On the Chemistry of α,α'-Bis(diazo) Ketones

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Abstract. The synthesis and decomposition of 2,6-bis(diazo)cyclohexanone (1) and 1,3-bis(diazo)-1,3-diphenylpropan-2-one (4) are reported. Cyclopropenones are established as intermediates in the photolytic decompositions. Thermal decomposition of 4 catalyzed by silver oxide and cuprous chloride also involves formation of 1,3-diphenylcyclopropenone. On the other hand, uncatalyzed thermal decomposition of 4 leads to 2,5-diphenyl-3,4-diazacyclopentadienone whose formation represents a novel electrocyclic ring closure. This fascinating intermediate behaves as both a dienophile with 2,3-dimethyl-1,3-butadiene and a diene with norbornene in cycloadditions. Control experiments associated with the above studies uncovered an unusually facile photodeconjugation of an α,β-unsaturated ester in which the normal intramolecular pathway is geometrically precluded.

1,n-Bis(diazo) compounds have the potential of being valuable intermediates for the synthesis of strained olefins as exemplified by eq 1. Two observations support such a


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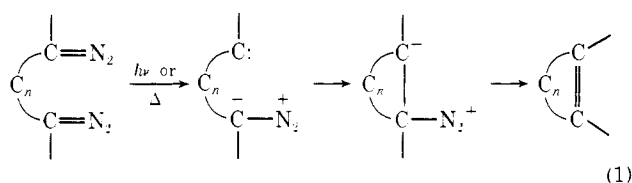
contention. Vicinal bis(diazo) compounds decompose *in situ* with production of acetylenes.[3-5] This route has led to the successful synthesis of a cycloheptyne[4] and an *in situ* trapping of cyclohexyne.[5] Alkynes may be considered to be the smallest cycloolefin (*i.e.*, eq 1, $n = 0$). Furthermore, generation of a potential electron-deficient carbon in close proximity to a diazo group has led to cyclization as illustrated by eq 2.[6,7] However, at the initiation of this work, no realization of the scheme represented by eq 1 existed.

(2)
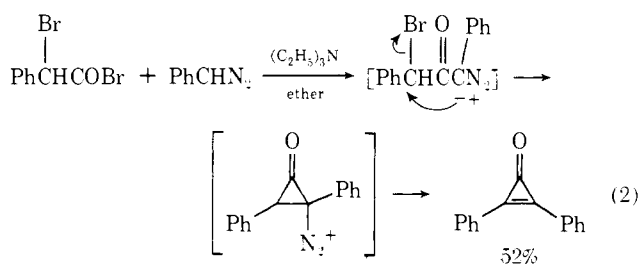
In 1959, Kirmse reported the ring contraction of 2,6-bis-(diazo)cyclohexanone (1, R = H) and interpreted the result on the basis of a Wolff rearrangement.[8] Later studies ob-


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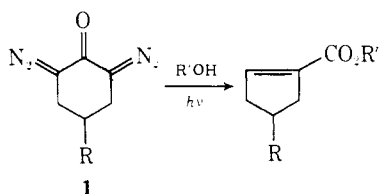
tained similar results.[9] An alternative explanation takes cognizance of the fact that in the proposed carbene intermediate, 1,3 overlap to form 2 which involves interaction of a carbanion with a carbene center should compete favorably with σ-bond migration. While 2 may fragment to the ketene 3, the exceedingly low activation energy associated with nitrogen disengagement for aliphatic diazonium salts suggests formation of the cyclopropenone would at least compete with (if not supercede) σ-bond cleavage. In this particular case, the facilitation of nitrogen disengagement by the eno-

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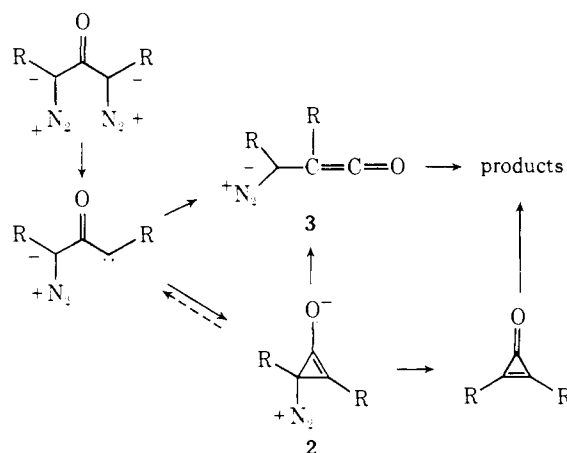
late should lower the activation energy of that process to such an extent that 2 may become an energy maximum (*i.e.*, a transition state). This possibility appeared to be an excellent point to begin our investigations of this approach to strained cycloolefins. In essence, it examines for the first time the effectiveness of a diazo function as a neighboring group to a carbene center.

Several successful cyclizations have been achieved,[10] most noteworthy being the formation of 3,3-dimethylcyclopropene.[11] Several reports indicate the decomposition of
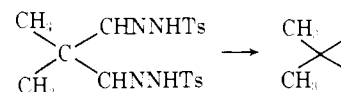
bis(diazo) compounds of 1,3,5-triketo systems to diacylacetylenes.[12] Cyclopropenones have been postulated as intermediates. α,ω-Bis(diazo) ketones have produced cyclic olefins in moderate yields although α,ω-bis(diazo) alkanes have been notably unsuccessful in such reactions.[13]

We wish to report our studies of the decomposition of a cyclic and an acyclic bis(diazo) ketone in which a cyclopropenone can be unambiguously established as the major primary product in at least the acyclic case. Furthermore, a facile synthetic route to the previously unknown 3,4-diazacyclopentadienone[14] has emerged.

Preparation of 1,3-Bis(diazo) 2-Ketones. We began our investigation with a detailed study of 2,6-bis(diazo)cyclohexanone. A brief discussion of the synthesis of this compound is in order since (1) no detailed experimental procedures are in the literature and (2) Tasovac, *et al.*,[9b] were unable to obtain this material.

Acid-catalyzed treatment of cyclohexanone in ether with methyl nitrite, prepared in an external generator *via* acidification of a methanolic aqueous sodium nitrite suspension,[15]

resulted in an 87% yield of 2,6-bis(oximino)cyclohexanone. Optimum yields require controlling the rate of generation of methyl nitrite so that the reaction temperature is kept at $10 \pm 5°$ with an external cooling bath. The exothermicity of the reaction caused darkening and total decomposition of the product if sufficient cooling was not provided.

Treatment of the bisoximino ketone with an alkaline chloramine solution[16] (prepared *in situ* from ammonium hydroxide, sodium hydroxide, and Chlorox) resulted in formation of the desired bis(diazo) ketone **1**, R = H, in 14% yield. Purification was accomplished by partial evaporation of solvent at room temperature or below followed by a very rapid elution through a silica gel column. Evaporation of all the solvent from the crude reaction mixture or slow elution through a silica gel or Florisil column resulted in rapid darkening of the material from which no diazo compound could be isolated. The spectral properties are in full accord with the assigned structure (see Experimental Section).

1,3-Bis(diazo)-1,3-diphenyl-2-propanone (**4**) was chosen as a system in which the proposed cyclopropenone would be directly detectable. The one-step diazo transfer method was attractive even though up to the initiation of our work bis(diazo) ketones had not been synthesized by this technique.[17,18] Treatment of dibenzyl ketone and sodium ethoxide in ethanol at $-3°$ with p-toluenesulfonyl azide, followed by addition of water, resulted in the formation of an orange precipitate of 1,3-bis(diazo)-1,3-diphenyl-2-propanone (see Scheme I). Because of the instability of **4**, purifi-

Scheme I. Generation and Characterization of 1,3-Bis(diazo)-1,3-diphenyl-2-propanone
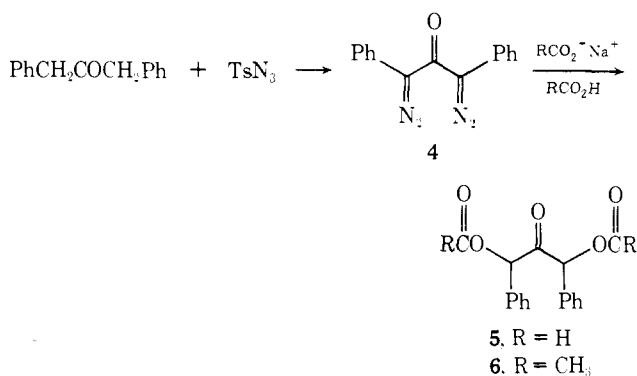

cation proved difficult. For example, thermal decomposition began to occur in hexane at room temperature within a few minutes. However, purification was achieved by swirling small portions in hexane for 1 min, filtering undissolved solid, and cooling the filtrate to $-20°$ to reprecipitate **4**. By this procedure, **4** could be recrystallized into long orange needles in 44% yield, which gave a satisfactory elemental analysis for $C_{15}H_{10}N_4O$. The infrared spectrum exhibited strong absorptions in the diazo region, a doublet at 2090 and 2085 cm^{-1}, and a singlet at 2040 cm^{-1}, as well as a medium intensity carbonyl stretching frequency at 1630 cm^{-1}, all characteristic of α,α'-bis(diazo) ketones.[9] Similarly, the ultraviolet absorption spectrum was typical of α,α'-bis(diazo) ketones;[9] maxima in methanol were observed at 264 and 328 nm with extinction coefficients of 21,000 and 10,000, respectively.

