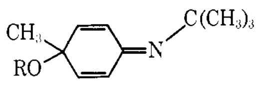
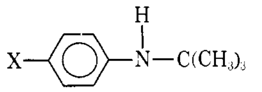
drawing substituents results in a marked decrease in the rate of rearrangement of the six anilines studied. The overall rate decrease in going from the para methyl derivative, **5**, to the para cyano case, **10**, was 1.8×10^6. This decrease in rate indicated that the transition state for the rearrangement of **2** involved the generation of a positive center adjacent to the aromatic ring. Confirmation of this concept was provided by Figure 1 which shows a plot of log K *vs.* the Brown σ^+ substituent constants.[7] For the six compounds studied, we obtained an excellent correlation with σ^+. The ρ for the reaction was -6.35 and the correlation coefficient was 0.996. Each of the compounds listed gave ortho chlorinated anilines as the major product. When the para position of the aniline was blocked the yields of ortho chlorinated products ranged from 65% for **10** to 85% for **5**. As previously noted,[2,3] **7** gave a mixture of ortho and para substitution. Two interesting facets of the product studies merit discussion. First, solvolysis of **5** in buffered ethanol gave 10% of **11a**, indicating the presence of positive charge on the ring. When the solvolysis of **5** was carried out in pure unbuffered methanol, we obtained 32% of **11b** and 61% of the normal ortho chlorinated aniline. The increased amount of 2,5-cyclohexadienone derivative,[8] **11**, formed in methanol was consistent with the difference in solvolytic properties between ethanol and methanol. The second interesting feature of the product studies was the amount of starting aniline, **12**, which was formed in the reaction. The amount of this amine gradually increased as the substituents became more electron withdrawing, going from 1% when X was methyl to 29% when X was cyano. This indicated that the presence of electron-withdrawing substituents decreased the amount of charge delocalized into the aromatic nucleus. Increased positive charge on nitrogen appeared to result in increased amounts of **12**.[9]



11a, R = CH_2CH_3
b, R = CH_3



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Investigation of the solvolysis of **5**–**10** in buffered ethanol showed that the mode of heterolytic cleavage involved the formation of an aryl nitrenium ion (anilenium ion) and chloride anion. The large ρ of -6.35 indicated that considerable delocalization of the charge onto the aromatic nucleus must have been present. This is consistent with the relative abilities of divalent nitrogen and trivalent carbon to bear a positive charge.[10] The solvolysis of *N*-chloroanilines to give anilenium ions adds still another category to the growing list of reactions which occur *via* nitrenium ion intermediates.[11]

Acknowledgment. We are indebted to the National Cancer Institute of the Public Health Service for a grant in support of this investigation.

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[7] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 80, 4979 (1958).

[8] We have recently shown that the reaction of **5** with silver ion in methanol produces **11b** in a 70% yield in a useful synthesis of 2,5-cyclohexadienone derivatives: P. G. Gassman and G. A. Campbell, *Chem. Commun.*, 427 (1970).

[9] In these cases it is unknown whether **12** arises *via* a hydride abstraction mechanism or *via* spin inversion of the singlet nitrenium ion to a hydrogen-abstracting triplet nitrenium ion. For an example of the latter see P. G. Gassman and R. L. Cryberg, *J. Amer. Chem. Soc.*, **91**, 5176 (1969).

[10] It is interesting to compare the solvolysis of derivatives of **2** with that of substituted 1-chloro-1-arylethanes. The ρ for the latter in 20:80 water–dioxane has been reported to be -4.50 (C. Mechelynck-David and P. J. C. Fierens, *Tetrahedron*, **6**, 232 (1959)). It would appear that the nitrogen cation was much more dependent on charge delocalization into the aromatic ring than was the analogous carbonium ion.

[11] For a recent review see P. G. Gassman, *Accounts Chem. Res.*, 3, 26 (1970).

[12] National Defense Education Act Fellow, 1967–1970; Stauffer Chemical Fellow, 1970–1971.

