Reactions of Tetramethyl-2-tetrazene with Diphenylketene and Isocyanates
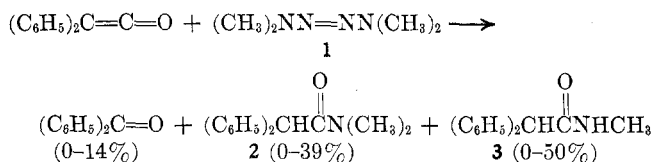
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Although the reactions of 2-tetrazenes with acids were first reported in 1878 and have received considerable attention since then,[1] reactions with other electrophiles, especially alkylating[2] and acylating[3] agents, have only recently begun to receive attention. Reaction in all of these cases is initiated by coordination of a terminal nitrogen of the tetrazene with the electrophilic reagent, followed by breaking of the N–N single bonds, with formation of molecular nitrogen and radical and/or ionic species. We here report the analogous reactions of tetramethyl-2-tetrazene (1) with diphenylketene and with phenyl and p-toluenesulfonyl isocyanates.

Diphenylketene and tetramethyl-2-tetrazene (1) react in carbon tetrachloride to afford variable yields of benzophenone, N,N-dimethyl-2,2-diphenylacetamide (2), and N-methyl-2,2-diphenylacetamide (3). The yields of the individual products varied widely in the several runs carried out, as did the time required to consume all the diphenylketene.

$$(C_6H_5)_2C=C=O + (CH_3)_2NN=NN(CH_3)_2 \longrightarrow$$
$$1$$

$$(C_6H_5)_2C=O + (C_6H_5)_2CHCN(CH_3)_2 + (C_6H_5)_2CHCNHCH_3$$
$$(0-14\%) \quad\quad 2\ (0-39\%) \quad\quad 3\ (0-50\%)$$

Phenyl isocyanate (4) reacts with the tetrazene 1 to yield 1-phenyl-3,3-dimethylurea (6) (94–100%), molecular nitrogen, and a small amount of another product which was assigned the structure 8 (Scheme I) on the basis of its spectra. The infrared spectrum of 8 had bands at 3.04 (NH), 6.00 (urea carbonyl), and 13.14 and 14.33 μ (monosubstituted phenyl). The nmr (CDCl₃) had peaks at δ 2.53 (s, 6 H), 2.92 (s, 3 H), and 6.92–7.62 (m, *ca.* 5 H). The ultraviolet spectrum had λ_{max} (EtOH) at 275 nm (ε 1200) and 240 (26,000). A model compound, 1-formyl-1,4,4-trimethyl-2-tetrazene, has λ_{max} (EtOH) at 275 nm (ε 18,800) and nmr peaks at 3.03 (s, 6 H) and 3.16 (s, 3 H).[4]

When the reaction of phenyl isocyanate and 1 was carried out in a flask with a low actinic coating (spectral transmission varies between 0 at 300 nm and 4% at 500 nm), the yield of 6 was sharply reduced (to 60%). This reaction also afforded a small amount of an oil whose nmr spectrum indicated that it contained 1,3,5-trimethylhexahydro-1,3,5-triazine, presumably formed from N-methylmethylenimine.[5]