Further characterization of **4** was achieved by treatment with sodium formate in formic acid and sodium acetate in glacial acetic acid resulting in 1,3-diformyloxy-1,3-diphenyl-2-propanone (**5**) and 1,3-diacetoxy-1,3-diphenyl-2-propanone (**6**), respectively, both obtained as a mixture of the meso and racemic diastereomers (see Scheme I).

Results

A methanolic solution of 2,6-bis(diazo)cyclohexanone (**1**, R = H) was irradiated at $-40°$ for 2 hr, at which point the disappearance of the diazo band in the infrared region was complete (see Scheme II). Separation was achieved by pre-

Scheme II. Decomposition of 2,6-Bis(diazo)cyclohexanone (**1**)
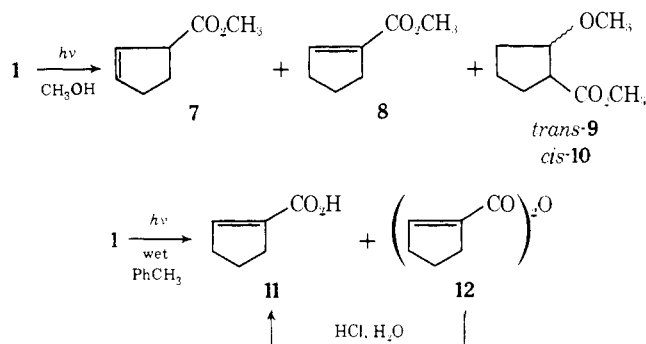
parative vpc to yield (in order of increasing retention time) methyl cyclopentene-3-carboxylate (**7**, 15%), methyl cyclopentene-1-carboxylate (**8**, 61%), methyl *trans*-2-methoxycyclopentanecarboxylate (**9**, 5%), and methyl *cis*-2-methoxycyclopentanecarboxylate (**10**, 10%). Control experiments demonstrate that **8**, **9**, and **10** are primary products. On the other hand, the unconjugated ester **7** appears to derive from **8**. Irradiation of a 1:4 mixture of **7** and **8** under conditions of the above photolysis resulted in complete isomerization into **7** in 4.5 hr.
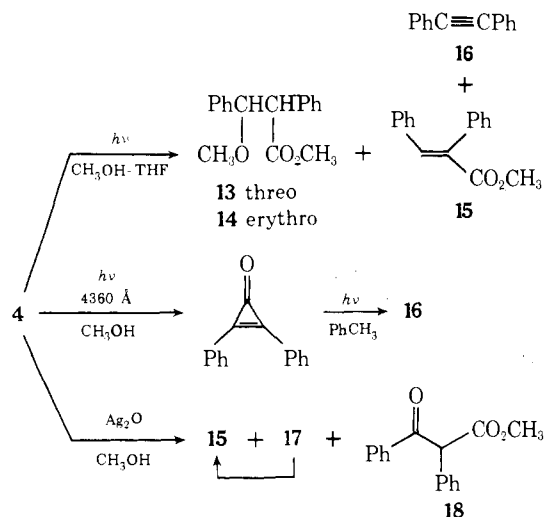
Structural assignments rested predominantly upon spectroscopic data (see Experimental Section). The assignments of the structures of **9** and **10** were confirmed by conversion of both into **8** upon treatment with methanolic sodium methoxide. The stereochemical assignments of these β-methoxy esters rest upon the nmr spectral shifts induced by europium tris(dipivaloylmethide) [Eu(dpm)$_3$]. The methyl singlets for the methoxy and carbomethoxy groups for the ester of shorter vpc retention time shifts from δ 3.19 and 3.60 to 3.77 and 4.97 upon addition of 30 mol % Eu(dpm)$_3$, whereas the shifts for the ester of longer vpc retention time are from δ 3.19 and 3.60 to 3.75 and 4.78.

Irradiation of **1** (R = H) in toluene or furan at $-40°$ or benzene at $10°$ containing a trace of water gave (in order of increasing vpc retention times) the ring contracted cyclopentene-1-carboxylic acid (**11**) and the corresponding anhydride **12** in a combined 65% yield (see Scheme II). The relative amounts of each varied with the amount of moisture in the solvent. Treatment of anhydride **12** with aqueous hydrochloric acid converts it quantitatively into the acid **11**. Photolysis of the bis(diazo) ketone in dry toluene or furan at $-40°$ or benzene at $10°$ yielded a yellow tar from which nothing could be characterized.

Irradiation of 1,3-bis(diazo)-1,3-diphenyl-2-propanone (**4**) at $-40°$ in a 4:1 (v/v) methanol–tetrahydrofuran solution for 4.5 hr and separation of the products by preparative tlc gave (in order of increasing R_f values) methyl *threo*-2,3-diphenyl-3-methoxypropionate (**13**, 41%), methyl *erythro*-2,3-diphenyl-3-methoxypropionate (**14**, 13%), methyl *trans*-2-phenylcinnamate (**15**, 5%), and diphenylacetylene (**16**, 24%) (see Scheme III).

An intense carbonyl stretching frequency at 1718 cm^{-1} in the ir spectrum and singlets in the nmr spectrum at δ 7.70 and 3.80 corresponding to the β proton of cinnamates and a methyl ester, respectively, are consistent with the assignment of **15**. This compound was shown to be identical with an authentic sample, prepared by the saponification of an authentic sample of ethyl α-phenylcinnamate and treat-

Scheme III. Photolytic and Catalytic Decomposition of
1,3-Bis(diazo)-1,3-diphenyl-2-propanone (4)

Table I. Effect of Solvent Composition on Photolytic
Decomposition of 4

% PhCH₃ in CH₃OH	% 16	% 13 + 14	Ratio 14:13	Ratio 16:(13 + 14)
0	20	57	4.2 ± 0.2	0.35
50	22	36	3.2 ± 0.3	0.61
80	26	32	3.9 ± 0.3	0.91
88	33	28	2.5 ± 0.5	1.14
100	65			

same conversion with sodium methoxide in methanol. The assignment of structure 18 rests on the spectral data and independent synthesis. Condensation of methyl phenylacetate with phenyl benzoate in the presence of sodamide yields a product identical with 18.[25] Decomposition of bis(diazo) ketone 4 with a methanolic cuprous chloride solution[26] at −15° led to a complex mixture from which the cyclopropenone 17 was the only identifiable product.

To complement the photochemical and metal ion induced decompositions, the bis(diazo) ketone 4 was decomposed thermally. In solution a rapid color change from orange-red to dark purple and ultimately to yellow was observed. The simple spectral properties and elemental analysis are consistent with both the "head-to-head trimer"[28] 1,4,6,7,8,10-hexaphenyl-2,3,11,12-tetraazatetracyclo[5.5.1.0²,⁶.0⁸,¹²]-trideca-3,10-diene-5,9,13-trione (19) and the "head-to-tail trimer" 1,4,6,7,10,12-hexaphenyl-2,3,8,9-tetraazatetracyclo[5.5.1.0.²,⁶.0⁸,¹²]trideca-3,9-diene-5,11,13-trione (20).

