Registry No.—**2**, 19991-27-6; **2** hydrochloride, 16175-40-9; **2a**, 20013-27-8; **5**, 19991-29-8; **6**, 16219-20-8; **7**, 16175-45-4; **9**, 16175-46-5; **12**, 16219-18-4; **13**, 16175-31-8; **14**, 16175-32-9; **15**, 19980-11-1; **15a**, 19980-12-2; **16**, 16175-38-5; **16a**, 19980-15-5; **17**, 19980-16-6; **18**, 16175-33-0; **19**, 16219-19-5.

Acknowledgments.—We wish to thank Mr. G. Bamert for assistance in the experimental work. We are very grateful to Mr. Urs Stoeckli and Mrs. N. Engstrom and their staff for the spectral and microanalytical work as well as for aid in the interpretation of the spectral data.

The Addition of Acetone Dimethylhydrazone to Dimethyl Acetylenedicarboxylate

STEPHEN F. NELSEN

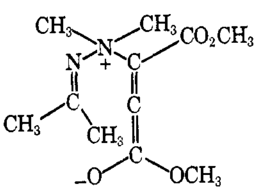
Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

Received November 8, 1968

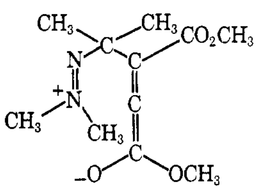
Acetone N,N-dimethylhydrazone and dimethyl acetylenedicarboxylate react at −30° to give 20% of the 1:2 adduct, 1-dimethylamino-2,2-dimethyl-3,4,5,6-tetracarbomethoxy-1,2-dihydropyridine, and 26% of a 1:1 adduct, dimethyl N-isopropylidine-N-dimethylamino-2-aminomaleate. At higher temperatures dimethyl 2-dimethylaminomaleate becomes an increasingly more important product. Dimethyloxalacetate dimethylhydrazone is a minor product at low temperatures. The 1:2 adduct gave upon photolysis the *cis* and *trans* forms of the azahexatriene, the former closing thermally at room temperature.

Hydrazones have three potentially nucleophilic centers: the amino nitrogen, the imino nitrogen, and the imino carbon. Alkylation of dimethylhydrazones takes place exclusively at the amino nitrogen,[1] which clearly ought to be the most nucleophilic center.

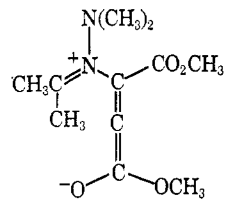
Dehydrodimerization of formaldehyde phenylhydrazone to glyoxal osazone, reported by von Pechmann,[2] presumably involves a nucleophilic attack at the carbon in the carbon–carbon bond-forming step. We felt that addition of dimethylhydrazones to dimethyl acetylenedicarboxylate[3] (1) would be an example of a nucleophilic reaction of a hydrazone which might give reaction at any of all of the nucleophilic centers. Since the initial addition to form zwitterions should be reversible, the products obtained would reflect the ease of subsequent reactions to give stable products. Dimethylamino nitrogen attack by acetone dimethylhydrazone (2) would yield zwitterion 3, which would be expected to undergo N–N$^+$ bond fission and give 2-dimethylamino dimethylmaleate. Attack by the imino carbon would give 4, which by analogy with enamine adducts[3] might be expected to close to the azacyclobutene structure, which would open to the azabutadiene form easily. Imino nitrogen attack would give 5, which would be expected to react as adducts of pyridines[3] and other imines,[4] and either add another molecule of dimethyl acetylenedicarboxylate in a "1,4-dipolar" reaction[4a] or transfer a C-methyl hydrogen.



