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DECARBONYLATION OF SOME TRICYCLO[3.2.1.0^{2,4}]OCTAN-8-ONE DERIVATIVES

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Abstract—The thermal decarbonylation of several cyclopropane containing carbonyl bridge compounds has been investigated in solution. The reactions are first order and the rate constants have been determined as well as the derived activation parameters. The relative rates of reaction are dependent on the configuration of the cyclopropane ring. For example, the first order rate constant for decarbonylation of *endo*-tricyclo[3.2.1.0^{2,4}]oct-6-en-8-one (**1**) is approximately 10^7 times greater than that for the isomeric *exo*-tricyclo[3.2.1.0^{2,4}]oct-6-en-8-one (**2**) and approximately 10^5 times greater than that for norborn-2-en-7-one (**6**). Differences in ground state energies may contribute to the relative high reactivity of the *endo*-tricyclo[3.2.1.0^{2,4}]octan-8-one derivatives but it is felt that the major cause involves favourable interaction of the *endo* orientated cyclopropane ring during cleavage of the bridgehead to carbonyl bridge bond.

Perhaps the most characteristic feature of norbornen-7-ones is the relative ease with which these carbonyl bridge compounds undergo thermal decarbonylation.[1,2] At approximately 150° to 250° these ketones readily lose carbon monoxide. As such, their reactivity lies roughly between the two extremes represented by the relatively unreactive norbornan-7-ones on the one hand and the extremely reactive norbornadien-7-ones on the other. Norbornan-7-ones have been described as thermally stable i.e. distillable. In contrast norbornadien-7-ones are extremely sensitive towards decarbonylation, so much so, that these ketones are more often than not, not isolable. Attempts to prepare such compounds via the Diels-Alder reaction,[1,2] acid hydrolysis of the corresponding ketal[3] or oxidation of the corresponding alcohol[4] lead to products formally derived from the intermediate carbonyl bridge compound with loss of carbon monoxide. This occurs almost without exception. A few exceptions have been recorded but Fuchs[5] has clearly demonstrated that the structural assignments are either incorrect or to be regarded with some skepticism.

The actual reasons for this increased ease of decarbonylation in the order norbornan-7-one < norbornen-7-one < norbornadien-7-one is a matter of some conjecture. Fuchs[5] has recently outlined the various conceivable explanations but in the absence of any systematic structure-reactivity studies no definitive conclusions could be formed. In this connection, Schmidt's double bond rule[1] may be reagrded as empirical and in effect simply summarizes the facility for norbornen-7-one to decarbonylate and/or undergo retro-Diels-Alder reaction.

We have recently reported[6] on the preparation of the tricyclic carbonyl bridge ketone **1** and commented upon its facile decarbonylation.* Qualitatively, the order of reactivity shown by **1** is greater than that of norbornen-7-one and approaches that of norbornadien-7-ones. It is therefore apparent that the cyclopropane ring in **1** is

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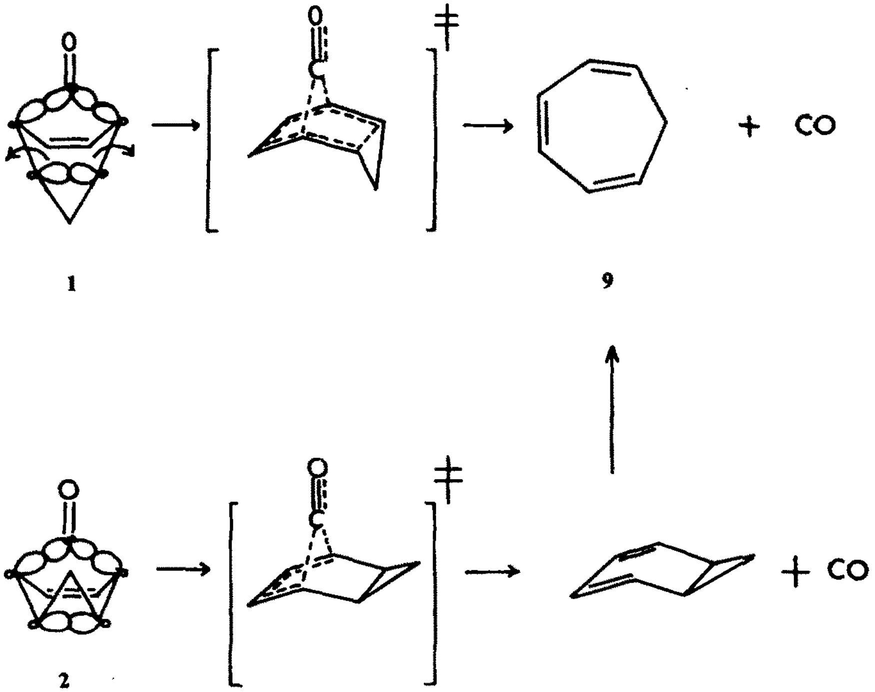
* Ketone **1** was also described by another group of workers: see Ref. 7

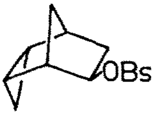
contributing to this reactivity and in an effort to gain some insight into the nature of this contribution we have made a systematic study of the thermal decarbonylation of **1** and several other cyclopropane containing carbonyl bridge compounds.