A satisfactory elemental analysis was obtained for C₄₅H₃₀N₄O₃. Mass spectrometry showed a small molecular ion peak at m/e 674, and a major peak at m/e 440 corresponding to a retrodiene reaction—loss of 2,5-diphenyl-3,4-diazacyclopentadienone (21). High resolution mass spectrometry confirmed the m/e 440 peak as having a molecular formula of C₃₂H₂₀N₂O₂ (440.15493). An appropriate metastable peak for the transformation 674 → 234 + 440 appeared at m/e 81.5. An osmometric molecular weight determination utilizing the quinone 22[27] (mol wt 648) as the standard was performed. By plotting ΔR/concentration (mmol/ml) vs. concentration, a k value of 405.5 was obtained for 22. Plotting ΔR/concentration (mg/ml) vs. concentration for 19 (or 20), an approximate zero concentration value of 0.60 was obtained. Using the equation, mol wt = k value/0.60, a molecular weight of 676 was obtained. Intense carbonyl stretching bands were observed at 1805 and 1733 cm⁻¹ and a band of medium intensity at 1672 cm⁻¹, consistent with a carbon-nitrogen double bond of a conjugated hydrazone. The nuclear magnetic resonance spectrum exhibited only aromatic absorptions.

ment of the α-phenylcinnamic acid with diazomethane. Diphenylacetylene (16) was shown to be identical in every respect with an authentic sample.

Spectral data (see Experimental Section) allow the assignment of structures 13 and 14 to the methoxy esters. Treatment of both esters with methanolic sodium methoxide effects elimination to methyl (E)-2-phenylcinnamate (15). Their nmr spectra allow assignment of stereochemistry.[19] The compound of smaller Rf value, 13, exhibited a methine coupling of 11.0 Hz, a methyl ester singlet at δ 3.68, and a methoxyl ether singlet at δ 3.20. The diastereomer of larger Rf value, 14, exhibited a methine coupling of 9.0 Hz, a singlet corresponding to the methyl ester at δ 3.40, and a singlet characteristic of a methoxyl ether at δ 3.00. In a comprehensive study of the nmr spectra of a series of 3-substituted 2,3-diphenylpropionates, the threo isomers have larger coupling constants of the methine hydrogens and a lower chemical shift for the methyl group of the ester than the corresponding erythro series.[19]

As a control experiment, irradiation of authentic diphenylcyclopropenone (17) in methanol-tetrahydrofuran (4:1, v/v) at −40° similar to the conditions of the photolysis of bis(diazo) ketone 4 resulted in the complete disappearance of starting material within 1 hr. Similar to earlier reports,[20,21] a quantitative yield of diphenylacetylene was obtained. Irradiation of bis(diazo) ketone 4 using either monochromatic light at 4360 Å or a visible region photoflood, conditions at which diphenylcyclopropenone was found to be photostable, indeed resulted in the isolation of diphenylcyclopropenone (see Scheme III). This material was easily identified by its characteristic infrared frequencies at 1850 and 1670 cm⁻¹.[22] Photolysis of 4 at −40° in an inert solvent such as toluene resulted in a 65% yield of the acetylene 16 as the only characterizable product.

Variation of the concentration of methanol in the toluene leads to a variation in the ratio of the acetylene to the methoxy esters as summarized in Table I. This ratio increases as the percentage of methanol decreases.

To compare the photolytic and catalytic decomposition, the bis(diazo) ketone 4 was treated with various metal salts. Reaction of a methanolic solution of freshly prepared silver oxide[9c,23] with 4 gives (in order of increasing Rf values) diphenylcyclopropenone (17, 11%), methyl benzoylphenylacetate (18, 8%), and methyl trans-α-phenylcinnamate (15, 36%) (see Scheme III). It was shown that under the reaction conditions 17 is slowly converted into 15, in general agreement with Bordwell and Crooks,[24] who effected the
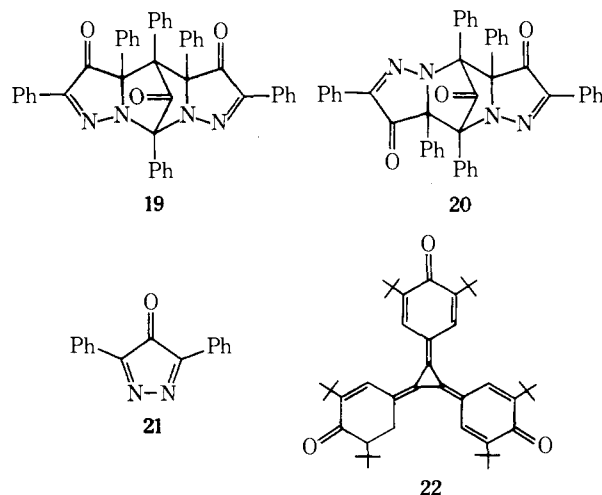

19

20

21

22

Cmr spectroscopy allows a differentiation between the "head-to-head trimer" structure **19** and the "head-to-tail" isomer **20**.[28] This spectrum exhibited three absorptions at δ 75.6, 80.8, and 87.2 characteristic of sp³ carbon atoms.[29] In addition, only two absorptions were observed for the sp² carbonyl carbons at δ 191.3 and 193.0 indicating either a plane or a C_2 axis of symmetry, *i.e.*, a bis-exo or a bis-endo structure. The sp² imine carbon absorptions fall in the same range as the sp² aromatic carbon absorptions[29] (δ 123.0–143.0), and the resultant complex absorptions in this region render interpretation useless. With the symmetry established by the carbonyl absorptions, only structure **19** allows three different sp³ carbons.

By following the thermal decomposition of **4** in hexane by ultraviolet absorption spectroscopy, isosbestic points were observed at 223, 243, and 353 nm. The ultraviolet absorption spectrum of **19** exhibited maxima at 236 and 325 nm with extinction coefficients of 21,000 and 5,400, respectively.

A number of possible mechanisms can account for this transformation, many invoking the intermediacy of 2,5-diphenyl-3,4-diazacyclopentadienone (**21**). When 1,3-bis-(diazo)-1,3-diphenyl-2-propanone (**4**) was allowed to decompose in hexane in the presence of 4–8 equiv of 2,3-dimethyl-1,3-butadiene or norbornene, only "trimer" **19** was obtained. However, utilizing these materials as solvent resulted in the formation of the corresponding adducts, 3,4-dimethyl-6,8-diphenyl-1,9-diazabicyclo[4.3.0]nona-3,8-dien-7-one (**23**) and 1,4-diphenyl-5,8-methylene-5,6,7,8-tetrahydrophthalazine (**24**) in 85 and 91% yield, respectively, as outlined in Scheme IV.

Scheme IV. Preparation and Trapping of 2,5-Diphenyl-3,4-diazacyclopentadienone (**21**)
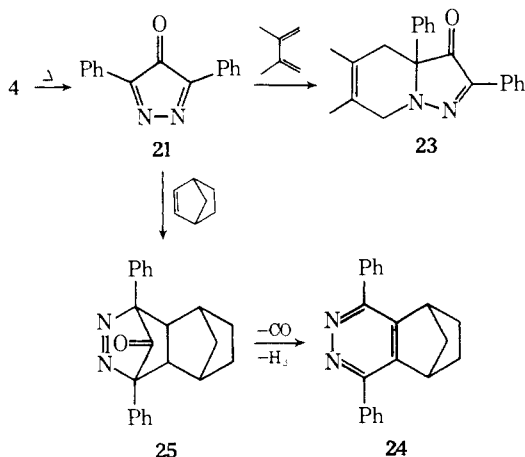

Discussion

The complexity of the behavior of α-ketocarbenes is underscored by the recent observations of their isomerizations to oxirenes.[30] In the present case, several features of the reaction detract from the straightforward rationale of a simple Wolff rearrangement. In addition to the arguments presented in the introduction, the exclusive formation of an α,β-unsaturated ester from the supposed precursor **26** is disturbing.
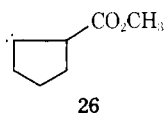

turbing. The accumulated evidence suggests electron-donating rather than electron-withdrawing groups facilitate hydrogen migration to a carbene center.[31] A reasonable perturbation on this mechanism is illustrated in Scheme V. The

Scheme V. An Alternative Wolff Rearrangement Mechanism
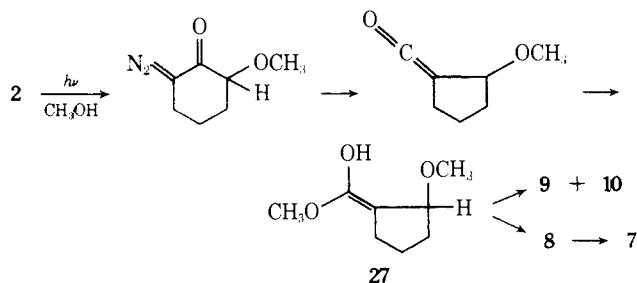
intermediate **27** economically accounts for formation of both the unsaturated and methoxy esters. Furthermore, it accommodates the exclusive formation of the conjugated ester. In accordance with this pathway, α'-substituted α-diazo ketones like **28**[32] and **29**[33] yield unsaturated esters as
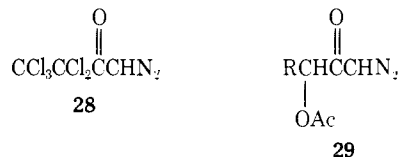
the major or exclusive products. However, the efficient (>91%) trapping of the initial carbene by solvent under photolysis conditions would be unprecedented. Furthermore, the results in moist toluene or furan are not in accord with such a mechanistic proposal. Some β-hydroxy carboxylic acid would have been expected to accompany the unsaturated acid. In acyclic systems such as **30**, solvent capture