3



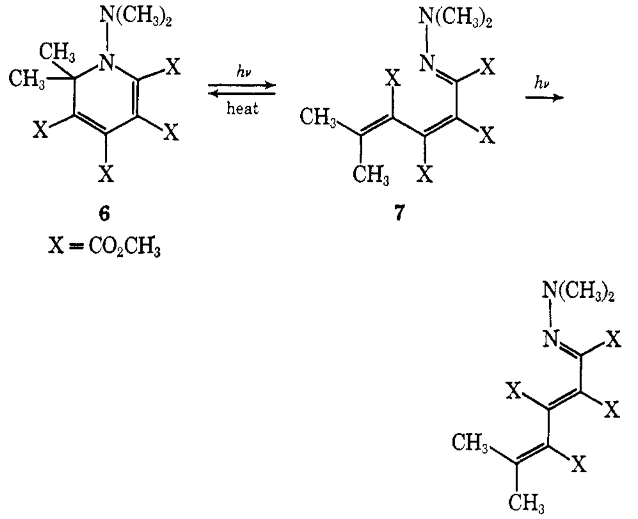
4



5

Results and Discussion

When 1 and 2 are mixed in methylene chloride at −30°, the reaction is complete in several hours. To consume all of the hydrazone, a molar ratio of 1.5:1 is required. Removal of solvent affords a yellow solid having spectral and analytical data consistent with 6, an expected product of initial imino nitrogen attack. The behavior of 6 upon ultraviolet irradiation confirms this structural assignment, for it is partially converted into an isomer, 7. The nmr spectrum of 7 shows the downfield shifted dimethylamino absorption and nonequivalent allylic methyls expected for simple ring opening of the azahexadiene ring of 6. At room temperature in carbon tetrachloride 7 reverts to 6 with a



6 7

X = CO_2CH_3

8

---

(1) (a) R. F. Smith and L. E. Walker, *J. Org. Chem.*, **27**, 4372 (1962); (b) P. A. S. Smith and E. E. Most, Jr., *J. Org. Chem.*, **22**, 358 (1957).

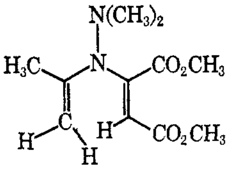
(2) H. von Pechmann, *Chem. Ber.*, **30**, 2459 (1897).

(3) For a recent review of such addition reactions, see E. Winterfeldt, *Angew. Chem. Intern. Ed. Engl.*, **6**, 423 (1967).

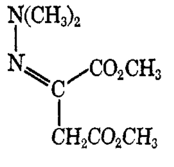
(4) (a) R. Huisgen and K. Herbig, *Ann. Chem.*, **688**, 98 (1965); (b) J. M. F. Gagan, *J. Chem. Soc., C*, 1966, 1121.

half-life of about 55 hr (analysis by nmr). Prolonged irradiation of **6** causes other products to be formed, of which the only one investigated was **8**, also an isomer. The nmr of **8** is quite similar to **7** but slightly shifted, and heating a mixture of **6**, **7**, and **8** with boiling acetone for 3 hr cyclized the **7** to **6** without affecting **8**. Thus **7** is the *cis* isomer, and **8** the *trans* isomer of the ring-opened material.

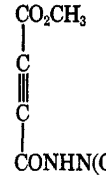
Only about 30% of the residue from the reaction of acetone dimethylhydrazone with dimethyl acetylenedicarboxylate after crystallization of **6** was distillable, and decomposition was apparent. The resinous pot residue was not investigated. The distillate consisted of two major components, **9** and **10**, which we could not separate analytically. Spectral data for **9** showed it to be dimethyl N-isopropylidine-N-dimethylamino-2-aminomaleate. That **9** has the maleic ester geometry is demonstrated by comparison of its nmr spectrum with those of the piperidine adducts of **1**[5] which have vinyl hydrogen absorption at δ 4.83 for the maleic, and 5.48 for the fumaric form (compared with 4.61 for **9**). The methoxyl separation substantiates the argument, for it is 0.22 ppm in the maleic and 0.00 ppm in the fumaric piperidine adduct, compared with 0.21 ppm for **9**. Thus **9** is the other expected product from **5**, the zwitterion formed by imino nitrogen attack.



9



10



11

The lower boiling component of the mixture had spectral data consistent with it being the N,N-dimethylhydrazone of oxalacetic acid (**10**). The corresponding phenylmethylhydrazone has been prepared by addition of 1-phenyl-1-methylhydrazine to dimethyl acetylenedicarboxylate.[6] The major product from addition of dimethylhydrazine to dimethyl acetylenedicarboxylate was, indeed, **10**. When this reaction is run at −30°, however, the major product is the solid monodimethylhydrazide (**11**), which was not detected in our reaction mixtures; so it is unlikely that **10** was formed by contamination of the acetone dimethylhydrazone with dimethylhydrazine. Adventitious hydrolysis of **9** is an obvious possibility.

