Addition of Some 1,3-Diaryltriazenes to Tetracyanoethylene

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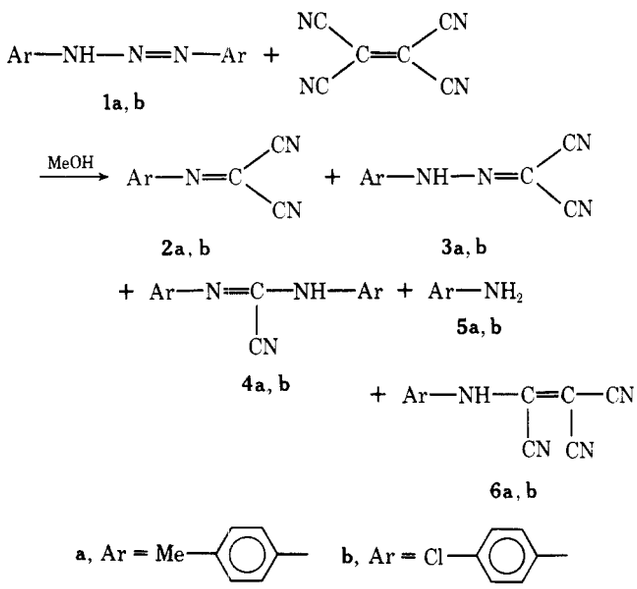
Received October 12, 1976

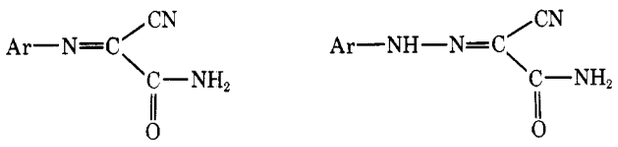
1,3-Diaryltriazenes react with tetracyanoethylene in methanol giving products derived from an addition–fragmentation mechanism. Experiments have been carried out to clarify the reaction scheme.

When equimolecular quantities of 1,3-diaryltriazene (1) and tetracyanoethylene (TCNE) in methanol are mixed at room temperature, an intense blue-green color develops, that quickly fades leaving a clear solution, from which products 2–4 can be separated by column chromatography (Scheme I).

Scheme I



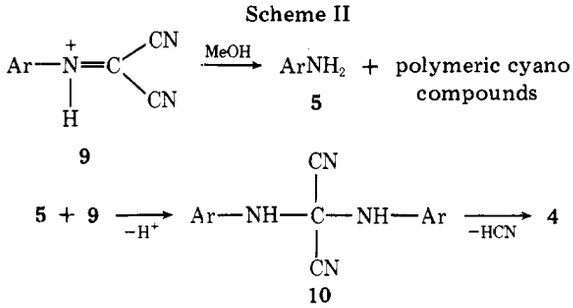
Compounds 2 and 3 are the main reaction products (50–80% yield); 5 and 6 were separated only in traces. In addition to the products reported above, it is possible to separate from the reaction mixture small quantities of the amides 7 and 8.



7 8

In excess TCNE the formation of 4 in the reaction is supressed, and the amount of tricyanovinylaniline (6) is greatly increased. This result suggests that 4 is not a primary product, and is formed by addition of aniline to the Schiff base 2, possibly in the protonated form 9. As discussed later, 2 or 9 is an intermediate in the reaction and a precursor of 5 (Scheme II).

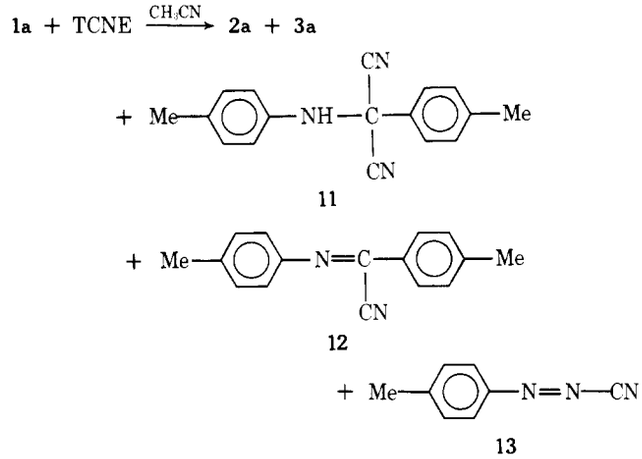
Scheme II



Compound 10 (Ar = *p*-chlorophenyl) was actually separated from the reaction between 1b and tetracyanoethylene in dry ether; it quickly loses HCN, giving 4, on dissolution in methanol. An increase in concentration of tetracyanoethylene in the reaction effectively scavenges the aniline, giving the addition product 6[1] and preventing the formation of 4. The preparation of amidines from imines carrying a nitrile function at the imino carbon atom is already known in the literature.[2]