R = Ar, PhCH₂, *i*-C₃H₇;

R' = BH₃, C₂H₅, C₃H₇
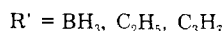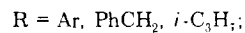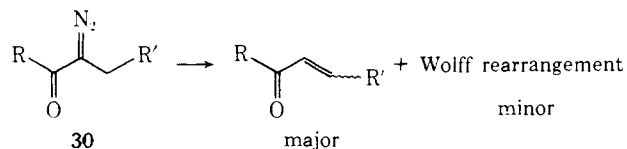
does not compete with hydrogen migration and Wolff rearrangement.[34] Thus, while the rationale proposed in Scheme V may account for some of the products, it cannot be the major pathway.

The intermediacy of the cyclopropenone **31** does provide a path to products through reaction with solvent. Such a reactive intermediate should be less strained than cyclopentyne (**32**) whose existence as a transient intermediate

seems reasonably secure.[35] All efforts to isolate products unambiguously derived from cyclopropenone **31** or its possible decomposition product **32** or to isolate adducts of **31** or **32** with toluene, furan, or benzene were unsuccessful.

The study of the acyclic derivative **4** provides support for the above interpretation. In addition to the β-methoxy esters and the conjugated ester, the products analogous to those obtained from **2**, a major product is diphenylacetylene. In the absence of a participatory solvent, the latter becomes the only isolable product of reaction. Control reactions clearly show, however, that the acetylene is a secondary product of photolysis. It arises from diphenylcyclopropenone. Under the conditions of the photolysis of the diazo compound, the latter is converted quantitatively to diphenylacetylene. More significantly, irradiation of **4** under con-

ditions in which the cyclopropenone is photolytically stable generates **17** as the exclusive product of the reaction. The origin of the methoxy esters **13** and **14** and the cinnamate **15** is less clear. Since basic methanol does cleave the cyclopropenone to methyl α-phenylcinnamate,[24] this intermediate accounts most economically for this product as well. On the other hand, no evidence suggests that this cyclopropenone (nor the cinnamate **15**) adds methanol to form the methoxy esters. Attempts to relate the formation of **13** and **14** to **16** led to ambiguous results. While a decrease in methanol concentration decreased the yields of **13** and **14** (see Table I), the yield of **16** did not increase proportionately. A common intermediate for the production of both types of products appears unlikely.

The metal salt induced decompositions reinforce the conclusion regarding cyclopropenone formation. Treatment of simple diazo ketones with silver oxide often leads to Wolff rearrangement,[23] whereas catalytic decomposition with copper salts produces quite different products.[26] In the case of the bis(diazo) ketone **4**, both methods gave results quite similar to the photolytic decomposition, namely, diphenylcyclopropenone or products derived therefrom, e.g., diphenylacetylene and/or methyl *trans*-α-phenylcinnamate. This lends credence to a very strong driving force for 1,3-π interaction which takes place regardless of the method of carbene generation.

A completely different behavior occurs upon the thermal decomposition of the bis(diazo) ketone **4**, a fact that suggests a carbene route is not operative. The formation of "trimer" **19** suggested the intermediacy of 2,5-diphenyl-3,4-diazacyclopentadienone (**21**).[18,36,37] The transient for-

mation of a deep purple color also supports such an intermediate since **21** has been obtained as a deep purple solid by the oxidation of 3,5-diphenyl-4-hydroxypyrazole.[37] Following the "trimerization" by uv spectroscopy, however, showed only replacement of the spectrum of starting material with that of product. Nevertheless, the formation of **21** in greater than 90% yield is unambiguously demonstrated by the successful trapping by 2,3-dimethylbuta-1,3-diene and norbornene. Diazacyclopentadienes **33** have been employed as dienes in a Diels–Alder reaction.[38]
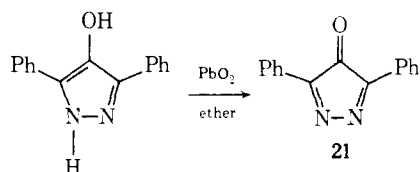

33. R = CH₃, Ph
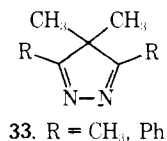
The most likely interpretation for the formation of **21** involves an electrocyclic ring closure of the bis(diazo) ketone to **34** followed by rapid disengagement of nitrogen to the
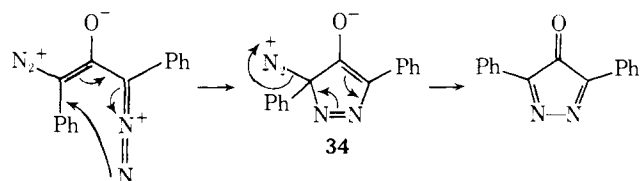
final product. This cyclization is isoelectronic with the facile pentadienyl to cyclopentenyl anion rearrangement.[39] This principle should be applicable to the synthesis of other heterocycles. The cyclization of vinyldiazomethane to pyrazole represents another example of this reaction type.[40]

A more perplexing problem is the origin of "trimer" **19**. The most direct pathway outlined in Scheme III involves the self-condensation of **21**.[41] Although such a mechanism has several deficiencies, the isolation of **21** as a purple solid eliminates this possibility.[37] The inability to trap **21** with 2,3-dimethylbuta-1,3-diene or norbornene unless these were used as solvents suggests that a different species present in these solutions such as the bis(diazo) ketone **4** has an unusual reactivity toward the diazacyclopentadienone **21**. A 1,3-dipolar mechanism as outlined in Scheme VI is espe-

Scheme VI. 1,3-Dipolar Pathway to "Trimer" **19**

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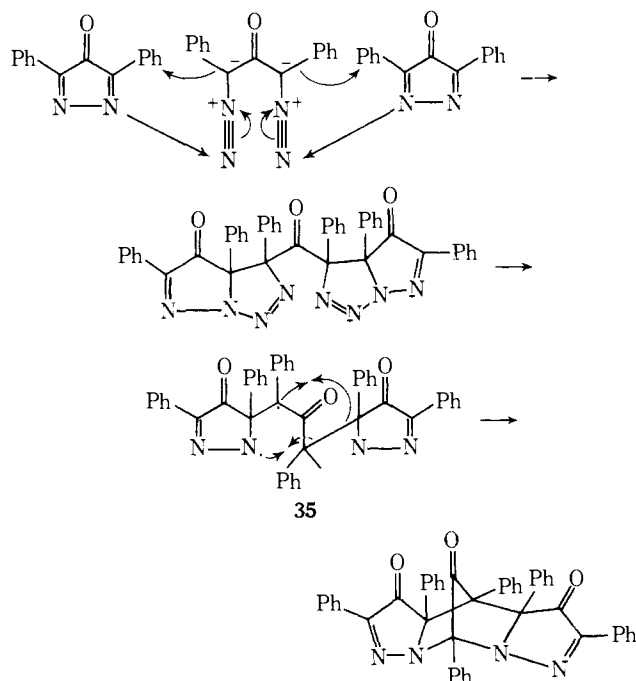
cially attractive because such additions of simple diazo compounds to imines are known.[42] Many variations on this theme involving the exact timing of bond making and breaking processes are possible. The scheme illustrated represents only the concept without making such detailed mechanistic judgments. Considerable precedent exists for the cleavage of the 2,3-bond of an aziridine even in a bicyclo[3.1.0] system somewhat analogous to **35**.[43]

In summary, three types of reactions of α,α'-bis(diazo) ketones involving 1,2-σ, 1,3-π, and 1,5-π interactions were observed. Strong evidence against a simple Wolff rearrangement developed. Indeed, when a nonparticipatory solvent is employed, the 1,3-pathway predominates and allows an approach to strained olefins. The complementary thermal behavior *via* a 1,5-π interaction provides a two-step synthesis of the difficultly accessible 3,4-diazacyclopentadienones and consequently many new heterocycles.