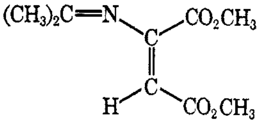
When the reaction of acetone dimethylhydrazone with dimethyl acetylenedicarboxylate is run at higher temperatures, **10** becomes a much less important product, and dimethyl 2-dimethylaminomaleate[5] (**12**) appears in isolable amounts. Yields calculated from the nmr spectra of the distillate and isolated weight of **6** are summarized in Table I. The bisenamine **9** is quite unstable to heating, vpc, or tlc, giving a variety of products, mostly intractable. The major nonvolatile products which come off an SE-30 vpc column upon injection of **9** are **10** and **13**. The spectral properties of **13** show it to be the acetone imine of dimethyl 2-aminomaleate. The downfield nmr shift for the vinyl hydrogen in comparison with **9** is expected since the imino nitrogen of **13** should be less capable of releasing electrons to the maleic ester system. A similar effect is reported by Truce and Brady,[7] who compare vinyl shifts for dialkylamino and ethylenimine adducts with **1**, although in this case nitrogen hybridization is changed by inclusion in a three-membered ring. The vinylic methyls remain a singlet in benzene, making it unlikely that an accidental shift correspondence is responsible; inversion at the imino nitrogen appears to be rapid. **13** would also have been a possible product from internal proton transfer by **5**, splitting out formaldehyde methylimine; no **13** was detected in the reactions of **1** with **2**, however.

TABLE I

PRODUCTS (PER CENT) OF THE REACTION OF 1 AND 2 IN METHYLENE CHLORIDE (1:1 MOLAR RATIO)

	Temp, °C		
Product	−30	0	40
6	16[a]	8	4
9	26	17	25
10	7	1	1
12	1	4	7

[a] Using a 1.26:1 ratio of 2:1, 22% was isolated.



13

The reaction of **1** with formaldehyde dimethylhydrazone was looked at briefly, but even at −50° no 1:1 or 2:1 products were observed. At higher temperatures small amounts of **12** were formed, as was the case with acetone dimethylhydrazone.

In conclusion, acetone dimethylhydrazone (**2**) reacts with **1** as an imine (through **5**), and no evidence for "azaenamine" reaction (proceeding through nucleophilic attack by carbon to give zwitterion **4**) was found. Above 0°, the product from N–N$^+$ fission of zwitterion **3** becomes increasingly important.

Experimental Section

Melting points were taken on a Fisher-Johns capillary apparatus, and are uncorrected. Nmr spectra were run on a Varian A-60A, and are reported as parts per million shift downfield from internal TMS. Ir spectra were taken using carbon tetrachloride on a Beckman IR-8, uv using a Cary 11, and mass spectra using a CEC 103 or AEI MS 9. Combustion analyses were by Microtech. Dimethyl acetylenedicarboxylate was distilled commercial material (Aldrich), and contained about 0.6% dimethylfumarate. Acetone N,N-dimethylhydrazone (bp 93–95°, lit.[8] bp 92–94°) was prepared by mixing equimolar quantities of acetone and N,N-dimethylhydrazine (untreated Aldrich), stirring for 4 hr, adding sodium hydroxide pellets until an aqueous layer stopped forming, and distilling from sodium hydroxide.

1-Dimethylamino-2,2-dimethyl-3,4,5,6-tetracarbomethoxy-1,2-dihydropyridine (**6**).—Acetone dimethylhydrazone (5.0 g, 0.05 mol) in 10 ml of methylene chloride was cooled to −30°, poured into a cooled solution of 9.0 g (0.063 mol) of **1** in 10 ml of methylene chloride, and stored 15 hr at −30°. Solvent was removed at aspirator pressure; the residue was stirred with 20 ml of carbon tetrachloride and filtered, washing well with carbon tetrachloride. The brown solid was crystallized once from chloroform–heptane

---

(5) R. Huisgen, K. Herbig, A. Siegl, and H. Huber, *Chem. Ber.*, **99**, 2526 (1966).

(6) R. M. Acheson and J. M. Vernon, *J. Chem. Soc.*, 1148 (1962).

(7) W. E. Truce and D. G. Brady, *J. Org. Chem.*, **31**, 3543 (1966).

(8) R. H. Wiley, S. C. Slaymaker, and H. Kraus, *ibid.*, **22**, 204 (1957).

to give 4.3 g (22%) of **6**, mp 141–143°. Two recrystallizations from $CHCl_3$ gave mp 142–143°; nmr ($CDCl_3$) δ 1.61 (s, 6, $C(CH_3)_2$), 2.87 (s, 6, $N(CH_3)_2$), 3.62 (s, 3, OCH_3), 3.68 (s, 3, OCH_3), 3.74 (s, 3, OCH_3), 3.84 (s, 3, OCH_3); ir (CCl_4) 5.76–5.90, 6.23, 6.51, 6.79 μ; uv max (MeOH) 271 nm (ε 1.10 × 10^4), 354 (5.8 × 10^3).

