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Registry No. Ia, 81875-81-2; Ib, 81875-82-3; Ic, 81875-83-4; IIa, 81875-84-5; IIb, 81875-85-6; IIc, 81875-86-7.

Structure of an Unusual 1:2 Carbene–Methacrylonitrile Adduct. Chemical Evidence for Nitrile Ylide Formation

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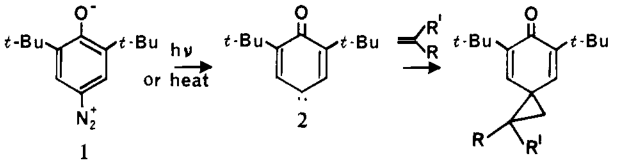
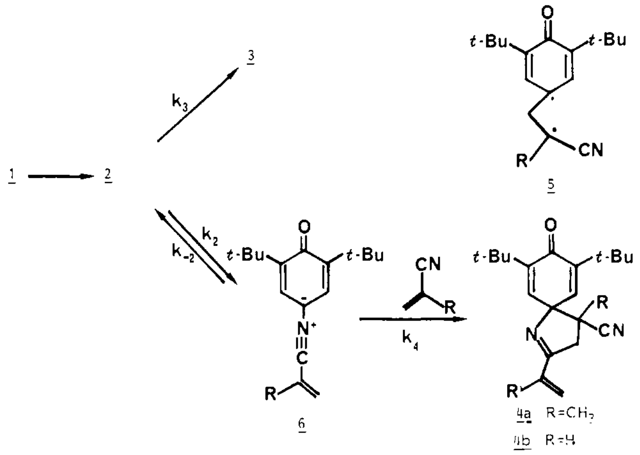
Current laser flash photolysis studies[1] of arylcarbenes in acetonitrile prompt us to describe the formation of unusual 1:2 cycloadducts between a carbene and unsaturated nitriles and to report evidence bearing on the reaction of a carbene with aliphatic nitriles.

It is well established from the work of the Nikiforov[2] and Pirkle[3] groups that thermal or photochemical decomposition of the *p*-diazo oxide **1** in the presence of substituted ethylenes leads to spirodienones (**3**) postulated to arise by cycloaddition of the carbene **2** to the olefinic bond.[4] Similar chemistry has been observed by Schechter's group for 10-diazoanthrone.[5]



3a, R = CH_3; R' = CN
b, R = H; R' = CN

In connection with a synthetic problem, we have conducted the thermolysis of **1** in pure methacrylonitrile (MAN) as solvent (4% **1**, reflux 2 h). To our surprise, two nonaromatic crystalline adducts, mp 149–150 and 147–149 °C, were isolated by Si gel chromatography in yields of 38% and 48%, respectively. The minor product had a molecular formula $C_{18}H_{25}ON$,[6] IR maxima ($CHCl_3$) at 1620, 1656, and 2240 cm^{-1}, λ_{max} (hexane) 272 nm (ϵ 18 000),[7] and ^1H NMR and ^{13}C NMR spectra[8] uniquely consistent with the spirodienone structure **3a**. The major product (**4a**) had the molecular formula $C_{22}H_{30}ON_2$[9] corresponding to the unexpected addition of *two MAN units to one of the carbene* **2**. Photolysis (4% **1**, >350 nm, 15 °C, 8 h) of *p*-diazooxide **1** in pure MAN also led to the formation of both adducts **3a** and **4a** in an approximately 1:1 ratio. When the *p*-diazooxide **1** was thermolyzed in pure acrylonitrile (4% **1**, reflux 14 h), a $C_{17}H_{23}ON$ adduct (**3b**), mp 122–123 °C,[2] and a $C_{20}H_{26}ON_2$ adduct (**4b**), mp 119–120.5 °C, were formed in yields of 43% and 28%, respectively. The spectroscopic properties of the adducts **3b**[10] and **4b**[11] closely paralleled those of the MAN series.



