J. Am. Chem. Soc. 1985, 107, 4553-4554

2-one addition was reduced to 5 min, the 1,4-diketone yield was 73%. Thus at −78 °C the acylcuprate reagent has only minimal stability but its reactions may be carried out at this higher temperature. This may be of advantage when less reactive organic electrophiles are to be acylated. Other experiments showed that there is no advantage to going to temperatures lower than −110 °C.

A procedure for the *direct* nucleophilic conjugate acylation of α,β-unsaturated carbonyl compounds is a useful new synthetic method for the organic chemist. It is clear that the scope and limitations of this procedure remain to be defined. Furthermore, this new class of nucleophilic acylating reagents presents interesting possibilities for applications in synthesis other than that reported here and we are investigating such possibilities both in the organic and organometallic direction.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for support of this work.

Registry No. $CH_2{=}CHAc$, 78-94-4; $CH_2{=}CHC(O)Et$, 1629-58-9; $CH_3CH{=}CHCHO$, 4170-30-3; $C_2H_5CH{=}CHCHO$, 764-39-6; $PrCH{=}CHCHO$, 505-57-7; $Bu_2(CN)CuLi_2$, 80473-69-4; (*sec*-Bu)$_2$(CN)CuLi$_2$, 86646-53-9; (*t*-Bu)$_2$(CN)CuLi$_2$, 87263-84-1; $BuC(O)(CH_2)_2Ac$, 25234-82-6; $BuC(O)(CH_2)_2C(O)Et$, 96948-54-8; $BuC(O)CH(Et)CH_2CHO$, 96948-55-9; $BuC(O)CH(Pr)CH_2CHO$, 92803-30-0; (*sec*-Bu)C(O)(CH$_2$)$_2$Ac, 96948-57-1; (*sec*-Bu)C(O)CH(Et)CH$_2$CHO, 96948-58-2; (*t*-Bu)C(O)(CH$_2$)$_2$Ac, 38453-95-1; (*t*-Bu)C(O)(CH$_2$)$_2$C(O)Et, 65199-78-2; (*t*-Bu)C(O)CH(Me)CH$_2$CHO, 96948-60-6; (*t*-Bu)C(O)CH(Et)CH$_2$CHO, 96948-61-7; (*t*-Bu)C(O)CH(Pr)CH$_2$CHO, 96948-62-8; (*t*-Bu)(CH$_2$)$_2$Ac, 14272-73-2; (*t*-Bu)(CH$_2$)$_2$C(O)Et, 5054-71-7; (*t*-Bu)CH(Me)CH$_2$CHO, 37179-52-5; 2-cyclohexenone, 930-68-7; 2-cyclopentenone, 930-30-3; 3-pentanoylcyclohexanone, 25234-78-0; 3-pentanoylcyclopentanone, 64277-97-0; 3-(2-methylbutanoyl)cyclohexanone, 96948-56-0; 3-pivaloylcyclohexanone, 62687-29-0; 3-pivaloylcyclopentanone, 96948-59-3.

Norborna-2,5-dien-7-one: A Covalent Benzene–Carbon Monoxide Adduct. A New Point on the Cycloreversion Structure–Reactivity Correlation Curve

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We ask whether any hypothetical full-valence molecule can fail to exist because the activation energy for its thermal cycloreversion to stable fragments is zero. Previous discussions[1,2] of a few experimental examples of cycloreversion have assumed[3] a correlation between exothermicities and rates, which, if generally correct, could guide efforts to answer this question by the synthesis of substances of increasing thermodynamic instability.

A broader survey (Figure 1) shows a monotonic relationship between activation free energy ($\Delta G^{\ddagger}$ at 300 K) and reaction enthalpy change (ΔH_r) for 17 orbital symmetry-"allowed" fragmentations.[4] The data correspond to rate and equilibrium constant ranges of 10^{27} and 10^{70}, respectively. In the present work, we have attempted to extend this curve toward lower $\Delta G^{\ddagger}$ values by the simultaneous synthesis of two substances of current theoretical and preparative interest, norborna-2,5-dien-7-one (**1**)[5] and ethylenedione (**2**),[6] whose predicted approximate $\Delta G^{\ddagger}$ values, 17 and 15 kcal/mol, for fragmentation (into benzene + CO and 2CO, respectively), are obtained by extrapolation (see Figure 1).