The formation of the α,β-unsaturated ester **7** as a secondary product of photolysis of **8** deserves special comment. Photochemical deconjugation normally involves a Norrish type II process involving a cyclic transition state as outlined below.[44-46] Thus, such a process would not be anticipated to
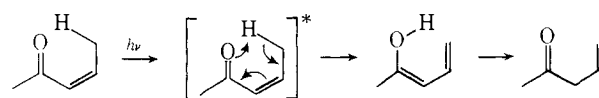
occur easily in cycloolefins. The photochemical deconjugation of acetylcyclooctene does occur and has been postulated to involve a *trans*-cyclooctene.[46] While photochemical isomerization of 1-acetyl-*cis*-cyclohexene to its trans isomer is proposed,[47] no evidence for the short-lived intermedi-

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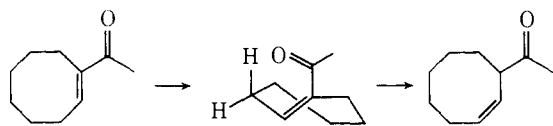
acy of a *trans*-cyclopentene has ever been reported.[48,49] Thus, it appears an intermolecular pathway would be more reasonable. The facility of such a process in cases in which the intramolecular pathway appears precluded has not been previously recognized.[50]

Experimental Section

Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra (ir) were determined on a Beckman IR-8 spectrophotometer, absorptions given in cm⁻¹. Ultraviolet spectra (uv) were recorded on Cary Model 11 and Model 15 spectrophotometers, absorptions given in nm. Proton magnetic resonance spectra (nmr) were determined on a Varian Associates Model A-60A spectrometer fitted with a variable-temperature probe. Chemical shifts are given in δ units, parts per million relative to tetramethylsilane as an internal standard. Mass spectra were taken on a MS-902 mass spectrometer at an ionizing current of 40 mA and ionizing voltage of 70 V. The molecular weight determination was performed on a Mechrolab osmometer, Model 301A.

Unless otherwise stated, all photolyses were carried out with a 450-W Hanovia lamp with a Pyrex filter. Two visible region photolyses were carried out using a Sylvania No. 2 photoflood; two photolyses were carried out using a Bausch and Lomb high intensity monochromator utilizing a wavelength of 4360 Å. All reactions were carried out under nitrogen. Preparative thin layer chromatography (tlc) was performed on 20 × 20 cm × 1.5 mm or 20 × 40 cm × 1.5 mm layers of Silica Gel PF-254 (E. Merck AG, Darmstadt).

2,6-Bis(oximino)cyclohexanone.[51] To a solution of 2.45 g (25 mmol) of cyclohexanone in 25 ml of ether was added 1 ml of concentrated hydrochloric acid, and the solution was cooled to 10°. Methyl nitrite, prepared from an external generator by the addition of a solution of 16.0 ml (290 mmol) of concentrated sulfuric acid and 28.5 ml of water to a suspension of 42.25 g (612 mmol) of sodium nitrite in 20 g (625 mmol) of methanol and 37.5 g of water, was added, maintaining the rate of addition so that the reaction temperature was kept between 5 and 15°. After neutralizing the reaction mixture with 1 ml of pyridine, the dioxime was removed by filtration, washed with acetone, and dried under vacuum to yield 3.4 g (87%) of a white solid, mp 175-190° dec (lit.[52] mp 160-200° dec) whose spectral data were consistent with the proposed structure: ir (Nujol) 3200-3400 (O-H), 1670 (C=O); nmr (DMSO-d_6) 9.42 (b, 2 H, NOH), 2.70 (distorted t, J = 3.5 Hz, 4 H, N=C-CH₂), 1.90 (distorted quintet, J = 3.5 Hz, 2 H, CH₂CH_2CH₂); uv, (H₂) 272 (ε 8600); uv (dilute potassium hydroxide) 336 (13,000); mass spectrum m/e (%) 41 (89), 44 (66), 95 (27), 111 (23), 124 (27), 140 (13), 156 (100).

2,6-Bis(diazo)cyclohexanone (1, R = H). To a solution of 140 ml of 15 *N* ammonium hydroxide and 50 ml of 5 *N* sodium hydroxide was added 3.20 g (20 mmol) of 2,6-bis(oximino)cyclohexanone. Keeping the reaction mixture between 10 and 20° with an external cooling bath, 240 ml of "Chlorox" was added over a 1-hr time period. The reaction mixture was stirred for an additional hour followed by addition of another 50 ml of "Chlorox" and stirring for 30 min. The reaction mixture was extracted extensively with ether, and the ethereal layer was washed with water until no ammonia aroma was detected, dried over sodium sulfate, filtered, and concentrated to 10 ml at water aspirator pressure at room temperature. After addition of 10 ml of benzene to the residue, the resultant solution was eluted with 1:1 benzene-ether (v/v) through a column containing 35 g of silica gel. The material in the yellow band was collected and evaporated to dryness to yield 410 mg (14%) of product whose spectral properties were consistent with the proposed structure: ir (CCl₄) 2080, 2060 (C-N₂), 1610 (C=O); nmr (CCl₄) 2.70 (t, J = 6.5 Hz, with further splitting, 4 H, N₂=C-CH₂), 1.85 (m, 2 H, CH₂CH_2CH₂); uv (95% ethanol) nm (ε) 259 (4000) and 325 (25,500).

1,3-Bis(diazo)-1,3-diphenyl-2-propanone (4). To a solution of 6.0 g (0.240 mol) of sodium in 300 ml of absolute ethanol cooled to

−3° was added 15.6 g (0.075 mol) of 1,3-diphenyl-2-propanone in one portion, followed by 33.6 g (0.170 mol) of p-toluenesulfonyl azide,[53] regulating the rate of addition so that the reaction temperature was kept below 0°. The reaction mixture was allowed to warm to 10°, whereupon 200 ml of water was added while the reaction mixture was cooled. The orange solid was filtered and recrystallized in small amounts by dissolving in hexane at room temperature and cooling to −20° to yield 8.66 g (44%) of orange needles, mp 93° dec: ir (CCl₄) 2090, 2040, 2035 (C-N₂), 1630 (C=O); nmr (CCl₄ at +7°) 7.40 (bs, Ar-H); uv (hexane) 264 (ε 23,500), 324 (7100); uv (methanol) 264 (ε 21,000), 328 (10,100). *Anal.* Calcd for C₁₅H₁₀N₄: C, 68.69; H, 3.84; N, 21.36. Found: C, 68.54; H, 3.87; N, 21.44 ("exploded violently on combustion").

1,3-Diformyloxy-1,3-diphenyl-2-propanone (5). To a solution of 2.0 g (29.4 mmol) of sodium formate in 100 ml of formic acid (dried by refluxing and distilling from phthalic anhydride) was slowly added 400 mg (1.5 mmol) of 1,3-bis(diazo)-1,3-diphenyl-2-propanone. After 10 min of stirring, the reaction mixture was evaporated to dryness at 25° (1 mm) and the residue taken up in a mixture of 25 ml each of water and ether. The ether was removed, and the aqueous fraction was extracted with ether. The combined ethereal extracts were washed successively with two 15-ml portions of saturated sodium carbonate solution and two 15-ml portions of water. The organic layer was dried over sodium sulfate, filtered, and evaporated to dryness to yield a yellow oily residue, unstable to thin layer chromatography. The oil was subjected to a vacuum of 0.1-mm pressure for several days, and partial crystallization occurred. Yellow needles were physically separated from the oil, yielding 45 mg (10%) of a solid, the spectral properties being in agreement with a mixture of *meso-* and *rac-* 1,3-diformyloxy-1,3-diphenyl-2-propanone: ir (CCl₄) 1710 (C=O); nmr (CCl₄) 8.00 and 7.90 (d, d, J = 1.0, J = 1.0 Hz, 2 H, H-C=O), 7.00-7.60 (m, 10 H, Ar-H), 6.30, 6.10 (d, d, J = 1.0, J = 1.0 Hz, 2 H, C-H); mass spectrum m/e (%) 50 (29), 77 (61), 105 (100), 122 (59), 298 (0.2); exact mass (calcd for C₁₇H₁₄O₅, 298.08411) 298.08103 ± 0.00792.