Our initial hypothesis, that the 1:2 carbene–MAN adduct **4a** might be a secondary reaction product arising from the interception of a second MAN unit by a thermally generated 1,3-diradical[12] (**5**) derived from opening of the cyclopropane ring of adduct **3a**, was quickly disproved. Prolonged heating of adduct **3a** in refluxing MAN led simply to recovery of **3a** in excellent yield. Moreover, detailed spectrometric analysis of **4a** demonstrated that the incorporation of a second MAN unit did not entail addition to the C=C bond of that unit. Thus the 400-MHz ^1H NMR of adduct **4a** not only showed the characteristic β-enone protons of a cyclohexadienone unit (δ 6.14 (d, J = 3Hz, 1 H), 6.65 (d, J = 3Hz, 1 H)) but revealed an isolated CH_2 group with diastereotopic protons (δ 2.98, 3.03, 3.53, 3.58; AB system, J = 18 Hz, 2 H) as well as a saturated CH_3 (δ 1.33 (s, 3 H)), an allylic CH_3 (δ 2.10 (br s, 3 H)), and terminal methylene (δ 5.55 (br s, 1 H), 5.68 (br s, H)). These data, taken with IR maxima at 1650, 1667, and 2240 cm^{-1} and λ_{max} (CH_3OH) 232 nm (ϵ 29 700) indicated that the adduct **4a** was probably formed by an addition to the C=C of one MAN unit and to the C≡N of another. A crystal of **4a**, grown from hexane and selected for intensity and unit cell measurements employing an Enraf-Nonius CAD-4 automatic X-ray diffractometer, was shown to be monoclinic in the space group $P2_1/c$: a = 12.177 (9) Å, b = 14.553 (9) Å, c = 13.014 (8) Å, β = 111.38 (3)°, Z = 4. From a total of 4462 reflections collected, 1291 were classified as observed [$F_o^2 > 3(\sigma(F_o)^2)$]. MULTAN 79 was utilized to locate all non-hydrogen atoms. The hydrogen atoms were located from difference Fourier maps. Subsequent refinement converged in four cycles to give R = 7.9%.

The structure **4a** thus shown for the 1:2 carbene–MAN adduct required a new mechanistic rationale. Control studies showed that the yield and ratio of adducts **3a** and **4a** from **1** were essentially unaffected by O_2, *p*-$(OMe)_2C_6H_4$, *m*-$(NO_2)_2C_6H_4$, 5% $CHBr_3$,

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(1) (a) Zupancic, J. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1980**, *102*, 5958; **1981**, *103*, 944. (b) Hadel, L. M.; Platz, M. S.; Senthilnathan, V. P.; Wrist, B. B.; Scaiano, J. C., submitted for publication. These workers find that the intersystem crossing rate of singlet 1-naphthylcarbene in CH_3CN is at least 5 times slower than in C_6H_6 and suggest the possible stabilization of the carbene in CH_3CN by reversible complexing with solvent to give a nitrile ylide. We are grateful to Professor Platz for communicating these results prior to publication.

(2) Nikiforov, G. A.; Sviridov, B. D.; Ershov, V. V. *Izvest. Akad. Nauk SSSR* **1968**, *3*, 558. This reference gives mp 118–119.5 °C for **3b**.

(3) Koser, G. F.; Pirkle, W. H. *J. Org. Chem.* **1967**, *32*, 1992. Pirkle, W. H.; Koser, G. F. *J. Am. Chem. Soc.* **1968**, *90*, 3598.

(4) Evidence for a ground-state triplet structure for carbene **2** has been discussed by Koser (Koser, G. F. *J. Org. Chem.* **1977**, *42*, 1474).

(5) Fleming, J. C.; Schechter, H. *J. Org. Chem.* **1969**, *34*, 3962.

(6) Found for **3a**: C, 79.63; H, 9.14; N, 5.00.

(7) This unusual λ_{max} is characteristic of such spiro[2,5]octa-3,6-diene-5-ones and has been ascribed to cyclopropane spiroconjugation. See, for example: Baird, R.; Winstein, S. *J. Am. Chem. Soc.* **1963**, *85*, 567.

(8) **3a**: ^1H NMR ($CDCl_3$) δ 1.23 (9 H, s), 1.27 (9 H, s), 1.59 (3 H, s), 1.70 (1 H, d, 5.4 Hz), 2.07 (1 H, d, 5.4 Hz), 6.12 (1 H, d, 3 Hz), 6.38 (1 H, d, 3 Hz); ^{13}C NMR ($CDCl_3$) δ 184.80, 151.74, 150.16, 139.72, 135.42, 120.91, 35.43, 35.13, 32.52, 30.58, 29.24 (corresponding to the $(CH_3)_6$ of *tert*-butyl groups) 22.69, 18.50.