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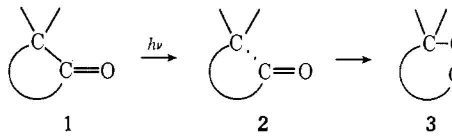
Received March 6, 1971

Mechanism of Photochemical Ring Expansion Reactions of Cyclic Ketones[1]

Sir:

A number of publications have appeared concerning the photochemical ring expansion reactions of selected cyclic ketones.[2–9] In most cases, the rearrangement was proposed to involve homolysis of a carbon–carbon bond α to the excited carbonyl function, followed by electronic rearrangement and rebonding to form an oxacarbene intermediate (eq 1). Evidence for intermediate **3** derives from its trapping by alcoholic solvents to yield acetals as isolable products. Yates has suggested[9] that ring expansion is associated with certain structural features which inhibit other competing intramolecular rearrangements; *i.e.*, ring expansion only occurs from **2** when other reactions of this species are disfavored. We present results here which demonstrate that while certain structural features are necessary for observation of photochemical ring expansion, the reaction can compete favorably with other common fates of **2**.[10]



(1)

Key compounds in this study are cyclopentanones **4**, **6**, **9**, and **11**, and cyclobutanones **15** and **17**. The photoproducts, efficiencies, and reactivities of the former set are listed in Table I. Photochemical ring expansion of **6** is in itself a rather unusual reaction[6,11]

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[1] Molecular Photochemistry. XLIV. Paper XLIII: K. Dawes, N. J. Turro, and J. M. Conia, *Tetrahedron Lett.*, in press. The authors are pleased to acknowledge the generous support of this research by the Air Force Office of Scientific Research (Grant No. AFOSR-70-1848).

[2] P. Yates and L. Kilmurry, *Tetrahedron Lett.*, 1739 (1964).

[3] P. Yates and L. Kilmurry, *J. Amer. Chem. Soc.*, **88**, 1563 (1966).

[4] (a) H. U. Hostettler, *Tetrahedron Lett.*, 687 (1965); (b) H. U. Hostettler, *Helv. Chim. Acta*, **49**, 2417 (1966).

[5] N. J. Turro and R. M. Southam, *Tetrahedron Lett.*, 545 (1967).

[6] D. R. Morton, E. Lee-Ruff, R. M. Southam, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 4349 (1970).

[7] G. Quinkert, G. Cimbollek, and G. Buhr, *Tetrahedron Lett.*, 4573 (1966).

[8] N. J. Turro and D. M. McDaniel, *J. Amer. Chem. Soc.*, **92**, 5727 (1970), and unpublished results.

[9] P. Yates, *Pure Appl. Chem.*, **16**, 93 (1968).

[10] It should be emphasized that our results do not necessarily invalidate the original suggestion made by Yates. That ring expansion is an inherently inefficient reaction in the bicyclo[2.2.1]heptan-2-one system is still quite plausible.

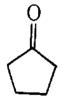
[11] J. K. Crandall and R. J. Seidewand, *J. Org. Chem.*, **35**, 697 (1970).

Table I. Quantum Yields[a] and Quenching Data[b] for Cyclic Ketones in CH_3OH[c]

Ketone	Aldehyde	Acetal	$k_q\tau_t$,[d] M^{-1}	$k_q\tau_t$,[e] M^{-1}	τ_t^{-1},[d,f] sec^{-1}	τ_t^{-1},[e,f] sec^{-1}	Φ[d]	Φ[e]
4	**5**		45		4.0×10^8		0.23	
6	**7**	**8**	39	37	4.5×10^8	4.8×10^8	0.16	0.12
9	**10**		<0.50		$>3.6 \times 10^{10}$		0.30	
11	**12**		0.44		4.0×10^{10}		0.29	

[a] Measured at 3130 Å for degassed solutions (*ca.* 0.1 *M*) of ketone in CH_3OH using benzophenone–benzhydrol actinometry. Generally, the average of two determinations. Per cent conversion $\leq 10\%$. [b] Determined at 3130 Å using purified 1,3-pentadiene as quencher. [c] All samples contained *ca.* 100 mg of anhydrous $NaHCO_3$/1.75 ml of solution to prevent ketal and acetal formation. [d] For formation of aldehyde. [e] For formation of acetal. [f] Assumes k_q for CH_3OH at 25° is 1.8×10^{10} M^{-1} sec^{-1} as calculated from the modified Debye equation (P. J. Wagner and I. Kochevar, *J. Amer. Chem. Soc.*, **90**, 2232 (1968)).