1,3-Diacetoxy-1,3-diphenyl-2-propanone (6). To a solution of 3.0 g (11 mmol) of sodium acetate in 150 ml of glacial acetic acid was slowly added 350 mg (1.3 mmol) of 1,3-bis(diazo)-1,3-diphenyl-2-propanone. After stirring for 30 min, the reaction mixture was added to 50 ml of water and extracted with five 25-ml portions of ether. The ethereal extract was washed with saturated potassium carbonate solution until basic, then with two 25-ml portions of water. After drying with sodium sulfate, the ethereal solution was filtered and evaporated to dryness to yield 135 mg of a pale yellow oil. The oil was purified by preparative tlc (R_f 0.80, 40% ether in benzene) to yield 40 mg (10%) of a mixture of *meso-* and *rac-* 1,3-diacetoxy-1,3-diphenyl-2-propanone (6): ir (CCl₄) 1748, 1710 (C=O); nmr (CCl₄) 7.00-7.50 (m, 10 H, Ar-H0, 6.00-6.30 (ss, 2 H, C-H), 2.10 and 2.00 (ss, 6 H, CH₃); mass spectrum m/e (%) 40 (27), 44 (22), 50 (20), 51 (36), 77 (70), 105 (100), 122 (69); 326 (trace); exact mass (calcd for C₁₉H₁₈O₅, 326.11541) 326.11372 ± 0.00528.

Photolysis of 2,6-Bis(diazo)cyclohexanone in Methanol. A solution of 296 mg (1.97 mmol) of 2,6-bis(diazo)cyclohexanone (1, R = H) in 450 ml of anhydrous methanol was irradiated for 2 hr at −40°, at which point no absorption was observed in the diazo region of the infrared spectrum. The solvent was evaporated under water aspirator pressure at 10° to yield 289 mg of a yellow-orange oil. The reaction mixture was separated by preparative vpc[54] to yield (in order of increasing retention time) 36 mg (15%) of methyl cyclopentene-3-carboxylate (7), 150 mg (61%) of methyl cyclopentene-1-carboxylate (8), 13 mg (5%) of methyl *trans*-2-methoxycyclopentanecarboxylate (9), and 26 mg (10%) of methyl *cis*-2-methoxycyclopentanecarboxylate (10). The spectral data of these compounds are consistent with the proposed structures. 7: ir (CCl₄) 1745 (C=O); nmr (CCl₄) 5.65 (m, 2 H, C=C-H), 3.60 (s, 3 H, CO₂CO₃), 3.40 (m, 1 H, C-H), 1.60-2.70 (m, 4 H, CH₂); mass spectrum m/e (%) 59 (60), 67 (100), 95 (16), 126 (24) (*cf.* ref 55 and 56). 8: ir (CCl₄) 1720 (C=O); nmr (CCl₄) 6.40 (b s, 1 H, C=C-H), 3.68 (s, 3 H, CO₂CH₃), 2.25-2.70 (m, 4 H, CH₂C=C), 1.80-2.20 (m, 2 H, CH₂CH_2CH₂); uv (95% ethanol) 223 (ε 7700), mass spectrum m/e (%) 67 (25), 95 (36), 126 (100) (*cf.* ref 55 and 57). 9: ir (CCl₄) 1740 (C=O); nmr (CCl₄) 3.90 (m, 1 H, CH-OCH₃), 3.60 (s, 3 H, CO₂CH₃), 3.19 (s, 3 H, OCH₃), 1.50-2.85 (m, 7 H, CH₂ and CHCO₂CH₃); [CCl₄ + 30

mol % Eu(DMP)₃] 4.97 (s, CO₂CH₃), 3.77 (s, OCH₃); mass spectrum m/e (%) 127 (38), 128 (55), 130 (22), 141 (30), 157 (23), 158 (100), 159 (11); exact mass (calcd for $C_8H_{14}O_3$, 158.09429) 158.09426 ± 0.00131. **10**: ir (CCl₄) 1740 (C=O); nmr (CCl₄) 3.90 (m, 2 H, C–H), 3.60 (s, 3 H, CO₂CH₃), 3.19 (s, 3 H, OCH₃), 1.50–2.80 (m, 7 H, CH₂ and CH–CO₂CH₃); [CCl₄ + 30 mol % Eu(DMP)₃] 4.78 (s, CO₂CH₃), 3.75 (s, OCH₃); mass spectrum m/e (%) 127 (38), 128 (54), 130 (21), 141 (29), 157 (22), 158 (100), 159 (13); exact mass (calcd for $C_8H_{14}O_3$, 158.09429) 158.09557 ± 0.00131.

Photolysis of 2,6-Bis(diazo)cyclohexanone in Moist Toluene, Furan, or Benzene. A solution of 296 mg (1.97 mmol) of 2,6-bis(diazo)cyclohexanone was irradiated in 450 ml of moist toluene or furan at −40° or benzene at 10° for 2 hr. Evaporation of the solvent at water aspirator pressure followed by separation by preparative vpc[58] yielded cyclopentene-1-carboxylic acid (**11**) and the corresponding anhydride **12** as the only volatile products in 65% combined yield.

11: mp 119–120° (lit. 119°,[56] 120–121°);[59] ir (CHCl₃) 2600–3400 (CO₂H), 1680 (C=O), 1630 (C=C); nmr (CDCl₃) 11.22 (broad s, 1 H, CO₂H), 6.95 (m, 1 H, C=CH), 2.60 (t, J = 6.8 Hz with further splitting, 4 H, CH₂C=C), 2.20 (distorted quintet, J = 6.8 Hz, 2 H, CH₂CH₂CH₂); mass spectrum m/e (%) 40 (30), 41 (97), 43 (26), 44 (24), 55 (29), 65 (34), 66 (60), 67 (100), 69 (28), 94 (25), 112 (86), 113 (6).

12: mp 89–90°; ir (CCl₄) 1775, 1710 (CO–O–CO), 1625 (C=C); nmr (CCl₄) 6.95 (broad s, 1 H, C=CH), 2.55 (m, 4 H, CH₂C=C), 2.10 (m, 2 H, CH₂CH₂CH₂); uv (95% ethanol) 220 (ε 10,000); mass spectrum m/e (%) 41 (34), 67 (43), 95 (100), 178 (7); 206 (~0.01); exact mass (calcd for $C_{12}H_{14}O_3$, 206.09429) 206.09367 ± 0.00338.

Conversion of Cyclopentene-1-carboxylic Anhydride (12) into Cyclopentene-1-carboxylic Acid (11). A solution of 21 mg (0.1 mmol) of cyclopentene-1-carboxylic anhydride (**12**) was stirred at room temperature for 2 hr in dilute hydrochloric acid solution. Extraction with ether, drying over sodium sulfate, filtration, and evaporation to dryness under water aspirator pressure yielded 22 mg (100%) of a white solid, identical in every respect with cyclopentene-1-carboxylic acid obtained above, mp 118–119°, mixture melting point with product from above reaction, 118–120°.

Photolysis of 1,3-Bis(diazo)-1,3-diphenyl-2-propanone (4) in Methanol. A solution of 260 mg (1.0 mmol) of 1,3-bis(diazo)-1,3-diphenyl-propanone in 450 ml of methanol–tetrahydrofuran (4:1 v/v) was irradiated at −40° for 4.5 hr at which time no absorption was observed in the diazo region of the infrared spectrum. The solvent was removed at 25° (1 mm) to yield 260 mg of a brown-yellow oil. An aliquot was purified by preparative tlc to yield in order of increasing polarity methyl *threo*-1,2,3-diphenyl-3-methoxypropionate (**13**, 41%), methyl *erythro*-2,3-diphenyl-3-methoxypropionate (b**14**, 13%), methyl *trans*-α-phenylcinnamate (**15**, 5%), and diphenylacetylene (**16**, 24%).

Methyl *threo*-2,3-diphenyl-3-methoxypropionate: mp 73–74°, ir (CCl₄) 1733 (C=O); nmr (CCl₄) 7.10 (b s, 10 H, Ar–H), 4.60 and 3.70 (AB pattern, J = 11.0 Hz, 2 H, –CH–CH–), 3.70 (s, 3 H, CO₂CH₃), 3.20 (s, 3 H, OCH₃); uv (methanol) 252 (ε 7000); mass spectrum m/e (%) 77 (14), 121 (100), 151 (17), 270 (0.04); exact mass (calcd for $C_{17}H_{18}O_3$, 270.12557) 270.12557 ± 0.00264; R_f 0.16, 4:1 chloroform–hexane.

