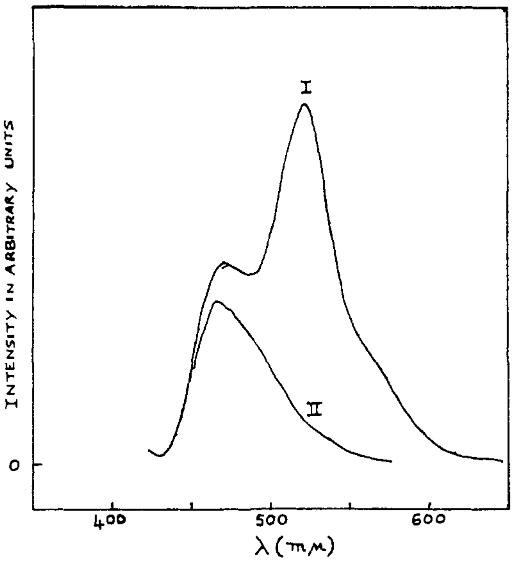

Figure 1. (I) Emission spectrum of 0.1 M biacetyl in aqueous solution. (II) Emission spectrum of 0.1 M biacetyl and 0.001 M $PtCl_4^{2-}$. Excitation at 405 mμ.

is more effective than $PtCl_4^{2-}$ (not shown in Figure 1). $PtCl_4^{2-}$ by itself did not show any luminescence. Thus the results of emission studies lead us to postulate triplet–triplet energy transfer from biacetyl to $PtCl_4^{2-}$. The quenching rate constant for the biacetyl–$PtCl_4^{2-}$ system calculated from the emission spectra (Figure 1) is about 3×10^7 $M^{-1}sec^{-1}$, which is considerably less than diffusion-controlled rates.

$PtCl_4^{2-}$ is known to undergo photoaquation with a quantum yield of 0.14 at 313, 404, and 472 mμ, and 0.65 at 254 mμ.[10] Photolysis of $PtCl_4^{2-}$ with 404-mμ radiation from a 1000-W xenon–mercury lamp yields $[PtCl_3 \cdot H_2O]^-$. The final spectrum of $[PtCl_3 \cdot H_2O]^-$ obtained by thermal equilibration of $PtCl_4^{2-}$ was found to be in complete agreement with the spectrum reported in the literature.[11]

Some quantitative measurements of the quantum yield for the photoaquation of $PtCl_4^{2-}$ both in the presence and in the absence of biacetyl as sensitizers have been made. With irradiation at 404 mμ and 0.034 M $PtCl_4^{2-}$ and 0.001 M $HClO_4$, a quantum yield of 0.16 ± 0.02 was obtained, which is in good agreement with the value of 0.14 reported in the literature.[10] A solution 0.5 M in biacetyl, 0.005 M in $PtCl_4^{2-}$, and 0.001 M in $HClO_4$ gave a value of 0.26 ± 0.02 with 404-mμ radiation, using reineckate[12] and ferrioxalate[13] actinometry. Balzani and Carassiti[10] interpreted the constancy of the quantum yield of 0.14 at 313, 404, and 472 mμ as due to a complete deactivation of the ligand field singlets (313, 404 mμ) and the triplet (472 mμ) to the lowest triplet (555 mμ) state, which could be the common precursor of the photoaquation having a quantum yield of 0.14. On the basis of our results on quantum yields the following scheme is proposed.

$$\text{(biacetyl)}_{S_0} \xrightarrow{h\nu} \text{(biacetyl)}_{S_1}$$
$$\text{(biacetyl)}_{S_1} \longrightarrow \text{(biacetyl)}_{T}$$
$$\text{(biacetyl)}_{T} \longrightarrow \text{(biacetyl)}_{S_0} + h\nu^1 \text{ (phosphorescence)}$$
$$\text{(biacetyl)}_{T} + \text{(complex)}_{S_0} \longrightarrow \text{(complex)}_{T}\ ({}^1A_{1g} \longrightarrow {}^3E_g)$$
$$\text{(complex)}_{T} \longrightarrow \text{product}$$

The higher yield of the sensitized reaction suggests the important result that the unsensitized reaction does not proceed by complete conversion of all higher excited states to the lowest triplet. In fact, since we report here a total yield for sensitized and direct reaction, it is true that the actual sensitized yield is larger than 0.26, and it may well be true that the quantum yield from the lowest triplet of the Pt complex is quite close to unity.

Acknowledgment. We thank the National Research Council (Canada) for support.