and is rendered all the more remarkable by the fact that its rate constants for rearrangement and for alkenal formation are comparable to those for alkenal formation for cyclopentanone. Furthermore, the ring expansion reaction is not appreciably more inefficient than alkenal formation from **6**. Finally, both ring expansion and alkenal formation from **6** can be totally quenched by 1,3-pentadiene, suggesting that both reactions occur exclusively from the triplet excited state of **6**. The photochemistry of **11** is in marked contrast to that observed for **6**. Specifically, initial α cleavage occurs only at the most highly alkyl-substituted carbon–carbon bond to afford alkenal **12**, there being no evidence for ring-expanded acetals. In addition, the quantum yields and rate data obtained for **11** are in excellent agreement with corresponding values for **9**.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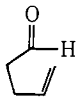
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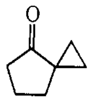
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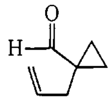
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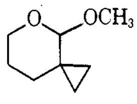
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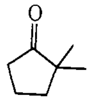
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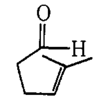
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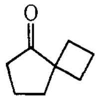
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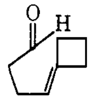
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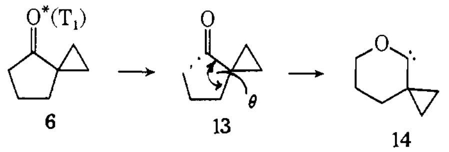
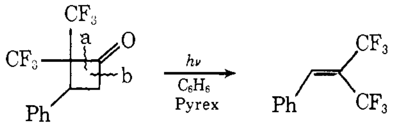
These findings suggest that the incorporation of the α spirocyclopropyl group in **6** facilitates bonding between the carbonyl oxygen and the alkyl radical center of the postulated acyl alkyl biradical intermediate **13**. This enhancement of ring expansion could be due to (1) the size of the angle θ in **13**[12] and/or (2) resonance stabilization of the acyl radical portion of **13**. The latter explanation would require that the carbonyl carbon undergo rehybridization from sp^2 to sp in order to achieve the preferred geometry[14] for maximum delocalization of the unpaired electron into the cyclopropane ring. Such rehybridization (which would "straighten out" the acyl radical and bring the carbonyl oxygen into closer proximity to the alkyl radical center) may favor ring expansion in the product-determining step from **13**. However, the rate of formation of **13** is not related to the types of different paths that it can explore, but rather, to structural features which stabilize its formation. This same reasoning can further account for the fact that photochemical ring expansion occurs to the virtual exclusion of other reactions in cyclobutanones containing an α spirocyclopropyl or α alkylidene group.[6]

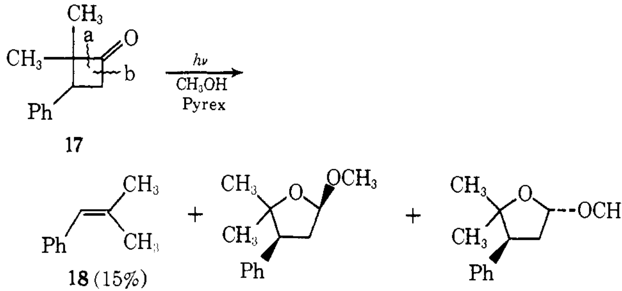


6 13 14

Photochemical ring expansion in cyclobutanones also appears to be facilitated by increasing α alkyl substitution.[5,6] The remarkable difference in behavior of the cyclobutanones **15**[15] and **17** leads us to suggest that although the photo-ring expansion reactions of cyclobutanones possess all the experimental characteristics of a concerted singlet state rearrangement,[8] a biradical-like transition state is more attractive to explain the lack of ring expansion from **15**[16] while **17** photorearranges in high yield, with regioselectivity of bond cleavage. Thus, both methyl and trifluoromethyl groups would be expected to stabilize breaking of bond "a" relative to bond "b." However, migration of the free-electron carbon to the carbonyl oxygen (expected to be nucleophilic attack by the carbon radical) should be favored for **17**. Indeed, for **15**, a competing reaction, cyclo-



15 16 (94-96%)



17 18 (15%) 19 (32%) 20 (55%)

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(12) Microwave studies[13] of substituted cyclopropanes suggest a value of *ca.* 116° for θ. This increase over the normal tetrahedral angle should make the transition state for alkenal formation from **6** poorer than the analogous transition state from **4**. This reasoning is supported by the quantum yield data in Table I.

