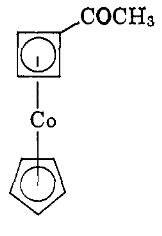
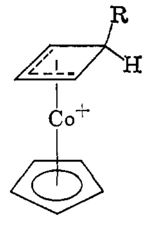


V



VI

mercury derivative of I in high yield, and again it appears that only the cyclobutadiene ring is attacked. Mercuration conducted in CH_3COOD followed by decomposition in D_2O afforded a mixture of mono-, di-, tri-, and tetradeuterio derivatives of complex I. Mass spectral analysis of this mixture clearly indicated that the great majority of the substitutions occurred on the cyclobutadiene ring, and little, if any, took place on the cyclopentadienyl ring. The reactivity of the C_4 ligand in this system could reasonably be associated with the well-established stability of π-allylcobalt complexes. An allylcobalt system such as VI could be expected to be a relatively stable intermediate in the substitution process and result in the greater reactivity of the cyclobutadiene ligand.

(9) The authors thank the National Science Foundation, the U. S. Army Research Office (Durham), and the Robert A. Welch Foundation for financial support. We also thank Badische Anilin und Soda Fabrik for a generous gift of cyclooctatetraene.

R. G. Amiet, R. Pettit[9]
Department of Chemistry, The University of Texas
Austin, Texas 78712

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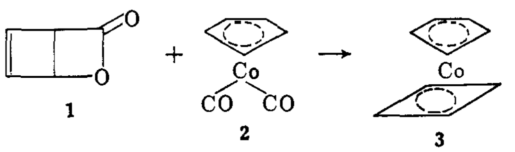
Photochemical Synthesis of Cyclobutadiene(cyclopentadienyl)cobalt

Sir:

Recently we reported the preparation of cyclobutadieneiron tricarbonyl[1] from iron pentacarbonyl or iron enneacarbonyl and photo-α-pyrone (**1**).[2] We now find that photolysis[3] of an ethereal solution of **1** and cyclopentadienylcobalt dicarbonyl (**2**) leads to the formation of cyclobutadiene(cyclopentadienyl)cobalt (**3**), a substance, isoelectronic with ferrocene, possessing an unsubstituted cyclobutadiene ring.[4]



Cyclobutadiene(cyclopentadienyl)cobalt (**3**) is a yellow, crystalline material, mp 88.5–89.0°, which sublimes readily at atmospheric pressure, is soluble in the common organic solvents, and exhibits a high degree of stability in air. *Anal.* Calcd for C_9H_9Co: C, 61.36; H, 5.11. Found: C, 61.25; H, 5.20.

The mass spectrum (70 ev) of **3** is relatively simple, with three intense peaks at m/e 176 (molecular ion), 150, and 124, lower intensity peaks at m/e 98, 85, and 59, and metastables at m/e 127.8, 102.5, and 77.5 for the transitions $176 \rightarrow 150$, $150 \rightarrow 124$, and $124 \rightarrow 98$. The molecular ion accounts for almost 40% of the total ion current, reflecting the high stability of the complex.

The presence of a cyclobutadiene ring in the complex is supported by its nmr spectrum (CCl_4), which exhibits two singlet peaks at τ 5.10 and 6.34 (relative areas 5:4) assigned to cyclopentadienyl and cyclobutadiene ring protons, respectively. The former are therefore significantly deshielded compared with those in ferrocene (τ 5.96, CCl_4),[5] while the latter are somewhat more shielded than the ring protons in cyclobutadieneiron tricarbonyl (τ 6.00, CCl_4).[2]

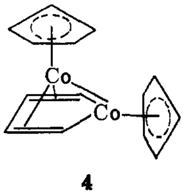
The most striking evidence for structure **3** is provided by its infrared spectrum (KBr) which exhibits peaks at 3090, 3060, 1408, 1308, 1210, 1101, 997, 926, 815, 787 (sh), 775, 749 (sh), and 739 (sh) cm^{-1}, in addition to a series of weak bonds between 1450 and 1800 cm^{-1}. Its spectrum is therefore very nearly a composite of the spectra of ferrocene (KBr, 3084, 1407, 1101, 999, 813, 787 cm^{-1}) and, excluding the carbonyl carbonyl bands, of cyclobutadieneiron tricarbonyl (CS_2, 3100, 1320, 1230, 934, 817, 770 cm^{-1}).

