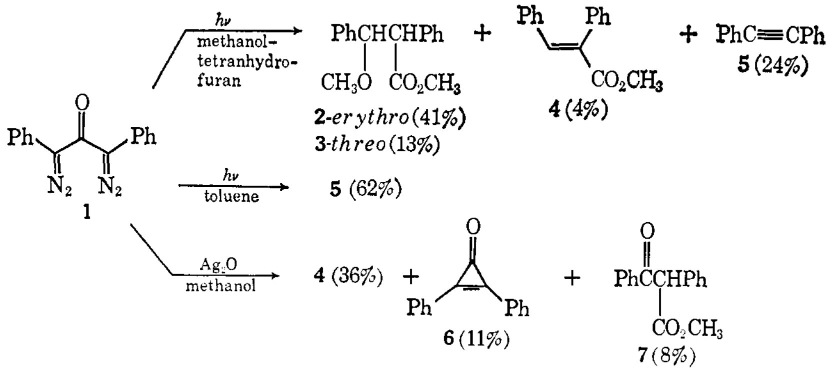
Scheme I



which generated the diformate and diacetate, respectively, provided further characterization.

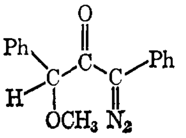
Irradiation of **1** in methanol–tetrahydrofuran (4:1) at −40° with a high-pressure Hanovia 450-W lamp with a Pyrex filter and separation of the products by preparative silica gel thin layer chromatography yielded *erythro*-methyl 2,3-diphenyl-3-methoxypropionate (**2**), *threo*-methyl 2,3-diphenyl-3-methoxypropionate (**3**), methyl α-phenylcinnamate (**4**), and diphenylacetylene (**5**) (Scheme I). Products **4** and **5** were identified by comparison with authentic samples; products **2** and **3** were characterized by spectral data; **2**: ir (CCl_4) 1733 cm^{-1} (C=O); nmr (CCl_4) τ 6.78 (singlet, 3 H), 6.29 (singlet, 3 H), 5.40, 6.35 (AB pattern, J = 11 Hz, 2 H), 2.92 (broad singlet, 10 H); mass spectrum: very small parent peak (<0.1%) at 270, base peak 121, exact mass, calcd: 270.12557, found: 270.12557 ± 0.00264; uv (methanol) λ_{max} 252 mμ (ϵ 7000); **3**: ir (CCl_4) 1733 cm^{-1} (C=O); nmr (CCl_4) τ 6.98 (singlet, 3 H), 6.61 (singlet, 3 H), 5.43, 6.30 (AB pattern, J = 9 Hz, 2 H); mass spectrum: very small parent peak (<0.1%) at 270, base peak 121, exact mass, calcd: 270.12557, found: 270.12557 ± 0.00264; uv (methanol) λ_{max} 252 mμ (ϵ 7150). Upon treatment with sodium methoxide in methanol **2** and **3** were converted into **4**.

It was determined that under the reaction conditions **4** is photostable and authentic diphenylcyclopropenone decarbonylates quantitatively to diphenylacetylene. Photolysis of **1** in toluene under similar conditions and separation by preparative silica gel thin layer chromatography resulted in isolation of **5** as the major product (Scheme I).

In order to determine whether **5** arises from diphenylcyclopropenone, **1** was irradiated at −40° with a monochromatic mercury vapor lamp at 4360 Å and with a No. 2 Sylvania photoflood, conditions at which authentic diphenylcyclopropenone was found to be stable. Using either light source, diphenylcyclopropenone was isolated with no trace of diphenylacetylene (**5**).

Decomposition of **1** in methanolic silver oxide, filtration, and separation by preparative silica gel thin layer chromatography resulted in isolation of methyl α-phenylcinnamate (**4**), diphenylcyclopropenone (**6**), and methyl benzoylphenylacetate (**7**), all identified by comparison with authentic samples. It was shown that under the reaction conditions, **6** is partially converted into **4** (Scheme I). Methanolic cuprous chloride decomposition of **1** also produced a small amount of **6**.