(1) (a) E. Fischer, *Justus Liebigs Ann. Chem.*, **190**, 67 (1878); (b) H. Weiland, *Ber.*, **41**, 3498 (1908); *Justus Liebigs Ann. Chem.*, **392**, 133 (1912); (c) W. R. McBride and W. E. Thun, *Inorg. Chem.*, **5**, 1846 (1966); (d) C. G. Overberger and B. S. Marks, *J. Amer. Chem. Soc.*, **77**, 4097 (1955).
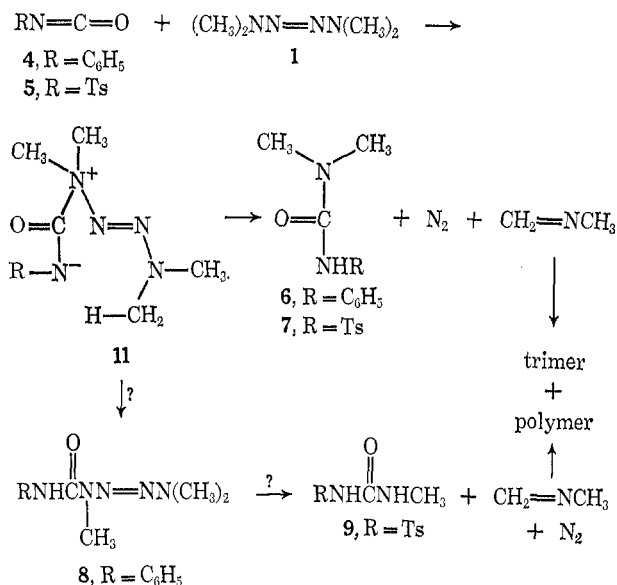
(2) (a) W. H. Bruning, C. J. Michejda, and D. Romans, *Chem. Commun.*, 11 (1967); (b) C. J. Michejda and D. Romans, *Tetrahedron Lett.*, 4213 (1969).

(3) (a) S. F. Nelsen, *J. Amer. Chem. Soc.*, **88**, 5666 (1966); (b) S. F. Nelsen, R. B. Metzler, and M. Iwamura, *ibid.*, **91**, 5103 (1969).

(4) W. E. Thun and W. R. McBride, *J. Org. Chem.*, **34**, 2997 (1969).

(5) E. A. Werner, *J. Chem. Soc.*, 844 (1917).

SCHEME I

$$RN=C=O + (CH_3)_2NN=NN(CH_3)_2 \longrightarrow$$
$$4, R = C_6H_5 \quad\quad\quad 1$$
$$5, R = Ts$$

p-Toluenesulfonyl isocyanate (5) reacts rapidly with 1 in carbon tetrachloride to yield 62% of 3,3-dimethyl-1-*p*-toluenesulfonylurea (7). This compound was identified by comparison of its infrared and nmr spectra with those of an authentic sample synthesized from 5 and dimethylamine. In addition to 7, a small amount of a material similarly identified as 3-methyl-1-*p*-toluenesulfonylurea (9) was obtained in one run.

Phenyl isocyanate and tetrabenzyl-2-tetrazene afforded after 11 days 3,3-dibenzyl-1-phenylurea (8%), unreacted tetrabenzyl-2-tetrazene (23%), and 6% of a white solid which was assigned the structure 10, analogous to the previously obtained 8. The infrared

$$\overset{O}{\underset{\|}{C_6H_5NHCNN=NN(CH_2C_6H_5)_2}}$$
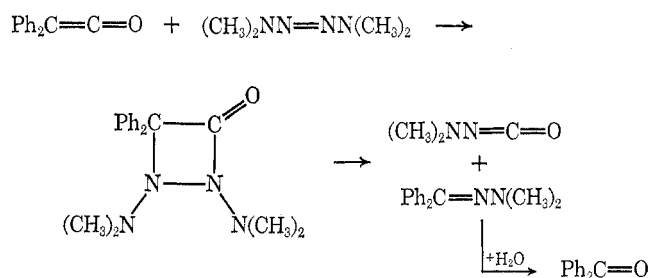$$\underset{CH_2C_6H_5}{|}$$
$$10$$
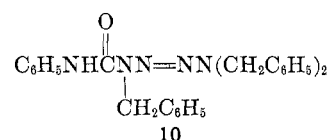
spectrum had bands at 2.99 (NH), 5.99 (urea carbonyl), and 13.32 and 14.45 μ (monosubstituted phenyl). The nmr spectrum (CDCl₃) had peaks at δ 4.50 (s, 4 H), 5.18 (s, 2 H), and 6.93–7.58 (m, *ca.* 20 H). The elemental analysis and a molecular weight determination were consistent with the proposed structure. The mother liquor from the recrystallization of 10 yielded on evaporation an oil which, when treated with 2,4-dinitrophenylhydrazine in strongly acidic ethanol, yielded the 2,4-dinitrophenylhydrazone of benzaldehyde (5%). This is presumed to have been produced from N-benzylbenzylidenimine.