The uv spectrum of the complex (95% EtOH) exhibits three absorption maxima at 258, 290, and 385 $m\mu$ (ϵ 20,000, 1200, and 320).

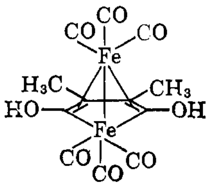
In addition to **3**, a dark green, air-sensitive crystalline material, mp 121–122°, is formed in the photolysis of **2** and **1**. *Anal.* Calcd for $C_{14}H_{14}Co_2$: C, 56.00; H, 4.67. Found: C, 56.21; H, 4.73.

Its mass spectrum (70 ev) exhibits principal peaks at m/e 300 (molecular ion), 241, 239, 222, 189, 143, 124, and 118. Its infrared spectrum shows all the peaks characteristic of the cyclopentadienyl ring, but there is no comparable correlation of spectral bands indicative of a cyclobutadiene ring chromophore. The nmr spectrum (CCl_4) of this substance exhibits an apparent triplet at unusually low field (τ 1.79, J = 3.5 Hz) and two singlet peaks at τ 5.04 (fine structure partially hidden underneath) and 5.16, with relative integrated areas of 2:7:5.

On the basis of these data, structure **4** is tentatively suggested for this substance. Such a structure is closely related to those of the iron complex **5**,[6] formed in the reaction of dimethylacetylene with an alkaline solution of iron carbonyl hydride, and the osmium complex **6**,[7] prepared by the reaction of $Os_3(CO)_{12}$ with 2,3-dimethylbutadiene. The chemistry of these new cobalt complexes is under investigation.



4



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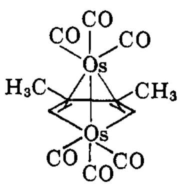

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[1] First reported by G. F. Emerson, L. Watts, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 131 (1965).

[2] M. Rosenblum and C. Gatsonis, *ibid.*, **89**, 5074 (1967).

[3] Irradiation was carried out with a mercury arc lamp (Hanovia, Type L, 450 W) with a Corex glass filter. The products were isolated and purified by column chromatography on alumina. All operations were conducted in a nitrogen atmosphere.

[4] The tetraphenyl derivative of **3**, prepared from cyclopentadienylcobalt dicarbonyl and diphenylacetylene, has been reported by A. Nakamura and H. Hagihara, *Bull. Chem. Soc. Japan*, **34**, 452 (1961).

[5] M. Rosenblum, "Chemistry of the Iron Group Metallocenes," Interscience Publishers, Inc., New York, N. Y., 1965.

[6] A. A. Hock and O. S. Mills, *Acta Cryst.*, **14**, 139 (1961).

[7] R. P. Dodge, O. S. Mills, and V. Schomaker, *Proc. Chem. Soc.*, 380 (1963).

Acknowledgment. We are indebted to Dr. C. Gatsonis and Mr. D. Ciappenelli for technical assistance. This research was supported by a grant (GM-05978) from the National Institutes of Health.

M. Rosenblum, B. North
Department of Chemistry, Brandeis University
Waltham, Massachusetts 02184

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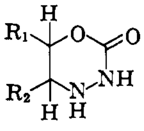
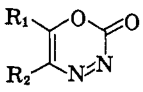
Photolytic Decomposition of Dihydrooxadiazinones

Sir:

The oxadiazinones I–V form a group of closely related heterocycles which until 1956 were unknown. At that time we described the preparation of IVa ($R_1 = R_2 = C_6H_5$; $R_3 = H$) from benzoin and carbethoxyhydrazine and reportedi ts thermal decomposition to *cis*- and *trans*-stilbenes.[1] Subsequently the diphenyl derivatives Ia ($R_1 = R_2 = C_6H_5$, *trans*) and Va ($R_1 = R_2 = C_6H_5$) were synthesized and transformed by oxidation with lead tetraacetate through the thermally unstable intermediates IIIa and IIa ($R_1 = R_2 = C_6H_5$) to *trans*-stilbene and tolane, respectively.[2] At the same time a number of other dihydrooxadiazinones (IV), derived from cyclic and acyclic α-ketols as well as from α-diketones, were also prepared and characterized.[2]

We wish now to report that dihydrooxadiazinones (IV) undergo smooth photolytic decomposition affording products which largely parallel those obtained pyrolytically.[3] These data are summarized in Table I.