(9) **4a**: found C, 78.07; H, 9.04; N, 8.27; ^{13}C NMR δ 185.47, 174.49, 150.10, 149.25, 138.39, 135.11, 123.89, 121.76, 76.63, 47.81, 47.20, 35.37, 35.23, 29.36, 29.24, 21.72, 19.11.

(10) **3b**: IR ($CHCl_3$) 1630, 1656, 2240 cm^{-1}; UV (hexane) λ_{max} 268 nm (ϵ 17 400); ^1H NMR ($CDCl_3$) δ 1.23 (9 H, s), 1.27 (9 H, s), 1.90 (2 H, m), 2.25 (1 H, dd, J = 9, 6 Hz), 5.85 (1 H, d, J = 3 Hz), 6.32 (1 H, d, J = 3 Hz).

(11) **4b**: IR ($CHCl_3$) 1650, 1668, 2240 cm^{-1}; UV (hexane) λ_{max} 229 nm (ϵ 30 000); ^1H NMR ($CDCl_3$) δ 1.26 (9 H, s), 1.28 (9 H, s), 3.25 (2 H, m), 3.45 (1 H, m), 5.84 (1 H, d, J = 17 Hz), 5.90 (1 H, d, J = 11 Hz), 6.30 (1 H, d, J = 3.6 Hz), 6.36 (1 H, d, J = 3.6 Hz), 6.71 (1 H, dd, J = 17, 11 Hz).

(12) The facile thermal and photochemical cis–trans isomerization of certain spiro[2,5]octa-3,6-dien-5-ones has been ascribed to the reversible formation and reclosure of such 1,3-diradical species. Pirkle, W. H.; Smith, S. G.; Koser, G. F. *J. Am. Chem. Soc.* **1969**, *91*, 1580.

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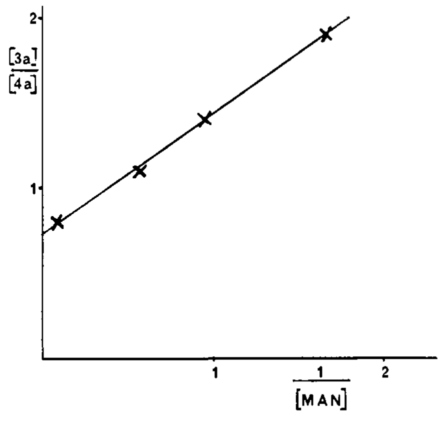
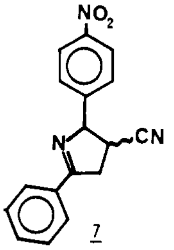


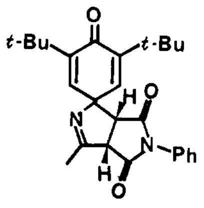
Figure 1.

or 1-5% EtOH, ruling out product dependence on radical chains, radical ions, intersystem crossing rates, or ionic intermediates. We propose that thermolysis of **1** (in the presence or absence of MAN) leads directly to the expected carbene **2** and that **2** reacts reversibly with MAN to yield a nitrile ylide intermediate (**6**).[13] In the presence of excess MAN this ylide may be captured by the double bond of a second MAN molecule to yield the stable diadduct **4a**. This process leading to adduct **4a** is in competition with the irreversible bimolecular cycloaddition of carbene **2** to MAN giving **3a**.

This mechanism is consistent with analogy, product ratio studies, and additional chemical evidence. Thus the formation of a halonium ylide during photolysis of diazo oxide **1** in the presence of 2,6-di-*tert*-butyl-4-bromophenol has been postulated.[14] Moreover, the regiochemistry of the trapping of our proposed ylide **6** by the acrylonitriles, to give **4a** or **4b**, conforms to that observed by Huisgen for the 1,3-dipolar addition of the electronically unsymmetrical benzonitrile 4-nitrobenzylylide to acrylonitrile yielding exclusively the regioisomer **7** (cis and trans).[15]



7



8

We have found that the molar product ratios ([**3a**]/[**4a**]) from thermolysis of **1** in MAN-heptane mixtures are proportional to 1/[MAN] as shown in Figure 1. These data give a linear plot of [**3a**]/[**4a**] vs. 1/[MAN] with an extrapolated intercept at 1/[MAN] = 0 of 0.7. Kinetic analysis of our proposed mechanism predicts that

$$\frac{d[3]/dt}{d[4]/dt} = \frac{k_3}{k_2} + \frac{k_{-2}k_3}{k_2k_4}(1/[\mathrm{MAN}])$$

which should indeed be linear with 1/[MAN] and give a nonzero intercept corresponding to k_3/k_2. The observed variations of the product ratios with [MAN] are thus in accord with the suggested mechanism and clearly preclude the irreversible formation of **6** (which predicts [**3a**]/[**4a**] to be independent of [MAN]), as well as any alternative mechanism in which **3** and **4** mutually arise from some irreversibly formed 1:1 adduct by competing unimolecular vs. bimolecular closures (this would predict a zero intercept at 1/[MAN] = 0).