At the inception of this work only one other example of the decarbonylation of a tricyclo[3.2.1.$0^{2,4}$]oct-6-en-8-one derivative had been recorded.[8] Since then Battiste *et al.*[9] have published the results of a study similar to ours. We report here a study covering a wider range of compounds including not only the tricyclic ketones but also two tetracyclo[3.3.1.$0^{2,4}$.$0^{6,8}$]nonan-9-ones and for comparison, norborn-2-en-7-one. The effect of several different solvents were also investigated. In those cases where thermal decarbonylation was not observed, photochemical decarbonylation was studied, but only with a view to determining pro



1 **9**

2



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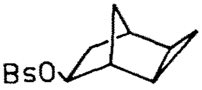

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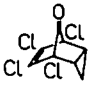
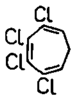
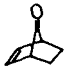
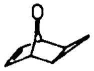
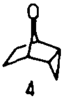
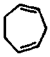
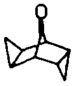
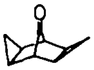
RESULTS AND DISCUSSION

Decarbonylation of the following bridge carbonyl compounds were investigated: the three unsaturated tricyclo[3.2.1.$0^{2,4}$]oct-6-en-8-ones **1**, **2** and **3**, the two saturated tricyclo[3.2.1.$0^{2,4}$]octan-8-ones **4** and **5**, norborn-2-en-7-one **6** and the two tetra-

TABLE 1. KINETIC AND THERMODYNAMIC DATA FOR THE THERMAL DECARBONYLATION OF THE CARBONYL BRIDGE COMPOUNDS

Reactant	Product	Solvent	Temp.,°C	k x10^5 sec^{-1}	E_a kcal mol^{-1}	logB	$\Delta H^{\ddagger}_{25°}$ kcal mol^{-1}	$\Delta S^{\ddagger}_{25°}$ eu	Relative rates at 25°	at 150°
 1	 9	Diglyme	25.6	2.75						
			32.3	7.22	26.1	14.5	25.5	6.0	1	1
			40.0	22.1			±0.7	±2.4		
		MeOH	25.6	1.98						
			31.6	4.92	25.6	14.0	25.0	3.5	0.83	0.55
			40.0	13.9			±0.7	±2.4		
		Cyclohexane	32.0	15.9						
		HOAc	32.0	4.27						
		DMSO	32.0	4.11						
		$MeOCH_2CH_2OH$	32.8	6.33						
 3	 10	Diglyme	35.5	2.85						
			50.0	17.4	23.9	12.4	23.3	-3.8	0.31	0.10
			56.2	32.2			±0.6	±2.0		
		MeOH	50.1	1.97						
			56.5	4.81	32.6	17.3	32.0	18.8	0.011	0.29
			65.7	20.1			0.8	2.5		
 6	 12	Diglyme	124.6	2.25						
			130.4	4.25	30.7	12.3	30.1	-4.4	$2.4x10^{-6}$	$2.3x10^{-5}$
			136.2	6.77			±1.7	±4.4		
 2	 9	Diglyme	130.4	1.42						
			136.2	2.49	32.2	12.7	31.6	-3.6	$4.8x10^{-7}$	$1.0x10^{-5}$
			141.1	4.35			±1.9	±4.6		
 4	 11	Diglyme	143.0	1.35						
			152.5	2.93	32.9	12.4	32.3	3.3	$9.2x10^{-8}$	$2.8x10^{-6}$
			161.5	8.12			±1.2	±2.7		
 7	 13	$MeOCH_2CH_2OH$	140.6	1.20						
			152.1	4.03	38.4	15.3	37.8	9.4	$5.6x10^{-8}$	$2.7x10^{-6}$
			159.9	9.98			±1.1	±2.5		
 5		Neat	no reaction at 280°C				relative rate at 280°C < $4 x 10^{-10}$			
 8		"								
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cyclo[3.3.1.0^{2,4}.0^{6,8}]nonan-8-ones **7** and **8**. Ketones **1**, **2**, **3**, **4**, **7** and **8** have been synthesized in these laboratories and the details have been published.[6b] Compounds **5**[10] and **6**[11] were prepared according to published procedures.