I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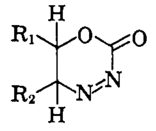
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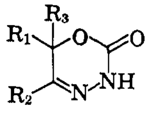
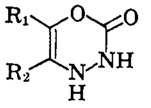

IV


V

The close similarity of products is particularly evident for those dihydrooxadiazinones derived from medium-ring α-ketols which, in addition to olefinic products, yield bicyclic compounds through apparent transannular reactions. These results are in striking contrast to the behavior of dihydrooxadiazinones derived from 1-acetylcyclohexanol and 3-methyl-3-hydroxybutanone (IVe,f). Photolytic decomposition of these substances affords moderate yields of the expected olefins, but their thermal decomposition results principally in the formation of unidentified high-boiling materials and virtually no olefinic product.

Table I

Dihydrooxadiazinone	Decomposition products[a]	Yield, % Thermal	Photochemical	Tosylhydrazones[b]
IVa, $R_1 = R_2 = C_6H_5$; $R_3 = H$	*cis*-Stilbene	38[c]	33	
	trans-Stilbene	32[c]	9	
IVb, $R_1 = R_2 = -(CH_2)_8-$; $R_3 = H$	*cis*-Cyclodecene	10	18	14
	trans-Cyclodecene	<1		6
	cis-Bicyclo[5.3.0]decane	55	44	62
	cis-Decalin	<1		18
	trans-Decalin	4	<1	
IVc, $R_1 = R_2 = -(CH_2)_7-$; $R_3 = H$	*cis*-Cyclononene	32	51	22
	trans-Cyclononene		5	
	cis-Hydrindan	24	2	66
	cis-Bicyclo[6.1.0]nonane			10
IVd, $R_1 = R_2 = -(CH_2)_6-$; $R_3 = H$	*cis*-Cyclooctene	75	65	45
	cis-Bicyclo[3.3.0]octane	7		46
	cis-Bicyclo[5.1.0]octane			9
IVe, $R_1 = CH_3$; $R_2 = R_3 = -(CH_2)_5-$	Ethylidenecyclohexane	<1	75	
IVf, $R_1 = R_2 = R_3 = CH_3$	3-Methyl-2-butene	<1	52	

[a] The identification of products was accomplished by glpc, ir, and nmr analyses. Comparison was made in all cases with authentic materials. The bicyclic compounds were prepared through Bamford–Stevens reactions on the corresponding ketones.[6] The medium-ring olefins were supplied by Dr. W. R. Moore, whose assistance is gratefully acknowledged. [b] L. Friedman and H. Shechter *J. Am. Chem. Soc.*, **83**, 3159 (1961); A. C. Cope, M. Brown, and G. L. Woo, *ibid.*, **87**, 3107 (1967). [c] M. Rosenblum, A. Longroy, M. Neveu, and C. Steel, *ibid.*, **87**, 5716 (1965).

The photolytic reactions of the dihydrooxadiazinones are more closely paralleled by their behavior under electron impact.[4] Decomposition of the molecular ion by the successive loss of CO_2 and N_2 is a common initial fragmentation path for all of the dihydrooxadiazinones examined and is a predominant process for IVe, IVf, and IVa in which structural factors may be expected to facilitate O–alkyl bond cleavage within the urethan function. By contrast, the loss of CO competes with the loss of CO_2 for those dihydrooxadiazinones (IVb–d) which are derived from secondary α-ketols.

We had previously adduced evidence for a very similar

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(1) M. Rosenblum and H. Moltzan, *Chem. Ind.* (London), 1480 (1956).

(2) M. Rosenblum, V. Nayak, S. K. DasGupta, and A. Longroy, *J. Am. Chem. Soc.*, **85**, 3874 (1963).

(3) Irradiation of ether solutions of IVa–f (λ_{max} ~240 mμ) were carried out in quartz vessels using Sylvania G8T5 gemicidal lamps. Solutions of IVa (λ_{max} 282 mμ) were irradiated with Rayonet R.P.R. 3000 Å lamps. Pyrolyses were conducted by subliming the compounds under high vacuum through a 8 mm × 30 cm tube packed with sand and heated to 400°. The pyrolysate was collected in a liquid nitrogen trap.

(4) Similar correspondence between photolytic reactions and the primary processes which occur in the mass spectrometer have been noted. For a discussion with leading references, see H. Budzikiewicz, C. Djerassi, and D. H. Williams Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967, p 26.