# Thermochemical Properties of Iodoacetone. Intramolecular Electrostatic Interactions in Polar Molecules[1]

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**Abstract:** Equilibrium constants for the system $CH_3COCH_3 + I_2 \rightleftharpoons CH_3COCH_2I + HI$ have been measured spectrophotometrically in the gas phase. From the van't Hoff plot of these equilibrium constants over the temperature range 314–430°, the best straight line obtained by a least-squares fit was log $K = (3.84 \pm 1.1)/2.303R - (13.03 \pm 0.76)/\theta$, where $\theta = 2.303RT$ in kilocalories/mole. Correcting these values to room temperature, using an estimate of $\overline{\Delta C_p}^\circ = 2.0$ gibbs/mol yields $\Delta S^\circ_{298} = 2.3$ gibbs/mol and $\Delta H_f{}^\circ{}_{298} = 12.1$ kcal/mol. By combining these with known values of $S^\circ$ and $\Delta H_f^\circ$ for $CH_3COCH_3$, $I_2$, and HI, $S^\circ_{298}(CH_3COCH_2I(g)) = 85.7$ gibbs/mol and $\Delta H_f{}^\circ{}_{298}(CH_3COCH_2I(g)) = -31.0$ kcal/mol are obtained. $\Delta(S^\circ_{298})_{int}$ and $\Delta(\Delta H_f{}^\circ{}_{298})$ on substitution of a hydrogen atom by an iodine atom are compared for a series of compounds containing hydrocarbon, ether, and ketone groups. As expected from the atom substitution rule, $\Delta(S^\circ_{298})_{int}$ is constant at 12.1 gibbs/mol with a small variation of ±0.8 gibbs/mol. However, the range of $\Delta(\Delta H_f{}^\circ{}_{298})$ is from 9.6 kcal/mol to 20.7 kcal/mol. An explanation for this large variation is presented as evidence for intramolecular coulombic interaction between partial charges in the polar molecules.

Thermochemical data and kinetic parameters may be obtained from a gas-phase spectroscopic study of the equilibrium[3]

$$RH + I_2 \rightleftharpoons RI + HI$$

As the number of organic iodides for which the thermochemical properties are known becomes more extensive, it is possible to estimate the corrections required for the atom substitution rule of estimating thermochemical properties. In this paper, we present the thermochemical data for iodoacetone and consider the effect of electrostatic interactions on the enthalpy of organic iodides.

## Experimental Section

**Materials.** $CH_3COCH_3$ was distilled and degassed at liquid nitrogen temperatures prior to use. No impurity could be detected by gas chromatography. $I_2$ was degassed at −10° and sublimed into a storage vessel attached to the inlet manifold. The $CH_3COCH_2I$ produced in the reaction mixture had the same retention time for gas chromatographic analysis on a silicone oil column as a sample prepared from $ClCH_2COCH_3$ and HI.[4]

**Apparatus and Procedure.** This has been described previously.[4] Equilibrium concentrations were determined from the optical density of $I_2$ at 450–500 nm and from the absorbance change at 230 nm. A pure sample of $ICH_2COCH_3$ could not be obtained in the gas phase for optical density calibrations. The absorbance at 230 nm is equal to

$$A_{230}/l = \epsilon_{I_2}([I_2]_0 - \Delta[I_2]) + \epsilon_A([A]_0 - \Delta[I_2]) + \epsilon_{HI}[HI] + \epsilon_{IA}[IA] \quad (1)$$

where $l$ is the cell path length, $[A]_0$ the initial concentration of acetone, [IA] the concentration of iodoacetone, and $\Delta[I_2]$ the change in $I_2$ concentration, which is assumed to be equal to $\Delta[A]$, [HI], and [IA]. Expressed as rates

$$\Delta A_{230}/\Delta t = l(\epsilon_{HI} + \epsilon_{IA} - \epsilon_A - \epsilon_{I_2})(\Delta[I_2]/\Delta t) \quad (2)$$