The apparently general reaction which gives rise to 2 from diphenylketene and 1, and to 7 from *p*-toluenesulfonyl isocyanate and 1, appears to be almost the exclusive path in the phenyl isocyanate–tetramethyltetrazene system. Therefore, our discussion will center on the latter reaction, assuming that the analogous products in the other cases arise by analogous routes. Since the reactions were carried out in carbon tetrachloride, the hydrogen bonded to the 1 nitrogen in the urea product must arise from one of the methyl groups of 1.

Also, since loss of molecular nitrogen occurs, initial attack by the 2 nitrogen of the tetrazene is unlikely. We have not undertaken any mechanistic study as such, but examination of the reaction products suggests a possible mechanism (Scheme I). Initial nucleophilic attack by one of the terminal nitrogens of 1 on the carbonyl of the isocyanate is followed by loss of nitrogen from the resulting species 11, with proton transfer from a methyl group on the other terminal nitrogen to the urea anion. Isolation, in small amounts, of the two compounds 8 and 10, in which the starting tetrazene structure has been maintained, indicates that a species like 11 is a likely intermediate in these reactions. These products (8 and 10) presumably arise from displacement of a methyl (or benzyl) group, presumably as a radical, from 11, followed by hydrogen abstraction from another molecule of tetrazene.

Since the yield of 3,3-dimethyl-1-phenylurea (6) was sharply reduced when light was excluded by carrying out the reactions in coated flasks, one or more reactions leading to this product must be light-induced. Indeed, this effect of light and the variability of the rates and products suggest the involvement of free radicals in the reaction. Perhaps breakup of 11 produces chain-initiating free radicals in addition to the paths sketched in Scheme I. The benzophenone produced from diphenylketene and tetramethyltetrazene might have been formed as a consequence of cycloaddition, the process which we sought (Scheme II). However, no evidence

SCHEME II

$$Ph_2C=C=O \ + \ (CH_3)_2NN=NN(CH_3)_2 \ \longrightarrow$$

Ph$_2$C——C$\overset{\displaystyle O}{\diagup\!\!\diagdown}$
| |
N——N
| |
(CH$_3$)$_2$N   N(CH$_3$)$_2$

$\longrightarrow$

$(CH_3)_2NN=C=O$
+
$Ph_2C=NN(CH_3)_2$
|
$\overset{+H_2O}{\longrightarrow} \ Ph_2C=O$

of the dimethylamino isocyanate fragment[6] was obtained. An alternative route to benzophenone would involve reaction of the ketene with oxygen; however, the presence of tetrazene appears to be necessary in order for benzophenone to be obtained in more than trace amounts.

The products 6, 7, and 9 could also have arisen by reaction of dimethylamine or methylamine, formed by acid-catalyzed decomposition of the tetrazene 1,[1] with the appropriate isocyanate. However, the tetrazene was stable in CCl$_4$ in the absence of isocyanate or ketene. Hydrolysis of the ketene by adventitious water would produce diphenylacetic acid, but the isocyanates, which reacted more rapidly, would not produce acids by this method; we therefore regard the acid-catalyzed route as improbable.

Experimental Section

All melting points and boiling points are uncorrected. The nuclear magnetic resonance spectra were measured with a Varian

(6) W. S. Wadsworth and W. D. Emmons, *J. Org. Chem.*, **32**, 1279 (1967).

A-60 spectrometer. Infrared spectra were determined on a Perkin-Elmer Infracord Model 137. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn.

Tetramethyl-2-tetrazene was prepared by oxidizing 1,1-dimethylhydrazine with mercuric oxide, according to a literature procedure.[7] Tetrabenzyl-2-tetrazene was prepared by oxidizing 1,1-dibenzylhydrazine with quinone.[8] Diphenylketene was prepared from diphenylacetic acid by conversion to the acid chloride, followed by dehydrohalogenation with triethylamine.[9] The phenyl isocyanate was Eastman White Label or redistilled practical grade. *p*-Toluenesulfonyl isocyanate was used as obtained from the Upjohn Co., Carwin Organic Chemicals, North Haven, Conn.

