stereomeric 1:1:1 products in a 5:1 ratio. Despite the fact that dimethyl acetylenedicarboxylate is a fairly good dipolarophile vs. **1**,[5,6,8] the copper-catalyzed procedure provided 58% of the dihydrofuran derivative **12** (mp 89–90 °C). Methyl phenylpropiolate, however, no longer successfully competed with benzaldehyde for the high-energy intermediate **2**.

Benzaldehyde has been replaced by anisaldehyde, 4-chlorobenzaldehyde, and furfural in analogous three-component reactions. For example, anisaldehyde, dimethyl fumarate, and **1** (Cu, 45 min, 125 °C) yielded 68% **5** and **6**, p-$C_6H_4OCH_3$ instead of C_6H_5 (mp 113.5–115 °C and 144–145 °C), in a 54:46 ratio, and the carbonyl ylide **2**, p-$C_6H_4OCH_3$ instead of C_6H_5, combined with fumaric ester 7.2 times faster than with anisaldehyde. Is it possible to substitute diazoacetic ester for diazomalonic ester? The pyrazoline formation with α,β-unsaturated carboxylic esters becomes the prominent reaction. Nevertheless, the Cu-catalyzed reaction of benzaldehyde, dimethyl fumarate, and methyl diazoacetate at 90 °C gave 14% of a tetrahydrofuran as 1:1:1 product. Experiments with more active metal catalysts are under way.

Registry No. 1, 6773-29-1; **3**, 82545-15-1; *cis*-**4**, 82545-16-2; *trans*-**4**, 82545-17-3; **5** (Ph), 82545-18-4; **5** ($C_6H_4OCH_3$-p), 82545-26-4; **6** (Ph), 82545-19-5; **6** ($C_6H_4OCH_3$-p), 82545-27-5; **7**, 82545-20-8; **8**, 82545-21-9; **9**, 82545-22-0; **10** (*N*-Me), 82545-23-1; **10** (*N*-Ph), 82545-24-2; **11** (*N*-Me), 82597-22-6; **11** (*N*-Ph), 82597-23-7; **12**, 82545-25-3; benzaldehyde, 100-52-7; dimethyl fumarate, 624-49-7; dimethyl maleate, 624-48-6; maleic anhydride, 108-31-6; *N*-methylmaleimide, 930-88-1; *N*-phenylmaleimide, 941-69-5; dimethyl acetylenedicarboxylate, 762-42-5; *p*-anisaldehyde, 123-11-5; methyl diazoacetate, 6832-16-2.

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(8) Bramley, R. K.; Grigg, R.; Guilford, G.; Milner, P. *Tetrahedron* **1973**, *29*, 4159–4167.

Chemistry of the Energy-Rich *m*-Quinomethane System. Formal (3 + 2) Cycloadditions to Olefins via a Singlet Intermediate

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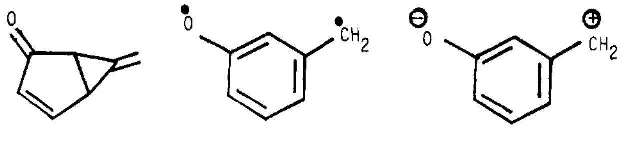
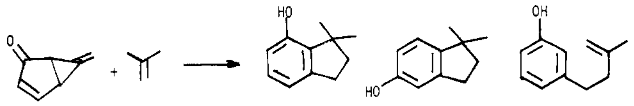
m-Quinomethane, a new non-Kekulé system, has been generated in two valency tautomeric forms, the bicyclic dienone **1** and the triplet state **2T** of the monocyclic biradical **2**.[1-3] The present paper reports a series of novel cycloadditions of this system and implicates a third species, a monocyclic singlet, **2S** or **3**, as the actual reactive intermediate.



1 2T: triplet 3
2S: singlet

Although **1** fails to give adducts with dimethyl acetylenedicarboxylate or dimethyl maleate, facile additions to electron-rich olefins occur either thermally (110 °C in benzene solution) or photochemically (0 °C in benzene solution, 300-nm radiation). With isobutylene, for example, three 1:1 adducts **4–6**, are formed in the kinetically controlled proportions 1.9:1.0:1.9, respectively.