The reaction between aromatic triazenes and TCNE is highly solvent sensitive. Compound 1a reacts with TCNE in dry ether or in acetonitrile much more slowly, giving 11 and 12 instead of 4a (Scheme III).

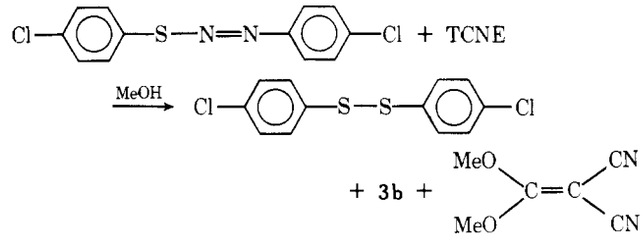
Scheme III



Details of the reaction in these nonprotic solvents are still unclear, although it probably involves a free-radical pathway. Mechanistic details must await further experimental work.

Substitution of the NH group of the triazenes by a sulfur atom retards strongly the reaction with TCNE. Alcoholysis of TCNE is competitive with the reaction between the areneazothiolate and TCNE (Scheme IV).

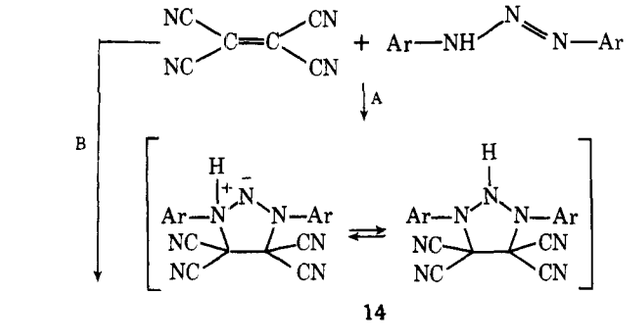
Scheme IV



Discussion

Two different mechanistic pathways can be devised to rationalize the products of the reaction in methanol: 1,3-cycloaddition of the aromatic triazene to TCNE, followed by a retro-cycloaddition (Scheme V, path A), or nucleophilic addition of the amino nitrogen to TCNE (path B).

Scheme V



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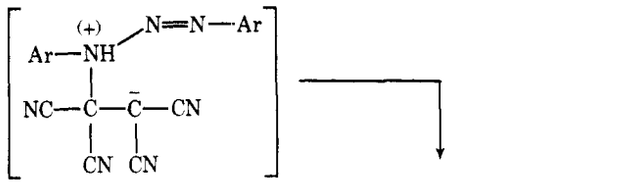

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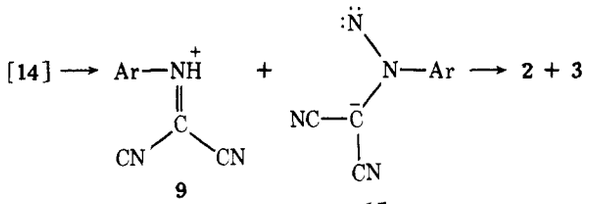

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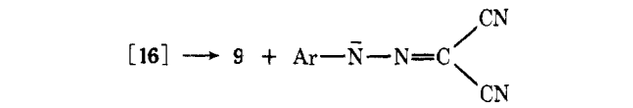
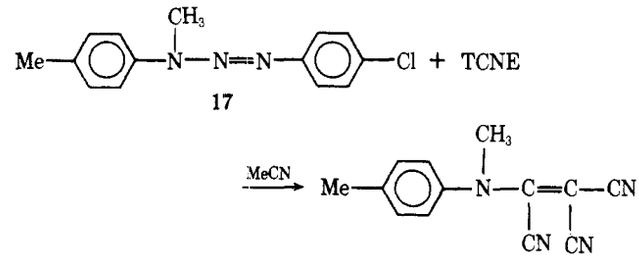