Reaction of Diphenylketene with Tetramethyl-2-tetrazene.— Diphenylketene (4.04 g, 21 mmol) and tetramethyl-2-tetrazene (3.01 g, 26 mmol) were stirred together in 75 ml of carbon tetrachloride for 3.5 days, after which time no band for diphenylketene (4.79 μ) remained in the infrared spectrum of the reaction mixture.

After the solvent had been stripped off at reduced pressure, the residue was chromatographed on a column of Florisil to afford (a) benzophenone (0.45 g, 12%, eluted with benzene), (b) *N,N*-dimethyl-2,2-diphenylacetamide (1.15 g, 23%, mp 128–131° from ligroin, eluted with benzene), and (c) *N*-methyl-2,2-diphenylacetamide (1.95 g, 39%, eluted with 5–50% ether in benzene, mp 164–166° from benzene–ligroin). The identity of each acetamide was shown by comparison of infrared and nmr spectra and mixture melting point with authentic samples prepared from diphenylacetyl chloride and dimethylamine or methylamine, respectively.

This reaction was rerun several times. The yields of the various products varied considerably from run to run, and the reaction time necessary to consume all of the diphenylketene also varied considerably (10–84 hr).

Reaction of Phenyl Isocyanate with Tetramethyl-2-tetrazene. —Tetramethyl-2-tetrazene (2.86 g, 25 mmol) and phenyl isocyanate (2.98 g, 25 mmol) were stirred together in 75 ml of carbon tetrachloride for 48 hr in a flask fitted with a reflux condenser and drying tube. There was no band for phenyl isocyanate (4.5 μ) in the infrared spectrum of the reaction mixture after this time.

The solution was filtered to remove a yellow precipitate which was shown to be crude 1-phenyl-3,3-dimethylurea by its infrared spectrum. This material was recrystallized once from a benzene–pentane mixture to give material of mp 120–131°. The mother liquor from this recrystallization and the reaction mixture were combined. After removal of the solvents, the residue was chromatographed on a column of Florisil.

Early fractions, eluted with benzene, afforded a low-melting solid, which was rechromatographed on a column of alumina. Elution with 1% ether in benzene yielded 146 mg of a material, mp 61–72°. This was recrystallized from a benzene–pentane mixture to mp 69–73°. The structure 8 was suggested by the spectra of this material: ir (Nujol) 3.04 (w, N–H), 6.00 (m, urea carbonyl), 6.23 (m), 7.43 (m), 7.68 (m), 8.14 (m), 8.43 (m), 8.67 (s), 8.98 (w), 9.54 (w), 9.81 (m), 10.65 (m), 11.02 (m), 11.73 (m), 12.22 (m), 13.14 (m), 13.75 (w), and 14.33 μ (m); nmr and uv in text.

The major product of the Florisil chromatography, eluted with ether, was 3,3-dimethyl-1-phenylurea (total yield 3.86 g, 94%, mp 129–132.5°). The identity of this urea was shown by comparison of its infrared and nmr spectra with those of authentic material which was prepared from phenyl isocyanate and dimethylamine.

When this reaction was rerun in a flask with a low actinic coating (spectral transmission varies between 0 at 300 nm and 4% at 500 nm), the yield of urea was reduced to 59%. Also isolated by chromatography on neutral alumina (eluted with methanol) was an oil whose nmr indicated that it contained 1,3,5-trimethyl-hexahydro-1,3,5-triazine.

The reaction was rerun on a vacuum line, and the evolved gas was collected and shown by its mass spectrum to be nitrogen (92% yield).

(7) E. Renouf, *Ber.*, **13**, 2169 (1880).

(8) H. Wieland and H. Fressel, *Justus Liebigs Ann. Chem.*, **392**, 144 (1912).

(9) We are grateful to Dr. J. C. Martin, Tennessee Eastman Co., for sending us details of this preparation.