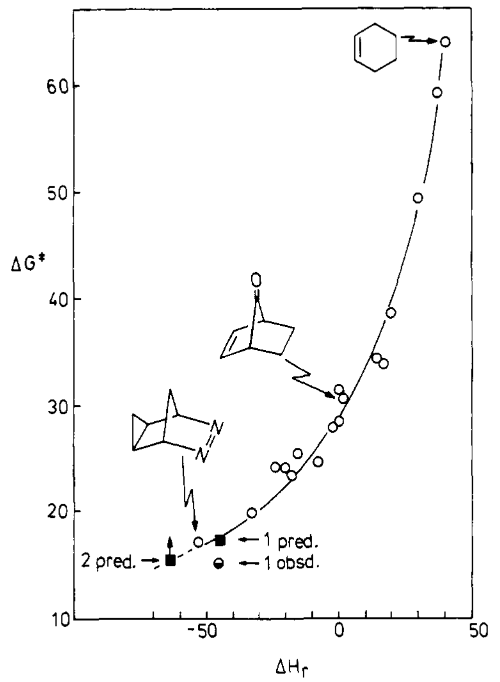
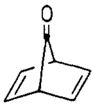


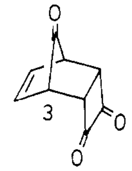
Figure 1. Dependence of $\Delta G^{\ddagger}$ (300 K) for fragmentation on reaction enthalpy. Values (kcal/mol) from the literature are shown as open circles. The actual $\Delta G^{\ddagger}$ value for triplet (ground state) **2** could be higher, since fragmentation of **2** is spin forbidden.[6a,b]



1

O=C=C=O

2



3

The synthesis of the pink, crystalline tricyclo[4.2.1.0^{2,5}]non-7-en-3,4,9-trione (**3**), mp 123–124 °C (dec), a potential precursor of both **1** and **2**, was achieved by a three-step sequence: Diels–Alder addition of 5,5-diethoxycyclopentadiene to diethyl maleate, acyloin condensation, and oxidation with Br_2.[7] Photolysis of CD_2Cl_2 solutions of **3** at 25 °C gave benzene as the only identified product, but photolysis of an argon matrix of **3** at 15 K with light of 313 nm, monitored by FT-IR, led to the disappearance of the bands of **3** (notably those of 1820 and 1772 cm^{-1}) and to the appearance of bands of CO at 2136 and 2121 cm^{-1}. Bands[8] of an unstable intermediate also grew in at 1846 (s), 1795 (s), 1327, 1317, 1206, 809, and 716 (s) cm^{-1}. The latter band is tentatively assigned to an olefinic C–H out-of-plane deformation mode. Warming the sample or prolonged irradiation produced benzene.

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(1) Rieber, N.; Alberts, J.; Lipsky, J. A.; Lemal, D. M. *J. Am. Chem. Soc.* **1969**, *91*, 5668.

(2) Berson, J. A.; Olin, S. S.; Pertrillo, E. W., Jr.; Bickart, P. *Tetrahedron* **1974**, *30*, 1639.

(3) This assumption is a corollary of the Hammond Postulate: (a) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334. (b) Farcasiu, D. *J. Chem. Educ.* **1975**, *52*, 76.

(4) (a) In most instances, ΔH_r data were calculated from group contributions in Benson's tables.[4b] References to kinetic data from which $\Delta G^{\ddagger}$(300 K) values were calculated are given in the supplementary material. (b) Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279.

(5) (a) Dewar, M. J. S.; Chantranupong, L. *J. Am. Chem. Soc.* **1983**, *105*, 7161. (b) Warrener, R. N.; Russell, R. A.; Pitt, I. G. *J. Chem. Soc., Chem. Commun.* **1984**, 1675 and references cited therein. (c) Landesberg, J. M.; Sieczkowski, J. *J. Am. Chem. Soc.* **1971**, *93*, 972 and references cited therein.

(6) (a) Haddon, R. C.; Poppinger, D.; Radom, L. *J. Am. Chem. Soc.* **1975**, *97*, 1645. (b) Raine, G. P.; Schaefer, H. F., III; Haddon, R. C. *Ibid.* **1983**, *105*, 194. (c) Rubin, M. B.; Weiner, M.; Scharf, H. D. *Ibid.* **1976**, *98*, 5699 and references cited therein.

(7) New compounds were characterized by elemental composition as well as IR and NMR spectroscopy.