$$\Delta[I_2]/\Delta t = q(\Delta A_{230}/\Delta t) \quad (3)$$

where $q$ is a constant at a given temperature.[5] Values of $q$ were calculated from eq 3 using $\Delta[I_2]/\Delta t$ measured in the visible prior to equilibrium. Using $q$, values of $(\Delta[I_2])_e$ were calculated from $(\Delta A_{230})_e$ after equilibrium had been established. Good agreement was obtained between equilibrium constants calculated from $(\Delta A_{230})_e$ and those obtained from $(\Delta[I_2])_e$ measured in the visible. This agreement supports the assumption that the reaction stoichiometry is unchanged from the initial stages to equilibrium. There was no decomposition of the $ICH_2COCH_3$ in the gas phase in the time required to reach equilibrium. At equilibrium, the absorbance was constant for a time of at least five half-lives of the reaction. In this time, there was no pressure change and no noncondensable gases were formed, further supporting the stability of $ICH_2COCH_3$. However, if the reaction time was extended to many multiples of the equilibrium time, some decomposition occurred, as was shown by small changes in the absorbance, the formation of noncondensable gases, and a pressure increase of the reaction mixture.

## Results and Discussion

Equilibrium data for the system $CH_3COCH_3 + I_2 \rightleftharpoons CH_3COCH_2I + HI$ are shown in Table I. Variation of the equilibrium constant, $K_{eq} = [ICH_2COCH_3]\cdot[HI]/[CH_3COCH_3][I_2]$, is within 30% for a 100-fold variation in the $[CH_3COCH_3]/[I_2]$ ratio. For all runs, $[ICH_2COCH_3]$ was assumed to be equal to [HI]. As the equilibrium lies well on the side of $CH_3COCH_3$ and $I_2$, no attempt was made to add HI to the initial reaction mixture. This would decrease $-\Delta[I_2]$ to the same order of magnitude as the errors in measuring the concentrations. A van't Hoff plot of this data yielded a reasonable straight line (see Figure 1), the equation of which was calculated by least squares: log $K = (3.84 \pm 1.1)/2.303R - (13.03 \pm 0.76)/\theta$, where $\theta = 2.303RT$ and the errors quoted are standard deviations.

No $C_p^\circ$ values are known for $ICH_2COCH_3$ and there are insufficient groups for group additivity estimates to be applied. We will use $\overline{\Delta C_p}^\circ = (\Delta C_p{}^\circ{}_{646} + \Delta C_p{}^\circ{}_{298})/2 = 2 \pm 1$ gibbs/mol for the system $RH + I_2 \rightarrow RI + HI$, by comparison with $\overline{\Delta C_p}^\circ = 2.18$ gibbs/mol for $R = CH_3CO$[6] and an estimate of

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[1] This work was supported in part by Grant No. 00353-05 of the Air Pollution Division, Public Health Service.

[2] Postdoctoral Research Associate.

[3] D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969).

[4] R. K. Solly, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kin.*, **2**, 11 (1970).

[5] $\epsilon_{I_2}$ may be pressure dependent at the experimental concentrations ($10^{-4}$ *M*), but as $\epsilon_{I_2} \ll (\epsilon_{HI} + \epsilon_{IA} - \epsilon_A)$, the effect on $q$ is negligible.

[6] R. Walsh and S. Benon, *J. Phys. Chem.*, **70**, 3751 (1966).