Compelling chemical evidence for the presence of the postulated nitrile ylide **6** derives from the reaction of carbene **2** in *acetonitrile solution containing a dipolarophile solute*. Thermolysis of **1** in CH_3CN at reflux or photolysis of **1** in CH_3CN at 15 °C in the presence of molar amounts of *N*-phenylmaleimide led in identical yields (48%) to a mixed diadduct shown by IR, ^1H NMR, and mass spectrometry to have the tricyclic spirodienone structure **8**.[16] We conclude that generation of carbene **2** in the presence of a saturated or unsaturated nitrile leads to a highly reactive nitrile ylide (cf. **6**) which can add to dipolarophiles. Although such chemistry will be more important for electrophilic carbenes, care must be taken in assuming that an aliphatic nitrile is an inert solvent for the spectroscopic studies of carbene structures and lifetimes.

Acknowledgment. We are grateful to Professor J. A. Kampmeier (University of Rochester) and Dr. R. Gallucci (General Electric Co.) for valuable discussions bearing on the reaction mechanism. Partial support of this work by Grant CA-11326 and postdoctoral fellowship CA-06787 (to B.H.T.) awarded by the National Cancer Institute, USPHS, is gratefully acknowledged.

Registry No. 1, 955-02-2; **2**, 21205-90-3; **3a**, 82065-50-7; **3b**, 19510-09-9; **4a**, 82065-51-8; **4b**, 82065-52-9; methacrylonitrile, 126-98-7; acrylonitrile, 107-13-1.

Supplementary Material Available: Structure of **4a** and listings of positional and thermal parameters and of interatomic distances and angles (14 pages). Ordering information is given on any current masthead page.

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[13] The half-lives for disappearance of **1** in heptane, in 10% MAN in heptane, and in neat MAN at 86 °C were found to be 30 ± 2, 35 ± 2, and 45 ± 3 min. These relatively small differences argue against the involvement of MAN in the decomposition of **1** (e.g., rate-determining formation of a pyrazoline) and are consistent with unimolecular formation of carbene **2** directly from **1**.

[14] Pirkle, W. H.; Koser, G. F. *J. Am. Chem. Soc.* **1968**, *90*, 3598.

[15] Huisgen, R. *Helv. Chim. Acta* **1967**, *50*, 2421 and references therein.

[16] **8**: found *m/e* 418.2254 (M^+); ^1H NMR ($CDCl_3$) δ 1.18 (9 H, s), 1.23 (9 H, s), 2.22 (3 H, s), 3.20 (1 H, d, J = 8 Hz), 3.93 (1 H, d, J = 8 Hz), 5.88 (1 H, d, J = 3 Hz), 5.96 (1 H, d, J = 3 Hz), 7.15 (2 H, m), 7.35 (3 H, m); IR ($CHCl_3$) 1640, 1670, 1720 cm^{-1}; UV (hexane) λ_{max} 228 nm (ϵ 16000). The ^{13}C NMR of **8** matches that of **4a** in appropriate respects. We thank Dr. T. Chang (Amer. Cyanamid Co.) for the high-resolution mass spectrum.

Synthesis and Electrophilic Reactivity of Dicarbonyl(cyclohexadienyl)nitrosylmanganese Cations

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A variety of nucleophiles are known[1] to add to the arene ring in (arene)$Mn(CO)_3^+$ to yield the corresponding cyclohexadienyl complex, from which the monofunctionalized arene can be obtained by oxidation or endo hydride abstraction in acid.[2] The addition of two nucleophiles to (arene)$Mn(CO)_3^+$ represents a possible route to difunctionalized 1,3-cyclohexadienes. Such double addition does not occur with most nucleophiles but is possible with strong hydride donors.[3,4] Double nucleophile addition to benzene has recently been shown[5] to occur with $(C_5H_5)Co(C_6H_6)^{2+}$, although in this case the usefulness is limited due to side reactions and the ready displacement of benzene by many nucleophiles.

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