(8) LeBlanc and Sheridan (LeBlanc, B. F.; Sheridan, R. S. *Abstr. Pap.—Am. Chem. Soc.* **1985**, *189th*, ORGN 178. LeBlanc, B.; Sheridan, R. *J. Am. Chem. Soc.*, following paper in this issue) have reported independent experiments toward the preparation of **1**. We thank Dr. Sheridan for making us aware of his activity in this area. In addition to IR bands at 1850, 1790, 1310, 1200, and 710 cm^{-1}, these authors report a band at 570 cm^{-1} which probably corresponds to one we observe at 575 cm^{-1}. The correspondence increases the degree of confidence in the assignment of the 575 cm^{-1} band to **1**.

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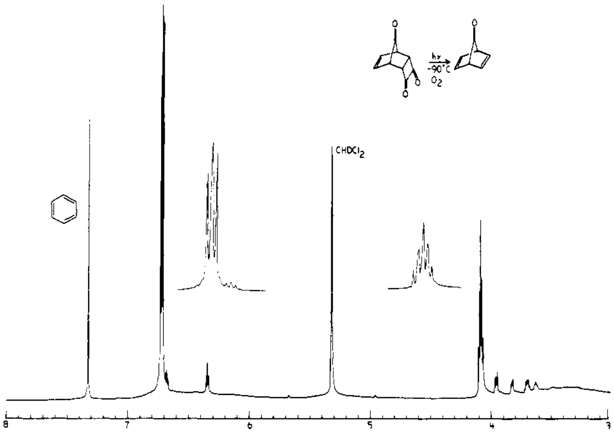

Figure 2. ^{1}H NMR spectrum (183 K, 250 Mhz) obtained by irradiation (192 K) of a CD_2Cl_2 solution of trione **3**. The major resonances are due to **1**. Small peaks near δ 6.3, 3.9, and 3.7 are due to unreacted **3** (~ 5–10%). The small peaks near δ 3.8 and 3.6 are associated with an impurity whose formation can be suppressed by degassing the sample before irradiation.

The asymmetric stretching vibration of **2** is predicted[6b] to produce an absorption band near 1745 cm^{-1}, and the two "carbonyl" bands at 1846 and 1795 cm^{-1} observed in the photolysate at first aroused our hopes that both **1** and **2** had indeed been generated. However, only **1** is formed, and neither band is in fact associated with **2**, since irradiation of **3**-d_6 under the same matrix-isolated conditions gave rise to an unstable species with a strong FT-IR absorption at 1808 cm^{-1} and a weak one at 1861 cm^{-1}. Since **2** contains no hydrogen, the observed deuterium perturbation is inconsistent with **2** as the carrier of the spectrum. The splitting observed in the undeuterated transient is reasonably ascribed to a Fermi resonance[9] in the spectrum of norbornadienone **1**. Similar smooth bisdecarbonylations are observed under matrix-isolated conditions in the photolyses of the 7,8-dihydro and 9-deoxy analogues of **3**, which lead, respectively, to norbornenone and norbornadiene. Again, only CO rather than C_2O_2 is formed.

Norbornadienone **1** can also be prepared in a polyethylene matrix, in which it is stable up to about 200 K. Photolysis of a CD_2Cl_2 solution of **3** at 192 K causes efficient conversion to **1**, whose ^{1}H NMR spectrum (Figure 2) shows only two absorptions: δ 6.72 (psuedo-t, 4 H, J = 2 Hz) and 4.08 (quintet, 2 H, J = 2 Hz). The ^{13}C spectrum shows three absorptions: δ 194.9 (s), 132.3 (d), and 55.4 (d). Norbornadienone decomposes to benzene and CO at higher temperature and has a half-life at 213 K of 25 min. From a study of the kinetics of decomposition (NMR), the activation parameters $\Delta G^{\ddagger}$ (300K) and E_a, 15 and 16 ± 2.5 kcal/mol, respectively, and log A = 13.0 ± 1.8 (A in s^{-1}), were obtained.[10] The $\Delta G^{\ddagger}$ value seems to be the lowest yet measured for a cycloreversion. The experimental $\Delta G^{\ddagger}$ value now may be compared with theoretical predictions[5a] of 21.5 and 25.7 kcal/mol derived, respectively, from MINDO/3 and MNDO calculations.

Free norbornadienone behaves similarly to the transient species implicated[5c] in the photochemistry of its Fe(CO)$_3$ complex, which forms 9,10-diphenylanthracene when generated in the presence of diphenylisobenzofuran. The same product now has been observed from the furan and **1** in the metal-free system.[11] Further studies of the chemistry of **1** are in progress.