The rates of decarbonylation could be followed conveniently by PMR spectroscopy. For the *exo*, *endo* tetracyclic ketone **7** the reaction was followed by VPC under conditions where both reactant and product were shown to be stable. The decarbonylation of each ketone occurred by a well behaved first order process. Table 1 summarizes all the rate constants and kinetic parameters for the various ketones.

The olefins resulting from decarbonylation of the ketones are known compounds and their identity was established either by comparison of spectral data with those of authentic samples or by comparison with the published data. Within the limits of experimentation all the products were formed in quantitative yield as determined by PMR spectroscopy. The saturated *exo* tricyclic ketone **5** and the *exo*, *exo* tetracyclic ketone **8** were stable at the maximum temperature tried. The rate constants listed in Table 1 for **5** and **8** are therefore estimates of the upper limit. The photochemical decarbonylation of these two ketones was investigated in a cursory manner only, mainly to demonstrate that the expected decarbonylation products were formed under favourable conditions. The products, 3.4-homotropylidene **13** and 1,4-cycloheptadiene **11**, were only partly stable under these conditions and therefore the yields were not good.

Several features of the thermal decarbonylation of the bridge carbonyl compounds listed in Table 1 are worthy of note. The rate of decarbonylation of the *endo* unsaturated tricyclic ketone **1** is almost insensitive to solvent change. Indeed, at 32° the largest rate constant observed (cyclohexane, $k = 15{\cdot}9 \times 10^{-5}\ \text{sec}^{-1}$) is greater by a factor of 3·9 only than the smallest observed rate constant (DMSO, $k = 4{\cdot}11 \times 10^{-5}\ \text{sec}^{-1}$). This insensitivity to solvent change indicates that the thermal decarbonylation of ketone **1** proceeds by a pathway involving homolytic bond cleavage rather than heterolytic bond cleavage. Thermal decarbonylation of the remaining ketones, except **3**, were studied in diglyme solvent only, and it is assumed that the decarbonylation also proceeds by one of two homolytic pathways.[12]

Changing the solvent from diglyme to methanol resulted in a marked decrease in the rate constant for the decarbonylation of the tetrachloroketone **3**. We believe that hemiacetal formation with ketone **3** in methanol is partly responsible for tnis decrease. Although ketone **1** in methanol could also be in equilibrium with some of the corresponding hemiacetal this may well be insignificant relative to the tetrachloroketone **3** which would be particularly prone to hemiacetal formation due to the presence of the electron attracting chlorine substituents at the bridgehead C atoms. If we denote the equilibrium constant between hemiketal and ketone by K and let $k_{C=O}$ equal the rate constant for decarbonylation from the ketone **3**, the apparent rate constant k is expressed by $[K/(1 + K)]k_{C=O}$. The apparent rate constant may therefore be well below the intrinsic $k_{C=O}$ and this could well be the case for the thermal decarbonylation of the tetrachloroketone **3** in methanol.

The other features of the thermal decarbonylation concern differences in reactivity dependent upon structure. Decarbonylation of the two *endo* unsaturated tricyclic ketones **1** and **3** occurs more readily than for norborn-2-en-7-one (**6**) whereas the *exo* unsaturated tricyclic ketone **2** undergoes decarbonylation with an order of reactivity close to that for norborn-2-en-7-one (**6**). It is therefore clear that the *endo* oriented cyclopropane ring in **1** and **3** is responsible for the enhanced rate of decarbonylation. In a similar vein we note that the ketones **4** and **7** each with an *endo* oriented cyclopropane ring are much more reactive than norbornan-7-one which is of the same order of reactivity as the ketones **5** and **8** containing only *exo* oriented cyclopropane rings. Clearly, the *endo* unsaturated tricyclic ketone **1** is more reactive than the isomeric *exo* ketone **2** just as the *endo* saturated ketone **4** is more reactive than the *exo* isomer **5**.