Methyl *erythro*-2,3-diphenyl-3-methoxypropionate: mp 98–99°; ir (CCl₄) 1733 (C=O); nmr (CCl₄) 7.30 (b s, 10 H, Ar–H), 4.60 and 3.70 (AB pattern, J = 9.0 Hz, 2 H, –CH–CH–), 3.40 (s, 3 H, CO₂CH₃), 3.00 (s, 3 H, OCH₃); uv (methanol) 252 (ε 7150); mass spectrum m/e (%) 77 (13), 121 (100), 238 (5), 270 (0.13); exact mass (calcd for $C_{17}H_{18}O_3$, 270.12557) 270.12557 ± 0.00264; R_f 0.18, 4:1 chloroform–hexane; mixture melting point of threo and erythro diastereomers, 70–72°.

Methyl *trans*-α-phenylcinnamate, mp 69–72° (lit.[24,60] mp 75–76°), and diphenylacetylene, mp 55–57° (lit.[61] mp 60–62°), had spectral properties identical with those reported in the literature.[24,60,61]

Conversion of Methyl 2,3-Diphenyl-3-methoxypropionate (13 and 14) into Methyl *trans*-α-Phenylcinnamate (15). To a mixture of 12 mg (0.044 mmol) of methyl *threo*- and *erythro*-2,3-diphenyl-3-methoxypropionate in 250 μl of methanol was added 10 mg (0.185 mmol) of sodium methoxide. After warming for 1 hr at approximately 40°, the reaction mixture was purified by preparative

tlc (successive elutions with chloroform) to yield 5 mg (42% recovery) of the diastereomeric reactants and 7 mg (50%) of methyl *trans*-α-phenylcinnamate.

Photolysis of Diphenylcyclopropenone. A solution of 250 mg (1.2 mmol) of diphenylcyclopropenone in 450 ml of methanol–tetrahydrofuran (4:1 v/v) was irradiated at −40°. After 1 hr, the solvent was evaporated to dryness to yield 215 mg (100%) of diphenylacetylene, mp 56–57° (lit.[61] mp 60–62°). The material had superimposable spectra with an authentic sample, as well as identical retention properties on tlc (successive elutions with 1:2 carbon tetrachloride–chloroform).

Photolysis of 1,3-Bis(diazo)-1,3-diphenyl-2-propanone (4) in Methanol at 4360 Å. A suspension of 39 mg (0.15 mmol) of **4** in 10 ml of methanol was irradiated at −50° at 4360 Å on a low-pressure mercury vapor lamp. After 10 hr, 34 mg (87% recovery) of starting material was filtered off at −78°, and the mother liquor was evaporated to dryness at 25° at water aspirator pressure to yield 5 mg of an oil whose infrared spectrum showed a cyclopropenone absorption (1850 cm⁻¹). The oil was purified by preparative tlc (R_f 0.08, chloroform) using a small analytical plate of 0.1-mm thickness to yield 4 mg (quantitative yield) of a white solid, identical in every respect with authentic diphenylcyclopropenone, mp 120–121° (lit.[22] mp 121°).

Photolysis of 1,3-Bis(diazo)-1,3-diphenyl-2-propanone (4) in Toluene. A suspension of 520 mg (2.0 mmol) of 1,3-bis(diazo)-1,3-diphenyl-2-propanone in 400 ml of toluene was irradiated at −40°. The infrared spectra of samples withdrawn every 15 min showed the appearance of a band at 2200 cm⁻¹, followed by the slow disappearance of the diazo bands, followed by the slow disappearance of the diazo bands, followed by the ultimate disappearance of the 2200-cm⁻¹ band. The solvent was removed at 25° (1 mm), and the red oily residue was purified by preparative tlc to yield 256 mg (62%) of diphenylacetylene. A few of the more than one dozen components (by tlc) were examined; however, attempts to characterize these minor components were unsuccessful.

Photolysis of 1,3-Bis(diazo)-1,3-diphenyl-2-propanone (4) in Various Methanol–Toluene Concentrations. Five suspensions of 50–100 mg of 1,3-bis(diazo)-1,3-diphenyl-2-propanone were irradiated for 4 hr in the following methanol–toluene concentrations (v/v): 100, 50, 20, 11.1, and 0%. The total percentages of ester products, calculated by nmr, the percentages of diphenylacetylene, based on product isolated by prep tlc, and the ratios of diphenylacetylene to esters were calculated and are summarized in Table I.

Decomposition of 1,3-Bis(diazo)-1,3-diphenyl-2-propanone (4) in Methanol with Silver Oxide. To a suspension of 1.0 g (4.0 mmol) of freshly prepared silver oxide in 175 ml of methanol cooled to −15° was slowly added a solution of 250 mg (0.95 mmol) of 1,3-bis-(diazo)-1,3-diphenyl-2-propanone in 12 ml of methanol–tetrahydrofuran (1:1 v/v). The reaction was allowed to warm to room temperature, followed by heating to reflux for 15 min until all gas evolution ceased. After filtration, the solvent was evaporated at water aspirator pressure and separated by preparative tlc (chloroform) to yield 21.2 mg (11%) of diphenylcyclopropenone (**17**), 18.0 mg (8%) of methyl benzoylphenylacetate (**18**) (R_f 0.75), and 80.1 mg (36%) of methyl *trans*-α-phenylcinnamate (**15**) (R_f 0.76). The spectra of **15** and **17** are identical with those of known samples. The spectra of methyl benzoylphenylacetate are in agreement with the proposed structure and superimposable with those of an authentic sample prepared by independent synthesis: ir (CCl₄) 1733 (ester C=O), 1678 (ketone C=O); nmr (CCl₄) 7.70–8.00 (m, 2 H, ortho O=C–Ar–H), 7.10–7.50 (m, 8 H, Ar–H), 5.40 (s, 1 H, C–H), 3.70 (s, 3 H, CO₂CH₃); uv (95% ethanol) 247 (ε 7100); mass spectrum m/e (%) 51 (20), 77 (52), 105 (100), 117 (20), 119 (19), 151 (28), 220 (4), 254 (0.6).

Reaction of Diphenylcyclopropenone (17) in Methanolic Silver Oxide. To a suspension of 1.0 g (4.0 mmol) of silver oxide in 50 ml of methanol cooled to −15° was slowly added a solution of 100 mg (0.48 mmol) of diphenylcyclopropenone in 10 ml of methanol–tetrahydrofuran (1:1 v/v). The reaction was allowed to warm to room temperature, followed by heating to reflux for 15 min. After filtration, the solvent was evaporated at water aspirator pressure and separated by preparative tlc (chloroform) to yield 57.1 mg (57%) of unreacted starting material (R_f 0.10) and 22.0 mg (45%) of methyl *trans*-α-phenylcinnamate (R_f 0.78).

Decomposition of 1,3-Bis(diazo)-1,3-diphenyl-2-propanone (4) with Cuprous Chloride in Methanol. To a suspension of 1.0 g (5.1

mmol) of cuprous chloride in 175 ml of methanol cooled to −15° was slowly added a solution of 250 mg (0.95 mmol) of 1,3-bis-(diazo)-1,3-diphenyl-2-propanone in 12 ml of methanol-tetrahydrofuran (1:1 v/v). After 3-min gas evolution ceased, and an aliquot showed the complete disappearance of the diazo band in the infrared region. After filtration, the solvent was evaporated at 25° (1 mm). Purification by preparative tlc (R_f 0.11, 4:1 carbon tetrachloride-ethyl acetate) yielded 21.5 mg (12%) of diphenylcyclopropenone as the only identifiable product.

Thermolysis of 1,3-Bis(diazo)-1,3-diphenyl-2-propanone (4). A suspension of 400 mg (1.5 mmol) of 1,3-diazo-1,3-diphenyl-2-propanone in 350 ml of hexane was heated to a gentle reflux for 2 hr, during which time the color of the solution underwent a change from orange-red to dark purple to yellow at which time yellow solid precipitated out of solution. The volume of solvent was reduced to 10 ml by evaporation at 40° under water aspirator pressure and filtered to yield 380 mg (97%) of a yellow powder, recrystallized from hexane to give 360 mg (93%) of a yellow crystalline material, mp 206–208° dec whose properties are in agreement with 1,4,6,7,8,10-hexaphenyl-2,3,11,12-tetraazatetracyclo-[5.5.1.0^{2,6}.0^{8,12}]trideca-3,10-diene-5,9,13-trione (**19**): ir (CH_2Cl_2) 1805 (C=O), 1733 (C=O), 1672 (C=N); nmr (DMSO-d_6) 7.20–7.80 (m, Ar–H); uv (hexane) 236 (ϵ 21,000), 395 (5400); mass spectrum m/e (%) 62 (42), 103 (18), 178 (73), 236 (100), 309 (43), 440 (38), 674 (0.1); exact mass for m/e 440 (calcd for $C_{30}H_{20}N_2O_2$, 440.15232), 440.15493. *Anal.* Calcd for $C_{45}H_{30}N_4O_3$: C, 80.10; H, 4.48; N, 8.30. Found: C, 79.81, 80.02; H, 4.46, 4.56; N, 8.20, 8.26.