Anal. Calcd for $C_{13}H_{24}N_2O_8$: C, 53.12; H, 6.29; N, 7.29. Found: C, 52.93; H, 6.26; N, 7.26.

Irradiation of 6.—A solution of 0.5 g of **6** in 350 ml of dry ether under N_2 was irradiated with a 450-W Hanovia "L" lamp, using a Pyrex well, for 50 min. Solvent was removed at aspirator pressure, and nmr indicated a 40% conversion into **7**. Recrystallization from CCl_4 gave **7**: mp 110-112° (resolidified and remelted 141–143°); nmr ($CDCl_3$) 1.79 (s, 3, —CCH_3), 2.07 (s, 3, =CCH_3), 3.06 (s, 6, $N(C_3)H_2$), 3.61 (s, 3, OCH_3), 3.66 (s, 3, OCH_3), 3.72 (s, 3, OCH_3); uv (MeOH) 282 nm (ε 7.8 × 10^3), 349 (3.2 × 10^3). In deuteriochloroform, the half-life for cyclization of **7** to **6** is about 55 hr at room temperature.

Irradiation of **6** for 24 hr gave other materials; the only one investigated (**8**) had an nmr spectrum very similar to that of **7**, though shifted—(CCl_4) δ 1.90 (s, 3, =CCH_3), 2.24 (s, 3, =CCH_3) 3.01 (s, 6, $N(CH_3)_2$), 3.60 (s, 3, OCH_3), 3.66 (s, 3, OCH_3), 3.71 (s, 3, OCH_3), 3.78 (s, 3, OCH_3). Heating a mixture of **6**, **7**, and **8** in chloroform with refluxing acetone for 3 hr converted the **7** into **6** without affecting the **8**. We never obtained **8** in crystalline form.

Dimethyl N-Isopropylidine-N-dimethylamino-2-aminomaleate (9).—The carbon tetrachloride solution from which **6** had been filtered (see above) was concentrated and distilled (short path, decomposition was apparent), giving an oil, bp 110–115° (1 mm). Redistillation through a 6-in. Vigreux column (bp 112–115°, 0.25 mm) gave an oil still contaminated with **12**. A sample collected 180°; decomposition is extensive) crystallized in needles from carbon tetrachloride–pentane at −25° after 3 weeks (mp 48–50°). The distillate crystallized when seeded. The analytical sample decomposed in transit, but gave for a parent peak *m/e* 242.1258 ± 0.0022 (calcd for $C_{11}H_{18}N_2O_4$, 242.1266); mass spectrum (70 eV) *m/e* (relative intensity) 242 (1), 199 (16), 184 (11), 166 (21), 140 (85), 109 (100), 108 (72), 107 (40); nmr (CCl_4) δ 5.18 (m, 1, vinyl), 4.93 (m, 1, vinyl), 4.61 (s, 1, vinyl), 3.75 (s, 3, OCH_3), 3.53 (s, 3, OCH_3), 2.55 (s, 6, $N(CH_3)_2$); ir (CCl_4) 5.72, 5.86, 6.29, 6.97 μ.

Dimethyloxalacetate Dimethylhydrazone (10).—A solution of 4.26 g of **2** in 20 ml of ether was dripped into 1.8 g of N,N-dimethylhydrazine in 10 ml of ether. When the refluxing had stopped the yellow solution was decanted from a black residue, concentrated, and distilled, bp 90–95° (0.5 mm), 2.1 g. This material was not obtained pure, but gave a parent having *m/e* 202.129 ± 0.037 (calcd for $C_8H_{14}N_2O_4$, 202.095); nmr (CCl_4) δ 3.73 (s, 3, OCH_3), 3.66 (s, 3, OCH_3), 3.57 (s, 2, CH_2), 2.88 (s, 6, $N(CH_3)_2$; ir 5.78–5.87, 6.35, 6.93 μ; uv (CH_3OH) maximum 291 nm (ε 6.3 × 10^3). This material had spectral properties identical with that isolated from reaction of **1** and **2** by tlc on silica gel which destroys **9**) followed by vpc on a 10 ft × 0.25 in. 10% FFAP column. The presence of **10** in the reaction mixtures was demonstrated by nmr of the methylene chloride solution before any work-up.