Reaction of *p*-Toluenesulfonyl Isocyanate with Tetramethyl-2-tetrazene.—Tetramethyl-2-tetrazene (2.95 g, 25 mmol) was dissolved in 50 ml of Spectrograde carbon tetrachloride and placed in a flask fitted with reflux condenser, drying tube, and syringe septum. *p*-Toluenesulfonyl isocyanate (5.00 g, 25 mmol) dissolved in 25 ml of Spectrograde carbon tetrachloride was introduced gradually into the tetrazene solution by syringe. The solution immediately turned orange and then yellow, and a solid separated out. Enough heat was evolved to cause the solution to reflux. The mixture was stirred for 0.5 hr. An infrared spectrum of the reaction mixture at this time showed no band for *p*-toluenesulfonyl isocyanate (4.4 μ). Methylene chloride was added to dissolve the precipitated solid, and the resulting mixture was extracted with three 50-ml portions of saturated aqueous sodium bicarbonate solution. These extracts were acidified with 2 N hydrochloric acid and extracted with three 50-ml portions of methylene chloride. Drying the latter extracts over magnesium sulfate and evaporation left 3.72 g (62%) of 1-(*p*-toluenesulfonyl)-3,3-dimethylurea (**7**) as a white solid, mp 146–160° dec. In another run, **7** was collected by filtration of the acidified sodium bicarbonate extracts. On standing the filtrate precipitated further solid, which was collected and dried, giving 0.28 g (5%) of 1-(*p*-toluenesulfonyl)-3-methylurea (**9**): mp 160–171° dec (lit.[10] mp 170–172°); ir (Nujol) 2.97 (m, N–H), 6.02 (s, C=O), 6.39 (m), 7.50 (m, -SO$_2$-), 8.59 (s, -SO$_2$-), 9.16 (w), 10.42 (m), 11.07 (m), 11.37 (m), and 12.27 μ (m); nmr (DMSO-d_6) δ 2.34 (s, 3 H), 2.60 (s, 3 H), 7.39 (d, 2 H), 7.93 (d, 2 H).

An authentic sample of **7** was prepared by reaction of *p*-toluenesulfonyl isocyanate with dimethylamine in chloroform and isolated by the extraction procedure described above: mp 156–170° dec; ir (Nujol) 3.03 (m, N–H), 5.90 (s, C=O), 6.25 (w), 7.43 (m, SO$_2$), 8.37 (w), 8.49 (m), 8.73 (s, -SO$_2$-) 9.16 (s), 9.78 (w), 11.09 (w), 11.65 (m), 12.29 (m), 13.27 (m), and 14.20 μ (w); nmr (CDCl$_3$) δ 2.41 (s, 3 H), 2.88 (s, 6 H), 7.29 (d, 2 H), 7.95 (d, 2 H).

Anal. Calcd for C$_{10}$H$_{14}$N$_2$O$_3$S: C, 49.58; H, 5.78; N, 11.57; S, 13.22. Found: C, 49.30; H, 5.91; N, 11.70; S, 12.99.

Melting of **7** was accompanied by evolution of a gas, presumably dimethylamine, which turned wet pH paper blue-green.

Reaction of Phenyl Isocyanate with Tetrabenzyltetrazene.—Tetrabenzyltetrazene (4.20 g, 0.010 mol) and phenyl isocyanate (1.12 g, 0.009 mol) were dissolved in 75 ml of carbon tetrachloride in a 125-ml erlenmeyer flask fitted with a reflux condenser and drying tube, and rubber septum fitted to a small side arm for ir sampling. After 11.5 days of stirring at room temperature, the isocyanate was consumed, as judged by ir. The solvent was stripped off, and the residue was chromatographed on silica gel. This yielded (a) unreacted tetrabenzyltetrazene (0.94 g, 23%, eluted with pentane–benzene mixtures) and (b) a pale yellow solid, eluted with benzene, mp 156–158° after recrystallization from ethanol (0.248 g, 6%), identified as **10** by its ir and nmr spectra (see text).

Anal. Calcd for C$_{28}$H$_{27}$N$_5$O: C, 74.83; H, 6.01; N, 15.59; mol wt, 449. Found: C, 75.51, 75.20; H, 5.99, 6.16; N, 15.72; mol wt, 420 (osmometric in chloroform).

