(ε 47 000), 247 (12 000) nm; NMR (CDCl$_3$) δ 7.60 (s, 1 H), 7.44 (br, s, 5 H), 3.99 (s, 3 H); mass spectrum (VLSI) *m/e* (relative intensity) 342 (4), 329 (1), 283 (100), 220 (59), 184 (10), 150 (32); GC $r_{n\text{-C}_{22}}$ (Dexsil 400, 200 °C) 4.6.

Anal. Calcd for $C_{15}H_9Cl_3O_3$: C, 52.44; H, 2.64; Cl, 30.95. Found: C, 52.67; H, 2.80; Cl, 31.03.

Because of the impurities evident in the gas chromatogram and the mass spectrum, **10b** was collected by preparative GC. Material collected off SE-52 at 220 °C gave IR and mass spectra essentially identical with the above.

Methyl 3,4,5-Trichlorobiphenyl-2-glyoxylate (9b) and Methyl 2,3,4-Trichlorobiphenyl-5-glyoxylate (10b) Directly from the Diels-Alder Adduct. *o*-Chloranil (1.09 g, 4.4 mmol) was reacted with 1.07 g (10.4 mmol) of phenylacetylene in 30 mL of benzene at reflux for 12 h. After the solution was cooled, 1.20 g of a commercial 25% NaOMe solution in methanol was added. After 5 min, the reaction was quenched with dilute aqueous NaHCO$_3$ and extracted thoroughly with several portions of pentane. The combined pentane extracts were washed with dilute aqueous NaHCO$_3$, dried with Na$_2$SO$_4$, and flash evaporated to an oil: 1.48 g (97% crude yield). GC analysis revealed two products comparable in retention times to the methyl esters **9b** and **10b** previously prepared separately. Mass spectrometry of samples collected off the gas chromatograph were identical for **9b** and **10b**. Gas chromatography gave the following: ortho ester **9b**, $r_{n\text{-C}_{22}}$ (Dexsil 400, 200 °C) 3.2, 21% yield; meta ester **10b**, *r* 4.7, 54% yield. Preparative high pressure liquid chromatography using 0.5% MeOH (v/v) in pentane gave the following: ortho ester **9b**, *k*′ 1.5, crystallized as colorless plates from cyclohexane, mp 88.5–90 °C (underpressed when mixed with pure **9b**); meta ester **10b**, *k*′ 2.9, a slightly yellow oil.

Registry No. 1, 2435-53-2; **4a**, 64253-27-6; **4a** Na salt, 70072-52-5; **4b**, 70072-53-6; **4c**, 70072-54-7; **5**, 29261-09-4; **9a**, 65531-05-7; **9a** Na salt, 70072-55-8; **9b**, 70072-56-9; **10a**, 65242-83-3; **10a** Na salt, 70072-57-0; **10b**, 70072-58-1; **11**, 70072-59-2; **12**, 3258-80-8; **13**, 6453-83-4; anthranilic acid, 118-92-3; phenylacetylene, 536-74-3; *o*-chloranil, 2435-53-2.

Periselective Addition of Mesoionic Compounds to Tetracyanoethylene. Preparation of [(Dicyanovinyl)hydrazono]malononitriles

Howard C. Berk* and John E. Franz

Monsanto Agricultural Products Company, Research Department, St. Louis, Missouri 63166

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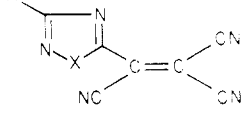
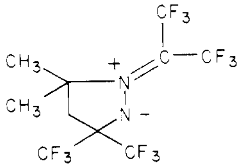
[(Dicyanovinyl)hydrazono]malononitriles are formed in moderate yields when sydnones are heated with tetracyanoethylene in inert solvents. An unstable bicyclic adduct, formed by a periselective 1,3-dipolar addition of the sydnone to the TCNE double bond, is proposed as a reaction intermediate. The [(dicyanovinyl)hydrazono]malononitriles undergo ready solvolysis under a variety of conditions to yield the corresponding hydrazonomalononitriles.

Tetracyanoethylene (TCNE) reacts with 1,3-dienes to form Diels–Alder adducts,[1] but the mode of cycloaddition to 1,3-dipoles is less predictable. As reported[2] earlier, nitrile sulfides and nitrile oxides react at the nitrile function of TCNE to yield the tricyanoethylenes **1a** and **1b**. Ethyl diazoacetate and the pyrazoline **2** react with TCNE in a similar manner to afford the products **3**[3] and



R = aryl, alkyl

1a, X = S
b, X = O



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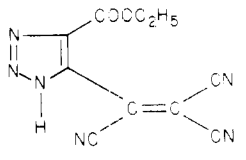

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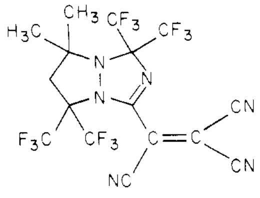

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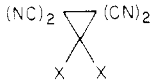
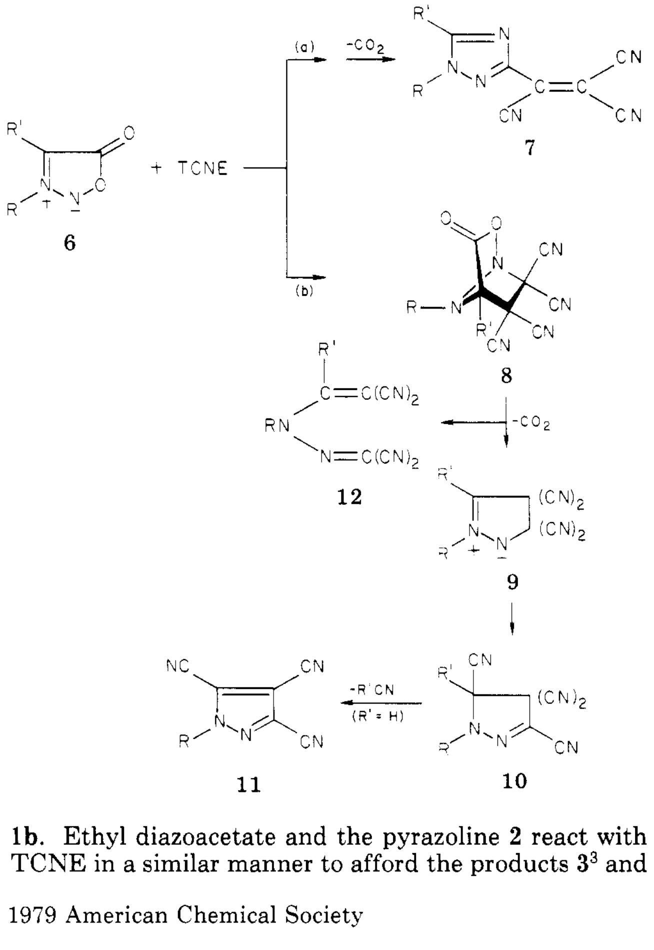


5a, X = H-
b, X = C$_6$H$_5$-

Scheme I



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[1] W. Middleton, R. Heckert, E. Little, and G. Krespan, *J. Am. Chem. Soc.*, **80**, 2783 (1958).

[2] J. E. Franz, R. K. Howe, and H. K. Pearl, *J. Org. Chem.*, **41**, 620 (1976).