A reaction scheme involving as the first step a nucleophilic addition to the electron-deficient double bond of TCNE is probably followed in the addition of the N-methylated triazene (**17**) to TCNE in acetonitrile as solvent; in this case the



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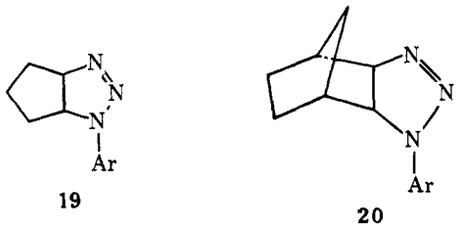
only identified reaction product was the tricyanovinylaniline (**18**), and no hydrazone (**3b**) was formed.

Nucleophilic addition to electron-deficient double bonds is also involved in the TCNE or diphenylketene catalyzed



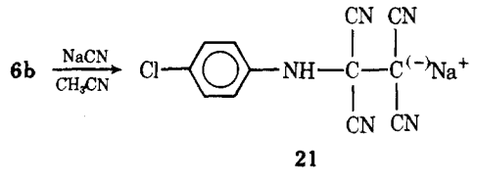
19 20

Table I. λ_{max} of the Charge-Transfer Bond in Ethereal Solutions of TCNE and Various Donors

Registry no.	Donor	λ_{max}, nm
785-86-4	1,3-Di-*p*-tolyltriazene (**1a**)	690
3470-39-1	1,3-Di-*p*-chlorophenyltriazene (**1b**)	590
62166-63-6	1-*p*-Chlorophenyl-1-methyl-3-*p*-tolyltriazene	640
62166-64-7	1-*p*-Tolyl-1-methyl-3-*p*-chlorophenyltriazene	670
106-49-0	*p*-Toluidine	705
106-47-8	*p*-Chloroaniline	610
932-96-7	*N*-Methyl-*p*-chloroaniline	650

decomposition of the cyclic triazenes **19** and **20** in methanol.[3]

In order to test if the azo derivative **16** may be also the precursor of **2** and **3**, NaCN was added to the tricyanovi-



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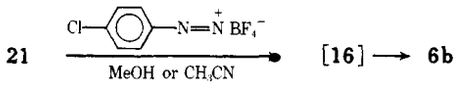

nylaniline (**6b**), and *p*-chlorophenyldiazonium tetrafluoroborate was added to the sodium salt of the anion **21**, previously separated and purified.

The only reaction product identified was the tricyanovinylaniline **6b**; no trace of **2b** or **3b** was found. For this reason we believe that Scheme V accounts only for the formation of tricyanovinyl amino derivatives, and not the formation of **2** and **3**.

The [2 + 3] cycloaddition mechanism (Scheme V, path A) is therefore probably the most satisfactory for explaining the products of Scheme I.

The rearrangement of **15** to the hydrazone (**3**) may be an example of aryl shift to an electron-deficient nitrogen. Unsuccessful attempts have been made to trap **15** by an ene reaction with a reactive double bond.

In the primary addition step the diazoamino derivative may behave as a 1,3 dipole with respect to the TCNE. No other examples of this behavior are reported in the literature; the only known cycloaddition of a triazene is the photochemically initiated [2 + 2] addition of the azo linkage of 1-phenyl-3,3-dimethyltriazene to diphenylketene.[4] In our case, a [2 + 2]

Scheme VI

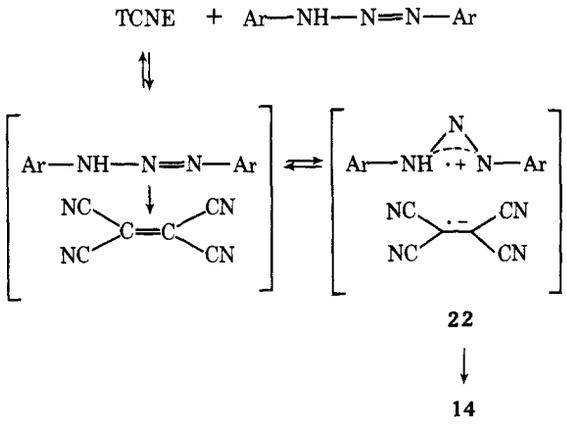

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Table II. Physical Constants[a]