**Table I.** Equilibrium Constants for the Equilibrium $CH_3COCH_3 + I_2 \rightleftarrows CH_3COCH_2I + HI$

| Temp, °C | $[CH_3COCH_3]_0$, Torr | $[I_2]_0$, Torr | $[CH_3COCH_3]_e$, Torr | $[I_2]_e$, Torr | $[CH_3COCH_2I]_e = [HI]_e$, Torr | $K_{eq} \times 10^5$ |
|---|---|---|---|---|---|---|
| 314.4 | 244.2 | 4.28 | 243.9 | 3.94 | 0.34 | 12.03 |
| 314.6 | 112.4 | 4.56 | 112.2 | 4.34 | 0.22 | 9.94 |
| 315.0 | 35.2 | 4.73 | 35.1 | 4.61 | 0.11 | 7.48 |
| 314.8 | 281.3 | 13.70 | 280.6 | 12.98 | 0.72 | 14.3 |
| 314.8 | 49.8 | 19.13 | 48.6 | 18.85 | 0.28[a] | 8.56 |
| 314.7 | 275.0 | 14.02 | 274.5 | 13.50 | 0.52[a] | 7.30 |
| 371.0 | 276.5 | 4.52 | 275.9 | 3.97 | 0.55 | 27.6 |
| 371.0 | 357.1 | 4.40 | 356.5 | 3.79 | 0.61 | 27.5 |
| 371.0 | 46.6 | 4.56 | 46.4 | 4.32 | 0.24 | 28.7 |
| 378.4 | 9.75 | 4.08 | 9.64 | 3.97 | 0.11 | 31.6 |
| 377.9 | 281.0 | 5.04 | 280.3 | 4.35 | 0.69 | 39.0 |
| 377.8 | 100.5 | 14.50 | 99.9 | 13.90 | 0.60 | 25.9 |
| 377.7 | 151.0 | 11.00 | 150.3 | 10.32 | 0.68 | 29.8 |
| 390.1 | 256.5 | 5.04 | 255.9 | 4.41 | 0.63 | 35.1 |
| 390.2 | 103.1 | 4.88 | 102.7 | 4.44 | 0.44 | 42.0 |
| 390.2 | 318.5 | 5.52 | 317.7 | 4.76 | 0.76 | 38.2 |
| 390.7 | 91.7 | 15.30 | 91.1 | 14.67 | 0.63 | 29.7 |
| 389.9 | 219.1 | 15.91 | 218.1 | 14.90 | 1.01[a] | 31.4 |
| 389.4 | 264.2 | 15.82 | 263.2 | 14.80 | 1.02 | 26.7 |
| 389.3 | 42.6 | 15.70 | 42.2 | 15.28 | 0.42 | 27.4 |
| 429.9 | 26.5 | 5.12 | 26.2 | 4.82 | 0.30 | 71.3 |
| 429.9 | 35.9 | 4.96 | 35.5 | 4.60 | 0.36 | 79.4 |
| 429.9 | 15.5 | 5.12 | 15.3 | 4.93 | 0.19 | 47.9 |
| 429.9 | 15.3 | 18.73 | 14.9 | 18.30 | 0.43[a] | 67.8 |
| 429.8 | 41.7 | 14.10 | 41.2 | 13.56 | 0.54[a] | 52.2 |
| 429.8 | 35.0 | 2.56 | 34.8 | 2.33 | 0.23 | 65.2 |

[a] Calculated from Δ (absorbance) at 230 nm.

$\overline{\Delta C_p}° = 1.6$ gibbs/mol for $R = CH_2CH{=}CH_2$.[7] Applying this estimate of $\overline{\Delta C_p}°$ to the van't Hoff parameters, we obtain $\Delta S°_{298} = 2.3 \pm 1.9$ gibbs/mol and $\Delta H_f°_{298} = 12.1 \pm 1.2$ kcal/mol. Combining these with the known values of $S°_{298}$ and $\Delta H_f°_{298}$ for $CH_3COCH_3$, $I_2$, and HI leads to $S°_{298}(ICH_2COCH_3(g)) = 85.7 \pm 2.0$ gibbs/mol and $\Delta H_f°_{298}(ICH_2COCH_3(g)) = -31.0 \pm 1.5$ kcal/mol.

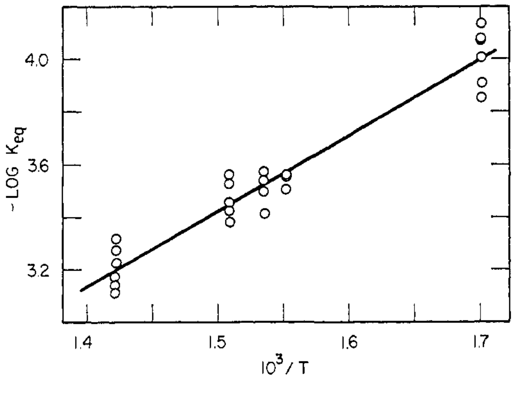


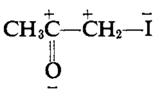
Figure 1. van't Hoff plot for the equilibrium $CH_3COCH_3 + I_2 \rightleftarrows CH_3COCH_2I + HI$.

All the fundamental vibrational frequencies have not been assigned for $ICH_2COCH_3$, so it is not possible to calculate $S°_{298}$ by statistical thermodynamics. Furthermore, $S°_{298}$ for the isoelectronic 2-methyl-3-iodopropene is not known. It would be possible to estimate this, using group contributions, from allyl iodide. However, the same result is obtained by comparing contributions to $S°_{298}$ by substituting an iodide atom for a hydrogen atom. As may be seen from Table II, excellent agreement is obtained for $\Delta S°_{int}(RI - RH)$ for R = acetonyl and allyl. All the values agree within $\Delta S°_{int} = 12.1 \pm 0.8$ gibbs/mol, the error limit generally being within the experimental error.