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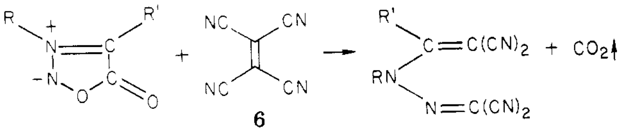
Table I. [(Dicyanovinyl)hydrazono]malononitriles from Sydnones and Tetracyanoethylene in *o*-Dichlorobenzene



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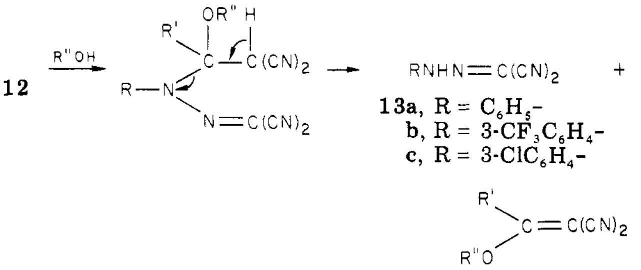
12

12	*R*	*R'*	mp, deg	% yield
a	C_6H_5	H	182.5-184.5	63
b	$4\text{-}ClC_6H_4$	H	161-162	33
c	$3\text{-}ClC_6H_4$	H	113-115	33
d	$3,4\text{-}Cl_2C_6H_3$	H	162.5-164.5	50
e	$4\text{-}FC_6H_4$	H	138-139	52
f	$3\text{-}FC_6H_4$	H	133.5-135	55
g	$2,4\text{-}F_2C_6H_3$	H	140-142	32
h	$4\text{-}BrC_6H_4$	H	191-192	50
i	$4\text{-}CH_3C_6H_4$	H	168-169	52
j	$3\text{-}CH_3C_6H_4$	H	158-159	41
k	$4\text{-}CNC_6H_4$	H	231	33
l	$3\text{-}F_3CC_6H_4$	H	179.5-181	55
m	$4\text{-}H_3COC_6H_4$	H	143-145	58
n	$4\text{-}H_3CSC_6H_4$	H	164-165	44
o	$2\text{-}C_2H_5C_6H_4$	H	172-174	11
p	$3,5\text{-}(F_3C)_2C_6H_3$	H	166-167	23
q	$3,4\text{-}(H_3C)_2C_6H_3$	H	162-163	56
r	C_6H_5	CH_3	198-200	17
s	C_6H_5	Br	140-142	62
t	C_6H_5	C_6H_5	183-184	30
u	CH_3	H	117-118	5
v	$CH_3\text{-}(CH_2)_3\text{-}$	H	91-92	34
x	$CH_3O\text{-}(CH_2)_3\text{-}$	H	97.5-98	34
y	cyclohexyl	H	176-178	20

4,[4] respectively. By contrast, however, diazomethane and diphenyldiazomethane undergo exclusive addition to the double bond of TCNE to produce intermediate pyrazolines and finally the substituted cyclopropanes **5a**[5] and **5b**.[2] In a continuation of our efforts to determine how the 1,3-dipolar structure influences the periselectivity of the cycloaddition reactions, we have investigated the mode of addition of TCNE to mesoionic sydnones.

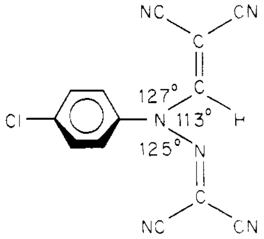
The sydnones **6**, which contain a "masked" azomethine imine function, generally were prepared by dehydration of the appropriate *N*-nitroso-α-amino acids with acetic[6] or trifluoroacetic anhydrides.[7] In accordance with related reactions of TCNE[2] and sydnones,[8,9] the formation of **7**, **10**, and/or **11** by the pathways indicated in Scheme I would appear potentially feasible. Pathway (a) represents 1,3-dipolar addition of the sydnone to the nitrile function of TCNE, and (b) indicates the expected mode of addition to the double bond. There is no precedence for the formation of a product of type **12** in reactions of this type, but this mode of cleavage would appear to be thermodynamically favorable. The cleavage of strained σ bonds in an analogous fashion has been reported by several groups.[10]

N-Phenylsydnone (**6a**, R = C_6H_5-; R' = H) and TCNE did not react in refluxing chlorobenzene, but in *o*-dichlorobenzene carbon dioxide was evolved at a moderate rate.[11] From the dark reaction mixture, a white solid was isolated in fair yield (63%). The elemental analysis of the product is consistent with the empirical formula $C_{13}H_6N_6$, and thus structures **8** and **11** are not tenable. The IR spectrum indicates the presence of nitrile and the absence of carbonyl functionality. The ^1H NMR spectrum exhibits resonances for five aromatic protons and one deshielded hydrogen at δ 8.8. The lack of color in the product and the magnitude of the shift of the low field proton in the ^1H NMR spectrum are not consistent for structures **7** and **10** but are tenable for **12** and/or **9**. Mesoionic products of type **9**, although postulated[8] as intermediates in sydnone–olefin reactions, have not been isolated. Hydrolytic experiments, however, strongly support the [(dicyanovinyl)hydrazono]malononitrile structure **12**. Thus, under a variety of conditions (Florisil chromatography, triethylamine in ethanol, HCl in methanol) solvolytic cleavage of the product occurs to yield the hydrazonomalononitrile **13a**.[12] The alkoxy dicyanoethylene coproduct undergoes secondary degradation and has not been isolated.



13a, R = C_6H_5-
b, R = $3\text{-}CF_3C_6H_4$-
c, R = $3\text{-}ClC_6H_4$-

An X-ray analysis of the *p*-chlorophenyl derivative **12b** confirms the [(dicyanovinyl)hydrazono]malononitrile structure as indicated below.[13]



A variety of [(dicyanovinyl)hydrazono]malononitriles prepared by the general procedure are summarized in Table I. Sydnones in which R' is hydrogen and R is aryl or alkyl require reaction times of 5–25 h at 170 °C for complete conversion. Evolution of carbon dioxide is generally impeded when the aryl groups contain electronegative substituents. When R' is alkyl or halogen (i.e.,

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(3) R. Scribner, G. Sauser, and W. Prichard, *J. Org. Chem.*, **25**, 1440 (1960).

(4) K. Burger, H. Schickaneder, and M. Pinzel, *Justus Liebigs Ann. Chem.*, 30 (1976).

(5) J. Bastus and J. Castells, *Proc. Chem. Soc., London*, 216 (1962).

(6) C. J. Thoman and D. J. Voaden, *Org. Synth.*, **45**, 96 (1965).

(7) W. Baker, W. D. Ollis, and V. D. Poole, *J. Chem. Soc.*, 1542 (1950).

(8) (a) R. Huisgen, H. Gotthardt, and R. Grashey, *Chem. Ber.*, **101**, 536 (1968); (b) H. Gotthardt and R. Huisgen, *ibid.*, **101**, 552 (1968); (c) R. Huisgen, R. Grashey, and H. Gotthardt, *ibid.*, **101**, 829 (1968); (d) R. Huisgen and H. Gotthardt, *ibid.*, **101**, 1059 (1968).