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Photolytic and Catalytic Decomposition of an α,α'-Bisdiazo Ketone. A Cyclopropenone Pathway

Sir:

Recent investigations into the photolysis[1,2] and silver oxide catalyzed decomposition[3] of α,α'-bisdiazocyclohexanones have resulted in isolation of the corresponding ring-contracted α,β-unsaturated acid or ester in yields ranging from 18 to 60% as the only characterized products. In each case, the products have been rationalized as having been formed *via* a Wolff rearrangement followed by a hydrogen migration, with no consideration given to the possibility of a cyclopropenone intermediate.

To study this possibility, the synthesis of 1,3-bisdiazo-1,3-diphenyl-2-propanone (**1**) was undertaken in the hope of isolating diphenylcyclopropenone. By the dropwise addition of *p*-toluenesulfonyl azide[4] to a solution of dibenzyl ketone and sodium ethoxide in ethanol at 0° followed by addition of water, orange solid was obtained and recrystallized in small amounts by dissolving in hexane at room temperature and cooling to −20° to give a 44% yield of **1**,[5] mp 93° dec. The spectral data were in agreement with the proposed structure:[6] ir (CCl_4) 2090, 2040, 2035 cm^{-1} ($C{=}N_2$), 1630 cm^{-1} ($C{=}O$); nmr (CCl_4)[7] τ 2.65 (broad singlet); uv (hexane) λ_{max} 264 mμ (ϵ 23,500), 324 (ϵ 7100); uv (methanol) λ_{max} 264 (ϵ 21,000), 328 (ϵ 10,100).

Treatment of **1** with sodium formate in concentrated formic acid and sodium acetate in glacial acetic acid

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(1) W. Kirmse, L. Horner, and K. Muth, unpublished; *cf.* W. Kirmse, *Angew. Chem.*, **71**, 539 (1959).

(2) R. Tasovac, M. Stefanovic, and A. Stojiljkovic, *Tetrahedron Letters*, 2731 (1967).

(3) R. F. Borch and D. Fields, *J. Org. Chem.*, **34**, 1481 (1969).

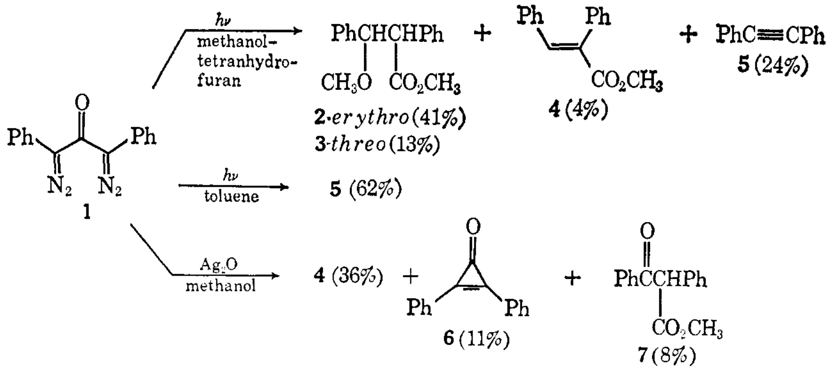
(4) W. von E. Doering and C. H. DePuy, *J. Am. Chem. Soc.*, **75**, 5956 (1953).

(5) J. B. Hendrickson and W. A. Wolf, *J. Org. Chem.*, **33**, 3611 (1968), obtained only the Wolff rearrangement product of the monodiazo ketone upon diazo group transfer to dibenzyl ketone.

(6) Elemental analysis confirms the composition.

(7) This nmr taken at +7° to avoid decomposition.

Scheme I



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

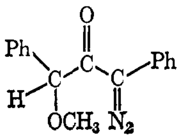
Irradiation of **1** in methanol-tetrahydrofuran (4:1) at −40° with a high-pressure Hanovia 450-W lamp with a Pyrex filter and separation of the products by preparative silica gel thin layer chromatography yielded *erythro*-methyl 2,3-diphenyl-3-methoxypropionate (**2**), *threo*-methyl 2,3-diphenyl-3-methoxypropionate (**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 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.



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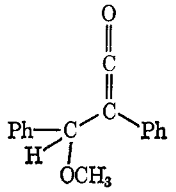

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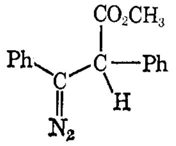

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Acknowledgments. We wish to thank the National Science Foundation for support of this work. P. J. W. expresses his appreciation to the National Institutes of Health for a predoctoral fellowship.

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[11] Alfred P. Sloan Foundation Fellow.

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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

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