(13) (a) J. P. Friend and B. P. Dailey, *J. Chem. Phys.*, **29**, 577 (1958); (b) R. G. Ford and R. A. Beaudet, *ibid.*, **48**, 4671 (1968); (c) F. M. K. Lam and B. P. Dailey, *ibid.*, **49**, 1588 (1968).

(14) W. G. Dauben and G. H. Berezin, *J. Amer. Chem. Soc.*, **89**, 3449 (1967).

(15) We thank Dr. C. G. Krespan (E. I. du Pont de Nemours and Co.) for a generous sample of this compound.

(16) Ketone **15** undergoes a dark reaction with methanol,[17] and consequently, an accurate mass balance could not be obtained in this solvent. However, control experiments show that styrene **16** is virtually the exclusive photoproduct formed. Previous results (ref 5) suggest that the percentage of cycloelimination in cyclobutanones is unaffected on going from methanol to benzene as solvent.

(17) Yu. A. Cheburkov, W. Mukhamadalier, and I. L. Knunyants, *Tetrahedron*, **24**, 1341 (1968).

elimination, completely predominates, even though concerted migration of bond "b" is possible.

(18) National Institutes of Health Predoctoral Fellow, 1968–present.

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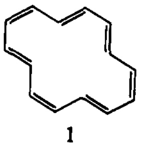
Reaction of [14]Annulene with Tricarbonyltriamminechromium(0). Synthesis and Structure of Hexacarbonyl-*trans*-6a,12a-dihydrooctalenedichromium(0)[1]

Sir:

Although organometallic complexes of cyclobutadiene, benzene, and cyclooctatetraene are well known, it has previously not been possible to prepare such complexes from the higher annulenes.[2] We now report the synthesis and structure determination of a carbonylchromium complex obtained from [14]annulene (**1**).[3] This substance has been shown to possess the hexacarbonyl-*trans*-6a,12a-dihydrooctalenedichromium(0) structure **2**, formally derived from *trans*-6a,12a-dihydrooctalene (**3**), a bicyclic valence isomer of [14]-annulene.



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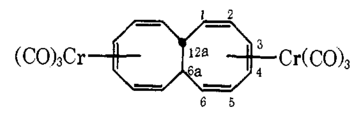

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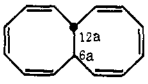

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A solution of [14]annulene (27 mg) in hexane (15 ml) was boiled under reflux with tricarbonyltriamminechromium(0) $[(NH_3)_3Cr(CO)_3]$[4] (300 mg) for 33 hr under nitrogen. Crystals of the complex **2** separated on the walls of the vessel, and one of these was used for the X-ray structure determination. The bulk of the complex **2** was isolated by evaporation, chromatography in benzene on Kieselgel (10 g), rapid elution with hexane–benzene (1:1), and finally crystallization from hexane–benzene. This procedure led to **2** (6 mg, ~10%) as reasonably stable bright red crystals, which decomposed on attempted melting point determination: mass spectrum, *m/e* 454 $[C_{14}H_{14}Cr_2(CO)_6]$; ultraviolet spectrum, λ_{max}^{EtOH} 230 sh (relative optical density, 1.00),[5] 283 (0.39), and 352 nm (0.36); $\lambda_{max}^{benzene}$ 354 nm (ϵ 9100); infrared spectrum (KBr), strong CO bands at 1955, 1895, and 1880 cm^{-1}.

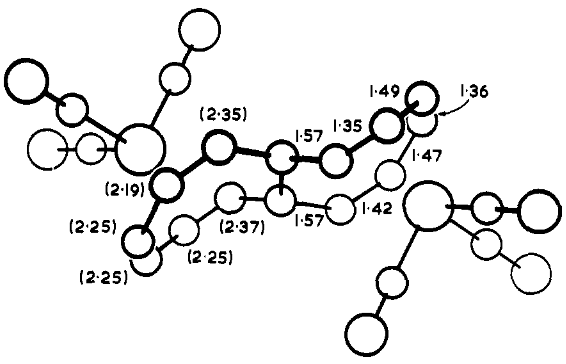

Figure 1. The molecular stereochemistry of hexacarbonyl-*trans*-6a,12a-dihydrooctalenedichromium(0) (**2**). The numbers in parentheses refer to C–Cr bond lengths (in ångströms), and the others to C–C bond lengths (in ångströms).