(9) (a) V. F. Vasil'eva, V. G. Yashunskii, and M. N. Sichukina, *Zh. Obshch. Khim.*, **30**, 698 (1960); *Chem. Abstr.*, **54**, 24674 (1960); (b) V. F. Vasil'eva, V. G. Yashunskii, and M. N. Sichukina, *Zh. Obshch. Khim.*, **31**, 1501 (1961); *Chem. Abstr.*, **55**, 22291 (1961); (c) V. F. Vasil'eva, V. G. Yashunskii, and M. N. Shchukina, *Zh. Obshch. Khim.* **33**, 3706 (1963); *Chem. Abstr.*, **60**, 8017 (1964).

(10) (a) H. D. Martin and M. Hekman, *Angew Chem.*, **84**, 995 (1972); *Angew Chem., Int. Ed. Engl.*, **11**, 926 (1972); (b) H. Matsukubo and H. Kato, *J. Chem. Soc., Perkin Trans 1*, 632 (1975); (c) K. T. Potts, J. Baum, and E. Houghton, *J. Org. Chem.*, **41**, 818 (1976); (d) A. Felzenstein, S. Sarel, and J. Yovell, *J. Chem. Soc., Chem. Commun.*, 918 (1975); (e) A. Huth, H. Straub, and F. Müller, *Tetrahedron Let.*, 2845 (1973); (f) F. Toda and H. Dan, *J. Chem. Soc., Chem. Commun.*, 30 (1976).

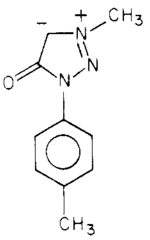
(11) As mentioned by the referee, Chinone and Ohta [*Bull. Chem. Soc. Jpn.*, **47**, 1032 (1974)] described the formation of a charge-transfer complex between sydnones and TCNE in solution. After removal of the solvent, each component was recovered unchanged. At lower temperatures, we also observed an orange color possibly characteristic of the complex.

(12) (a) N. V. Maatschappij, *Chem. Abstr.*, **63**, 13278 (1965); (b) A. L. Fenner, *ibid.*, **72**, 6257c (1965).

(13) The X-ray analysis of **12b** was performed by Frank L. May and Donald J. Dahm of the Corporate Research Department of Monsanto. For the data see: Crystal Structure Communications, in press.

6r and **6s**), however, the formation of **12** is complete in 25 min at 140 °C. The activating effect of alkyl and halogen substituents in the 4 position of the sydnone ring is somewhat surprising in view of the opposing inductive effects of these groups. By contrast, liberation of carbon dioxide is not facilitated when R′ is aryl. The very slow rate of reaction observed when R is an ortho substituted aryl group presumably is due to steric inhibition of the 1,3-dipolar cycloaddition reaction. In contrast to **12a** and **12l**, **12s** reacted appreciably slower with dilute hydrochloric acid in methanol at room temperature. At 60–65 °C, however, hydroytic cleavage of **12s** yielded **13a**.

In contrast to our findings concerning the 1,3-dipolar addition of sydnones to TCNE, other mesoionic compounds[14] have been reported to react in a different manner. Thus, the triazole[14a] **14** and TCNE yielded the tricyanoethylene **15** and the thiazolone[14b] **16** afforded the adduct **17**. These systems (**14** and **16**) have two structural features in common: (1) carbon dioxide is not the heterocumulene potentially capable of elimination and (2) each mesoionic structure possesses a labile proton. Work is in progress to better define the importance of these features.



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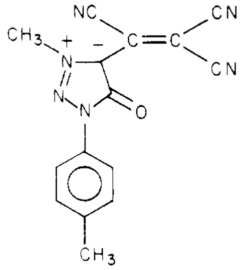

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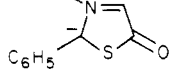

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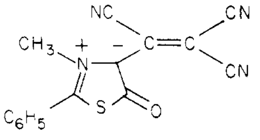

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Experimental Section

Melting points were taken in open capillaries in a Mel-Temp apparatus and are uncorrected. The tetracyanoethylene used in this work was Eastman white label grade. CAC analyses were performed on a Ford M Scientific 720 dual column programmed gas chromatograph using 2-ft columns packed with 10% OV-17. Programming was generally carried out from 50 to 300 °C, at 15 °C/min.

α-[2-(2,2-Dicyanovinyl)-2-phenylhydrazono]malononitrile (12a). A mixture of 6.5 g (0.04 mol) of 3-phenylsydnone,[8] 5.2 g (0.04 mol) of TCNE, and 50 mL of *o*-dichlorobenzene was heated at 170 °C under nitrogen with good agitation. After 3 h, the mixture was cooled to room temperature and allowed to remain overnight. The reaction mixture was diluted with 50 mL of ether and filtered. The residue was washed with ether and air dried. The yield of brown powder, mp 181–182 °C, was 7.0 g (71%). The IR spectrum indicated essentially pure **12a**. An analytical sample was prepared by decolorization with charcoal as follows: a mixture of 2 g of crude product, 1 g of decolorizing charcoal, and 35 mL of benzene was heated to boiling, and the mixture was filtered after 1–2 min. The residue was extracted with two 15-mL portions of hot benzene, and the combined filtrate was allowed to cool. After crystallization was complete, the product was collected and washed with ether. The yield of pure α-[2-(2,2-dicyanovinyl)-2-phenylhydrazono]malononitrile (**12a**), mp 182.5–184.5 °C, was 1.5 g. From the benzene filtrates there was recovered 0.4 g of additional product with the same IR spectrum: ν (Nujol) 3030, 2222, 1613, 1582, 1515, 1449, 1351, 1220, 1188, 1152, and 730 cm^{-1}.

Anal. Calcd for $C_{13}H_6N_6$: C, 63.40; H, 2.46; N, 34.14. Found: C, 62.91; H, 2.43; N, 33.98.

α-[2-(*p*-Chlorophenyl)-2-(2,2-dicyanovinyl)hydrazono]malononitrile (12b). A solution of 3-(*p*-chlorophenyl)sydnone[15] (2.1 g, 0.011 mol) and tetracyanoethylene (1.4 g, 0.011 mol) in *o*-dichlorobenzene (20 mL) was heated in a 170 °C bath for 5.5 h. The reaction mixture was allowed to stand overnight and then diluted with petroleum ether. The resulting black precipitate was collected and dried in the air. The black solid was dissolved in hot benzene, treated with charcoal, and boiled for 10 min. After filtration, the yellow solution was concentrated to one-third volume and diluted with petroleum ether, and the resulting precipitate was collected and dried in the air to yield 0.8 g (55%) of **12b**. Recrystallization from benzene–petroleum ether yielded an analytically pure sample of **12b**: mp 161–162 °C; NMR δ_{Me_4Si} ($CDCl_3$) 7.3–8.0 (m, 5).

Anal. Calcd for $C_{13}H_5N_6Cl$: C, 55.63; H, 1.80; N, 29.94. Found: C, 55.54; H, 1.85; N, 29.90.

α-[2-(*m*-Chlorophenyl)-2-(2,2-dicyanovinyl)hydrazono]malononitrile (12c). A solution of 3-(*m*-chlorophenyl)sydnone[16] (4.2 g, 0.021 mol) and tetracyanoethylene (2.94 g, 0.023 mol) in *o*-dichlorobenzene (30 mL) was heated at 165 °C for 6 h. Workup as in preparation of **12b** afforded 2.0 g (33%) of **12c**: mp 113–115 °C; NMR δ_{Me_4Si} (Me_2SO-d_6) 7.69 (m, 3, ArH), 7.88 (m, 1, ArH) and 8.73 (s, 1, vinyl H).