Compd	Mp, °C	Mass spectrum, *m/e*
2a	98–100	169, $C_{10}H_7N_3^+\cdot$ (base); 142, $C_9H_6N_2^+\cdot$; 91, $C_7H_7^+$
2b	136–138	189, $C_9H_4ClN_3^+\cdot$ (base); 163, $C_8H_4ClN_2^+$; 154, $C_9H_4N_3^+$; 137, C_7H_4ClN; 111, C_6H_4Cl
3a	168–170 dec	184, $C_{10}H_8N_4^+\cdot$; 157, $C_9H_7N_3^+\cdot$; 119, $C_7H_7N_2^+$; 106, $C_7H_8N^+$; 91, $C_7H_7^+$ (base)
3b	189–190 dec	204, $C_9H_5ClN_4^+\cdot$; 177, $C_8H_4ClN_3^+\cdot$; 139, $C_6H_4ClN_2^+$; 126, $C_6H_5ClN^+$; 111, $C_6H_4Cl^+$ (base)
4a	124–125	249, $C_{16}H_{15}N_3^+\cdot$; 248, $C_{16}H_{14}N_3^+$; 222, $C_{15}H_{14}N_2^+\cdot$; 143, $C_9H_7N_2^+$; 91, $C_7H_7^+$ (base)
4b	174–175	289, $C_{14}H_9Cl_2N_3^+\cdot$; 288, $C_{14}H_8Cl_2N_3^+$; 262, $C_{13}H_8Cl_2N_2^+\cdot$; 163, $C_8H_4ClN_2^+$; 111, $C_6H_4Cl^+$ (base)
7a	147–149	187, $C_{10}H_9N_3O^+\cdot$; 143, $C_9H_7N_2^+$ (base); 91, $C_7H_7^+$; 44, $CONH_2^+$
8a	237–238 dec	202, $C_{10}H_{10}N_4O^+\cdot$ (base); 185, $C_{10}H_7NO_3^+\cdot$; 157, $C_9H_7N_3^+\cdot$; 119, $C_7H_7N_2^+$; 105, $C_7H_7N^+\cdot$; 91, $C_7H_7^+$
8b	258–259 dec	222, $C_9H_7N_4OCl^+\cdot$ (base); 205, $C_9H_4N_3OCl^+\cdot$; 177, $C_8H_4N_3Cl^+\cdot$; 139, $C_6H_4N_2Cl^+$; 125, $C_6H_4NCl^+\cdot$; 111, $C_6H_4Cl^+$; 44, $CONH_2^+$
10b	187–188	316, $C_{15}H_{10}N_4Cl_2^+\cdot$; 315, $C_{15}H_9N_4Cl_2^+$
11	155–157	261, $C_{17}H_{15}N_3^+\cdot$; 234, $C_{16}H_{14}N_2^+\cdot$; 219$^+$; 208, $C_{15}H_{14}N^+$; 106, $C_7H_8N^+$ (base); 91, $C_7H_7^+$
12	130–131	234, $C_{16}H_{14}N_2^+\cdot$ (base); 219$^+$; 208, $C_{15}H_{14}N^+$; 91, $C_7H_7^+$
18	179–181	222, $C_{13}H_{10}N_4^+\cdot$ (base); 207, $C_{12}H_7N_4^+$; 196, $C_{12}H_{10}N_3^+$; 91, $C_7H_7^+$

[a] Satisfactory analytical data for all compounds in table (±0.4% for C, H, N, and for **b** series, Cl) were reported for all compounds except **2a** (N: calcd, 24.84; found, 23.90), **4b** (C: calcd, 57.93; found 57.28), **10b** (C: calcd, 56.78; found, 56.25), and **18** (C: calcd, 70.24; found, 69.72).

cycloaddition to the azo linkage of the aromatic triazene can be easily discounted by examining the results of the reaction with N-methylated triazenes, in which the products are not consistent with this kind of initial step (see Experimental Section). In addition, it must be noted that the triazaallyl anion[5] does not react with TCNE in this way.

An alternative pathway to the cycloadduct **14** may involve the solvation of an initial charge-transfer complex, giving a radical ion pair **22** that can collapse to **14** via an "aromatic" transition state (Scheme VI).