Thermolysis of 1,3-Bis(diazo)-1,3-diphenyl-2-propanone (4) in 2,3-Dimethyl-1,3-butadiene. Formation of 3,4-Dimethyl-6,8-diphenylbicyclo[4.3.0]-1,9-diazanona-3,8-dien-7-one (23). A suspension of 131 mg (0.5 mmol) of 1,3-bis(diazo)-1,3-diphenyl-2-propanone in 10 ml of 2,3-dimethyl-1,3-butadiene was heated to reflux for 1 hr. The reaction mixture was evaporated to dryness under water aspirator pressure to yield 200 mg of an oily residue. Crystallization was induced by scratching; the yellow solid was recrystallized from methanol to yield 135 mg (85%) of pale yellow crystals: mp 157–159° [lit.[37] mp 159–160°]; ir ($CHCl_3$) 3040 (C=C-H), 1705 (C=O); nmr ($CDCl_3$) 8.20 (m, 2 H, ortho N=C-Ar-H), 7.40 (m, 8 H, Ar-H), 4.36 (m, 2 H, C=C-CH$_2$N), 2.70 (AB q, J = 17.1 Hz, 2 H, C=C-CH$_2$-C), 1.63 (m, 6 H, CH$_3$); uv (95% ethanol) 268 (ϵ 17,600), 390 (3500); mass spectrum m/e (%) 40 (28), 41 (38), 43 (22), 44 (26), 55 (22), 67 (36), 81 (17), 82 (100), 103 (38), 121 (15), 123 (20), 178 (91), 179 (16), 199 (17), 200 (23), 202 (29), 222 (21), 316 (12), 317 (3).

Thermolysis of 1,3-Bis(diazo)-1,3-diphenyl-2-propanone (4) in Norbornene. Formation of 1,4-Diphenyl-5,8-methano-5,6,7,8-tetrahydrophthalazine (24). To a solution of 6 ml of norbornene and 1 ml of hexane heated to 45° was slowly added 131 mg (0.5 mmol) of 1,3-bis(diazo)-1,3-diphenyl-2-propanone; the mixture was heated to reflux for 1 hr. The reaction mixture was evaporated under water aspirator pressure to yield 142 mg (95%) of a white solid, mp 203–225°. The solid was recrystallized from methanol to yield 135 mg (91%) of white crystals: mp 229–230° (lit.[37] mp 230.5–231.5°): ir ($CHCl_3$) 3060 (Ar-H), 2960 (C-H); nmr ($CDCl_3$) 7.70–8.10 (m, 4 H, ortho Ar–H), 7.35–7.68 (m, 6 H, meta and para Ar–H), 3.75 (m, 2 H, C–H), 1.30–1.82 (m, 6 H, CH$_2$); uv (95% ethanol) 261 (ϵ 23,700); mass spectrum m/e (%) 66 (15), 77 (12), 104 (10), 165 (10), 236 (17), 241 (33), 242 (32), 297 (31), 298 (100), 299 (20), 300 (3).

References and Notes

(1) Camille and Henry Dreyfus Teacher–Scholar Grant Recipient, 1970–1975.
(2) National Institutes of Health Predoctoral Fellow.
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Structures of the [*n*. 2.2]Propellanes. I. 2-Hydroxy[4.2.2]propellane *p*-Nitrobenzoate

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Abstract: The complete crystal structure of the *p*-nitrobenzoate of 2-hydroxytricyclo[4.2.2.0^{1,4}]dodecane has been determined. The bond common to all three rings of this [4.2.2]propellane is longer (1.578 Å) than is normal for a bond between sp^3-hybridized carbon atoms, and there is considerable angular distortion from tetrahedral values at the bridgehead atoms. The observed geometry and molecular orbital calculations indicate a greater than normal admixture of p-type orbitals in the bridgehead bond. Crystal data: $P2_1/n$, $a = 10.976$ (1), $b = 7.135$ (1), $c = 19.740$ (1) Å; $\beta = 90.43$ (1)°; $Z = 4$; $d_x = 1.294$ g cm^{-3}; $d_m = 1.28$ (1) g cm^{-3}; Cu Kα radiation (λ 1.5418 Å). The structure was solved by direct methods using counter-measured X-ray intensity data (max sin $\theta/\lambda = 0.61$ Å^{-1}, 2209 reflections, 461 unobserved). Refinement by full-matrix least-squares was terminated at $R = 0.043$.

The propellanes^1 are compounds containing three rings that have one bond in common. There has been much speculation as to the molecular geometry of such systems when one or more of these rings is small (<5), particularly at the two carbon atoms that are common to all three rings.^{2} The chemistry of "small ring propellanes," *i.e.*, those with less than 11 carbon atoms in the fused rings, has been reviewed by Ginsburg.^{3} Very interesting questions have been raised as to the hybridization of the bridgehead carbons.^{2} The energy of a [2.2.2]propellane has been calculated as a function of the length of the central bond.^{4} The bridgehead carbon atoms might be expected to be coerced by geometry factors into a hybridization approximating sp^2, in which case the bridgehead bond would be formed by a σ overlap of the remaining p orbitals. This would suggest that the propellane bond should be longer and weaker than is normal for a carbon-carbon single bond. Indeed, Wiberg^5 and Eaton^2 and their respective coworkers have found that the central bond in small ring propellanes is very reactive. For example, [3.2.2]- and [4.2.2]propellanes have been shown to add bromine readily at room temperature across the central single bond.^{2} There are therefore good reasons for embarking on a detailed X-ray crystallographic study of a set of small ring propellanes with a view to measuring precise bond lengths and angles and to considering how these vary with ring size. We report now our results on the first of the set of [*n*. 2.2]propellanes (*n* = 4, 3, 2) that we have available and under investigation^2 (see structure I).

NO$_2$PhCOO

1
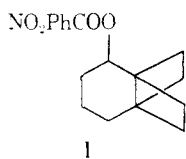
Experimental Section

Data measured are as follows: empirical formula, C$_{17}$H$_{19}$NO$_4$; mp 115.5–116.5°;^{3} space group $P2_1/n$ (no. 14); cell dimensions (least-squares refinement using reflections measured at ±θ) $a = 10.976$ (1), $b = 7.135$ (1), $c = 19.740$ (1) Å; $\beta = 90.43$ (1)°; $V = 1546$ Å^3; $Z = 4$; $d_x = 1.294$ g/cc; $d_m = 1.28$ (1) g/cc (flotation in aqueous KI); radiation, Cu Kα (graphite monochromator, λ 1.5418 Å); μ 4.69 cm^{-1}; crystal habit, monoclinic prismatic elongated along *b*; diffractometer, Nonius CAD4; crystal size for data collection, 0.125 X 0.150 X 0.570 mm. The intensity data were collected by a $\theta/2\theta$ scan with automatic scan and aperture expansion. A reflection was measured at the highest possible speed and then, if necessary, at a speed designed to achieve 2000 counts above background (a limit of 4 min was placed on measurement time). Reflections less than 20 counts above background (*ca.* 1σ) in the preliminary scan were regarded as unobserved and not measured further. An attenuator was automatically inserted if the preliminary scan indicated a count rate greater than 50,000 counts/sec (the 1% linearity limit of the electronics). Three standard reflections, (028), (2$\bar{1}$9), and (505), were measured sequentially at hourly intervals and also after every 51 reflections. The total drop in standard intensity was 3.5%, and two scale factors were assigned (approximately equal groups of reflections). For the purpose of structure determination and refinement, all reflections with $\theta < 50°$ were included but only "observed" reflections (> 3σ) for 50° < $\theta \le 65°$ (1748 "observed" and 461 "unobserved" reflections). Lorentz and polarization corrections were applied by local programs, but no absorption corrections were made (azimuth scans indicated no significant intensity variation).

Structure Determination and Refinement

Quasi-normalized structure factor magnitudes (*E* values) were calculated by DATFIX program of the XRAY67 system^6 (programs from this system were used for all calculations unless otherwise noted), and the structure was solved by symbolic addition as detailed by Silverton.^{7} The function minimized in least-squares refinement was $\Sigma[w(F_o - F_c)]^2$ Since the background, at the limit