Anal. Calcd for $C_{13}H_5N_6Cl$: C, 55.63; H, 1.80; N, 29.94. Found: C, 55.53; H, 1.89; N, 29.91.

α-[2-(3,4-Dichlorophenyl)-2-(2,2-dicyanovinyl)hydrazono]malononitrile (12d). A mixture of 4.6 g (0.02 mol) of 3-(3,4,-dichlorophenyl)sydnone,[17] 2.8 g (0.022 mol) of TCNE, and 50 mL of *o*-dichlorobenzene was heated at the reflux temperature under nitrogen for 7 h. The black solution was diluted with petroleum ether, and the gummy black precipitate was stored under ether overnight. The dark brown powder which formed under the ether was collected and washed with ether. The air-dried product, mp 153–157 °C weighed 3.5 g. An additional quantity of crude product (0.5 g) was recovered from the combined filtrates for a total yield of 4.0 g (63%). Attempts to purify the crude product by chromatography on Florisil resulted in extensive hydrolysis. Purification was achieved by decolorization with activated carbon. A mixture of 1 g of crude product, 1.5 g of decolorizing charcoal, and 35 mL of benzene was boiled for 1–2 min and then filtered. The residue was extracted with 15 mL of hot benzene, and the combined filtrate was concentrated at reduced pressure. The residue was washed with ether to yield 0.8 g of pure **12d**, mp 162.5–164 °C. An analytical sample, mp 162.5–164.5 °C, was prepared by recrystallization from benzene: ν (Nujol) 3049, 2222, 1608, 1567, 1515, 1449, 1348, 1220, 1163, 1126, and 769 cm^{-1}.

Anal. Calcd for $C_{13}H_4Cl_2N_6$: C, 49.54; H, 1.28; N, 26.67. Found: C, 49.64; H, 1.30; N, 26.60.

α-[2-(2,2-Dicyanovinyl)-2-(*p*-fluorophenyl)hydrazono]malononitrile (12e). A mixture of 3-(*p*-fluorophenyl)sydnone[18] (2.0 g, 0.011 mol) and tetracyanoethylene (1.55 g, 0.012 mol) in *o*-dichlorobenzene (22 mL) was heated at 170 °C for 7 h. Workup as in preparation of **12b** led to isolation of 1.5 g (52%) of **12e**: mp 138–139 °C; NMR δ_{Me_4Si} (Me_2SO-d_6) 7.3–7.83 (m, 4, ArH), 8.79 (s, 1, vinyl H); ν (CH_2Cl_2) 2225 cm^{-1}.

Anal. Calcd for $C_{13}H_5N_6F$: C, 59.09; H, 1.91; N, 31.81. Found: C, 58.98; H, 1.98; N, 31.96.

α-[2-(2,2-Dicyanovinyl)-2-(*m*-fluorophenyl)hydrazono]malononitrile (12f). A solution of 3-(*m*-fluorophenyl)sydnone[18]

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(14) (a) K. T. Potts and S. Husain, *J. Org. Chem.*, **35**, 3451 (1970); (b) K. T. Potts, J. Baum, E. Houghton, D. N. Roy, and V. P. Singh, *ibid.*, **39**, 3619 (1974); (c) K. T. Potts and M. Sorm, *ibid.*, **36**, 8 (1971). (d) For a different mode of addition see: P. Rajagopalan and P. Penev, *J. Chem. Soc., Chem. Commun.*, 490 (1971).

(15) W. Baker, W. D. Ollis, and V. D. Poole, *J. Chem. Soc.*, 307 (1949).

(16) V. G. Yashunskii, V. F. Vasil'eva, and Yu. N. Sheinker, *Zh. Obshch. Khim.*, **29**, 2712 (1959).

(17) R. W. Pütter and G. Wolfrom, German Patent 1 057 124 (May 4, 1959); *Chem. Abstr.*, **55**, 7436 (1961).

(18) M. Bellas and H. Suschitsky, *J. Chem. Soc. C.*, 189 (1966).

(1.0 g, 0.0055 mol) and tetracyanoethylene (0.78 g, 0.006 mol) in *o*-dichlorobenzene (11 mL) under nitrogen was heated in a 165 °C bath for 4.5 h. Workup as in the preparation of **12b** afforded 1.0 g (33%) of **12f**: mp 133.5–135 °C; NMR δ_{Me_4Si} (Me_2SO-d_6) 7.5–7.9 (m, 4, ArH) and 8.83 (s, 1, vinyl H); ν (Nujol) 2250, 1580, and 1560 cm^{-1}.

Anal. Calcd for $C_{13}H_5N_6F$: C, 59.09; H, 1.91; N, 31.81. Found: C, 59.13; H, 1.79, N, 31.88.

α-[2-(2,4-Difluorophenyl)-2-(2,2-dicyanovinyl)hydrazono]malononitrile (12g). A solution of 1.3 g (0.0065 mol) of 3-(2,4-difluorophenyl)sydnone and tetracyanoethylene (0.83 g, 0.0065 mol) in *o*-dichlorobenzene (11 mL) was heated in a 170 °C bath for 7.5 h. Workup as in the preparation of **12b** afforded 0.58 g (32%) of **12g**: mp 140–142 °C; NMR δ_{Me_4Si} (Me_2SO-d_6) 7.37–7.83 (m, 3, ArH) and 9.0 (s, 1, vinyl H); ν (CH_2Cl_2) 2225 cm^{-1}.

Anal. Calcd for $C_{13}H_4N_6F_2$: C, 55.33; H, 1.43; N, 29.78. Found: C, 55.10; H, 1.46; N, 29.60.

α-[2-(*p*-Bromophenyl)-2-(2,2-dicyanovinyl)hydrazono]malononitrile (12h). A solution of 3-(*p*-bromophenyl)sydnone[19] (3.0 g, 0.0124 mol) and tetracyanoethylene (1.74 g, 0.0136 mol) in *o*-dichlorobenzene (40 mL) was heated in a 170 °C bath for 7 h. The workup was as in the preparation of **12b** and afforded 2.0 g (50%) of **12h**: mp 191–192 °C; NMR δ_{Me_4Si} (Me_2SO-d_6) 7.7 (A_2 of A_2B_2, J = 8 Hz, 2, ArH), 7.9 (B_2 of A_2B_2, J = 8 Hz, 2, ArH).

Anal. Calcd for $C_{13}H_5N_6Br$: C, 48.02; H, 1.55; N, 25.85. Found: C, 47.97; H, 1.58; N, 25.93.

α-[2-(2,2-Dicyanovinyl)-2-(*p*-tolyl)hydrazono]malononitrile (12i). A solution of 3-(*p*-tolyl)sydnone[15] (2.5 g, 0.0142 mol) and tetracyanoethylene (2.4 g, 0.0156 mol) in *o*-dichlorobenzene (25 mL) was heated in a 165 °C bath for 7 h. The workup was as in the preparation of **12b** and afforded 1.9 g (52%) of **12i**: mp 168–169 °C; NMR δ_{Me_4Si} (Me_2SO-d_6) 2.36 (s, 3, CH_3), 7.46 (br s, 4, ArH), and 8.73 (s, 1, vinyl H).