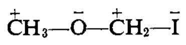
The small variation in $\Delta S°_{int}$ supports the much larger variations which are obtained for $\Delta(\Delta H_f°)(RI - RH)$. $\Delta(\Delta H_f°)$ ranges from 9.6 kcal/mol for $R = CH_3CO$ to 20.7 kcal/mol for $R = CH_3COCH_2$. The model compounds have similar structural differences so steric interaction cannot account for the 11.1-kcal/mol variation in $\Delta(\Delta H_f°)$.

The results are best explained by the increased electrostatic interaction on substituting the more electronegative iodine atom for a hydrogen atom. Using methane as our model, $CH_3I$ is 21.1 kcal/mol more endothermic than $CH_4$. All other iodides are more stable relative to the parent hydrogen compound. In the hydrocarbon series, the decreased $\Delta(\Delta H_f°)$ relative to $CH_4$-$CH_3I$ may be explained by stabilizing of a partial negative charge on the iodine atom by alkyl substitution on the α-carbon atom.

In the oxygen-atom series, by comparison of $\Delta(\Delta H_f°)$ for RH − RI, $ICH_2COCH_3$ and $ICH_2OCH_3$ are less and more stable, respectively, relative to $ICH_2CH_2CH_3$. We propose this relative stability may be explained by electrostatic interaction of partial charges



$\mathrm{CH_3\underset{\underset{\underset{-}{O}}{\|}}{\overset{+}{C}}-\overset{+}{C}H_2-\overset{-}{I}}$



$\mathrm{\overset{+}{C}H_3-\overset{-}{O}-\overset{+}{C}H_2-\overset{-}{I}}$

The adjacent charges in $ICH_2COCH_3$ decrease the stability, while $CH_3OCH_2I$ is stabilized by the alternate charge sequence.

Values for the partial charges may be calculated from group dipole moments.[8] Using 1.9 D for the

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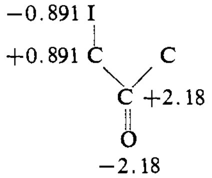
[7] A. S. Rodgers, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **88**, 3194 (1966).

**Table II**

| R | | $S°$, gibbs/mol | $S°_{int}$,[c] gibbs/mol | $\Delta S_{int}$(RI − RH), gibbs/mol | $\Delta H_f°_{298}$, kcal/mol | $\Delta H_f°$(RI − RH), kcal/mol |
|---|---|---|---|---|---|---|
| $CH_3$ | RH | 44.5 | 49.4 | 13.3 | −17.9 | 21.1 |
| | RI | 60.5 | 62.7 | | 3.3 | |
| $C_2H_5$ | RH | 54.9 | 60.7 | 12.2 | −20.2 | 18.1 |
| | RI | 70.7 | 72.9 | | −2.1 | |
| $C_3H_7$ | RH | 64.5 | 70.3 | 12.9 | −24.8 | 17.4 |
| | RI | 81.0 | 83.2 | | −7.4 | |
| $C_3H_5$ | RH | 63.8 | 66.0 | 11.5 | 4.9 | 18.0 |
| | RI | 77.5 | 77.5 | | 22.9 | |
| $CH_3CO$ | RH | 63.2 | 65.4 | 12.8 | −39.7 | 9.6 |
| | RI | 76.0 | 78.2 | | −30.3 | |
| $CH_3OCH_2$ | RH | 63.7 | 69.5 | | −44.0 | |
| | RI | 79.3[a] | 81.5 | 12.0[a] | −28.6 | 15.4[a] |
| | | 77.6[b] | 79.8 | 10.3[b] | −29.3 | 14.7[b] |
| $CH_3COCH_2$ | RH | 70.5 | 76.3 | 11.6 | −51.7 | 20.7 |
| | RI | 85.7 | 87.9 | | −31.0 | |

[a] Calculated from $K_{eq}$ for $CH_3OCH_3 + I_2 \rightleftarrows CH_3OCH_2I + HI$ by fixing $\Delta S_{int}(RI - RH) = 12.0$ gibbs/mol. [b] From F. R. Cruickshank and S. W. Benson, *J. Amer. Chem. Soc.*, **91**, 2487 (1969). Calculated from $K_{eq}$ by fixing $S°_{298}(CH_3OCH_2I) = S°_{298}(C_3H_7I) - 2.5$ gibbs/mol. [c] $S°_{int} = S° + R \ln (\sigma/n)$, where $\sigma$ = total symmetry number and $n$ = number of optical isomers.