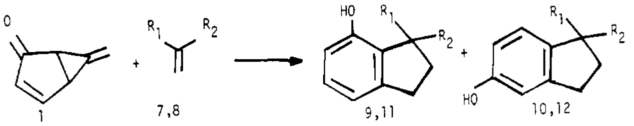


1 4 5 6

Their structures are established by elemental compositions, spectroscopic properties, and independent syntheses.[4] At low conversion (3.7% depletion of **1**), the absolute yield of 1:1 cycloadducts in the thermal reaction is 86 ± 15% by gas chromatographic (GC) analysis. This drops to 24% at 100% conversion, although the proportions of products **4**:**5**:**6** change only slightly (2.2:1.0:2.6). The photochemical reaction gives 54% yield of the same cycloadduct mixture after 100% conversion.

The diminished yields of 1:1 adduct in the high-conversion runs are caused by a secondary reaction in which another molecule of enone alkylates the first product either on oxygen or on carbon to give a 2:1 adduct. This problem can be mitigated in the photochemical addition by in situ protection of the 1:1 adducts. Inclusion of 6 equiv of trimethylsilyl chloride (Me_3SiCl) and 9 equiv of 2,6-lutidine in the reaction mixture traps the initial adducts **4–6** as their Me_3Si ethers, which under these conditions are relatively resistant to attack by a second molecule of **1**. Methanolysis of the Me_3Si ethers at 45 °C gives **4–6** in the combined yield of 70°.[5]

The highly specific Markovnikov-like orientation observed in the isobutylene additions occurs also in the reactions with isoprene (**7**) and with ethyl vinyl ether (**8**), which give products **9** + **10** (about equal amounts) and **11** + **12** (about 2:1), respectively.



1 7,8 9,11 10,12

7, **9**, **10**, $R_1 = Me$; $R_2 = CH{=}CH_2$
8, **11**, **12**, $R_1 = H$; $R_2 = OEt$

Without the Me_3SiCl in situ protection, the (unoptimized) absolute yields of **9** + **10** are 22% and 30% in the thermal and photochemical modes, respectively; **11** + **12** are correspondingly formed in 37% and 51% yields. O-methylation of **11** and **12** and of the dihydro derivatives of **9** and **10** give the corresponding ethers. Independent syntheses[4] of the latter confirm the spectroscopically based structural assignments. Products resulting from formal (3 + 2) addition to the conjugated diene system of isoprene, if present, constitute <3% of the adduct mixture.

Superficially, the cycloaddition reactions leading to phenolic indans and the hydrogen-transfer process leading to the olefin **6** resemble a Diels–Alder reaction and a vinylogous ene reaction, respectively, in which a σ bond plays a π-like role. However, the analogy implies a bimolecular mechanism, which is now shown to be incompatible with the kinetics of the thermal reaction.

Disappearance of enone **1** in benzene solution in the presence of a large excess of methanol or isoprene follows clean pseudo-first-order kinetics (analyses by GC and NMR). Measurements at seven temperatures between 100 and 129 °C give the Arrhenius equation $k = 10^{14.0} \exp(-30600 \pm 600\ (\mathrm{cal/mol})/RT)\ \mathrm{s}^{-1}$. At high methanol concentration a trace of 4-methoxy-6-methylenebicyclo[3.1.0]hexan-2-one is formed. Otherwise, the sole product in the methanol reaction is *m*-hydroxybenzyl methyl ether. The rate is *independent of the methanol concentration* in the range 0.0–1.73 M. At 105 °C, the rate in the presence of 0.5 M isoprene is the same as that in the presence (or absence) of methanol.

These data suggest that unimolecular formation of a reactive intermediate is the rate-determining step. A priori, the candidates

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(1) Rule, M.; Matlin, A. R.; Hilinski, E. F.; Dougherty, D. A.; Berson, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 5098.

(2) Seeger, D. E.; Hilinski, E. F.; Berson, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 720.

(3) Rule, M. Matlin, A. R.; Seeger, D. E.; Hilinski, E. F.; Dougherty, D. A.; Berson, J. A. *Tetrahedron* **1982**, *38*, 787.