Anal. Calcd for $C_{14}H_8N_6$: C, 64.61; H, 3.10. Found: C, 64.55; H, 3.14.

α-[2-(2,2-Dicyanovinyl)-2-(*m*-tolyl)hydrazono]malononitrile (12j). A solution of 3-(*m*-tolyl)sydnone[20] (2.0 g, 0.0113 mol) and tetracyanoethylene (1.6 g, 0.0125 mol) in *o*-dichlorobenzene (22 mL) was heated in a 165 °C bath for 7.5 h. Workup as in the preparation of **12b** afforded 1.2 g (41%) of **12j**: mp 158–159 °C; NMR δ_{Me_4Si} (Me_2SO-d_6) 2.46 (s, 3, CH_3), 7.3 (br s, 4, ArH), and 8.83 (s, 1, vinyl H); ν ($CDCl_3$) 2250 cm^{-1}.

Anal. Calcd for $C_{14}H_8N_6$: C, 64.61; H, 3.10. Found: C, 64.57; H, 3.15.

α-[2-(4-Cyanophenyl)-2-(2,2-dicyanovinyl)hydrazono]malononitrile (12k). A solution of *N*-(4-cyanophenyl)sydnone (2.01 g, 0.0035 mol) and TCNE (1.20 g, 0.0093 mol) in *o*-dichlorobenzene (40 mL) was heated in a 165 °C bath for 6 h. The cooled reaction mixture was diluted with petroleum ether (150 mL), and the dark brown precipitate was collected after the solution was left standing overnight. The material was taken up as a suspension in hot benzene and filtered. The residue was identified as the desired product (0.1 g. 4%). The filtrate was concentrated in vacuo to yield 1.5 g of a mixture of sydnone (80%) and product (20%). A solution of this mixture (1.5 g), TCNE (0.60 g, 0.0047 mol) in *o*-dichlorobenzene (30 mL), was heated in a 175 °C bath for 16 h. After cooling the solution and diluting it with petroleum ether, the resulting precipitate was collected, dried, and recrystallized from methylene chloride–petroleum ether with charcoal clarification. The resulting light tan product which contained a trace of sydnone was taken up in boiling benzene, and after cooling the resulting precipitate was collected and dried to yield 0.8 g (29.4%) of **12k**: mp 231 °C; NMR δ_{Me_4Si} (Me_2SO-d_6) 8.2 (m, 4, ArH) and 8.8 (s, 1, vinyl H).

Anal. Calcd for $C_{14}H_5N_7$: C, 61.99; H, 1.86. Found: C, 61.89; H, 1.89.

α-[2-(2,2-Dicyanovinyl)-2-(3-(trifluoromethyl)phenyl)hydrazono]malononitrile (12l). A mixture of 9.5 g (0.04 mol) of recrystallized *N*-(3-(trifluoromethyl)phenyl)sydnone,[21] 5.2 g (0.04 mol) of TCNE, and 100 mL of *o*-dichlorobenzene was heated with stirring under nitrogen at the reflux temperature for 7.5 h. Sublimation of TCNE into the condenser during this period made it difficult to complete the reaction. The reaction mixture was cooled to room temperature and filtered. The residue was washed with benzene and petroleum ether. The air-dried brown-gray solid, mp 179–180 °C, weighed 8.5 g (67%). The IR spectrum indicated that the crude product was nearly pure **12l**. A sample of the product (0.5 g) was dissolved in a minimum amount of acetonitrile, and the solution was put on a column of Florisil developed with benzene. The column was eluted with benzene and ether, and the combined eluate was concentrated at reduced pressure. The yellow residue was washed with benzene until a nearly colorless solid (0.4 g) was obtained. The IR spectrum indicated pure **12l**. An analytical sample, mp 179.5–181 °C, was prepared by recrystallization from benzene: ν (Nujol) 3049, 2222, 1612, 1587, 1515, 1503, 1449, 1433, 1316, 1232, 1190, 1170, 1160, 1133, 1093, 1064, and 766 cm^{-1}.

Anal. Calcd for $C_{14}H_5F_3N_6$: C, 53.50; H, 1.61; N, 26.75. Found: C, 53.52; H, 1.68; N, 26.72.

The benzene washes were concentrated at reduced pressure, and 0.05 g of bright yellow solid was recovered. The product was recrystallized from hexane to yield an analytically pure sample of α-[2-(*m*-(trifluoromethyl)phenyl)hydrazono]malononitrile (**13b**): mp 150 °C dec; NMR δ_{Me_4Si} (Me_2SO-d_6) 7.65 (m, 5, ArH) and N–H); ν (Nujol) 3248, 3175, 3106, 2222, 1626, 1608, 1567, 1488, 1466, 1333, 1299, 1279, 1179, 1136, 1064, 891, 798, and 699 cm^{-1}.

Anal. Calcd for $C_{10}H_5N_4F_3$: C, 50.43; H, 2.12; N, 23.52. Found: C, 50.41; H, 2.14; N, 23.60.

The remaining 8 g of crude product was purified in the same manner to yield 6.5 g of **12l** and 0.7 g of byproduct **13b**.

α-[2-(2,2-Dicyanovinyl)-2-(*p*-methoxyphenyl)hydrazono]malononitrile (12m). A solution of 3-(*p*-methoxyphenyl)sydnone[22] (1.92 g, 0.01 mol) and tetracyanoethylene (1.41 g, 0.011 mol) in *o*-dichlorobenzene (22 mL) was heated in a 170 °C bath for 7 h. The workup was as in the preparation of **12b** and afforded 1.6 g (58%) of **12m**: mp 143–4 °C; NMR δ_{Me_4Si} (Me_2SO-d_6) 3.8 (s, 3, CH_3), 7.1 (A_2 of A_2B_2, J = 9 Hz, 2, ArH), 7.6 (B_2 of A_2B_2, 2, ArH), and 8.8 (s, 1, vinyl H).

Anal. Calcd for $C_{14}H_8N_6O$: C, 60.87; H, 2.92; N, 30.42. Found: C, 60.88; H, 2.92; N, 30.50.

α-[2-(2,2-Dicyanovinyl)-2-(*p*-(thiomethyl)phenyl)hydrazono]malononitrile (12n). A solution of 3-(*p*-(thiomethyl)phenyl)sydnone (2.5 g, 0.012 mol) and tetracyanoethylene (1.7 g, 0.0132 mol) in *o*-dichlorobenzene (25 mL) was heated in a 170 °C bath for 6 h. Workup as in the procedure for **12b** afforded 1.6 g (29%) of **12n**, mp 164–165 °C, and 0.45 g (15%) of crude **12n**. For **12n**: NMR δ_{Me_4Si} (Me_2SO-d_6) 2.53 (s, 3, CH_3-S), 7.53 (m, 4, ArH), and 8.75 (s, 1, vinyl H).

Anal. Calcd for $C_{14}H_8N_6S$: C, 57.52; H, 2.72; N, 28.75. Found: C, 57.74; H, 2.82; N, 28.56.