C–I group and 2.7 D for the C=O group, we calculate the following charges



All values are electrostatic units × $10^{10}$. Considering these as point charges centered on the atoms, the electrostatic interaction is given by

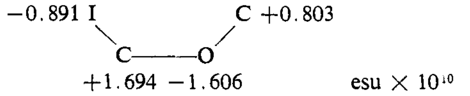
$$E = (q_1q_2/Ds) \times 1.44 \times 10^{13} \text{ kcal/mol}$$

where $q$ is the charge in electrostatic units, $D$ the dielectric constant, and $s$ the distance between the charges in centimeters. By assuming a uniform dielectric constant of one, and summing the 1–2, 1–3, and 1–4 interactions, 3.7-kcal/mol repulsion is calculated for the *trans* configuration. This value is in reasonable agreement with the experimentally measured value of 2.7 kcal/mol (using 18.0 kcal/mol as a standard for $\Delta(\Delta H_f°)$ of (RI − RH)). The discrepancy may be decreased by introducing a dielectric constant along the C–C bond. The charge interaction is attenuated due to the higher electron density along the bonds, as compared to the nonbonded charge interaction. Values of the dielectric constant may be calculated from the bond index of refraction,[9] but the number of model compounds that have been investigated is limited.

Using the same partial charges as shown in the diagram, we calculate 6.3-kcal/mol electrostatic repulsion for the configuration with the iodine atom *cis* to the carbonyl group. The energy difference of 2.6 kcal/mol between the *trans* and *cis* configuration represents an electrostatic energy barrier to rotation of the $CH_2I$ group along the C–C bond.

Cruickskank and Benson have previously considered the electrostatic interaction of iodomethyl methyl ether.[10] In their calculations, they consider the attraction between the partially negative iodine atom and the partial positive charge on the opposite carbon atom. This does not represent the stabilization of the molecule as they claim, but rather an electrostatic potential energy barrier to rotation of the $CH_2I$ group. The nonbonded carbon–iodine distance varies from 2.7 Å for the iodine atom *cis* to the adjacent carbon, to 4.3 Å with the iodine atom in the *trans* configuration. Using partial charges calculated from group dipole moments, there is a difference of 1.4 kcal/mol in the attractive potential for the two configurations.

The assignment of partial charges in iodomethyl methyl ether is complicated. There is no bond between the CI dipole and the CO dipole, as was the case for iodoacetone. As a first approximation, we have simply added the partial charges and obtain the values shown in the diagram. With the exception of the carbon–iodine nonbonded attraction, all potentials are independent of configuration. With the charges shown in the diagram, we have 7.9-kcal/mol attraction, plus the attraction over the variable nonbonded carbon–iodine distance. As in the previous discussion, the attraction is relative to $\Delta(\Delta H_f°)$ of RI − RH, using $\Delta(\Delta H_f°)$ = 18 kcal/mol as a standard. The *gauche* conformation, for which the carbon–iodine distance is 3.3 Å, is favored sterically. In this conformation, the total attraction is 11 kcal/mol.



This is much higher than the experimental value of 2.6 kcal/mol. There are two refinements which we can introduce into the calculation to reduce the

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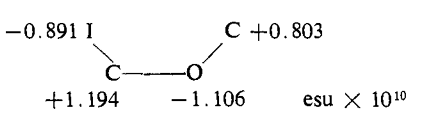
(8) C. J. F. Böttcher, "Theory of Electric Polarisation," Elsevier Publishing Co., Amsterdam, 1952.

(9) W. T. Creswell, G. H. Geffery, J. Leicester, and A. I. Vogel, *Research*, 1, 719 (1948); 2, 46 (1949); *J. Chem. Soc.*, 514 (1952).