Initial formation of charge transfer complexes has been previously postulated for other cycloaddition reaction of TCNE.[6]

Experimental Section

The diaryltriazenes were synthesized in the usual way.[7] Reaction products were identified on the basis of elemental analysis and spectral data: 60-MHz NMR (JEOL C60HL), mass spectra (JEOL JMS D100), IR, or by comparison with authentic specimens prepared in an independent way.

Reactions between 1,3-Diaryltriazenes and TCNE. The triazene (0.01 M) was dissolved in 100 mL of the solvent (methanol, acetonitrile, or diethyl ether) and TCNE (0.01 M) was added under stirring at room temperature. In every case it developed an intense blue-green color (see Table I for λ_{max} in dry ether) that faded quickly in methanol (5 min) and more slowly in acetonitrile or ether (12 h in dry ether). The solvent was then evaporated and the residue was chromatographed on silica gel. The products reported below were separated by using *n*-pentane/ethyl ether gradient, with the exception of the amides **7** and **8** and of the tricyanovinylamines **6** and **18**, eluted with methanol. Table II reports analytical data and mass spectra for the separated compounds; elemental composition of fragment Ions are obtained from exact mass measurement, resolution 7500 (10% valley, mean error <5 ppm). NMR and IR data are consistent with the proposed structures. The symmetrical NMR spectrum obtained for the amidines **4a** and **4b** can be rationalized on the basis of the known tautomerism of this kind of compound.[8]

1a and TCNE in Methanol. Elution of the chromatographic column with *n* pentane/ether (90:10) gave 0.5 g of *N*-dicyanomethylene-*p*-toluidine (**2a**). The IR spectrum of this product ($CHCl_3$) shows characteristic bands at 2210 (m, cyano group), 1610 (m, >C=N– stretching), and 1530 cm^{-1} (s); NMR spectrum ($CHCl_3$) 2.40 (s, 3, CH_3), 7.25 ppm (AA′BB′, 4). Elution with *n* pentane/ether (50:50) gave N^1,N^2-di-*p*-tolylaminocyanoformamide (**4a**), 0.5 g. IR spectrum ($CHCl_3$) 3440 and 3350 (m, N–H stretching), 2230 (m, C=N), 1640 and 1615 cm^{-1} (s, >C=N– stretching). The literature reports similar absorption for N^1,N^2-substituted amidines. NMR ($CHCl_3$) 2.29 (s, 6, 2 CH_3), 7.0 (s, 8, aromatics), 7.2 ppm (broad singlet, 1, NH). Elution with ether gave 1.7 g of *p*-dicyanomethylenehydrazinotoluene (**3a**), identical with an authentic specimen synthesized from malononitrile and diazotized *p*-toluidine: IR ($CHCl_3$) 3270 (m, NH stretching), 2220 (s, –C≡N) 1605 (m), 1545 (s), 1460 cm^{-1} (s). Traces of *p*-toluidine were also detected in intermediate fractions by TLC (R_f and color reaction). Elution with methanol gave a mixture of products, then separated by a new chromatographic column. Using a continuous gradient ether/methanol were separated **7a** (traces) [IR ($CHCl_3$) 3510, 3400 (m, NH stretching), 2220 (w, CN), 1710 (s, amide I), 1565 cm^{-1} (s, amide II)]; **8a**, traces [IR ($CHCl_3$) 3510, 3400 (m, NH stretching), 2210 (s, –CN), 1665 (s, amide I), 1590 cm^{-1} (m, amide II)]; and *N*-tricyanovinyl-*p*-toluidine (**6a**), traces, identical with an authentic model prepared from *p*-toluidine and TCNE.

1a and TCNE in acetonitrile gave **2a**, 0.2 g; *N*-cyano-*p*-xylylene *p*-toluidine (**12**), 0.6 g [IR ($CHCl_3$) 2210 (m, C≡N), 1600 and 1565 cm^{-1} (s); NMR ($CDCl_3$) 2.40 (s, 3, $-CH_3$), 2.45 (s, 3, $-CH_3$), 7.22 (AA′BB′ multiplet, 4), 7.70 ppm (AA′BB′ multiplet, 4)]; α,α-dicyano-α-toluidino-*p*-xylene (**11**), 0.5 g [IR ($CHCl_3$) 3400 (m, NH stretching), 2240 cm^{-1} (w, CN); NMR ($CDCl_3$) 2.30 (s, 3, CH_3), 2.40 (s, 3, CH_3), 4.0 (broad s, 1, NH), 7.08 (AA′BB′ multiplet, 4), 7.58 ppm (AA′BB′ multiplet, 4); this product dissolved in methanol gives **12** and hydrogen cyanide]; **3a**, 0.7 g; **13**, traces.