α-[2-(2,2-Dicyanovinyl)-2-(*o*-ethylphenyl)hydrazono]malononitrile (12o). A mixture of 3-(*o*-ethylphenyl)sydnone[20] (1.0 g, 0.0052 mol) and TCNE (0.2 g, 0.0052 mol) in *o*-dichlorobenzene (11 mL) was heated at 165–170 °C for 24 h. To the cooled reaction mixture was added TCNE (0.3 g, 0.002 mol) with 4 mL of *o*-dichlorobenzene, and the mixture was heated at 165–170 °C for 20 additional hours. Workup as in the preparation of **12b** led to isolation of 0.16 g (11%) of **12o** as a nearly white solid: mp 172–174 °C; NMR δ_{Me_4Si} ($CDCl_3$) 1.33 (t, J = 8 Hz, 3, CH_3), 2.47 (g, 2, CH_2), 7.2–7.9 (m, 4, ArH), and 8.0 (s, 1, vinyl H).

Anal. Calcd for $C_{15}H_{10}H_6$: C, 65.68; H, 3.67. Found: C, 65.91; H, 3.38.

α-[2-(3,5-Bis(trifluoromethyl)phenyl)-2-(2,2-dicyanovinyl)hydrazono]malononitrile (12p). A solution of 3-[(3,5-bis(trifluoromethyl)phenyl]sydnone (1.5 g, 0.005 mol) and TCNE (0.7 g, 0.0055 mol) in *o*-dichlorobenzene (15 mL) was heated in a 165 °C bath for 17 h. Workup as in the preparation of **12b** yielded 0.45 g (23%) of **12p**: mp 166–167 °C; NMR δ_{Me_4Si} (Me_2SO-d_6) 8.6 (br s, 3, ArH) and 8.8 (s, 1, vinyl H); m/e 382.0 (M^+, 68.81), 363.1 (8.11), 305.0 (15.86), and 304.0 (44.41).

Anal. Calcd for $C_{15}N_6H_4F_6$: C, 47.13; H, 1.05; N, 21.99. Found: C, 47.28; H, 1.13; N, 21.77.

α-[2-(3,4-Dimethylphenyl)-2-(2,2-dicyanovinyl)hydrazono]malononitrile (12q). A solution of 3-(3,4-dimethylphenyl)sydnone (2.5 g, 0.013 mol) and tetracyanoethylene (1.8

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(19) R. A. Eade and J. C. Earl, *J. Chem. Soc.*, 2307 (1948).

(20) D. L. Hammick and D. J. Vooden, *J. Chem. Soc.*, 3303 (1961).

(21) K. W. Ratts and J. W. Worley, unpublished results.

(22) R. A. Eade and J. C. Earl, *J. Chem. Soc.*, 591 (1946).

g, 0.014 mol) in *o*-dichlorobenzene (25 mL) was heated in a 170 °C bath for 6.5 h. After the solution was left standing overnight, the crude reaction mixture was diluted with petroleum ether, and the resulting precipitate was purified as in the procedure for preparation of **12b** to afford 2.0 g (56%) of **12q**: mp 162–163 °C; NMR $\delta_{\mathrm{Me_4Si}}$ ($\mathrm{Me_2SO}$-d_6) 2.36 (s, 3, CH_3), 2.20 (s, 3, CH_3), 7.46 (br s, 3, Ar**H**), and 8.83 (s, 1, vinyl H).

Anal. Calcd for $C_{15}H_{10}N_6$: C, 65.68; H, 3.67. Found: C, 65.63; H, 3.72.

α-**[2-(1-Methyl-2,2-dicyanovinyl)-2-phenylhydrazono]malononitrile (12r).** A solution of 3-phenyl-4-methylsydnone[23] (2.0 g, 0.011 mol) and tetracyanoethylene (1.6 g, 0.012 mol) in *o*-dichlorobenzene was heated for 1 h in a 140 °C bath at which point the evolution of carbon dioxide ceased. After an additional hour at 140 °C, the solution was cooled, petroleum ether was added, and a solid separated. Workup as in the preparation of **12b** led to isolation of 0.5 g (17%) of **12r**: mp 190–192 °C; NMR $\delta_{\mathrm{Me_4Si}}$ ($CDCl_3$) 2.5 (s, 3, CH_3) and 7.2–7.9 (m, 5, ArH); ν (Nujol) 2225 cm^{-1}.

Anal. Calcd for $C_{14}H_8N_6$: C, 64.61; H, 3.10. Found: C, 64.59; H, 3.13.

α-**[2-(1-Bromo-2,2-dicyanovinyl)-2-phenylhydrazono]malononitrile (12s).** A solution of 3-phenyl-4-bromosydnone[24] (1.7 g, 0.007 mol) and tetracyanoethylene (0.98 g, 0.0077 mol) in *o*-dichlorobenzene (15 mL) was heated in a 140 °C bath for 60 min. However, no carbon dioxide evolution was noted after the first 25 min. The cooled reaction mixture was diluted with petroleum ether, and the resulting precipitate separated. Workup as in preparation of **12b** afforded 1.4 g (62%) of **12s**: mp 140–142 °C; NMR $\delta_{\mathrm{Me_4Si}}$ ($CDCl_3$) 7.2–7.8 (m, 5, ArH); ν (CH_2Cl_2) 2225 cm^{-1}.

Anal. Calcd for $C_{13}H_5N_6Br$: C, 48.02; H, 1.55; N, 25.85. Found: C, 48.31; H, 1.68; N, 25.69.

α-**[2-(1-Phenyl-2,2-dicyanovinyl)-2-phenylhydrazono]malononitrile (12t).** A solution of 3,4-diphenylsydnone[15] (1.5 g, 0.0063 mol) and tetracyanoethylene (1.0 g, 0.0078 mol) in *o*-dichlorobenzene (20 mL) was heated in a 170 °C bath for 7 h. After the solution was left standing at room temperature overnight, petroleum ether was added to the reaction mixture, and a black precipitate separated. Workup as in the preparation of **12b** yielded 0.4 g (20%) of **12t**, mp 180–182 °C, and 0.2 g (10%) of crude **12t**. Further recrystallization from benzene–petroleum ether yielded an analytically pure sample of **12t**: mp 183–184 °C; NMR $\delta_{\mathrm{Me_4Si}}$ ($\mathrm{Me_2SO}$-d_6) 7.55 (m, 10, ArH); ν (Nujol) 2225, 1560, 1525, 1340, 1275, 1210, and 1180 cm^{-1}.

Anal. Calcd for $C_{19}H_{10}H_6$: C, 70.80; H, 3.13. Found: C, 70.58; H, 3.20.

α-**[2-(2,2-Dicyanovinyl)-2-methylhydrazono]malononitrile (12u).** A solution of 3-methylsydnone[20] (2.9 g, 0.029 mol) and tetracyanoethylene (4.1 g, 0.032 mol) in *o*-dichlorobenzene (25 mL) was heated in a 165 °C bath for 6 h. After the solution was left standing at room temperature overnight, petroleum ether was added, and a black precipitate separated. Workup as in preparation of **12b** afforded 0.25 g (5%) of **12u**: mp 117–118 °C; NMR $\delta_{\mathrm{Me_4Si}}$ ($\mathrm{Me_2SO}$-d) 3.95 (s, 3, CH_3) and 8.35 (s, 1, vinyl H).