In the methanol photolysis, products **2**, **3**, and **4** appear to arise *via* a Wolff rearrangement process. That **2** and **3** greatly predominated over **4** suggests their origin from Wolff rearrangement of the diazo compound **8** formed by methanol insertion into the initially produced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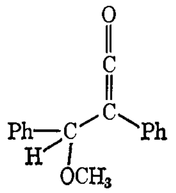
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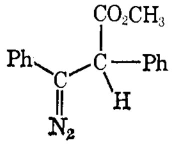
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carbene. Reaction of the formed ketene **9** with methanol could lead to the small amount of **4** as well as **2** and **3**. If diazo compound **10** had been formed (in analogy to the suggestions in the bisdiazocyclohexanone cases[1-3]), **4** would be anticipated to be the predominant product.[8] Thus, the results suggest that the cyclopropenone is the sole precursor of diphenylacetylene in the photolysis and of **4** in the silver oxide catalyzed decomposition.[9] These observations require consideration be given to a cyclopropenone pathway in the bisdiazocyclohexanone cases as well. Straining the cyclopropenone by bridging the olefin carbons with a short chain would enhance the reactivity of the carbonyl group toward water and alcohol addition, leading ultimately to α,β-unsaturated acids and esters.[10] Our studies in this regard are continuing.

Acknowledgments. We wish to thank the National Science Foundation for support of this work. P. J. W. expresses his appreciation to the National Institutes of Health for a predoctoral fellowship.

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Free-Radical Acetoxy Group Migration[1]

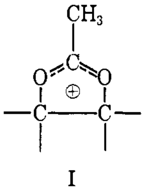
Sir:

The rearrangement of a group from one carbon atom to another has been recognized in a large number of free-radical reactions.[2,3] The ionic counterparts of

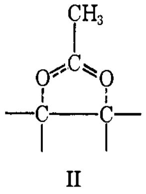
(1) Taken in part from the M.S. Thesis of F. C. P. Law, University of Alberta, 1969.

many 1,2 rearrangements have been shown to involve bridged intermediates[4–6] while free-radical migrations have failed, with the possible exception of the halogens, to show the involvement of nonclassical intermediates.[2,7]

We wish to report the preliminary results of our studies on the mechanism of a new example of a free-radical rearrangement, a 1,2-acyloxy migration. Acyloxy participation has been elegantly demonstrated, in carbonium ion systems, to proceed through the bridged intermediate I.[8] The generation of a radical center on a carbon atom adjacent to a neighboring acyloxy group could allow us to observe the formation of the bridged radical species, II, analogous to I.



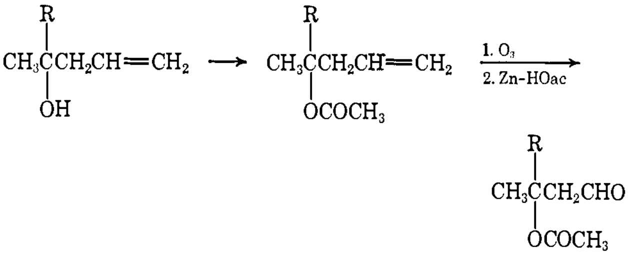
I



II

The benzoyl peroxide initiated decarbonylation of β-acetoxy-β-methylbutyraldehyde (III) and β-acetoxybutyraldehyde (IV) affords an opportunity to observe the reactions of two such radicals.