(4) Methyl ethers of compounds **4** and **5** by H_2SO_4-catalyzed cyclization of 4-(3-methoxyphenyl)-2-methyl-2-butanol; methyl ether of compound **6** by Wittig methylenation of 4-(3-methoxyphenyl)-2-butanone; methyl ethers of dihydro-**9** and of dihydro-**10** by acid-catalyzed cyclization of 1-(3-methoxyphenyl)-3-hydroxy-3-pentane.

(5) The method fails in the thermal mode, however, because **1** reacts with Me_3SiCl at 110 °C to give a high yield of *m*-(trimethylsiloxy)benzyl chloride.

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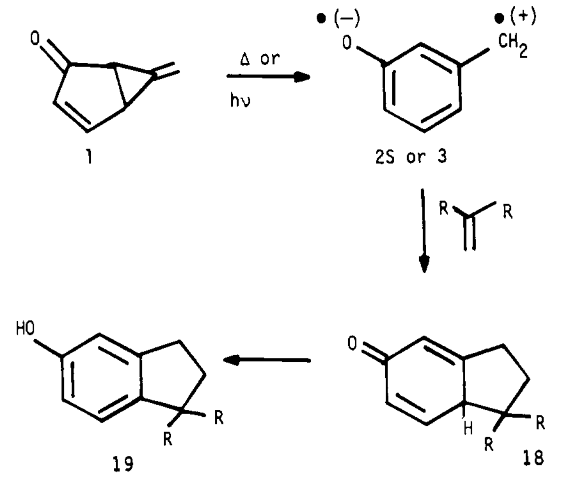
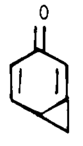
Scheme I



for the role of the intermediate might include the previously observed[1,3] triplet **2T**, but this seems unlikely in view of the normal Arrhenius preexponential term observed here. Violation of the spin prohibition in the reaction **1** → triplet **2T** should have resulted in a sharply diminished *A* factor.[6] Other formally possible candidates might be the ketones **13** and **14**, which are valency tautomers of **1**.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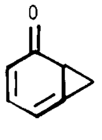
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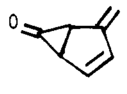
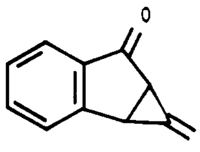

15

A perhaps more plausible candidate is the cyclopropanone **15**. Bond additivity calculations,[7] using the assumption of equal strain in **1** and **15**, suggest that the reaction **1** → **15** is nearly thermoneutral. That **15** indeed may be thermally accessible from **1** is strongly suggested by the observation that fulvene is a product of the pyrolysis of **1** under more drastic conditions (350 °C, 0.02 s, 10^{-4} torr).[8] However, if the methanolysis and cycloaddition of **1** proceed through **15** as an obligatory intermediate, the activation energy (E_a) for the corresponding reactions of the benzoenone **16** should be greater than that for **1** by the endothermicity of the cyclopropanone-forming step **16** → **17** ($\Delta H_r \sim 28$ kcal/mol). This would predict that **16** should react many orders of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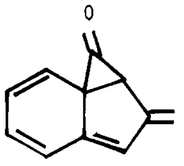
17

magnitude slower than **1**. In fact, however, we find the reaction of **16** with methanol at 105 °C gives 1-hydroxy-3-(methoxymethyl)naphthalene at a rate about 10 times *faster* than the methanolysis of **1**. Pending a basis for formal rejection of **13** and **14**, we consider the weight of evidence to favor a monocyclic singlet valency tautomer of **1**, either the singlet biradical **2** or the zwitterion **3**[9] as the reactive intermediate in the addition mechanism (Scheme I).

The addition reactions of the enone **1** are extraordinarily exothermic. With alcohols, **1** reacts to give *m*-hydroxybenzyl ethers,[1-3] a process that is exothermic by 72 kcal/mol.[7] This value is far greater than the exothermicity (ΔH_r) of addition of an alcohol to a simple olefin (31 kcal/mol) and comparable in magnitude to that of addition of an alcohol to a carbene (71 kcal/mol). In the cycloaddition of Scheme I, the overall ΔH_r is 89 kcal/mol, of which 69 kcal/mol is released in the actual cyclization to the ketonic precursor (**18**) of the phenolic indan (**19**). The overall energy yield is 50 kcal/mol greater than that in an archetypal Diels–Alder reaction. It is difficult to name any cycloaddition of a kinetically stable organic molecule that is nearly so exothermic.