Anal. Calcd for $C_8H_4N_6$: C, 52.18; H, 2.19. Found: C, 52.15; H, 2.21.

α-**[2-*n*-Butyl-2-(2,2-dicyanovinyl)hydrazono]malononitrile (12v).** A solution of 3-*n*-butylsydnone[17,25] (3.0 g, 0.021 mol) and tetracyanoethylene (2.96 g, 0.023 mol) in *o*-dichlorobenzene (20 mL) was heated in a 163 °C bath for 7 h. The cooled reaction mixture was allowed to stand overnight, and petroleum ether was added to yield a precipitate which was purified as in the preparation of **12b** to afford 1.6 g (34%) of **12v**: mp 91–92 °C; NMR $\delta_{\mathrm{Me_4Si}}$ ($\mathrm{Me_2SO}$-d_6) 0.7–2.1 (m, 7), 4.3 (distorted t, J = 8 Hz, 2, CH_2–N), and 8.5 (s, 1, vinyl H).

Anal. Calcd for $C_{11}H_{10}N_6$: C, 58.40; H, 4.46. Found: C, 58.53; H, 4.53.

α-**[2-(2,2-Dicyanovinyl)-2-(3-methoxypropyl)hydrazono]malononitrile (12x).** A solution of 3-(3-methoxypropyl)sydnone[26] (1.0 g, 0.0063 mol) and tetracyanoethylene (0.9 g, 0.0070 mol) in *o*-dichlorobenzene (20 mL) was heated in a 170 °C bath for 6 h. After the solution was left standing at room temperature overnight, the workup as described in the synthesis of **12b** yielded 0.52 g (34%) of **12x**, mp 97.5–98 °C.

Anal. Calcd for $C_{11}H_{10}N_6O$: C, 54.54; H, 4.16; N, 34.69. Found: C, 54.41; H, 4.21; N, 34.54.

α-**[2-Cyclohexyl-2-(2,2-dicyanovinyl)hydrazono]malononitrile (12y).** A solution of 3-cyclohexylsydnone[15,17,19] (1.0 g, 0.006 mol) and tetracyanoethylene (0.85 g, 0.0066 mol) in *o*-dichlorobenzene (11 mL) was heated at 169 °C for 6.5 h. Workup as in the preparation of **12b** afforded 0.3 g (20%) of **12y**: mp 176–178 °C; NMR $\delta_{\mathrm{Me_4Si}}$ ($\mathrm{Me_2SO}$-d_6) 1.0–2.2 (m, 10, –CH_2–), 4.62 (m, 1, C–**H**), and 8.38 (s, 1, vinyl H); ν (Nujol) 2225, 1600, 1290, and 1235 cm^{-1}.

Anal. Calcd for $C_{13}H_{12}N_6$: C, 61.89; H, 4.79. Found: C, 61.83; H, 4.68.

Reaction of α-[2-(2,2-Dicyanovinyl)-2-(3-(trifluoromethyl)phenyl)hydrazono]malononitrile (12l) with Triethylamine in Methanol. A solution of **12l** (500 mg, 1.59 mmol) in methanol (10 mL) under nitrogen was treated with triethylamine (81 mg, 0.8 mmol) and stirred at room temperature for 24 h. The methanol was removed in vacuo, and the residue was chromatographed on silica gel. Elution with 50% ether/pentane yielded 250 mg (66%) of α-[2-(3-(trifluoromethyl)phenyl)hydrazono]malononitrile (**13b**).

In a similar reaction, **12c** yielded α-[2-(3-chlorophenyl)hydrazonol]malononitrile (**13c**): NMR $\delta_{\mathrm{Me_4Si}}$ ($\mathrm{Me_2SO}$-d_6) 7.5 (m, 5, Ar**H** and N–**H**).

Anal. Calcd for $C_9H_5N_4Cl$: C, 52.83; H, 2.46; N, 27.38. Found: C, 52.92; H, 2.50; N, 27.35.

Reaction of 12l with 10% HCl in Methanol. A solution of **12l** (500 mg, 1.59 mmol) in methanol (5 mL) was treated with 10% HCl (5 mL), and the resulting suspension was heated to 90 °C. Homogeneity was attained in 5 min, but a new suspension was then quickly observed. After 4 h at 90 °C, the cooled solution was filtered to yield hydrazonomalononitrile **13b**; 260 mg (69%).

Reaction of 12l with Triethylamine in Ethanol. A solution of **12l** (500 mg, 1.59 mmol) in dry ethanol (10 mL) was treated under nitrogen with triethylamine (101 mg, 1.0 mmol) and stirred at room temperature for 24 h. The oil was concentrated in vacuo and chromatographed on Florisil. Elution with 50% ether/petroleum ether yielded 230 mg (61%) of **13b**.

Reaction of 12a with 10% Hydrochloric Acid and Methanol. A solution of **12a** (1.0 g, 0.0041 mol) in methanol (50 mL) and 10% hydrochloric acid (25 mL) was stirred at room temperature for 6 h. Addition of an equal volume of water produced precipitate which was isolated by filtration and dried in the air to yield 550 mg (80%) of **13a**. Recrystallization of **13a** from ether–petroleum ether produced an analytically pure sample of α-(2-phenylhydrazono)malononitrile: mp 140–144 °C; NMR δ ($\mathrm{Me_2SO}$-d_6) 7.5 (m); m/e 171 ($M^+ + 1$, 6.61), 170.0 (M^+, 57.81), 143.0 (1.94), and 105.0 ($C_6H_5N_2^{+\cdot}$, 27.55).

Anal. Calcd for $C_9H_6N_4$: C, 63.52; H, 3.55. Found: C, 63.60; H, 3.56.

Reaction of 12s with 10% Hydrochloric Acid and Methanol at 60–65 °C. A solution of **12s** (100 mg, 0.3 mmol) in 10% hydrochloric acid (2.5 mL) and methanol (5 mL) was heated at 60–65 °C for 5.75 h. The cooled solution was neutralized with sodium bicarbonate and extracted with methylene chloride three times. The organic layers were dried ($MgSO_4$) and concentrated to a dark yellow residue which was analyzed by NMR and TLC to contain only **13a**. Chromatography on Florisil elution 50% ether–petroleum ether yielded 40 mg (76%) of **13a**. A reaction did not occur when **12s** was stirred with 10% hydrochloric acid and methanol at room temperature for 4–5 h: NMR $\delta_{\mathrm{Me_4Si}}$ ($CDCl_3$) 1.3 (t, J = 7 Hz, 3), 3.9 (s, 2), 4.3 (q, 2), 4.9 (br s, 1, N–H), 6.55 (A_2 of A_2B_2, J = 9 Hz, 2, ArH), and 7.5 (B_2 of A_2B_2, 2, ArH).

Anal. Calcd for $C_{11}H_{12}N_2O_2$: C, 64.69; H, 5.92; N, 13.72. Found: C, 64.54; H, 5.93; N, 13.69.

Registry No. **6a**, 120-06-9; **6b**, 829-31-2; **6c**, 52827-07-3; **6d**, 68657-44-3; **6e**, 5352-95-4; **6f**, 5319-48-2; **6g**, 68657-45-4; **6h**, 26537-61-1; **6i**, 3483-19-0; **6j**, 3483-17-8; **6k**, 68657-48-7; **6l**, 26537-62-2; **6m**,

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[23] J. C. Earl and A. W. Mackney, *J. Chem. Soc.*, 899 (1935).