There are two possible causes for the increased reactivity of the *endo* tricyclic ketones (**1** and **4**) over the isomeric *exo* ketone and both causes could be partly or solely operative. Ground state energy differences between the *exo* and *endo* isomers such that the *exo* isomer is more stable could be responsible for the observed reactivity differences. Alternatively the decarbonylation of the *endo* isomer could proceed via a concerted mechanism involving participation of the C-2 to C-4 cyclopropane bond whereas the *exo* isomer decarbonylates via a nonconcerted mechanism involving no stabilization of the transition state by the cyclopropane bond. It is difficult to assess the relative gound state energies of the *exo* and *endo* isomers and it is even more difficult to gauge the extent to which these ground state energy differences might be responsible for the rate enhancement of the *exo* over the *endo* isomer. In this regard, Wiberg[13] has found that acetolysis of *endo*-tricyclo[3.2.1.0^{2,4}]octan-*exo*-6-yl brosylate (**14**) occurred with some isomerization to the *exo* brosylate (**15**) whereas during acetolysis of **15** there was no evidence for isomerization to **14**. Presumably the *exo* isomer **15** is more stable than the *endo* isomer **14** and one might expect therefore that the *exo* ketones **2** and **5** would be more stable than their corresponding *endo* isomers **1** and **4**. Certainly this qualitative assessment of the relative ground state energies does add some credibility to the explanation that ground state energy differences contribute to the observed rate differences for the *exo* versus the isomeric *endo* tricyclic ketones. However, in the absence of more precise data this explanation cannot be persued further.

The alternative explanation proposed originally by Battiste[9] *et al.* appears more attractive. Concerted cyclopropane ring opening occurs in a disrotatory fashion[14] and for the ketone **1** only one of the two possible disrotatory modes is energetically possible: the mode which results in formation of *cis* double bonds in the product. For *endo* ketone **1** this mode of cyclopropane ring opening allows for favourable overlap of the orbitals of the cyclopropane bond with the developing orbitals at C-1 and C-5 during the decarbonylation process. Decarbonylation occurs in a one step concerted process and the transition state will be stabilized by overlap not only with the π orbitals of the double bond but also with the orbitals of the C-2, C-4 bond of the cyclopropane ring. Six electrons will be delocalized over six C atoms two of which are not directly bonded and as such the transition state resembles a monohomobenzene structure[15] with loosely bound carbon monoxide.

For the isomeric *exo* tricyclic ketone the energetically feasible mode of disrotatory cyclopropane ring opening does not allow overlap of the cyclopropane C-2 to C-4 orbitals with the developing orbitals at C-1 and C-5, at least until some rehybridization at C-1 and C-5 has occurred further on in the reaction pathway and beyond the rate determining step. The initial transition state is stabilized by overlap involving the olefinic π orbitals only and presumably the reaction proceeds via a norcaradiene intermediate in a two step process. The differences in reactivity between the *endo* and *exo* saturated tricyclic ketones **4** and **5**, and that between the *exo*, *endo* and the *exo*, *exo* tetracyclic isomers **7** and **8** may be rationalized along similar lines.

Finally, it may be pointed out that there is no conclusive evidence to suggest that both bridgehead carbon to carbonyl carbon bonds have cleaved simultaneously in the transition state. Baldwin[12] has reported that thermal decarbonylation of dicyclopentadien-1,8-dione occurs with $\Delta S^{\ddagger} = +9{\cdot}8 \pm 2{\cdot}3$ e.u. and he has noted that this value lies close to the rotational entropy of carbon monoxide suggestive of a decarbonylation transition state in which both bonds to the carbon monoxide moiety have been broken. In the present study only the tetracyclic ketone **7** has a $\Delta S^{\ddagger}$ value in this vicinity. Except for tetrachloroketone **3** in methanol, the entropies of activation are relatively low and suggest that only one of the bonds between bridgehead carbon to the carbon monoxide moiety is broken in the transition state. In either event, the *endo* orientated cyclopropane ring may be expected to contribute some conjugative stabilization to the transition state.

EXPERIMENTAL

PMR spectra were recorded with a Varian A-60 NMR spectrometer equipped with a variable temp probe. Analytical VPC was carried out using a Perkin–Elmer 880 gas chromatograph (FID) with the following column: 1. 10ft × 0·125 in O.D. copper column of 5% Ucon 50 HB 2000 on 80/100 non acid washed Chromosorb W. Preparative VPC was performed using a Wilkens Aerograph A-700 "Autoprep" with the following column: 2. 10 ft × 0·25 in O.D. aluminium column of 15% Ucon 50 HB 2000 on 60/80 non acid washed Chromosorb W.