Acknowledgment. We are grateful for the support of this work by the National Institutes of Health (GM 23375) and the National Science Foundation (CHE-8011399). We also thank the National Science Foundation for its support of the NSF Regional NMR Facility at Yale University (CHE-7916210).

Registry No. 1, 71946-85-5; **4**, 82615-36-9; **5**, 77366-77-9; **6**, 82615-37-0; **7**, 78-79-5; **8**, 109-92-2; **9**, 82615-38-1; **10**, 82615-39-2; **11**, 82621-38-3; **12**, 82615-40-5; isobutylene, 115-11-7.

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(6) (a) Mazur, M. R.; Berson, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 684. (b) Mazur, M. R.; Berson, J. A. *Ibid.* **1982**, *104*, 2217. (c) Rule, M.; Lazzara, M. G.; Berson, J. A. *Ibid.* **1979**, *101*, 7091. (d) Rule, M.; Mondo, J. A.; Berson J. A. *Ibid.* **1982**, *104*, 2209.

(7) (a) Estimated by using group contributions to heats of formation from Benson's tables (ref 7b). (b) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley-Interscience: New York, 1976.

(8) Goodman, J.; Berson, J. A., unpublished results.

(9) (a) Although the rate constant k_r for methanolysis of **1** responds to the polarity of the solvent only weakly and in the direction opposite to that expected if charge separation were far advanced in the transition state (k_r in $CH_3CN = 0.67k_r$ in benzene at 105 °C), a zwitterionic intermediate is not necessarily excluded. An "early" transition state is suggested by the observed E_a for **1**, 30 kcal/mol, which hardly differs from the E_a of about 28 kcal/mol found[10] for the unimolecular rearrangement of the ethylene ketal of **1** to that of **15**. Thus, the reaction of **1** shows little of the kinetic driving force potentially available from aromatization. (b) A zwitterionic intermediate is favored as the reactive species in the cycloadditions of cyclopropanones: Edelson, S. S.; Turro, N. J. *J. Am. Chem. Soc.* **1970**, *92*, 2770. (c) Intermediates related to **3** have been discussed in connection with other reactions: Leitich, J.; Wessely, F. *Montash. Chem.* **1964**, *95*, 129. Seiler, P.; Wirz, J. *Helv. Chim. Acta* **1972**, *55*, 2693. We are indebted to Professor Laren Tolbert, University of Kentucky, for calling the latter reference to our attention.

(10) Matlin, A. R.; Berson, J. A., unpublished work.

Photolysis of $Re_2(CO)_{10}$ in the Presence of Simple Olefins. Reactions of (μ-Hydrido)-(μ-alkenyl)-dirhenium Carbonyl Compounds

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UV photolysis of $M_2(CO)_{10}$, M = Mn or Re, in the presence of phosphine or phosphite ligands results in formation of the disubstituted dinuclear compounds 1,2-$M_2(CO)_8L_2$.[1] The reaction is believed to occur via thermal substitution of photogenerated $M(CO)_5\cdot$ radicals (eq 1–3). Substitution has also been effected

$$M_2(CO)_{10} \xrightarrow{h\nu} 2M(CO)_5\cdot \tag{1}$$

$$M(CO)_5\cdot \xrightarrow{L} M(CO)_4L\cdot + CO \tag{2}$$

$$2M(CO)_4L\cdot \rightarrow 1{,}2\text{-}M_2(CO)_8L_2 \tag{3}$$

by thermal means[2] or through use of Me_3NO.[3] It has recently been shown in these laboratories that 1,2-*dieq*-$Re_2(CO)_8(py)_2$ (py

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(1) (a) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 2065. (b) Morse, D. L.; Wrighton, M. S. *Ibid.* **1976**, *98*, 3931. (c) Byers, B. H.; Brown, T. L. *Ibid.* **1975**, *97*, 947. (d) Kidd, D. R.; Brown, T. L. *Ibid.* **1978**, *100*, 4095.

(2) (a) Osborne, A. G.; Stiddard, M. H. B. *J. Chem. Soc.* **1964**, 634. (b) Jolly, P. W.; Stone, F. G. A. *Ibid.* **1965**, 5259.

(3) Koelle, U. *J. Organomet. Chem.* **1978**, *155*, 53.

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