1a and TCNE in dry ether gave **2a**, 1.3 g; **3a**, 1.4 g; **11**, 0.11 g; **12**, 0.1 g.

1b and TCNE in methanol gave *N*-dicyanomethylene-*p*-chloroaniline (**2b**), 0.1 g; *p*-dicyanomethylenehydrazinochlorobenzene (**3b**), 1.8 g; N^1,N^2-di-*p*-chloroanilinocyanoformamidine (**4b**), 0.7 g; *N*-tricyanovinyl-*p*-chloroaniline (**6b**), traces; **8b**, traces.

1b and TCNE in dry diethyl ether gave **2b**, 0.5 g; **3b**, 1.8 g; dicyanodi-*p*-chloroanilinomethane (**10**), traces; **4b**, 0.5 g. Using wet diethyl ether, no **10** was obtained.

1-*p*-Tolyl-1-methyl-3-*p*-chlorophenyltriazene (17) and TCNE in methanol gave **3b**, 1.5 g; *N*-methyl-*p*-toluidine, 0.6 g; **8b**, traces.

1-*p*-Tolyl-1-methyl-3-*p*-chlorophenyltriazene (17) and TCNE in acetonitrile gave *N*-methyl-*N*-tricyanovinyl-*p*-toluidine (**18**), 0.4 g, and unidentified tars.

1-*p*-Chlorophenylamino-2-*p*-chlorophenyldiazotetracyanoethane (16). To a suspension of sodium cyanide (1.1 g) in dry acetonitrile was slowly added at 0 °C a solution of *N*-tricyanovinyl-*p*-chloroaniline (5 g) in dry acetonitrile. Dry ethyl ether was then added to the homogeneous solution and the precipitate was filtered and washed with dry ether. The solid product (5.4 g) was completely free from *N*-tricyanovinyl-*p*-chloroaniline.

This compound (2.2 g) was then treated in acetonitrile and—separately—in methanol with 1.3 g of *p*-chlorobenzendiazonium tetrafluoroborate. From both reactions the only identified product was *N*-tricyanovinyl *p*-chloroaniline; no traces of **2b** or **3b** were detected by TLC.

***p*-Chlorophenylthio-*p*-chlorophenyldiimide and TCNE in Methanol.** To a solution of *p*-chlorophenylthio-*p*-chlorophenyldiimide (2.8 g) in methanol (100 mL) was added TCNE (2.3 g) and the reaction mixture was refluxed for 24 h. Column chromatography of the residue after evaporation of the solvent gave 4,4′-dichlorodiphenyl disulfide, (**3b**) and 1,1-dimethoxydicyanoethylene, identified by comparison with authentic specimens.

Registry No.—**2a**, 62166-65-8; **2b**, 62166-66-9; **3a**, 40257-94-1; **3b**, 946-76-9; **4a**, 58078-43-6; **4b**, 62166-67-0; **7a**, 62166-68-1; **8a**, 3665-

89-2; **8b**, 20931-91-3; **10b**, 62166-69-2; **11**, 62166-70-5; **12**, 31429-31-9; **18**, 62166-71-6; TCNE, 670-54-2.

References and Notes

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Rapid and Unequivocal Determination of Syn–Anti Stereochemistry for Toluenesulfonylhydrazones and Other Imine Derivatives via Carbon-13 Nuclear Magnetic Resonance Spectroscopy. A Synthetic Adjunct

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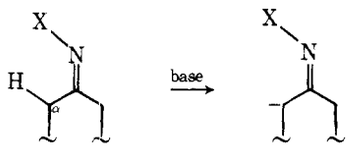
Received February 10, 1977

Measurement of the ^{13}C NMR chemical shift differences between the α carbons of ketone and imine derivatives (toluenesulfonylhydrazones, dimethylhydrazones, and oximes) provides a convenient and reliable means of assigning imine stereochemistry. It has been found that carbons syn to the imine "X" moiety are shifted to higher field (Δ syn α = 12–15 ppm) than are carbons anti to the imine "X" moiety (Δ anti α' = 3–6 ppm).