Preparation of carbonyl bridge compounds

endo-*Tricyclo*$[3.2.1.0^{2,4}]$*oct-6-en-8-one*[6,7] (**1**), exo-*tricyclo*$[3.2.1.0^{2,4}]$*oct-6-en-8-one*[6b,9] (**2**), 1,5,6,7-*tetrachloro*-endo-*tricyclo*$[3.2.1.0^{2,4}]$*oct-6-en-8-one*[6b,16] (**3**), endo-*tricyclo*$[3.2.1.0^{2,4}]$*octan-8-one*[6,7,16] (**4**), exo-*tricyclo*$[3.2.1.0^{2,4}]$*octan-8-one*[10] (**5**), *norborn-2-en-7-one*[11] (**6**), endo, exo-*tetracyclo*$[3.3.1.0^{2,4}.0^{6,8}]$-*nonan-9-one*[6b] (**7**) and exo, exo-*tetracyclo*$[3.3.1.0^{2,4}.0^{6,8}]$*nonan-9-one*[6b] (**8**) were prepared according to published procedures. Analytical samples of ketones **1**, **2**, **4** and **7** were prepared by repeated crystallizations and the remaining ketones were purified by distillation and/or preparative VPC. Purity was checked by PMR spectroscopy.

Kinetic methods. The following general procedure was used for all the ketones. A soln of the ketone (*ca* 0·5 to 1·0 M) in the appropriate solvent containing a small percentage of benzene was sealed in an NMR tube and heated for appropriate periods. The sample was analysed by PMR spectroscopy with a variable temp probe maintained at some 30° (at least) below the temp of the kinetic run. PMR integration, relative to the added benzene standard, of each sample were performed in both directions at least 5 times and the average integration taken for each point.

For most of the ketones this procedure gave reproducible data. However, for the more reactive ketones **1** and **3** the procedure was understandably less reproducible. More satisfactory results were obtained using the following alternate procedure. Some twelve NMR samples were prepared from a stock soln of the ketone and then these were immersed in the rate bath. At appropriate intervals a sample was withdrawn and stored at −78°. After all the samples had been collected they were analysed as above.

The kinetic data was processed in the usual manner to yield the Arrhenius parameters shown in Table 1 and these parameters were used to calculate the activation enthalpies and entropies. Estimated errors in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated by the method of Peterson *et al.*[17]

For each of the ketones and their corresponding decarbonylation product the following PMR signals were used to monitor the extent of reaction. In most cases both the disappearance of reactant and the appearance of product could be monitored.

Ketone	PMR signal	Product	PMR signal
1	Vinyl	**9**	Low field 2 proton vinyl "triplet"
2	Vinyl	**9**	Low field 2 proton vinyl "triplet"
3	Highest field multiplet—one proton	**10**	Vinyl
4	—	**11**	Vinyl
5	Bridgehead	**11**	Vinyl
6	Vinyl	**12**	Vinyl

Thermal decarbonylation of the *exo, endo* tetracyclic ketone **7** was followed by VPC (column 1, programmed from 65° to 135°). Ketone **7** (22 mg) and cyclooctane (17 mg, VPC standard) were made up to 1·0 ml with 2-methoxyethanol in a volumetric flask. Samples were sealed into ampoules and then heated for appropriate intervals in a thermostated bath. VPC areas of the standard, reactant and the product were calculated by the tracing and weighing procedure.

Products. In all cases the yields as determined by PMR spectroscopy or VPC were quantitative. Isolation and characterization of tropilidine **9** (from ketone **7**) and tetrachlorotropilidine **10** (from ketone **3**) were described previously.[6b] The remaining ketones were decarbonylated for ten half-lives and the products isolated by preparative VPC (column 2). 1,4-Cycloheptadiene **11** (from ketone **4**) was shown to be identical (PMR and IR) to a sample of this cyclic olefin prepared according to the published procedure.[18] 1,3-Cyclohexadiene **12** (from ketone **6**) displayed a PMR spectrum identical with that reported[19] and 3,4-homotropilidine **13** (from ketone **7**) gave characteristic PMR and IR data in agreement with that published.[18]

Photolytic decarbonylation of exo-*tricyclo*[3.2.1.$0^{2,4}$]*octan-8-one* (**5**). A soln of **5** (0·370 g) in pentane (120 ml) containing cyclooctane (0·168 g, VPC standard) was irradiated through quartz windows for 3/4 hr with a Hanovia 90 W medium pressure mercury lamp. The progress of the reaction was monitored by VPC as described above (column 1, 60°). The soln was filtered from insoluble polymeric material and concentrated under vacuum. Preparative VPC (column 2, 60°) gave **11** (0·10 g) which was identified as before.

Photolytic decarbonylation of exo, exo-*tetracyclo*[3.3.1.$0^{2,4}$.$0^{6,8}$]-*nonan-9-one* (**8**). In a manner similar to that described above, ketone **8** was irradiated (2 hr) to yield **13** (33% yield) which was isolated by preparative VPC (column 2, 85°C) and identified as described above.

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