The nmr spectrum of **2** ($CDCl_3$, 100 MHz), using a time-averaged computer, showed singlets at τ 3.88 and 4.38 due to [14]annulene,[3] formed during determination of the spectrum (see below); in addition, the spectrum exhibited multiplets at τ 3.75–4.3, 4.7–4.95, 5.05–5.3, and 5.45–5.7 (olefinic protons of **2**), as well as at τ 6.3–6.8 (methine protons of **2**).

It is interesting that [14]annulene was regenerated when solutions of **2** in ether, ethyl alcohol, benzene, or deuteriochloroform were allowed to stand at room temperature. The reaction could be followed conveniently by the typical change of the ultraviolet spectrum, and in ether was complete after ~24 hr. Evidently, *trans*-6a,12a-dihydrooctalene (**3**) is thermodynamically less stable than [14]annulene (**1**), and is transformed to this valence isomer.

The structure of the complex **2** was established by an X-ray crystallographic analysis. It crystallizes in the space group $P\bar{1}$, with $a = 11.334$, $b = 7.101$, and $c = 9.674$ Å, $\alpha = 102.10$, $\beta = 135.51$, and $\gamma = 100.14°$, and $Z = 1$. The crystals gave relatively weak diffraction spectra, but 693 independent reflections with $F_{obsd}^2/\sigma(F_{obsd}^2) > 1.0$ ($\sin\theta_{max}/\lambda = 0.45$) have been observed by automatic four-circle diffractometer methods (Mo Kα). The structural analysis was based on conventional Fourier and full-matrix least-squares methods, the molecular stereochemistry being shown in Figure 1 [present unweighted discrepancy index, $R = 0.12$; esd's in bond lengths average 0.02 (Cr–C) and 0.04 Å (C–C and C–O)].

The complex **2** has exact C_i symmetry in the crystal. Each tricarbonylchromium fragment is seen to be bonded to a triene group, the isomerization of [14]annulene to a bicyclic hexaene being dictated by the charge requirements of the metal (18-electron "rule"). Apart from the bond C(6a)–C(12a), which has a length of 1.32 Å ($\sigma = 0.06$ Å), carbon–carbon bond lengths are close to ones which could be predicted from related systems.[6] The shortness of C(6a)–C(12a) is largely due to inadequate resolution in the X-ray data, since this cannot be a double bond in view of the mass spectral data, the regeneration of [14]annulene from the complex, and the general stereochemistry of C(6a) and C(12a). Chromium–carbon bond lengths to C(2), C(3), C(4),

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(1) Unsaturated Macrocyclic Compounds. LXXXI. For part LXXX, see F. Sondheimer, *Accounts Chem. Res.*, submitted for publication.

(2) For instance, no complexes could be isolated when [14]annulene or [18]annulene was treated with hexacarbonylchromium(0 thermally or photochemically (E. P. Woo and K. Stöckel, unpublished experiments from these laboratories). On the other hand, carbonylchromium and carbonylmolybdenum complexes of 1,6-methano[10]annulene have been synthesized [E. O. Fischer, H. Rühle, E. Vogel, and W. Grimme, *Angew. Chem.*, **78**, 548 (1966); *Angew. Chem., Int. Ed. Engl.*, **5**, 518 (1966); P. E. Baikie and O. S. Mills, *J. Chem. Soc. A*, 328 (1969); P. F. Lindley and O. S. Mills, *ibid.*, 1286 (1969)], as well as a carbonylchromium complex of *anti*-1,6:8,13-bismethano[14]annulene [E. Vogel, personal communication; M. J. Barrow and O. S. Mills, *Chem. Commun.*, 220 (1971)].

(3) See F. Sondheimer, *Proc. Roy. Soc., Ser. A*, **297**, 173 (1967).

(4) W. Hieber, W. Abeck, and H. K. Platzer, *Z. Anorg. Allg. Chem.*, **280**, 252 (1955).

(5) Accurate ϵ values could not be obtained in ethyl alcohol, due to the low solubility of **2** in this solvent.

(6) See M. R. Churchill and R. Mason, *Advan. Organometal. Chem.*, **5**, 93 (1967).