withdrawing ligands are absent. In a few calculations square pyramidal geometries were considered as deviations from ideal T or TBP structures. The spin densities, however, cannot be calculated accurately with CNDO/2. A π-electron model is proposed to calculate spin densities in tetracoordinated π-ligand phosphorus complexes, in which the five 3d orbitals of phosphorus are included in the calculation. These spin densities are found to be in good agreement with ESR experiments. The success of this model, where only π electrons are explicitly calculated, is explained.

Recently much interest has arisen in the characterization of pentacoordinated phosphorus compounds. In the case of alkyl-alkoxy phosphoranyl radicals, Davies et al.[1] and Krusic et al.[2] have established by ESR measurements that the radicals have a trigonal bipyramidal (TBP) configuration, in which the unpaired electron is situated in an equatorial (basal) position. This was concluded from the large phosphorus splitting constants (a_P) of 700-1000 G.

Recent work by Schipper et al.,[3] Rothuis et al.,[4,5] and Boekestein et al.[6] and also results from Lucken and Mazeline[7,8] indicate that much smaller (<40 G) a_P's are found when one or more ligands consist of a π-electron system. This suggests an essential difference in coordination in both types of radicals. We performed CNDO/2 calculations[9-11] on these radicals. With the help of a SIMPLEX procedure[12] the energetically best configuration was calculated, with optimal distances and bond angles. The first type of phosphorus radicals was found to have a TBP geometry, in accordance with experimental data. The odd electron and the ligands were all found to be situated in the positions that were experimentally established by Krusic et al.[2] When one or more of the ligands consist of a π-electron system the configuration is confirmed to be tetrahedron (T) like.[3-6] Recently, it has been established by Davies et al.[13] that in the case of phenylphosphoranyl radicals high splitting constants (500-1000 G) can be observed with electron-withdrawing ligands (2,2,2-trifluoroethoxy, chlorine, hydrogen, and methyl sulfide) linked to phosphorus. By repeating Boekestein's[6] experiments, Davies et al.[13] confirmed his observations and proposal for T geometry if no electron-withdrawing substituent is present. In both cases the geometry of the phenylphosphoranyl radicals has been confirmed by our CNDO/2 calculations. From the calculated spin densities it was then attempted to calculate phosphorus splitting constants. The pentacoordinated radicals have high a_P's (~700 G) and the tetracoordinated radicals have low a_P's (<80 G). The exact values of the small a_P's for some of the π-ligand radicals, in which we are especially interested, showed no good agreement with the results from the ESR experiments. In order to explain the low phosphorus splitting constants, we propose a model in which the phosphorus has sp_3 hybridization and the odd electron (the fifth "ligand") is delocalized over the five 3d orbitals of the phosphorus atom and the π-electron system. This implies a T-like configuration.[14]

Geometry Optimization with CNDO/2

In determining the geometry of the radicals, different trial configurations were chosen, i.e., T and TBP with different choices of apical (ap) and equatorial (eq) positions for the ligands. For some radicals we also calculated geometries which correspond with square pyramidal configurations. The bond lengths and a few bond angles were then optimized. This was not done for the bond angles at the