The residue from evaporating the mother liquor from the recrystallization of **10** gave 0.145 g (5%) of benzaldehyde 2,4-dinitrophenylhydrazone on treatment with 2,4-dinitrophenylhydrazine reagent.

Further elution of the chromatography column with ether–benzene mixtures yielded (c) 1,1-dibenzyl-3-phenylurea, 0.243 g, (8%), mp 126–128° after recrystallization from benzene–ligroin (lit.[11] mp 125°).

Registry No.—**1**, 6130-87-6; **7**, 26093-79-8; **8**, 28321-01-9; **9**, 13909-69-8; **10**, 28321-03-1; diphenylketene, 525-06-4.

(10) H. Ruschig, *Arzneim.-Forsch.*, **8**, 448 (1958); *cf. Chem. Abstr.*, **53**, 1316*i* (1959).

(11) T. Mukaiyama, S. Ozaki, and Y. Hobayashi, *Bull Chem. Soc Jap.*, **29**, 51 (1956).

# Reduction of Tertiary Halides to Hydrocarbons with Sodium Borohydride in Sulfolane

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The use of sodium borohydride in polar aprotic solvents as convenient systems for the selective removal of aliphatic halides and tosylates was recently reported from our laboratories[2a] and also independently by Bell and coworkers,[2b] and more recently, by Vol'pin, Dvolaitzky, and Levitin.[2c] In the course of our study, the tertiary halide cumyl chloride was observed to undergo dehydrohalogenation followed by hydroboration. The intermediate alkylborane could be converted to the expected alcohol with alkaline peroxide or to isopropylbenzene by refluxing with valeric acid. This latter procedure results in overall reduction of tertiary halides to the hydrocarbon as shown in Scheme I.

SCHEME I
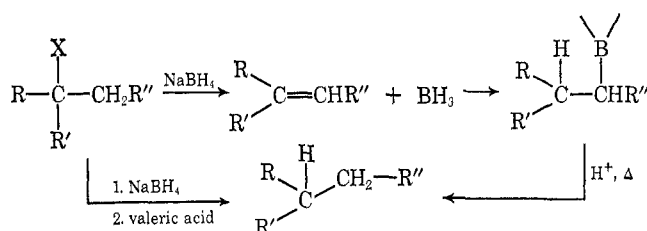
This note describes the utility of sodium borohydride in sulfolane as a convenient one-step procedure for direct removal of tertiary halides by way of elimination, hydroboration, and protonolysis. Recently, Jacobus[3] has reported use of the procedure (in DMSO) to reduce 3-chloro-3,7-dimethyloctane to 2,6-dimethyloctane in unspecified yield.

After conducting some preliminary experimentation, the general reaction conditions represented in Table I were chosen to provide adequate yields with reasonable reaction times. The use of a large excess of borohydride does not appear to be necessary as borohydride/compound ratios of 1:1 to 2:1 were entirely sufficient. Using temperatures of 120° for reaction with borohydride (100° for the benzyl halide, cumyl chloride) and 190–200° (reflux) for the subsequent protonolysis, a total reaction time of about 20 hr was realized. The reaction mixtures were worked up by simply pouring into water and extracting with cyclohexane or ether. Isolation is easily accomplished by washing the organic solution with water and dilute carbonate, drying, and removing the solvent.

The ease of the reductive procedure coupled with the good to excellent yields obtainable recommends the

(1) (a) Undergraduate Research Participant, 1969–1970; (b) Undergraduate Research Participant, 1968–1969.

(2) (a) R. O. Hutchins, D. Hoke, J. Keogh, and D. Koharski, *Tetrahedron Lett.*, 3495 (1969); (b) H. M. Bell, C. W. Vanderslice, and A. Spehar, *J. Org. Chem.*, **34**, 3923 (1969); (c) M. Vol'pin, M. Dvolaitzky, and H. Levitin, *Bull. Soc. Chim. Fr.*, 1526 (1970).

(3) J. Jacobus, *Chem. Commun.*, 338 (1970).