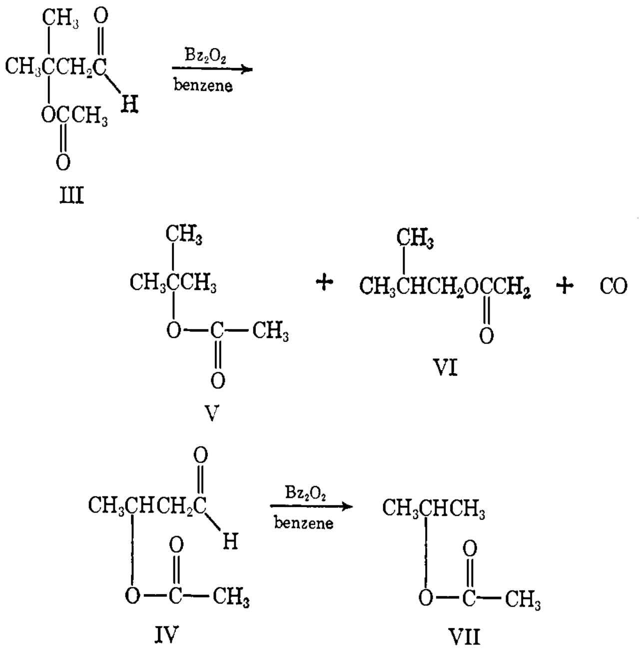
The syntheses of III (bp 71–72° (13 mm), n^{25}D 1.4210) and IV (bp 66–67° (10 mm), lit. 70–72° (12 mm[9]), n^{25}D 1.4183) were achieved by acetylation of the corresponding unsaturated alcohols followed by the reductive ozonolysis of the esters. The structures and purity of the aldehydes were verified by their microanalysis, nmr spectra, and glpc analysis.



III, R = CH$_3$
IV, R = H

The radical chain decarbonylation of III in benzene or chlorobenzene solution at 75° yielded both the unrearranged and the rearranged acetates, V and VI, while the decarbonylation of IV under the same conditions yielded only the unrearranged acetate VII.

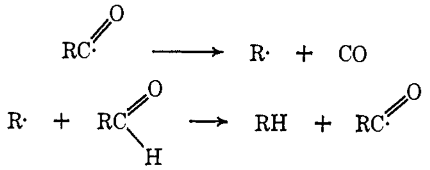
The individual components of each reaction mixture were identified by a comparison of their glpc retention times with those of authentic materials on three separate columns (Ucon Polar, SF-96, SE-30), and by their mass spectrum which was shown to be identical with those of the assigned materials.



III V VI IV VII

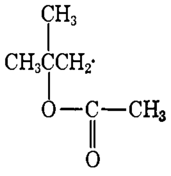
The observation of acetoxyl migration during the decarbonylation of III prompted us to investigate the mechanism of this rearrangement in greater detail.

The well-known mechanism[10] (eq 1 and 2) for free-radical chain decarbonylation of aldehyde III generates, with the loss of carbon monoxide, a radical whose possible structure is either A or B.

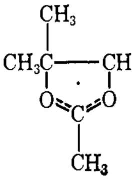


(1)

(2)

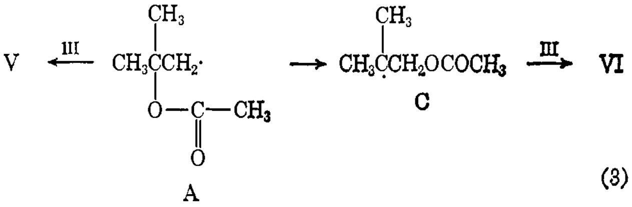


A



B

The classical radical, A, has a choice of chain transfer with III or rearrangement to a tertiary radical, C, prior to transfer (eq 3). The bridged radical, B, upon formation, would present a common intermediate for transfer with III to yield either the rearranged or unrearranged acetate VI and V (eq 4).



A C (3)

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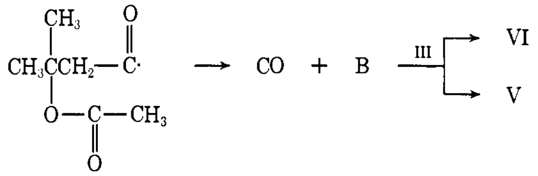
Table I. Products from the Benzoyl Peroxide Initiated Decarbonylation of III at 75°