[24] C. V. Greco, M. Pesce, and J. M. Franco, *J. Heterocycl. Chem.*, **3**, 391 (1966).

[25] J. Fugger, J. M. Tien, and I. M. Hunsberger, *J. Am. Chem. Soc.*, **77**, 1843 (1955); C. V. Greco, W. H. Nyberg, and C. C. Cheing, *J. Med. Pharm. Chem.*, **5**, 851 (1962).

[26] F. H. C. Stewart, *J. Org. Chem.*, **27**, 687 (1962).

3815-80-3; **6n**, 68657-46-5; **6o**, 68657-43-2; **6p**, 68657-47-6; **6q**, 66947-48-6; **6r**, 3483-16-7; **6s**, 13183-09-0; **6t**, 3815-83-6; **6u**, 6939-12-4; **6v**, 64180-21-8; **6x**, 70377-79-6; **6y**, 20600-69-5; **12a**, 68657-26-1; **12b**, 68657-30-7; **12c**, 68657-31-8; **12d**, 68657-28-3; **12e**, 68657-34-1; **12f**, 68657-29-4; **12g**, 68657-33-0; **12h**, 68657-39-6; **12i**, 68657-36-3; **12j**, 68657-32-9; **12k**, 68657-41-0; **12l**, 68657-27-2; **12m**, 68657-35-2; **12n**, 68657-38-5; **12o**, 68657-25-0; **12p**, 68657-40-9; **12q**, 70415-61-1; **12r**, 70377-80-9; **12s**, 70428-84-1; **12t**, 70377-81-0; **12u**, 70377-82-1; **12v**, 70377-83-2; **12x**, 70377-84-3; **12y**, 70377-85-4; **13a**, 306-18-3; **13b**, 3720-41-0; **13c**, 555-60-2; TCNE, 670-54-2.

Chemistry of Carbanions. 34. Alkylation of a 1-Decalone Enolate with Abnormal Geometry[1]

Herbert O. House,* William V. Phillips, and Don VanDerveer

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

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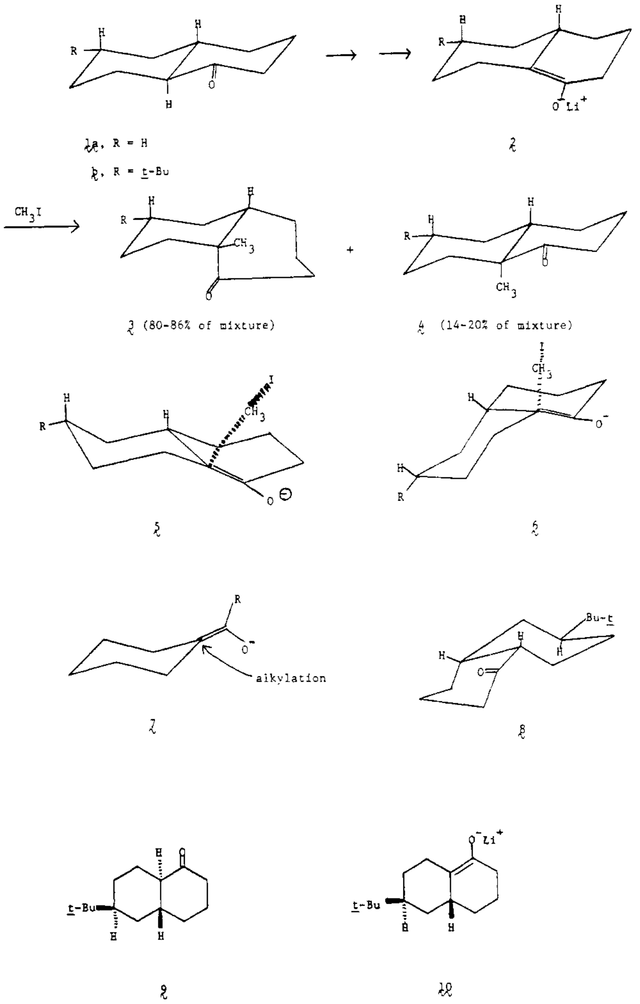
Solutions of the lithium enolate **10** have been prepared by appropriate transformations of the ketones **8** and **9**. Both an X-ray structure determination of the derived enol ester **26** and conformational calculations on the related olefin **27** suggest that the favored conformations of the enolate **10** are the twist-boat conformers **28a** and **28b**. Reaction of this enolate **10** with methyl iodide formed predominantly the cis-fused decalone **17**. This result is in better agreement with an early, reactant-like transition state for the alkylation reaction rather than a late, product-like transition state that resembles the geometry of the products in their initially formed conformations.

The alkylation of the 1-decalone enolates **2** (Scheme I) to form predominantly the cis-fused monoalkylated products **3**[2] conforms to the ideas that the alkylation stereochemistry can be explained by invoking transition states **5** and/or **6** with reactant-like geometries and that the preferred direction for alkylation normally introduces the alkyl substituent equatorial to the saturated cyclohexane ring (see structure **7**). It was of interest to examine the alkylation of a 1-decalone enolate whose geometry was distorted from that normally found (i.e., **5** or **6**) to learn what factor seemed best to account for the alkylation stereochemistry. For that purpose, we have synthesized the 1-decalone derivatives **8** and **9**[3] and report here the result of reaction of the corresponding lithium enolate **10** with methyl iodide.

A suitable precursor **11** (Scheme II) for the enolate **10** could be obtained by enol acetylation of ketone **8**[3] followed by separation of the enol acetates **11** and **12** by low-pressure liquid chromatography. However, as found in an earlier study,[2] methylation of the lithium enolate **10** (accompanied by 1 equiv of *t*-BuOLi) formed from the enol acetate **11**, and MeLi was accompanied by the formation of di- and trimethylated products that complicated the separation and analysis of the reaction products. To diminish the amount of polyalkylation, we chose to use the enol silyl ether **14** as a precursor for the enolate **10** in order to avoid excess base (*t*-BuOLi) in the reaction mixture.[4] Although the direct reaction of the ketone **8** with Me_3SiCl and Et_3N[4b] formed only the unwanted silyl enol ether **13**, the indirect method, involving generation of the enolate **10** from the enol acetate **11** and subsequent quenching of the enolate **10** with Me_3SiCl,[4,5] afforded the desired silyl enol ether **14**.

Scheme I



Reaction of the enolate **10**, generated from the silyl enol ether **14**, with MeI for a short period of time (40–60 s) afforded mixtures containing small amounts of the recovered unalkylated ketones **8** and **9** and two dialkylated products tentatively assigned structures **15** and **16**. The major product was the monomethylated ketone **17** isolated

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[2] See H. O. House and M. J. Umen, *J. Org. Chem.*, **37**, 2841 (1972), and references cited therein.

[3] H. O. House and W. V. Phillips, *J. Org. Chem.*, **43**, 3851 (1978).

[4] (a) G. Stork and P. F. Hudrlik, *J. Am. Chem. Soc.*, **90**, 4462, 4464 (1968); (b) H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **34**, 2324 (1969).

[5] C. R. Krüger and E. G. Rochow, *J. Organomet. Chem.*, **1**, 476 (1964).

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