(10) See F. R. Cruickshank and S. W. Benson, Table II, footnote *b*.

discrepancy between the theoretical and the experimental values. Assigning a dielectric constant to the bonds will reduce the attraction between nearest neighbor bonded atoms, while the repulsion of alternate nonbonded atoms will remain unchanged. Using the C–I and C–O bond-refractive indices of Creswell, *et al.*,[9] the overall electrostatic interaction is reduced to 2 kcal/mol repulsion. We can eliminate the discrepancy between our calculated attraction and the experimental value by assigning a bond refractive index of $n$ = 1.15 to the O–CI bond, compared to 1.51 measured for dimethyl ether. Our calculations assume a dielectric constant of 1 for the repulsions of like charges on alternate atoms. With a larger $\epsilon$ than 1, we can assign a value for $n$ of the O–CI bond more like that of the parent ether, and obtain good agreement with the experimental value.

As an alternative to increasing the dielectric constant between the partial charges, we can reduce the degree of additivity of the partial charges. For example, using the partial charges shown below, and a uniform dielectric constant of unity, we calculate 2.5-kcal/mol attraction in the *gauche* conformation.



## Conclusion

By assuming an electrostatic model, the relative stability of iodoacetone has been calculated with good agreement to that found experimentally. Partial charges were calculated from group dipole moments and potentials obtained by simple coulombic interaction. Similar calculations for iodomethyl methyl ether are complicated as the interacting dipoles are not separated by at least one bond. Assuming that the partial charges are additive and with a uniform dielectric constant of 1, the predicted relative stability is too high. Good agreement is obtained with the experimental value by introducing a dielectric constant for potentials along bonds, or by a mutual reduction from simple addition of concurrent dipole charges.

Both refinements can be determined experimentally from the bond-refractive indices and overall dipole moments of iodo compounds. However, this information is not available at present. On a qualitative basis, a system of alternate positive and negative partial charges imparts stability to a molecule, while destabilization is associated with adjacent like charges. From Table II it may be seen that, relative to the parent hydrogen compound, the most stable iodo compound is acetyl iodide. The negative iodine atom is adjacent to the positively polarized carbon atom of the carbonyl group.

The entropy and enthalpy of $ICH_2COCH_3(g)$ has been calculated as $S°_{298}$ = 85.7 ± 2.0 gibbs/mol and $\Delta H_f°_{298}$ = −31.0 ± 1.5 kcal/mol. From these results we can obtain the group contribution of the iodo ketone group.[11]

| | $\Delta H_f°_{298}$, kcal/mol | $S°_{298}$, gibbs/mol |
|---|---|---|
| C—(CO)(I)($H_2$) | 10.6 | 42.5 |

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[11] S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).

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# The Photochemistry of 2,6-Cyclooctadienone and 2,4-Cyclooctadienone[1]

**Thomas S. Cantrell and John S. Solomon**

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**Abstract:** Irradiation of 2,6-cyclooctadienone (**1**) in inert solvents affords in modest yield tricyclo[3.2.1.0$^{2,6}$]-octan-8-one, whose structure was proven by chemical degradation. Irradiation of **1** in reactive solvents such as methanol or furan gives addition products derived from a ground-state intermediate, 2-*trans*,6-*cis*-cyclooctadienone. Photolysis of 2,4-cyclooctadienone, **2**, in inert solvents gives low yields of the *trans*, head-to-head, 2 + 2 dimer, **16**, resulting from dimerization at the $\alpha,\beta$ positions of each dienone molecule. In methanol and furan adducts resulting from trapping of a mono-*trans*-dienone are formed. Possible pathways for the formation of the various products are discussed.

As part of the tremendous amount of investigation into the photochemistry of carbonyl compounds, cyclic enones of various ring sizes have received considerable attention.[2] Recent studies of the photochemical behavior of medium-ring unsaturated ketones have uncovered a multitude of interesting transformations. The eight-membered ring conjugated enones 2-cycloocten-1-one[3] and 2,4,6-cyclooctatrien-1-one[4] have been found to undergo isomerization to strained *trans* enones, which in turn undergo thermal cycloadditions and dimerizations, and in the latter case,

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[1] Supported in part by a grant from the Robert A. Welch Foundation.

[2] See, for example, R. O. Kan, "Organic Photochemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, Chapters 3 and 4.

[3] (a) P. E. Eaton and K. Lin, *J. Amer. Chem. Soc.*, **86**, 2087 (1964); (b) R. Noyori, A. Watanabe, and M. Kato, *Tetrahedron Lett.*, 5443 (1968).

[4] L. L. Barber, O. L. Chapman, and J. Lassila, *J. Amer. Chem. Soc.*, **91**, 531 (1969).