Reaction	$[III]^0$ × 10^2 M	Solvent	Concn × 10^2 $M^{a,b}$ of products C_4H_7CHO	CH_3CO_2H	V	VI	III^f	VI:V
1	270.0	C_6H_6	44	6	26	2.5	108	0.09
2	94.06	C_6H_6	15	4.7	17	2.9	52	0.17
3	71.31	C_6H_6	14	4.4	13	2.7	33	0.20
4	50.38	C_6H_6	6.2	2.0	5.2	1.4	31	0.27
5	50.20	C_6H_5Cl		4.2	5.3	1.3	22	0.25
6	19.11	C_6H_6	4.4	1.0	1.5	0.6	4.4	0.43
7	18.80	C_6H_5Cl		2.0	1.4	0.8	11	0.57
8	10.76	C_6H_6	3.3		0.7	0.5	1.8	0.71
9	10.69	C_6H_5Cl			0.5	0.4	6.5	0.80

[a] Products V and VI were quantitatively analyzed on a 5% 1/8 in. × 13 ft SF-96 glpc column. The remaining products were quantitated using a 5% 1/8 in. × 13 ft Ucon Polar glpc column. The response of all products to the flame ionization detector was calibrated with an added standard, bromobenzene. [b] The symbols $[III]^0$ and $[III]^f$ refer to the initial and final concentration of aldehyde III after the reaction had been carried out for 72 hr.

In principle it is possible to distinguish between these two mechanistic possibilities since the relative rates of formation of the two products VI and V would be independent of aldehyde concentration if a common intermediate, B, were involved in their respective formations.



(4)

When benzene or chlorobenzene solutions containing varying concentrations of II (2.7–0.1 M) were heated (75°) with benzoyl peroxide (10 mol %) in sealed degassed Pyrex ampoules, for 72 hr, it was found that, aside from carbon monoxide, acetic acid, β-methylcrotonaldehyde, and unreacted starting material, only compounds VI and V where formed (see Table I). A material balance accounted for up to 93% of the starting aldehyde. Both the rearranged (VI) and the unrearranged (V) acetates were shown to be stable under the reaction conditions, while the starting aldehyde slowly yielded β-methylcrotonaldehyde by a concomitant thermal elimination. When isobutylene was added to the reaction mixture prior to reaction, it could be quantitatively reisolated at the conclusion of the reaction. Furthermore (see Table I), as the concentration of III was increased the ratio of V:VI increased uniformly.

The rapid rate of acetoxy radical decarboxylation,[11,12] the absence of isobutylene as a reaction product, and the lack of reaction of added isobutylene make an elimination–readdition process an unattractive mechanism for the observed rearrangement although this type of pathway, as a cage process, cannot be ruled out.[13–15]

The concentration dependence of the ratio of V:VI clearly demonstrated the absence of a common intermediate in the formation of both products and necessitates that structure B serves as a transition state, or an unreactive intermediate, on the path to the formation of the rearranged radical, C, the driving force for the reaction being the transformation of a primary radical into a more stable tertiary radical. Alternatively, structure B plus one of the other intermediate radicals (A or C) can function as the precursers for the formation of V and VI. Since bis(α-alkoxyalkyl) radicals have been proposed as stable species,[16] the involvement of B as an intermediate must be considered.

Under conditions identical with the ones necessary to produce rearranged acetate from the decarbonylation of III, the decarbonylation of IV yields only isopropyl acetate (VII), and it appears that the stability gained by the rearrangement of an acetoxy group from a secondary to a primary position is insufficient to overcome the activation energy necessary for its migration.

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A Novel Nitrosyl-Substituted Metal Carbonyl Cluster

Sir:

Metal nitrosyls and metal carbonyl clusters both are attractive potential homogeneous catalysts. The nitrosyls are frequently more reactive than isoelectronic carbonyls, and this tendency has been exploited in catalytic applications.[1,2] Clusters offer the possibility of catalysis involving more than one metal center, similar to the mechanism proposed recently by Schrauzer[3] for the catalysis of the dimerization of bicyclo[2.2.1]-heptadiene-2,5 by $Zn(Co(CO)_4)_2$. Unfortunately, clusters sufficiently robust to survive typical conditions for catalytic processes have in our experience often proved unreactive. In view of the apparent activating effect of coordinated nitrosyl, a reasonable synthetic objective is then the preparation of nitrosyl carbonyl clusters.

The well-known affinity of ruthenium for nitrosyl ligands suggested an investigation of the reaction of

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