The empirical correlation of Figure 1, slightly modified to incorporate the observed value for **1**, would seem to offer reliable predictions in the range covered by experiment to date. We hope to extend the correlation by further experiments to permit more firmly based predictions for substances of still lower stability, including C_2O_2.

Acknowledgment. We thank the National Science Foundation for support of this research and the Dox Foundation for a fellowship.

Registry No. 1, 22773-11-1; **3**, 96866-88-5; diethyl (*endo,endo*)-7,7-diethoxy-2,3-norborn-5-endicarboxylate, 96866-89-6; *endo*-9,9-diethoxytricyclo[4.2.1.0^{2,5}]non-7-en-3,4-dione, 96866-90-9; diethyl maleate, 141-05-9; 5,5-diethoxycyclopentadiene, 2931-32-0; 9,10-diphenylanthracene, 1499-10-1; diphenylisobenzofuran, 5471-63-6.

Supplementary Material Available: Data on ΔH_r and $\Delta G^{\ddagger}$ for 17 cycloreversions (7 pages). Ordering information is given on any current masthead page.

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[9] (a) Herzberg, G. "Infrared and Raman Spectra of Polyatomic Molecules"; Prentice-Hall: New York, 1939. (b) Davis, R. E.; Kim, K. S. *Theor. Chim. Acta* **1972**, *25*, 89.

[10] The E_a and log A values were obtained over the temperature range 200–213 K.

[11] Photolysis of a solution of **3** in Et_2O at −90 °C was followed by treatment with cold ethereal diphenylisobenzofuran. Workup[5c] gave 9,10-diphenylanthracene, recognized by its fluorescence and identified by 250-Mhz ^{1}H NMR spectroscopic comparison with an authentic sample.

Photochemical Generation and Direct Observation of 7-Norbornadienone

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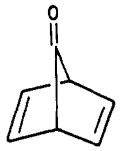
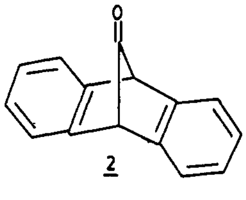
The novel ketone 7-norbornadienone (bicyclo[2.2.1]hepta-2,5-dien-7-one, **1**) holds a key position in the lore of cheletropic reactions,[1] yet this elusive molecule has not been previously observed.[2] Landesberg and Sieczkowski[3] have reported suggestive evidence for the intermediacy of **1** in photolysis or oxidation of its iron tricarbonyl complex, although the molecule eluded spectroscopic detection. Warrener and co-workers[4] recently reported observation of a highly substituted derivative of **1** which decarbonylated above −30 °C. In contrast, dibenzo derivatives of **1**, such as **2**, are modestly stable at room temperature.[5,6] On the basis of semiempirical calculations, Dewar and Chantranupong[7] have predicted that **1** should have an activation barrier of 21.4 kcal/mol (MINDO/3; 25.6 by MNDO; at 300 K) toward cheletropic loss of CO. We now wish to report the generation of **1** from two independent precursors, its spectroscopic observation, and details of its reactivity.[8]



1



2

Our approach to **1** was based on known reactions of norbornadienes[9] and quadricyclanes[10] with triazolinediones. Azo

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[1] Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry", 2nd ed.; Harper and Row: New York, 1981; p 849.

[2] Yankelevich, S.; Fuchs, B. *Tetrahedron Lett.* **1967**, 4945.

[3] Landesberg, J. M.; Sieczkowksi, J. *J. Am. Chem. Soc.* **1969**, *91*, 2120; *Ibid.* **1971**, *93*, 972.

[4] Warrener, R. N.; Russel, R. A.; Pitt, I. G. *J. Chem. Soc., Chem. Commun.* **1984**, 1675.

[5] Meinwald, J.; Miller, E. G. *Tetrahedron Lett.* **1961**, 253.

[6] Irie, T.; Tanida, A. *J. Org. Chem.* **1979**, *44*, 1002.

[7] Dewar, M. J. S.; Chantranupong, L. *J. Am. Chem. Soc.* **1983**, *105*, 7161.

[8] J. A. Berson and D. Birney have obtained similar results to ours from an alternate precursor: Berson, J. A.; Birney, D. *J. Am. Chem. Soc.*, preceding communication. We thank these authors for providing us with these results before publication.

0002-7863/85/1507-4554$01.50/0