α-Metalated imine derivatives (**2a–c**), including dimethylhydrazones,[1] oximes,[2] and toluenesulfonylhydrazones,[3] are becoming increasingly important intermediates in organic synthesis. The deprotonation reactions of these imines (**1a–c**) exhibit a substantial preference for selective removal of α hydrogens which are syn to the imine X group (**1a–c** → **2a–c**).

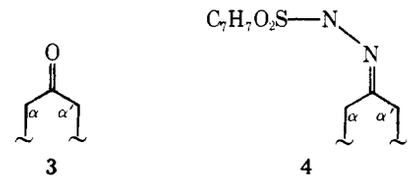


1a, X = $N(CH_3)_2$ 2a, X = $N(CH_3)_2$
b, X = OH b, X = O^-
c, X = $NHSO_2C_7H_7$ c, X = $N^-SO_2C_7H_7$

Utilization of this directing effect in a synthetically rational manner clearly requires an unambiguous method for the determination of syn–anti stereochemistry for imine derivatives of unsymmetrical ketones.

In connection with several synthetic projects in the area of tosylhydrazone chemistry,[3a,b] it became apparent that the traditional ^1H NMR spectral methods for assigning syn and anti isomers, such as differential solvent shifts[4a] (including benzene, a medium in which tosylhydrazones are only sparingly soluble) and lanthanide shift reagent studies,[4b,c] were neither uniformly unambiguous nor particularly convenient.

Several literature reports on the ^{13}C NMR spectra of hydrazones[5] and oximes[6] have indicated a substantial chemical shift difference between the syn and anti carbons α to the imine moiety. We have measured the ^{13}C NMR of a large number of imine derivatives (Tables I–V) based on the hypothesis that the major factor responsible for affecting chemical shift differences between syn and anti carbons is a steric compression effect,[7] which results in upfield shifts for syn α carbons. We have also measured the ^{13}C NMR of the parent ketone in each case. Comparison of the chemical shift differences between the ketone (**3**) and its imine derivative (**4**) *for each α carbon* readily shows that α carbons syn to the tosylhydrazone moiety are substantially shifted upfield (Δ syn α = 12–15 ppm) by comparison to the ketone, while α carbons



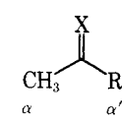
3 4

Δ syn α = (δ ketone 3 for C_α) – (δ hydrazone 4 for C_α)
Δ anti α' = (δ ketone 3 for $C_{\alpha'}$) – (δ hydrazone 4 for $C_{\alpha'}$)

anti to the tosylhydrazone moiety are shifted upfield only slightly (Δ anti α' = 3–6 ppm) (Tables I–IV).

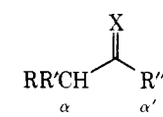
These observations can be qualitatively explained by postulating that the small upfield shift of the anti carbons is primarily due to an inductive effect resulting from the electronegativity difference between ketone and tosylhydrazone. The larger upfield shift of the syn α carbons results from a combination of the inductive effect *plus* a steric compression effect[6b,7] which, in turn, results in additional shielding. Use of this comparison of ketone and tosylhydrazone shifts allows the ketone to serve as an "internal standard"; therefore, the primary structural contributions to the chemical shift which are present both in the ketone and the tosylhydrazone tend to cancel out. The only major effect remaining is that which results from, and hence defines, the hydrazone stereochemistry.

Inspection of Tables I–IV for the structural types **5–11** demonstrates the validity of this approach. Table V indicates



5

a, R = Me
b, R = CH_2Cl
c, R = CH_2Br
d, R = CH_2OAc
e, R = Et
f, R = CH_2Ph
g, R = CH_2CO_2Me
h, R = CH_2CO_2tBu
i, R = *t*-Bu
j, R = Ph



6

a, R = H; R′ = Me; R″ = Et
b, R = R′ = Me; R″ = *i*-Pr
c, R = R′ = Me; R″ = Ph
d, R = R′ = Me; R″ = CH_2CO_2Et
e, R = H; R′ = Et; R″ = CH_2CO_2Et
f, R = H; R′ = Me; R″ = $CH(Me)CO_2Me$