Methyl Dimethylacetylenedicarboxylate N,N-Dimethylhydrazide.—When 4.26 g (0.03 mol) of **1** and 1.80 g (0.03 mol) of N,N-dimethylhydrazine were allowed to react in 15 ml of methanol at −30° for 7 hr, 2.3 g of a solid, mp 170–193 dec, was isolated after evaporation. Two crystallizations from chloroform gave colorless rods: mp 200° dec; nmr ($CDCl_3$) δ 7.05 (s, 1, NH), 3.94 (s, 3, OCH_3), 3.50 (s, 6, $N(CH_3)_2$); ir ($CHCl_3$) 3.0 (w, broad), 5.78, 6.04, 6.20 μ.

Acetone dimethyl 2-aminomaleate imine (13) was isolated in small amounts by collection from a 10 ft × 0.25 in. 10% SE-30 vpc column when **9** was injected. Thermal decomposition of **9** in a flow system (230–265°) or neat (250°) gave only traces of **13**: nmr (CCl_4) δ 5.91 (s, 1, vinyl H), 3.77 (s, 3, OCH_3), 3.67 (s, 3, OCH_3), 1.98 (6, $NCCH_3)_2$); ir (CCl_4) 5.73, 5.89, 6.32 μ; uv (CH_3OH) 282 nm (ε 8.8 × 10^3); mass spectrum (70 eV) *m/e* (relative intensity) 199 (3), 167 (12), 141 (13), 137 (13), 123 (149), 109 (100), 108 (31), 183 (13).

Registry No.—**1**, 762-42-5; **2**, 13483-31-3; **6**, 19987-67-8; **7**, 19988-62-6; **9**, 19988-63-7; **10**, 19987-68-9; **11**, 19987-69-0; **13**, 19988-64-8.

Acknowledgment.—We thank the Petroleum Research Fund and the Wisconsin Alumnia Research Foundation for support of this work.

Cycloaddition Reactions of Isocyanates. The Addition of Sulfonyl Isocyanates to Carbodiimides[1]

HENRI ULRICH, B. TUCKER, F. A. STUBER, AND A. A. R. SAYIGH

The Upjohn Company, Donald S. Gilmore Research Laboratories, North Haven, Connecticut 06473

Received January 6, 1969

The polar cycloaddition reaction of arenesulfonyl isocyanates (**1**) with dialkylcarbodiimides (**2**) gives rise to the formation of six-membered ring cycloadducts **6** and **8**. The latter compound arises from interception of an acyclic polar 1:1 adduct by arenesulfonylalkylcarbodiimide (**9**), which is generated *via* an exchange sequence. Simultaneous cycloaddition of **1**, **2**, and **9** forms cycloadducts **6**, **8**, and **12**. Cycloadduct **12** is a 2:1 adduct of **9** and **2**. All cycloadducts readily thermolyze above 100° to lose alkyl isocyanate and give arenesulfonylcarbodiimides in good yield.

The cycloaddition reactions of arenesulfonyl isocyanates with double-bonded substrates often occur in a stepwise fashion.[1-4] The initially generated acyclic 1:1 adducts can undergo ring closure to produce four-membered ring cycloadducts or they can be intercepted by a double bond containing dipolarophile to yield six-membered ring cycloadducts. The possibility of interception is enhanced if the lifetime of the acyclic 1:1 adduct is increased by effective delocalization of the generated charges. In the arenesulfonyl isocyanate–dialkylcarbodiimide system delocalization of the generated charges in the initially formed acyclic adducts can occur readily, and since sulfonylheterocumulenes are excellent dipolarophiles the six-membered ring cycloadducts are obtained exclusively. The elucidation of structure of the six-membered ring cycloadducts is complicated by the ambident character of the generated acyclic 1:1 adducts and by the possibility of addition across either one of the double bonds in the heterocumulene substrates.

On mixing of equimolar amounts of arenesulfonyl isocyanate (**1**) and dialkylcarbodiimides (**2**), with or without a solvent, an immediate reaction occurs, as evidenced by the appearance of two double-bond absorptions at 1869 (medium) and 1724 cm^{-1} (strong),

---

(1) Part of this work appeared as a communication: H. Ulrich, B. Tucker, and A. A. R. Sayigh, *J. Amer. Chem. Soc.*, **90**, 528 (1968).

(2) W. Bartmann, *Chem. Ber.*, **100**, 2938 (1967).

(3) E. J. Moriconi and W. C. Crawford, *J. Org. Chem.*, **33**, 370 (1968).

(4) R. Gompper, A. Studeneer, and W. Elsner, *Tetrahedron Lett.*, 1019 (1968).